$$
\begin{aligned}
\frac{1}{[A]_t} &= \left(5.76 \times 10^{-2}\ \text{L mol}^{-1}\ \text{min}^{-1}\right)(10\ \text{min}) + \frac{1}{0.200\ \text{mol}^{-1}} \\
\frac{1}{[A]_t} &= \left(5.76 \times 10^{-1}\ \text{L mol}^{-1}\right) + 5.00\ \text{L mol}^{-1} \\
\frac{1}{[A]_t} &= 5.58\ \text{L mol}^{-1} \\
[A]_t &= 1.79 \times 10^{-1}\ \text{mol L}^{-1}
\end{aligned}
$$

Therefore 0.179 mol/L of butadiene remain at the end of 10.0 min, compared to the 0.200 mol/L that was originally present.

Check Your Learning

If the initial concentration of butadiene is 0.0200 *M*, what is the concentration remaining after 20.0 min?

Answer: 0.0195 mol/L

The integrated rate law for second-order reactions has the form of the equation of a straight line:

$$
\begin{aligned}
\frac{1}{[A]_t} &= kt + \frac{1}{[A]_0} \\
y &= mx + b
\end{aligned}
$$

A plot of $\frac{1}{[A]_t}$ versus t for a second-order reaction is a straight line with a slope of k and a y-intercept of $\frac{1}{[A]_0}$. If the plot is not a straight line, then the reaction is not second order.

Example 17.9

Graphical Determination of Reaction Order and Rate Constant

The data below are for the same reaction described in Example 17.8. Prepare and compare two appropriate data plots to identify the reaction as being either first or second order. After identifying the reaction order, estimate a value for the rate constant.

Solution

Trial	Time (s)	$[C_4H_6]$ (*M*)
1	0	1.00×10^{-2}
2	1600	5.04×10^{-3}
3	3200	3.37×10^{-3}
4	4800	2.53×10^{-3}
5	6200	2.08×10^{-3}

In order to distinguish a first-order reaction from a second-order reaction, prepare a plot of $\ln[C_4H_6]_t$ versus t and compare it to a plot of $\frac{1}{[C_4H_6]_t}$ versus t. The values needed for these plots follow.

Time (s)	$\frac{1}{[C_4H_6]}$ (M^{-1})	ln[C_4H_6]
0	100	−4.605
1600	198	−5.289
3200	296	−5.692
4800	395	−5.978
6200	481	−6.175

The plots are shown in **Figure 17.10**, which clearly shows the plot of ln$[C_4H_6]_t$ versus t is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[C_4H_6]_t}$ versus t is linear, indicating that the reaction is second order.

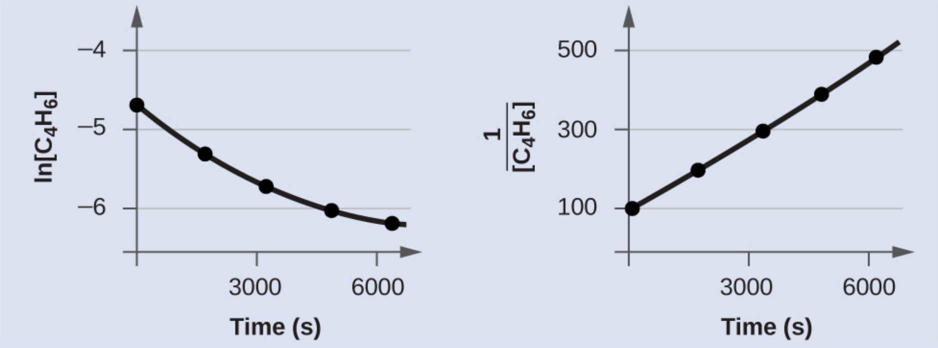


Figure 17.10 These two graphs show first- and second-order plots for the dimerization of C_4H_6. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

According to the second-order integrated rate law, the rate constant is equal to the slope of the $\frac{1}{[A]_t}$ versus t plot. Using the data for t = 0 s and t = 6200 s, the rate constant is estimated as follows:

$$k = \text{slope} = \frac{(481\,M^{-1} - 100\,M^{-1})}{(6200\,\text{s} - 0\,\text{s})} = 0.0614\,\text{M}^{-1}\ \text{s}^{-1}$$

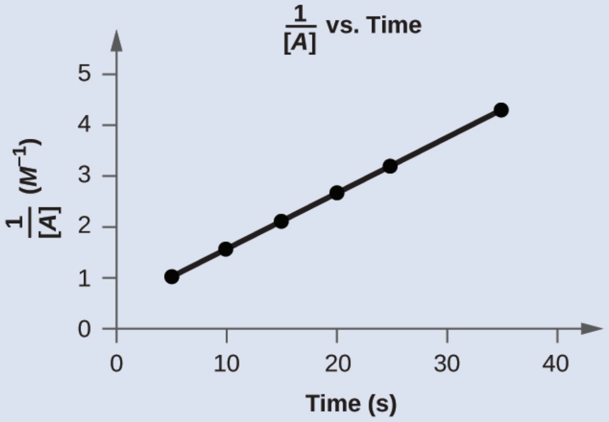
Check Your Learning

Do the following data fit a second-order rate law?

Trial	Time (s)	[*A*] (*M*)
1	5	0.952
2	10	0.625
3	15	0.465
4	20	0.370
5	25	0.308

Trial	Time (s)	[*A*] (*M*)
6	35	0.230

Answer: Yes. The plot of $\frac{1}{[A]_t}$ vs. t is linear:



Zero-Order Reactions

For zero-order reactions, the differential rate law is:

$$\text{rate} = k$$

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactant(s). This may seem counterintuitive, since the reaction rate certainly can't be finite when the reactant concentration is zero. For purposes of this introductory text, it will suffice to note that zero-order kinetics are observed for some reactions only under certain specific conditions. These same reactions exhibit different kinetic behaviors when the specific conditions aren't met, and for this reason the more prudent term *pseudo-zero-order* is sometimes used.

The integrated rate law for a zero-order reaction is a linear function:

$$\begin{aligned} [A]_t &= -kt + [A]_0 \\ y &= mx + b \end{aligned}$$

A plot of $[A]$ versus t for a zero-order reaction is a straight line with a slope of $-k$ and a y-intercept of $[A]_0$. **Figure 17.11** shows a plot of $[NH_3]$ versus t for the thermal decomposition of ammonia at the surface of two different heated solids. The decomposition reaction exhibits first-order behavior at a quartz (SiO_2) surface, as suggested by the exponentially decaying plot of concentration versus time. On a tungsten surface, however, the plot is linear, indicating zero-order kinetics.

Example 17.10

Graphical Determination of Zero-Order Rate Constant

Use the data plot in **Figure 17.11** to graphically estimate the zero-order rate constant for ammonia decomposition at a tungsten surface.

Solution

The integrated rate law for zero-order kinetics describes a linear plot of reactant concentration, $[A]_t$, versus time, t, with a slope equal to the negative of the rate constant, $-k$. Following the mathematical approach of previous examples, the slope of the linear data plot (for decomposition on W) is estimated from the graph. Using the ammonia concentrations at $t = 0$ and $t = 1000$ s:

$$k = -\text{slope} = -\frac{(0.0015\ \text{mol L}^{-1} - 0.0028\ \text{mol L}^{-1})}{(1000\ \text{s} - 0\ \text{s})} = 1.3 \times 10^{-6}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Check Your Learning

The zero-order plot in **Figure 17.11** shows an initial ammonia concentration of 0.0028 mol L^{-1} decreasing linearly with time for 1000 s. Assuming no change in this zero-order behavior, at what time (min) will the concentration reach 0.0001 mol L^{-1}?

Answer: 35 min

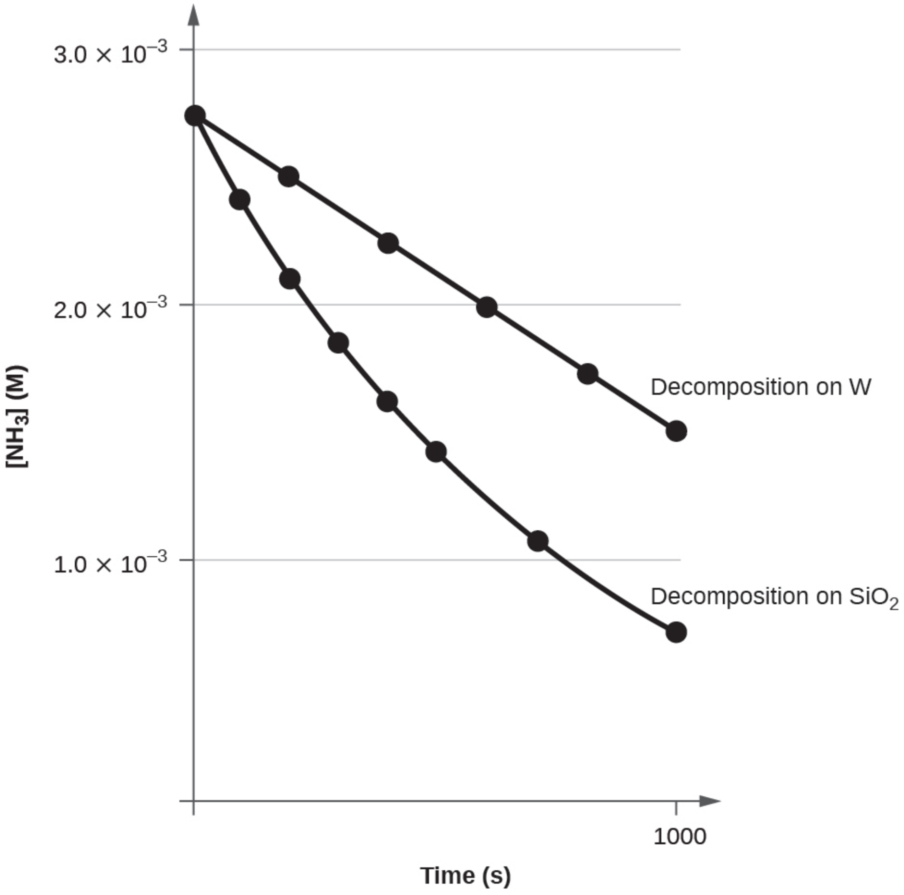


Figure 17.11 The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

The Half-Life of a Reaction

The **half-life of a reaction ($t_{1/2}$)** is the time required for one-half of a given amount of reactant to be consumed. In each succeeding half-life, half of the remaining concentration of the reactant is consumed. Using the decomposition of hydrogen peroxide (**Figure 17.2**) as an example, we find that during the first half-life (from 0.00 hours to 6.00 hours), the concentration of H_2O_2 decreases from 1.000 *M* to 0.500 *M*. During the second half-life (from 6.00 hours to 12.00 hours), it decreases from 0.500 *M* to 0.250 *M*; during the third half-life, it decreases from 0.250 *M* to 0.125

M. The concentration of H_2O_2 decreases by half during each successive period of 6.00 hours. The decomposition of hydrogen peroxide is a first-order reaction, and, as can be shown, the half-life of a first-order reaction is independent of the concentration of the reactant. However, half-lives of reactions with other orders depend on the concentrations of the reactants.

First-Order Reactions

An equation relating the half-life of a first-order reaction to its rate constant may be derived from the integrated rate law as follows:

$$\begin{aligned} \ln \frac{[A]_0}{[A]_t} &= kt \\ t &= \ln \frac{[A]_0}{[A]_t} \times \frac{1}{k} \end{aligned}$$

Invoking the definition of half-life, symbolized $t_{1/2}$, requires that the concentration of *A* at this point is one-half its initial concentration: $t = t_{1/2}, \quad [A]_t = \frac{1}{2}[A]_0$.

Substituting these terms into the rearranged integrated rate law and simplifying yields the equation for half-life:

$$\begin{aligned} t_{1/2} &= \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k} \\ &= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k} \\ t_{1/2} &= \frac{0.693}{k} \end{aligned}$$

This equation describes an expected inverse relation between the half-life of the reaction and its rate constant, *k*. Faster reactions exhibit larger rate constants and correspondingly shorter half-lives. Slower reactions exhibit smaller rate constants and longer half-lives.

Example 17.11

Calculation of a First-order Rate Constant using Half-Life

Calculate the rate constant for the first-order decomposition of hydrogen peroxide in water at 40 °C, using the data given in **Figure 17.12**.

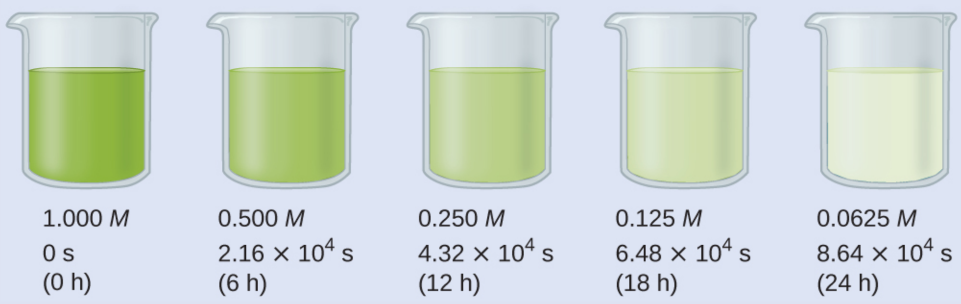


Figure 17.12 The decomposition of H_2O_2 $(2H_2O_2 \longrightarrow 2H_2O + O_2)$ at 40 °C is illustrated. The intensity of the color symbolizes the concentration of H_2O_2 at the indicated times; H_2O_2 is actually colorless.

Solution

Inspecting the concentration/time data in **Figure 17.12** shows the half-life for the decomposition of H_2O_2 is 2.16×10^4 s:

$$\begin{aligned} t_{1/2} &= \frac{0.693}{k} \\ k &= \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4 \text{ s}} = 3.21 \times 10^{-5} \text{ s}^{-1} \end{aligned}$$

Check Your Learning

The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1}. What is the half-life for this decay?

Answer: 5.02 d.

Second-Order Reactions

Following the same approach as used for first-order reactions, an equation relating the half-life of a second-order reaction to its rate constant and initial concentration may be derived from its integrated rate law:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

or

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

Restrict t to $t_{1/2}$

$$t = t_{1/2}$$

define $[A]_t$ as one-half $[A]_0$

$$[A]_t = \frac{1}{2}[A]_0$$

and then substitute into the integrated rate law and simplify:

$$\begin{aligned} \frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ \frac{2}{[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ \frac{1}{[A]_0} &= kt_{1/2} \\ t_{1/2} &= \frac{1}{k[A]_0} \end{aligned}$$

For a second-order reaction, $t_{1/2}$ is inversely proportional to the concentration of the reactant, and the half-life increases as the reaction proceeds because the concentration of reactant decreases. Unlike with first-order reactions, the rate constant of a second-order reaction cannot be calculated directly from the half-life unless the initial concentration is known.

Zero-Order Reactions

As for other reaction orders, an equation for zero-order half-life may be derived from the integrated rate law:

$$[A] = -kt + [A]_0$$

Restricting the time and concentrations to those defined by half-life: $t = t_{1/2}$ and $[A] = \frac{[A]_0}{2}$. Substituting these terms into the zero-order integrated rate law yields:

$$\begin{aligned}\frac{[A]_0}{2} &= -kt_{1/2} + [A]_0 \\ kt_{1/2} &= \frac{[A]_0}{2} \\ t_{1/2} &= \frac{[A]_0}{2k}\end{aligned}$$

As for all reaction orders, the half-life for a zero-order reaction is inversely proportional to its rate constant. However, the half-life of a zero-order reaction increases as the initial concentration increases.

Equations for both differential and integrated rate laws and the corresponding half-lives for zero-, first-, and second-order reactions are summarized in **Table 17.2**.

Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	First-Order	Second-Order
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	$M\ \mathrm{s}^{-1}$	s^{-1}	$M^{-1}\ \mathrm{s}^{-1}$
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ vs. t
relationship between slope of linear plot and rate constant	$k = -\text{slope}$	$k = -\text{slope}$	$k = \text{slope}$
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Table 17.2

Example 17.12

Half-Life for Zero-Order and Second-Order Reactions

What is the half-life (ms) for the butadiene dimerization reaction described in **Example 17.8**?

Solution

The reaction in question is second order, is initiated with a 0.200 mol L^{-1} reactant solution, and exhibits a rate constant of 0.0576 L mol^{-1} min^{-1}. Substituting these quantities into the second-order half-life equation:

$$\begin{aligned}t_{1/2} &= \frac{1}{[(0.0576\ \mathrm{L\ mol}^{-1}\ \mathrm{min}^{-1})(0.200\ \mathrm{mol\ L}^{-1})]} = 0.0115\ \mathrm{min} \\ t_{1/2} &= 0.0115\ \mathrm{min}\left(\frac{60\ \mathrm{s}}{1\ \mathrm{min}}\right)\left(\frac{1000\ \mathrm{ms}}{1\ \mathrm{s}}\right) = 690\ \mathrm{ms}\end{aligned}$$

Check Your Learning

What is the half-life (min) for the thermal decomposition of ammonia on tungsten (see **Figure 17.11**)?

Answer: 18 min

17.5 Collision Theory

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

- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- Define the concepts of activation energy and transition state
- Use the Arrhenius equation in calculations relating rate constants to temperature

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates.

Collision theory is based on the following postulates:

1. The rate of a reaction is proportional to the rate of reactant collisions:

$$\text{reaction rate} \propto \frac{\text{\# collisions}}{\text{time}}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species’ valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:

$$2\,\text{CO}(g) + \text{O}_2(g) \longrightarrow 2\,\text{CO}_2(g)$$

Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. It is also a side reaction of the combustion of gunpowder that results in muzzle flash for many firearms. If carbon monoxide and oxygen are present in sufficient amounts, the reaction will occur at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$\text{CO}(g) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) + \text{O}(g)$$

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in **Figure 17.13**. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms $(\text{O}=\text{C}=\text{O})$. This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.

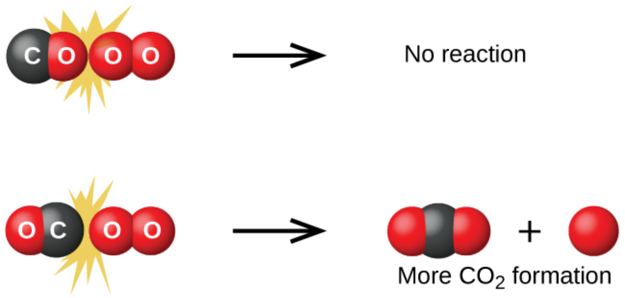


Figure 17.13 Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. In addition to a proper orientation, the collision must also occur with sufficient energy to result in product formation. When reactant species collide with both proper orientation and adequate energy, they combine to form an unstable species called an **activated complex** or a **transition state**. These species are very short lived and usually undetectable by most analytical instruments. In some cases, sophisticated spectral measurements have been used to observe transition states.

Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

Activation Energy and the Arrhenius Equation

The minimum energy necessary to form a product during a collision between reactants is called the **activation energy (**E_a**)**. How this energy compares to the kinetic energy provided by colliding reactant molecules is a primary factor affecting the rate of a chemical reaction. If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly since only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, a large fraction of molecules will be adequately energetic and the reaction will proceed rapidly.

Figure 17.14 shows how the energy of a chemical system changes as it undergoes a reaction converting reactants to products according to the equation

$$A + B \longrightarrow C + D$$

These **reaction diagrams** are widely used in chemical kinetics to illustrate various properties of the reaction of interest. Viewing the diagram from left to right, the system initially comprises reactants only, $A + B$. Reactant molecules with sufficient energy can collide to form a high-energy activated complex or transition state. The unstable transition state can then subsequently decay to yield stable products, $C + D$. The diagram depicts the reaction's activation energy, E_a, as the energy difference between the reactants and the transition state. Using a specific energy, the *enthalpy* (see chapter on thermochemistry), the enthalpy change of the reaction, ΔH, is estimated as the energy difference between the reactants and products. In this case, the reaction is exothermic ($\Delta H < 0$) since it yields a decrease in system enthalpy.

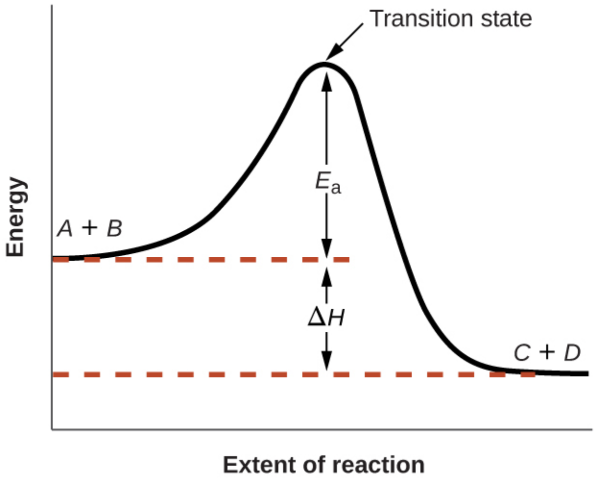


Figure 17.14 Reaction diagram for the exothermic reaction $A + B \longrightarrow C + D$.

The **Arrhenius equation** relates the activation energy and the rate constant, *k*, for many chemical reactions:

$$k = Ae^{-E_a/RT}$$

In this equation, *R* is the ideal gas constant, which has a value 8.314 J/mol/K, T is temperature on the Kelvin scale, E_a is the activation energy in joules per mole, *e* is the constant 2.7183, and *A* is a constant called the **frequency factor**, which is related to the frequency of collisions and the orientation of the reacting molecules.

Postulates of collision theory are nicely accommodated by the Arrhenius equation. The frequency factor, *A*, reflects how well the reaction conditions favor properly oriented collisions between reactant molecules. An increased probability of effectively oriented collisions results in larger values for *A* and faster reaction rates.

The exponential term, $e^{-Ea/RT}$, describes the effect of activation energy on reaction rate. According to kinetic molecular theory (see chapter on gases), the temperature of matter is a measure of the average kinetic energy of its constituent atoms or molecules. The distribution of energies among the molecules composing a sample of matter at any given temperature is described by the plot shown in **Figure 17.15**(**a**). Two shaded areas under the curve represent the numbers of molecules possessing adequate energy (*RT*) to overcome the activation barriers (E_a). A lower activation energy results in a greater fraction of adequately energized molecules and a faster reaction.

The exponential term also describes the effect of temperature on reaction rate. A higher temperature represents a correspondingly greater fraction of molecules possessing sufficient energy (*RT*) to overcome the activation barrier (E_a), as shown in **Figure 17.15**(**b**). This yields a greater value for the rate constant and a correspondingly faster reaction rate.

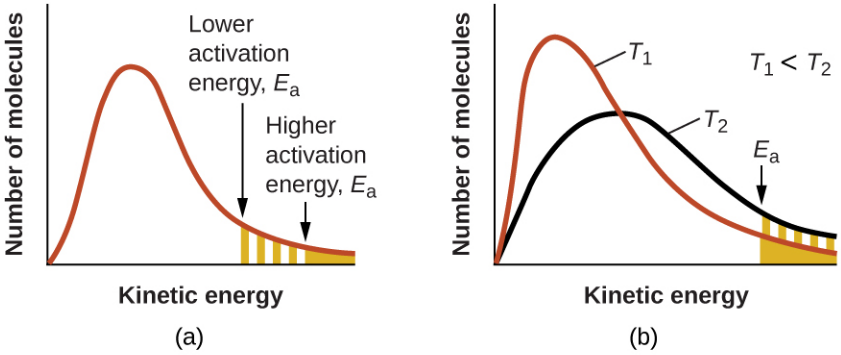


Figure 17.15 Molecular energy distributions showing numbers of molecules with energies exceeding (a) two different activation energies at a given temperature, and (b) a given activation energy at two different temperatures.

A convenient approach for determining E_a for a reaction involves the measurement of k at two or more different temperatures and using an alternate version of the Arrhenius equation that takes the form of a linear equation

$$\begin{aligned} \ln k &= \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \\ y &= mx + b \end{aligned}$$

A plot of ln k versus $\frac{1}{T}$ is linear with a slope equal to $\frac{-E_a}{R}$ and a y-intercept equal to ln A.

Example 17.13

Determination of E_a

The variation of the rate constant with temperature for the decomposition of HI(g) to $H_2(g)$ and $I_2(g)$ is given here. What is the activation energy for the reaction?

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

T **(K)**	***k*** **(L/mol/s)**
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}
781	3.95×10^{-2}

Solution

Use the provided data to derive values of $\frac{1}{T}$ and ln k:

$\frac{1}{\mathrm{T}}\ (\mathrm{K}^{-1})$	**ln *k***
1.80×10^{-3}	−14.860
1.74×10^{-3}	−13.617
1.55×10^{-3}	−9.362
1.43×10^{-3}	−6.759
1.28×10^{-3}	−3.231

Figure 17.16 is a graph of ln k versus $\frac{1}{T}$. In practice, the equation of the line (slope and y-intercept) that best fits these plotted data points would be derived using a statistical process called regression. This is helpful for most experimental data because a perfect fit of each data point with the line is rarely encountered. For the data here, the fit is nearly perfect and the slope may be estimated using any two of the provided data pairs. Using the first and last data points permits estimation of the slope.

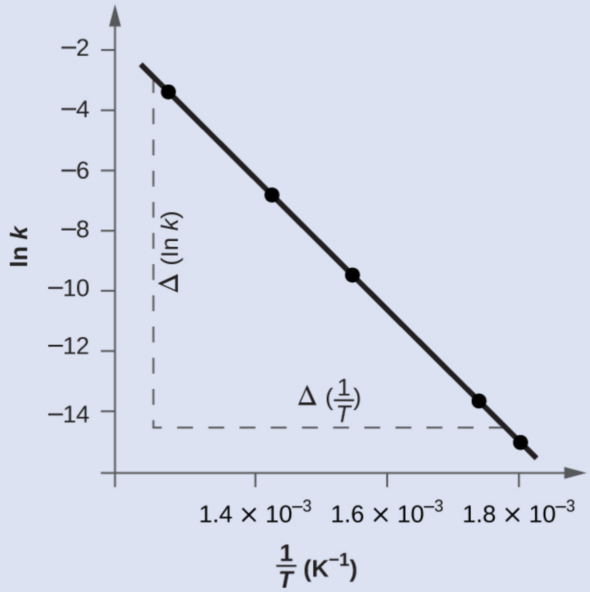


Figure 17.16 This graph shows the linear relationship between ln *k* and $\frac{1}{T}$ for the reaction $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$ according to the Arrhenius equation.

$$\begin{aligned}
\text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\
&= \frac{(-14.860)\ -\ (-3.231)}{\left(1.80 \times 10^{-3}\ \text{K}^{-1}\right) - \left(1.28 \times 10^{-3}\ \text{K}^{-1}\right)} \\
&= \frac{-11.629}{0.52 \times 10^{-3}\ \text{K}^{-1}} = 2.2 \times 10^{4}\ \text{K} \\
&= -\frac{E_\text{a}}{R} \\
E_\text{a} &= -\text{slope} \times R = -\left(-2.2 \times 10^{4}\ \text{K} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\right) \\
& \quad 1.8 \times 10^{5}\ \text{J mol}^{-1}\ \text{or}\ 180\ \text{kJ mol}^{-1}
\end{aligned}$$

Alternative approach: A more expedient approach involves deriving activation energy from measurements of the rate constant at just two temperatures. In this approach, the Arrhenius equation is rearranged to a convenient two-point form:

$$\ln\frac{k_1}{k_2} = \frac{E_\text{a}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Rearranging this equation to isolate activation energy yields:

$$E_\text{a} = -R\left(\frac{\ln k_2\ -\ \ln k_1}{\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right)}\right)$$

Any two data pairs may be substituted into this equation—for example, the first and last entries from the above data table:

$$E_\text{a} = -8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\left(\frac{-3.231 - (-14.860)}{1.28 \times 10^{-3}\ \text{K}^{-1}\ -\ 1.80 \times 10^{-3}\ \text{K}^{-1}}\right)$$

and the result is $E_\text{a} = 1.8 \times 10^{5}\ \text{J mol}^{-1}$ or $180\ \text{kJ mol}^{-1}$

This approach yields the same result as the more rigorous graphical approach used above, as expected. In practice, the graphical approach typically provides more reliable results when working with actual experimental data.

Check Your Learning

The rate constant for the rate of decomposition of N_2O_5 to NO and O_2 in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:

$$2N_2O_5(g) \longrightarrow 4NO(g) + 3O_2(g)$$

Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

Answer: 1.1×10^5 J mol^{-1} or 110 kJ mol^{-1}

17.6 Reaction Mechanisms

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

- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

Chemical reactions very often occur in a step-wise fashion, involving two or more distinct reactions taking place in sequence. A balanced equation indicates what is reacting and what is produced, but it reveals no details about how the reaction actually takes place. The **reaction mechanism** (or reaction path) provides details regarding the precise, step-by-step process by which a reaction occurs.

The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$O_3(g) \longrightarrow O_2(g) + O$$
$$O + O_3(g) \longrightarrow 2O_2(g)$$

Each of the steps in a reaction mechanism is an **elementary reaction**. These elementary reactions occur precisely as represented in the step equations, and they must sum to yield the balanced chemical equation representing the overall reaction:

$$2O_3(g) \longrightarrow 3O_2(g)$$

Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called **intermediates**.

While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction *does not involve the direct collision and reaction of two ozone molecules*. Instead, one O_3 decomposes to yield O_2 and an oxygen atom, and a second O_3 molecule subsequently reacts with the oxygen atom to yield two additional O_2 molecules.

Unlike balanced equations representing an overall reaction, the equations for elementary reactions are explicit representations of the chemical change taking place. The reactant(s) in an elementary reaction's equation undergo only the bond-breaking and/or making events depicted to yield the product(s). For this reason, *the rate law for an elementary reaction may be derived directly from the balanced chemical equation describing the reaction*. This is not the case for typical chemical reactions, for which rate laws may be reliably determined only via experimentation.

Unimolecular Elementary Reactions

The **molecularity** of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a **unimolecular reaction** involves the reaction of a *single* reactant species to produce one or more molecules of product:

$$A \longrightarrow \text{products}$$

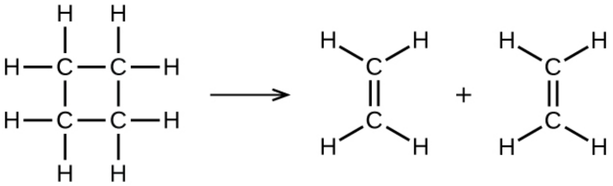
The rate law for a unimolecular reaction is first order:

$$\text{rate} = k[A]$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

$$\text{O}_3 \longrightarrow \text{O}_2 + \text{O}$$

illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism as described above. However, some unimolecular reactions may be the only step of a single-step reaction mechanism. (In other words, an "overall" reaction may also be an elementary reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, is represented by the following chemical equation:



This equation represents the overall reaction observed, and it might also represent a legitimate unimolecular elementary reaction. The rate law predicted from this equation, assuming it is an elementary reaction, turns out to be the same as the rate law derived experimentally for the overall reaction, namely, one showing first-order behavior:

$$\text{rate} = -\frac{\Delta[\text{C}_4\text{H}_8]}{\Delta t} = k[\text{C}_4\text{H}_8]$$

This agreement between observed and predicted rate laws is interpreted to mean that the proposed unimolecular, single-step process is a reasonable mechanism for the butadiene reaction.

Bimolecular Elementary Reactions

A **bimolecular reaction** involves two reactant species, for example:

$$A + B \longrightarrow \text{products}$$

and

$$2A \longrightarrow \text{products}$$

For the first type, in which the two reactant molecules are different, the rate law is first-order in A and first order in B (second-order overall):

$$\text{rate} = k[A][B]$$

For the second type, in which two identical molecules collide and react, the rate law is second order in A:

$$\text{rate} = k[A][A] = k[A]^2$$

Some chemical reactions occur by mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$\text{NO}_2(g) + \text{CO}(g) \longrightarrow \text{NO}(g) + \text{CO}_2(g)$$

(see **Figure 17.17**)

Figure 17.17 The probable mechanism for the reaction between NO_2 and CO to yield NO and CO_2.

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is the second step of the two-step ozone decomposition mechanism discussed earlier in this section:

$$\mathrm{O}(g) + \mathrm{O}_3(g) \longrightarrow 2\mathrm{O}_2(g)$$

Termolecular Elementary Reactions

An elementary **termolecular reaction** involves the simultaneous collision of three atoms, molecules, or ions. Termolecular elementary reactions are uncommon because the probability of three particles colliding simultaneously is less than one one-thousandth of the probability of two particles colliding. There are, however, a few established termolecular elementary reactions. The reaction of nitric oxide with oxygen appears to involve termolecular steps:

$$\begin{array}{l} 2\mathrm{NO} + \mathrm{O}_2 \longrightarrow 2\mathrm{NO}_2 \\ \text{rate} = k[\mathrm{NO}]^2[\mathrm{O}_2] \end{array}$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$\begin{array}{l} 2\mathrm{NO} + \mathrm{Cl}_2 \longrightarrow 2\mathrm{NOCl} \\ \text{rate} = k[\mathrm{NO}]^2[\mathrm{Cl}_2] \end{array}$$

Relating Reaction Mechanisms to Rate Laws

It’s often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the **rate-limiting step** (or rate-determining step) of the reaction Figure 17.18.

Figure 17.18 A cattle chute is a nonchemical example of a rate-determining step. Cattle can only be moved from one holding pen to another as quickly as one animal can make its way through the chute. (credit: Loren Kerns)

As described earlier, rate laws may be derived directly from the chemical equations for elementary reactions. This is not the case, however, for ordinary chemical reactions. The balanced equations most often encountered represent the overall change for some chemical system, and very often this is the result of some multistep reaction mechanisms. In every case, the rate law must be determined from experimental data and the reaction mechanism subsequently deduced from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

$$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$$

For temperatures above 225 °C, the rate law has been found to be:

$$\text{rate} = k[NO_2][CO]$$

The reaction is first order with respect to NO_2 and first-order with respect to CO. This is consistent with a single-step bimolecular mechanism and it is *possible* that this is the mechanism for this reaction at high temperatures.

At temperatures below 225 °C, the reaction is described by a rate law that is second order with respect to NO_2:

$$\text{rate} = k[NO_2]^2$$

This rate law is not consistent with the single-step mechanism, but is consistent with the following two-step mechanism:

$$\begin{gathered} NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)\ (\text{slow}) \\ NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)\ (\text{fast}) \end{gathered}$$

The rate-determining (slower) step gives a rate law showing second-order dependence on the NO_2 concentration, and the sum of the two equations gives the net overall reaction.

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving a rapidly reversible reaction the rate law for the overall reaction may be more difficult to derive.

As discussed in several chapters of this text, a reversible reaction is at *equilibrium* when the rates of the forward and reverse processes are equal. Consider the reversible elementary reaction in which NO dimerizes to yield an intermediate species N_2O_2. When this reaction is at equilibrium:

$$\begin{aligned} &NO + NO \rightleftharpoons N_2O_2 \\ &\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}} \\ &k_1[NO]^2 = k_{-1}[N_2O_2] \end{aligned}$$

This expression may be rearranged to express the concentration of the intermediate in terms of the reactant NO:

$$\left(\frac{k_1[NO]^2}{k_{-1}}\right) = [N_2O_2]$$

Since intermediate species concentrations are not used in formulating rate laws for overall reactions, this approach is sometimes necessary, as illustrated in the following example exercise.

Example 17.14

Deriving a Rate Law from a Reaction Mechanism

The two-step mechanism below has been proposed for a reaction between nitrogen monoxide and molecular chlorine:

$$\begin{array}{ll} \text{Step 1: } NO(g) + Cl_2(g) \rightleftharpoons NOCl_2(g) & \text{fast} \\ \text{Step 2: } NOCl_2(g) + NO(g) \longrightarrow 2NOCl(g) & \text{slow} \end{array}$$

Use this mechanism to derive the equation and predicted rate law for the overall reaction.

Solution

The equation for the overall reaction is obtained by adding the two elementary reactions:

$$2NO(g) + Cl_2(g)\ 2NOCl(g)$$

To derive a rate law from this mechanism, first write rates laws for each of the two steps.

$$\begin{aligned} \text{rate}_1 &= k_1[NO][Cl_2] \text{ for the forward reaction of step 1} \\ \text{rate}_{-1} &= k_{-1}[NOCl_2] \text{ for the reverse reaction of step 1} \\ \text{rate}_2 &= k_2[NOCl_2][NO] \text{ for step 2} \end{aligned}$$

Step 2 is the rate-determining step, and so the rate law for the overall reaction should be the same as for this step. However, the step 2 rate law, as written, contains an intermediate species concentration, $[NOCl_2]$. To remedy this, use the first step's rate laws to derive an expression for the intermediate concentration in terms of the reactant concentrations.

Assuming step 1 is at equilibrium:

$$\begin{aligned} \text{rate}_1 &= \text{rate}_{-1} \\ k_1\,[NO][Cl_2] &= k_{-1}\,[NOCl_2] \\ [NOCl_2] &= \left(\frac{k_1}{k_{-1}}\right)[NO][Cl_2] \end{aligned}$$

Substituting this expression into the rate law for step 2 yields:

$$\text{rate}_2 = \text{rate}_{\text{overall}} = \left(\frac{k_2 k_1}{k_{-1}}\right)[NO]^2[Cl_2]$$

Check Your Learning

The first step of a proposed multistep mechanism is:

$$F_2(g) \rightleftharpoons 2F(g) \text{ fast}$$

Derive the equation relating atomic fluorine concentration to molecular fluorine concentration.

Answer: $[F] = \left(\frac{k_1[F_2]}{k_{-1}}\right)^{1/2}$

17.7 Catalysis

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

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

Catalysts Do Not Affect Equilibrium

A catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year.

Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Portrait of a Chemist

Fritz Haber

In the early 20th century, German chemist Fritz Haber (**Figure 17.19**) developed a practical process for converting diatomic nitrogen, which cannot be used by plants as a nutrient, to ammonia, a form of nitrogen that is easiest for plants to absorb.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (N_2) is nutritionally unavailable due the tremendous stability of the nitrogen-nitrogen triple bond. For plants to use atmospheric nitrogen, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation).

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures. For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate. Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008.

Figure 17.19 The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country."[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H = -92.2\text{ kJ}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly.

In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (**Figure 17.20**).

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[1] Herrlich, P. "The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?" *EMBO Reports* 14 (2013): 759–764.

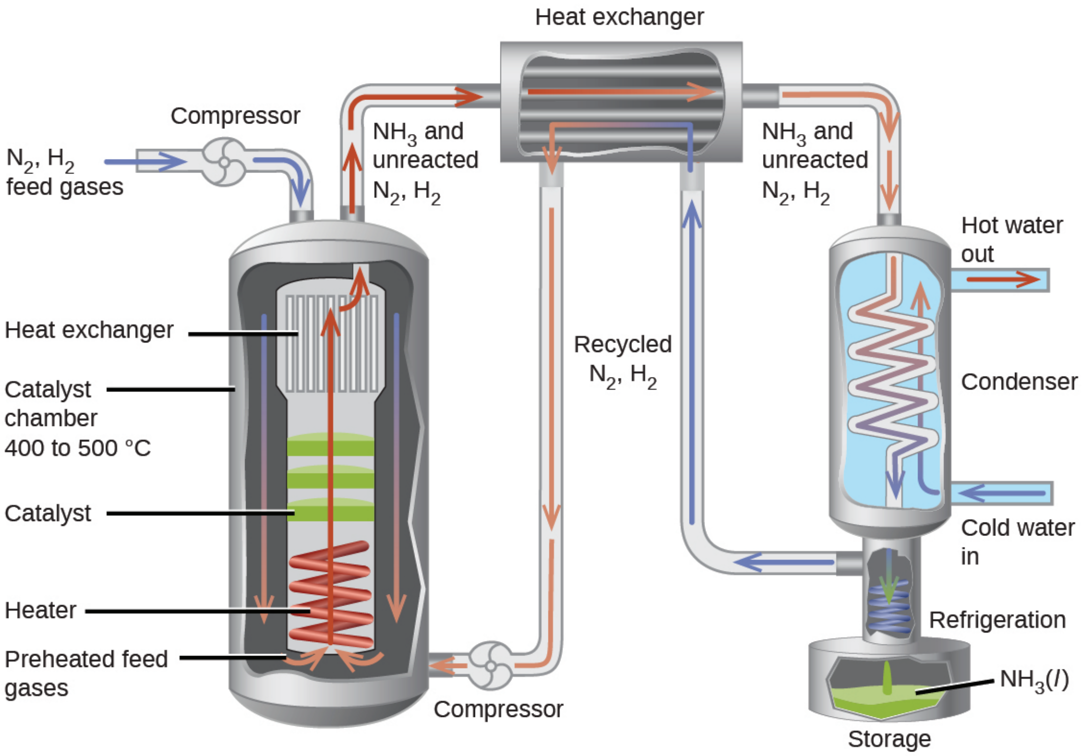


Figure 17.20 Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

Among the factors affecting chemical reaction rates discussed earlier in this chapter was the presence of a *catalyst*, a substance that can increase the reaction rate without being consumed in the reaction. The concepts introduced in the previous section on reaction mechanisms provide the basis for understanding how catalysts are able to accomplish this very important function.

Figure 17.21 shows reaction diagrams for a chemical process in the absence and presence of a catalyst. Inspection of the diagrams reveals several traits of these reactions. Consistent with the fact that the two diagrams represent the same overall reaction, both curves begin and end at the same energies (in this case, because products are more energetic than reactants, the reaction is endothermic). The reaction mechanisms, however, are clearly different. The uncatalyzed reaction proceeds via a one-step mechanism (one transition state observed), whereas the catalyzed reaction follows a two-step mechanism (two transition states observed) with *a notably lesser activation energy*. This difference illustrates the means by which a catalyst functions to accelerate reactions, namely, by providing an alternative reaction mechanism with a lower activation energy. Although the catalyzed reaction mechanism for a reaction needn’t necessarily involve a different number of steps than the uncatalyzed mechanism, it must provide a reaction path whose rate determining step is faster (lower E_a).

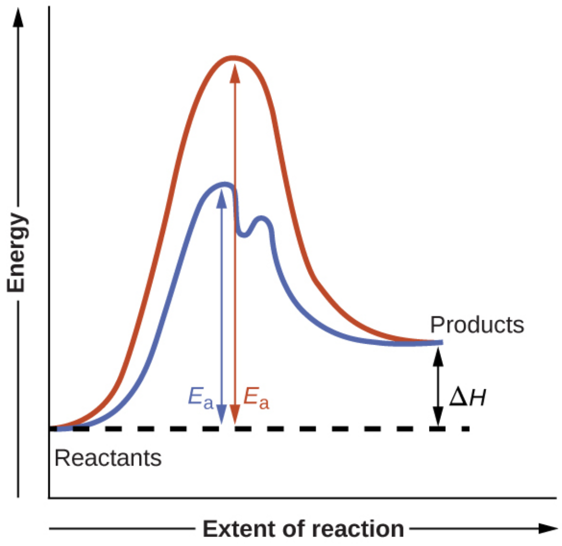
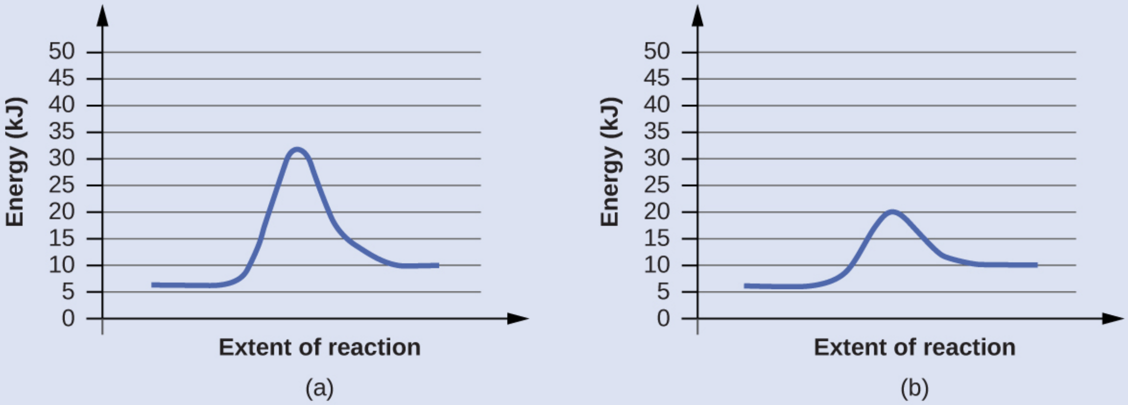


Figure 17.21 Reaction diagrams for an endothermic process in the absence (red curve) and presence (blue curve) of a catalyst. The catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Example 17.15

Reaction Diagrams for Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Estimate the activation energy for each process, and identify which one involves a catalyst.



Solution

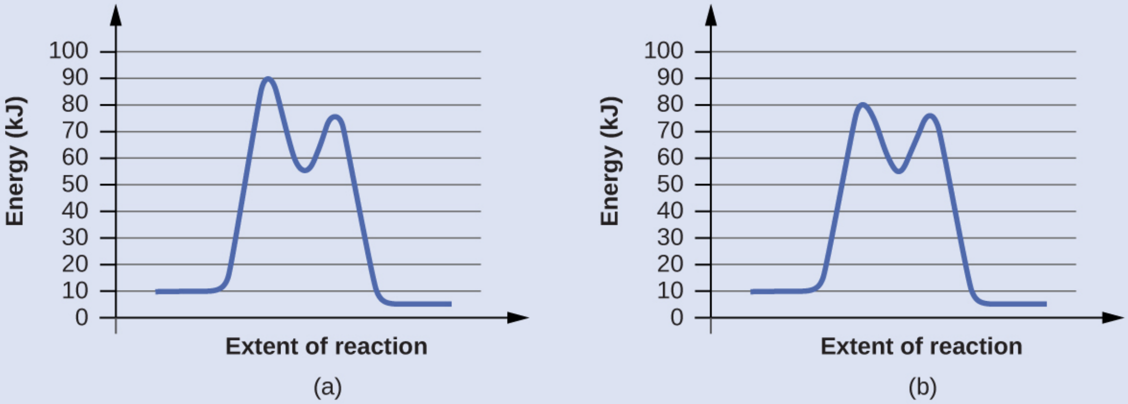
Activation energies are calculated by subtracting the reactant energy from the transition state energy.

$$\text{diagram (a)}: E_a = 32\text{ kJ} - 6\text{ kJ} = 26\text{ kJ}$$
$$\text{diagram (b)}: E_a = 20\text{ kJ} - 6\text{ kJ} = 14\text{ kJ}$$

The catalyzed reaction is the one with lesser activation energy, in this case represented by diagram (b).

Check Your Learning

Reaction diagrams for a chemical process with and without a catalyst are shown below. Both reactions involve a two-step mechanism with a rate-determining first step. Compute activation energies for the first step of each mechanism, and identify which corresponds to the catalyzed reaction. How do the second steps of these two mechanisms compare?



Answer: For the first step, E_a = 80 kJ for (a) and 70 kJ for (b), so diagram (b) depicts the catalyzed reaction. Activation energies for the second steps of both mechanisms are the same, 20 kJ.

Homogeneous Catalysts

A **homogeneous catalyst** is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product.

As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:

$$3O_2(g) \xrightarrow{hv} 2O_3(g)$$

Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following two-step mechanism:

$$\begin{aligned} &O_3 \longrightarrow O_2 + O \\ &O + O_3 \longrightarrow 2O_2 \end{aligned}$$

A number of substances can catalyze the decomposition of ozone. For example, the nitric oxide -catalyzed decomposition of ozone is believed to occur via the following three-step mechanism:

$$\begin{aligned} &NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g) \\ &O_3(g) \longrightarrow O_2(g) + O(g) \\ &NO_2(g) + O(g) \longrightarrow NO(g) + O_2(g) \end{aligned}$$

As required, the overall reaction is the same for both the two-step uncatalyzed mechanism and the three-step NO-catalyzed mechanism:

$$2O_3(g) \longrightarrow 3O_2(g)$$

Notice that NO is a reactant in the first step of the mechanism and a product in the last step. This is another characteristic trait of a catalyst: Though it participates in the chemical reaction, it is not consumed by the reaction.

Portrait of a Chemist

Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (**Figure 17.22**), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."[2] Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).

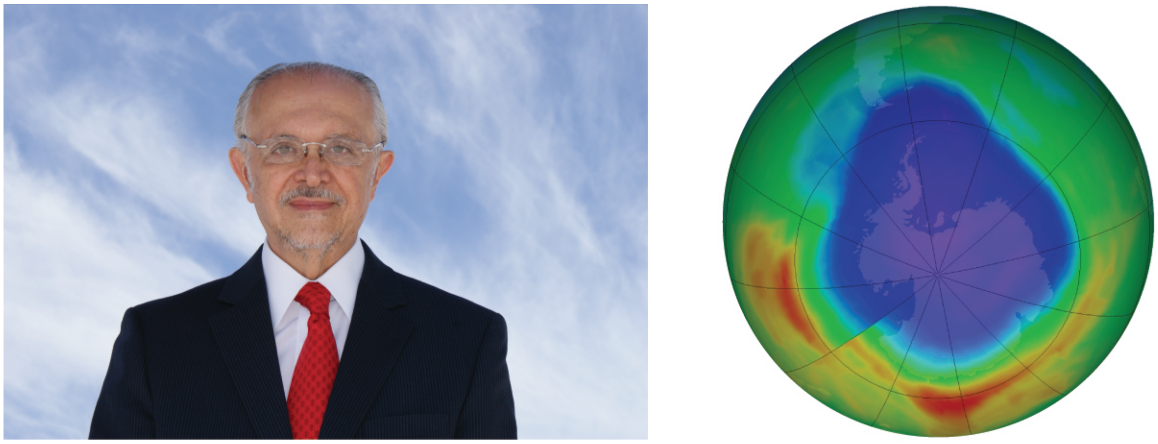

(a) (b)

Figure 17.22 (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

In 1974, Molina and Rowland published a paper in the journal *Nature* detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth's upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable "hole" forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—reaches earth's surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

$$\mathrm{CH_3Cl + OH \longrightarrow Cl + other\ products}$$

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$\begin{aligned}&\mathrm{Cl + O_3 \longrightarrow ClO + O_2}\\&\mathrm{ClO + O \longrightarrow Cl + O_2}\\&\text{overall Reaction: }\mathrm{O_3 + O \longrightarrow 2O_2}\end{aligned}$$

A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and $ClONO_2$.

Since receiving his portion of the Nobel Prize, Molina has continued his work in atmospheric chemistry at MIT.

How Sciences Interconnect

Glucose-6-Phosphate Dehydrogenase Deficiency

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in **Figure 17.23**, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (**Figure 17.24**).

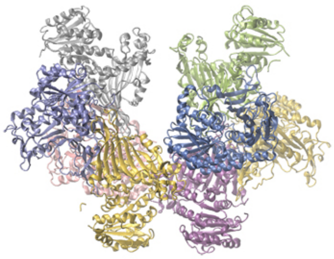


Figure 17.23 Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.

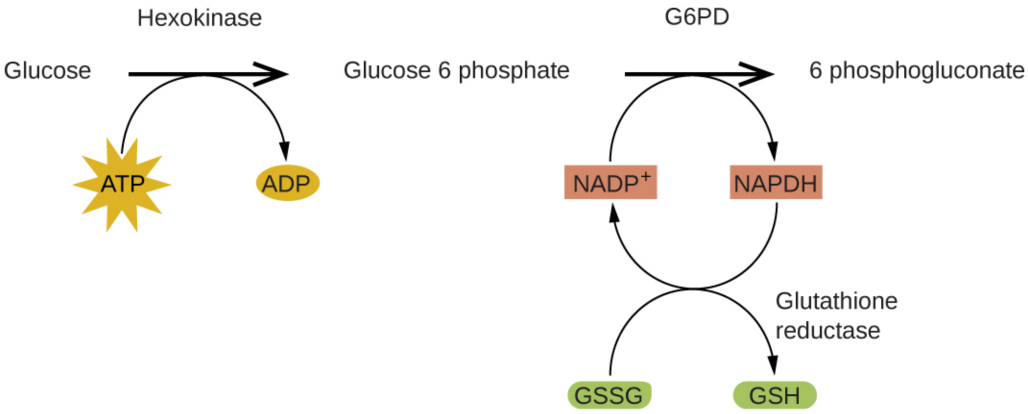


Figure 17.24 In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

Heterogeneous Catalysts

A **heterogeneous catalyst** is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. Gas and liquid phase

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2. “The Nobel Prize in Chemistry 1995,” Nobel Prize.org, accessed February 18, 2015, http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1995/.

reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

Heterogeneous catalysis typically involves the following processes:

1. Adsorption of the reactant(s) onto the surface of the catalyst
2. Activation of the adsorbed reactant(s)
3. Reaction of the adsorbed reactant(s)
4. Desorption of product(s) from the surface of the catalyst

Figure 17.25 illustrates the steps of a mechanism for the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).

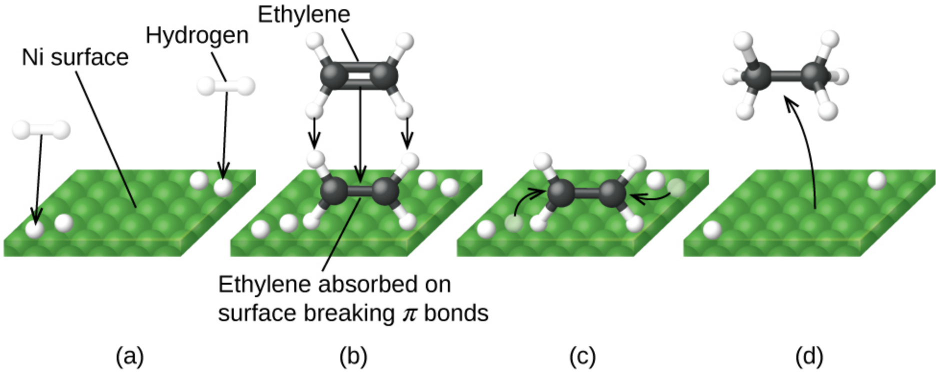


Figure 17.25 Mechanism for the Ni-catalyzed reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the C-C π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d) C_2H_6 molecules desorb from the Ni surface.

Many important chemical products are prepared via industrial processes that use heterogeneous catalysts, including ammonia, nitric acid, sulfuric acid, and methanol. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (**Figure 17.26**).

Chemistry in Everyday Life

Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (**Figure 17.26**).

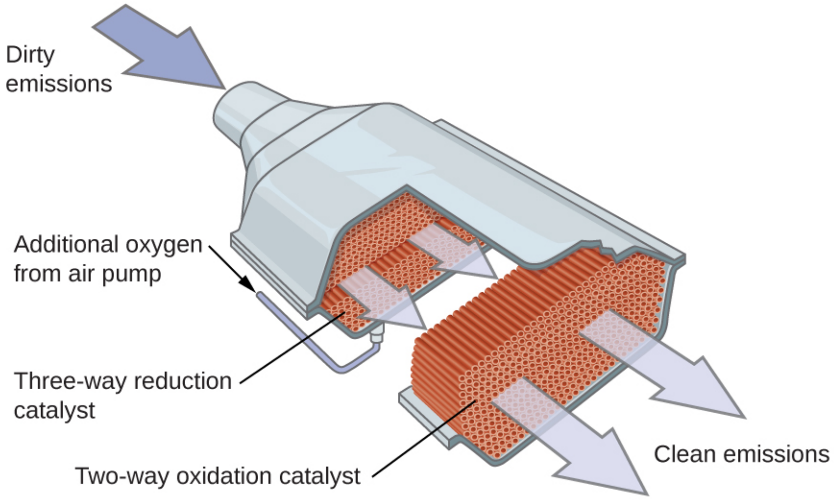


Figure 17.26 A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion of nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

$$2NO_2(g) \longrightarrow N_2(g) + 2O_2(g)$$
$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$
$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

Link to Learning

The University of California at Davis' "ChemWiki" provides a **thorough explanation (http://openstax.org/l/16catconvert)** of how catalytic converters work.

How Sciences Interconnect

Enzyme Structure and Function

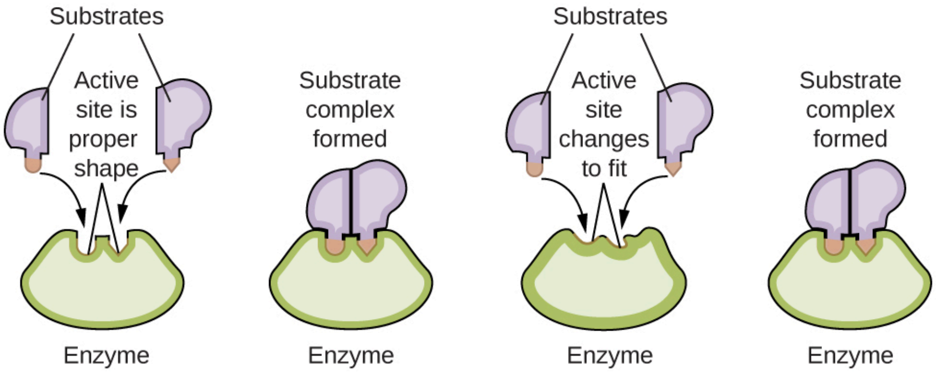
The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in **Table 17.3**.

Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Table 17.3

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (**Figure 17.27**).



(a) Lock-and-key model (b) Induced fit model

Figure 17.27 (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

Link to Learning

The **Royal Society of Chemistry (http://openstax.org/l/16enzymes)** provides an excellent introduction to enzymes for students and teachers.

The connection between the rate of a reaction and its equilibrium constant is one we can easily determine with just a bit of algebraic substitution. For a reaction where substance A forms B (and the reverse)

$$A \rightleftharpoons B$$

The rate of the forward reaction is

$$\text{Rate}(f) = k(f)[A]$$

And the rate of the reverse reaction is

$$\text{Rate}(r) = k(r)[B]$$

Once equilibrium is established, the rates of the forward and reverse reactions are equal:

$$\text{Rate}(f) = \text{Rate}(r) = k(f)[A] = k(r)[B]$$

Rearranging a bit, we get

$$\text{Rate}_f = \text{Rate}_r \text{ so } k\left(f\right)\left[A\right] = k\left(r\right)\left[B\right]$$

Also recall that the equilibrium constant is simply the ratio of product to reactant concentration at equilibrium:

$$\frac{k(f)}{k(r)} = \frac{[B]}{[A]}$$

$$K = \frac{[B]}{[A]}$$

So the equilibrium constant turns out to be the ratio of the forward to the reverse rate constants. This relationship also helps cement our understanding of the nature of a catalyst. That is, a catalyst does not change the fundamental equilibrium (or the underlying thermodynamics) of a reaction. Rather, what it does is alter the rate constant for the reaction – that is, both rate constants, forward and reverse, equally. In doing so, catalysts usually speed up the rate at which reactions attain equilibrium (though they can be used to slow down the rate of reaction as well!).

Key Terms

activated complex (also, transition state) unstable combination of reactant species formed during a chemical reaction

activation energy (E_a) minimum energy necessary in order for a reaction to take place

Arrhenius equation mathematical relationship between a reaction's rate constant, activation energy, and temperature

average rate rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

bimolecular reaction elementary reaction involving two reactant species

catalyst substance that increases the rate of a reaction without itself being consumed by the reaction

collision theory model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

elementary reaction reaction that takes place in a single step, precisely as depicted in its chemical equation

frequency factor (A) proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

half-life of a reaction ($t_{1/2}$) time required for half of a given amount of reactant to be consumed

heterogeneous catalyst catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

homogeneous catalyst catalyst present in the same phase as the reactants

initial rate instantaneous rate of a chemical reaction at $t = 0$ s (immediately after the reaction has begun)

instantaneous rate rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

integrated rate law equation that relates the concentration of a reactant to elapsed time of reaction

intermediate species produced in one step of a reaction mechanism and consumed in a subsequent step

method of initial rates common experimental approach to determining rate laws that involves measuring reaction rates at varying initial reactant concentrations

molecularity number of reactant species involved in an elementary reaction

overall reaction order sum of the reaction orders for each substance represented in the rate law

rate constant (k) proportionality constant in a rate law

rate expression mathematical representation defining reaction rate as change in amount, concentration, or pressure of reactant or product species per unit time

rate law (also, rate equation) (also, differential rate laws) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

rate of reaction measure of the speed at which a chemical reaction takes place

rate-determining step (also, rate-limiting step) slowest elementary reaction in a reaction mechanism; determines the rate of the overall reaction

reaction diagram used in chemical kinetics to illustrate various properties of a reaction

reaction mechanism stepwise sequence of elementary reactions by which a chemical change takes place

reaction order value of an exponent in a rate law (for example, zero order for 0, first order for 1, second order for 2, and so on)

termolecular reaction elementary reaction involving three reactant species

unimolecular reaction elementary reaction involving a single reactant species

Key Equations

- relative reaction rates for $a\text{A} \longrightarrow b\text{B} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = \frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t}$
- integrated rate law for zero-order reactions: $[A]_t = -kt + [A]_0$,
- half-life for a ___-order reaction $t_{1/2} = \frac{[A]_0}{2k}$
- integrated rate law for first-order reactions: $\ln[A]_t = -kt + \ln[A]_0$,
- half-life for a ___-order reaction $t_{1/2} = \frac{0.693}{k}$
- integrated rate law for second-order reactions: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$,
- half-life for a ___-order reaction $t_{1/2} = \frac{1}{[A]_0 k}$
- $k = Ae^{-E_\text{a}/RT}$
- $\ln k = \left(\frac{-E_\text{a}}{R}\right)\left(\frac{1}{T}\right) + \ln A$
- $\ln\frac{k_1}{k_2} = \frac{E_\text{a}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Summary

17.1 Chemical Reaction Rates

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction.

17.2 Factors Affecting Reaction Rates

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway with a lower activation energy.

17.3 Rate Laws

Rate laws (*differential rate laws*) provide a mathematical description of how changes in the concentration of a substance affect the rate of a chemical reaction. Rate laws are determined experimentally and cannot be predicted by reaction stoichiometry. The order of reaction describes how much a change in the concentration of each substance affects the overall rate, and the overall order of a reaction is the sum of the orders for each substance present in the reaction. Reaction orders are typically first order, second order, or zero order, but fractional and even negative orders are possible.

17.4 Integrated Rate Laws

Integrated rate laws are mathematically derived from differential rate laws, and they describe the time dependence of reactant and product concentrations.

The half-life of a reaction is the time required to decrease the amount of a given reactant by one-half. A reaction's half-life varies with rate constant and, for some reaction orders, reactant concentration. The half-life of a zero-order reaction decreases as the initial concentration of the reactant in the reaction decreases. The half-life of a first-order reaction is independent of concentration, and the half-life of a second-order reaction decreases as the concentration increases.

17.5 Collision Theory

Chemical reactions typically require collisions between reactant species. These reactant collisions must be of proper orientation and sufficient energy in order to result in product formation. Collision theory provides a simple but effective explanation for the effect of many experimental parameters on reaction rates. The Arrhenius equation describes the relation between a reaction's rate constant, activation energy, temperature, and dependence on collision orientation.

17.6 Reaction Mechanisms

The sequence of individual steps, or elementary reactions, by which reactants are converted into products during the course of a reaction is called the reaction mechanism. The molecularity of an elementary reaction is the number of reactant species involved, typically one (unimolecular), two (bimolecular), or, less commonly, three (termolecular). The overall rate of a reaction is determined by the rate of the slowest in its mechanism, called the rate-determining step. Unimolecular elementary reactions have first-order rate laws, while bimolecular elementary reactions have second-order rate laws. By comparing the rate laws derived from a reaction mechanism to that determined experimentally, the mechanism may be deemed either incorrect or plausible.

17.7 Catalysis

Catalysts affect the rate of a chemical reaction by altering its mechanism to provide a lower activation energy, but they do not affect equilibrium. Catalysts can be homogenous (in the same phase as the reactants) or heterogeneous (a different phase than the reactants).

Exercises

17.1 Chemical Reaction Rates

1. What is the difference between average rate, initial rate, and instantaneous rate?

2. Ozone decomposes to oxygen according to the equation $2O_3(g) \longrightarrow 3O_2(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

3. In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $Cl_2(g) + 3F_2(g) \longrightarrow 2ClF_3(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3.

4. A study of the rate of dimerization of C_4H_6 gave the data shown in the table:

$$2C_4H_6 \longrightarrow C_8H_{12}$$

Time (s)	0	1600	3200	4800	6200
$[C_4H_6]$ (*M*)	1.00×10^{-2}	5.04×10^{-3}	3.37×10^{-3}	2.53×10^{-3}	2.08×10^{-3}

(a) Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.

(b) Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus $[C_4H_6]$. What are the units of this rate?

(c) Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

5. A study of the rate of the reaction represented as $2A \longrightarrow B$ gave the following data:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
$[A]$ (*M*)	1.00	0.775	0.625	0.465	0.360	0.285	0.230

(a) Determine the average rate of disappearance of *A* between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.

(b) Estimate the instantaneous rate of disappearance of *A* at 15.0 s from a graph of time versus [*A*]. What are the units of this rate?

(c) Use the rates found in parts (a) and (b) to determine the average rate of formation of *B* between 0.00 s and 10.0 s, and the instantaneous rate of formation of *B* at 15.0 s.

6. Consider the following reaction in aqueous solution:

$$5Br^{-}(aq) + BrO_3{}^{-}(aq) + 6H^{+}(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

If the rate of disappearance of $Br^{-}(aq)$ at a particular moment during the reaction is 3.5×10^{-4} mol L^{-1} s^{-1}, what is the rate of appearance of $Br_2(aq)$ at that moment?

17.2 Factors Affecting Reaction Rates

7. Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

8. Explain why an egg cooks more slowly in boiling water in Denver than in New York City. (Hint: Consider the effect of temperature on reaction rate and the effect of pressure on boiling point.)

9. Go to the **PhET Reactions & Rates (http://openstaxcollege.org/l/16PHETreaction)** interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red plunger to release the atom and observe the results. Then, click on “Reload Launcher” and change to “Angled shot” to see the difference.

(a) What happens when the angle of the collision is changed?

(b) Explain how this is relevant to rate of reaction.

10. In the **PhET Reactions & Rates (http://openstaxcollege.org/l/16PHETreaction)** interactive, use the “Many Collisions” tab to observe how multiple atoms and molecules interact under varying conditions. Select a molecule to pump into the chamber. Set the initial temperature and select the current amounts of each reactant. Select “Show bonds” under Options. How is the rate of the reaction affected by concentration and temperature?

11. In the **PhET Reactions & Rates (http://openstaxcollege.org/l/16PHETreaction)** interactive, on the Many Collisions tab, set up a simulation with 15 molecules of A and 10 molecules of BC. Select “Show Bonds” under Options.

(a) Leave the Initial Temperature at the default setting. Observe the reaction. Is the rate of reaction fast or slow?

(b) Click “Pause” and then “Reset All,” and then enter 15 molecules of A and 10 molecules of BC once again. Select “Show Bonds” under Options. This time, increase the initial temperature until, on the graph, the total average energy line is completely above the potential energy curve. Describe what happens to the reaction.

17.3 Rate Laws

12. How do the rate of a reaction and its rate constant differ?

13. Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:

(a) What is the order of the reaction with respect to that reactant?

(b) Tripling the concentration of a different reactant increases the rate of a reaction three times. What is the order of the reaction with respect to that reactant?

14. Tripling the concentration of a reactant increases the rate of a reaction nine-fold. With this knowledge, answer the following questions:

(a) What is the order of the reaction with respect to that reactant?

(b) Increasing the concentration of a reactant by a factor of four increases the rate of a reaction four-fold. What is the order of the reaction with respect to that reactant?

15. How much and in what direction will each of the following affect the rate of the reaction: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\mathrm{NO_2}]^2$?

(a) Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.

(b) Increasing the concentration of CO from 0.01 *M* to 0.03 *M*.

16. How will each of the following affect the rate of the reaction: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\mathrm{NO_2}][\mathrm{CO}]$?

(a) Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm

(b) Increasing the concentration of CO from 0.02 *M* to 0.06 *M*.

17. Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to depletion of the ozone layer. The reaction $\mathrm{NO} + \mathrm{O_3} \longrightarrow \mathrm{NO_2} + \mathrm{O_2}$ is first order with respect to both NO and O_3 with a rate constant of 2.20×10^7 L/mol/s. What is the instantaneous rate of disappearance of NO when [NO] = 3.3×10^{-6} *M* and [O_3] = 5.9×10^{-7} *M*?

18. Radioactive phosphorus is used in the study of biochemical reaction mechanisms because phosphorus atoms are components of many biochemical molecules. The location of the phosphorus (and the location of the molecule it is bound in) can be detected from the electrons (beta particles) it produces:

$${}^{32}_{15}\mathrm{P} \longrightarrow {}^{32}_{16}\mathrm{S} + \mathrm{e}^-$$

$$\text{rate} = 4.85 \times 10^{-2}\ \text{day}^{-1}\left[{}^{32}\mathrm{P}\right]$$

What is the instantaneous rate of production of electrons in a sample with a phosphorus concentration of 0.0033 *M*?

19. The rate constant for the radioactive decay of ^{14}C is 1.21 × 10^{-4} year^{-1}. The products of the decay are nitrogen atoms and electrons (beta particles):

$$^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + \text{e}^{-}$$

$$\text{rate} = k\left[^{14}_{6}\text{C}\right]$$

What is the instantaneous rate of production of N atoms in a sample with a carbon-14 content of 6.5 × 10^{-9} *M*?

20. The decomposition of acetaldehyde is a second order reaction with a rate constant of 4.71 × 10^{-8} L mol^{-1} s^{-1}. What is the instantaneous rate of decomposition of acetaldehyde in a solution with a concentration of 5.55 × 10^{-4} *M*?

21. Alcohol is removed from the bloodstream by a series of metabolic reactions. The first reaction produces acetaldehyde; then other products are formed. The following data have been determined for the rate at which alcohol is removed from the blood of an average male, although individual rates can vary by 25–30%. Women metabolize alcohol a little more slowly than men:

[C_2H_5OH] (*M*)	4.4 × 10^{-2}	3.3 × 10^{-2}	2.2 × 10^{-2}
Rate (mol L^{-1} h^{-1})	2.0 × 10^{-2}	2.0 × 10^{-2}	2.0 × 10^{-2}

Determine the rate law, the rate constant, and the overall order for this reaction.

22. Under certain conditions the decomposition of ammonia on a metal surface gives the following data:

[NH_3] (*M*)	1.0 × 10^{-3}	2.0 × 10^{-3}	3.0 × 10^{-3}
Rate (mol L^{-1} h^{-1})	1.5 × 10^{-6}	1.5 × 10^{-6}	1.5 × 10^{-6}

Determine the rate law, the rate constant, and the overall order for this reaction.

23. Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.

$$2\text{NOCl}(g) \longrightarrow 2\text{NO}(g) + \text{Cl}_2(g)$$

Determine the rate law, the rate constant, and the overall order for this reaction from the following data:

[NOCl] (*M*)	0.10	0.20	0.30
Rate (mol L^{-1} h^{-1})	8.0 × 10^{-10}	3.2 × 10^{-9}	7.2 × 10^{-9}

24. From the following data, determine the rate law, the rate constant, and the order with respect to *A* for the reaction $A \longrightarrow 2C$.

[*A*] (*M*)	1.33 × 10^{-2}	2.66 × 10^{-2}	3.99 × 10^{-2}
Rate (mol L^{-1} h^{-1})	3.80 × 10^{-7}	1.52 × 10^{-6}	3.42 × 10^{-6}

25. Nitrogen monoxide reacts with chlorine according to the equation:
$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$

The following initial rates of reaction have been observed for certain reactant concentrations:

[NO] (mol/L^1)	[Cl_2] (mol/L)	Rate (mol L^{-1} h^{-1})
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate law that describes the rate's dependence on the concentrations of NO and Cl_2? What is the rate constant? What are the orders with respect to each reactant?

26. Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation: $H_2(g) + 2NO(g) \longrightarrow N_2O(g) + H_2O(g)$

Determine the rate law, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (*M*)	0.30	0.60	0.60
[H_2] (*M*)	0.35	0.35	0.70
Rate (mol L^{-1} s^{-1})	2.835×10^{-3}	1.134×10^{-2}	2.268×10^{-2}

27. For the reaction $A \longrightarrow B + C,$ the following data were obtained at 30 °C:

[*A*] (*M*)	0.230	0.356	0.557
Rate (mol L^{-1} s^{-1})	4.17×10^{-4}	9.99×10^{-4}	2.44×10^{-3}

(a) What is the order of the reaction with respect to [*A*], and what is the rate law?

(b) What is the rate constant?

28. For the reaction $Q \longrightarrow W + X,$ the following data were obtained at 30 °C:

[*Q*]$_{\text{initial}}$ (*M*)	0.170	0.212	0.357
Rate (mol L^{-1} s^{-1})	6.68×10^{-3}	1.04×10^{-2}	2.94×10^{-2}

(a) What is the order of the reaction with respect to [*Q*], and what is the rate law?

(b) What is the rate constant?

29. The rate constant for the first-order decomposition at 45 °C of dinitrogen pentoxide, N_2O_5, dissolved in chloroform, $CHCl_3$, is 6.2×10^{-4} min^{-1}.
$2N_2O_5 \longrightarrow 4NO_2 + O_2$

What is the rate of the reaction when [N_2O_5] = 0.40 *M*?

30. The annual production of HNO_3 in 2013 was 60 million metric tons Most of that was prepared by the following sequence of reactions, each run in a separate reaction vessel.

(a) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

(b) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(c) $3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$

The first reaction is run by burning ammonia in air over a platinum catalyst. This reaction is fast. The reaction in equation (c) is also fast. The second reaction limits the rate at which nitric acid can be prepared from ammonia. If equation (b) is second order in NO and first order in O_2, what is the rate of formation of NO_2 when the oxygen concentration is 0.50 *M* and the nitric oxide concentration is 0.75 *M*? The rate constant for the reaction is 5.8×10^{-6} L^2 mol^{-2} s^{-1}.

31. The following data have been determined for the reaction:
$I^- + OCl^- \longrightarrow IO^- + Cl^-$

	1	2	3
$[I^-]_{initial}$ (*M*)	0.10	0.20	0.30
$[OCl^-]_{initial}$ (*M*)	0.050	0.050	0.010
Rate (mol L^{-1} s^{-1})	3.05×10^{-4}	6.20×10^{-4}	1.83×10^{-4}

Determine the rate law and the rate constant for this reaction.

17.4 Integrated Rate Laws

32. Describe how graphical methods can be used to determine the order of a reaction and its rate constant from a series of data that includes the concentration of *A* at varying times.

33. Use the data provided to graphically determine the order and rate constant of the following reaction:
$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

Time (s)	0	5.00×10^3	1.00×10^4	1.50×10^4
$[SO_2Cl_2]$ (*M*)	0.100	0.0896	0.0802	0.0719
Time (s)	2.50×10^4	3.00×10^4	4.00×10^4	
$[SO_2Cl_2]$ (*M*)	0.0577	0.0517	0.0415	

34. Pure ozone decomposes slowly to oxygen, $2O_3(g) \longrightarrow 3O_2(g)$. Use the data provided in a graphical method and determine the order and rate constant of the reaction.

Time (h)	0	2.0×10^3	7.6×10^3	1.00×10^4
$[O_3]$ (*M*)	1.00×10^{-5}	4.98×10^{-6}	2.07×10^{-6}	1.66×10^{-6}
Time (h)	1.23×10^4	1.43×10^4	1.70×10^4	
$[O_3]$ (*M*)	1.39×10^{-6}	1.22×10^{-6}	1.05×10^{-6}	

35. From the given data, use a graphical method to determine the order and rate constant of the following reaction: $2X \longrightarrow Y + Z$

Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
[*X*] (*M*)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125

36. What is the half-life for the first-order decay of phosphorus-32? $\left({}^{32}_{15}\text{P} \longrightarrow {}^{32}_{16}\text{S} + \text{e}^{-}\right)$ The rate constant for the decay is 4.85×10^{-2} day^{-1}.

37. What is the half-life for the first-order decay of carbon-14? $\left({}^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + \text{e}^{-}\right)$ The rate constant for the decay is 1.21×10^{-4} year^{-1}.

38. What is the half-life for the decomposition of NOCl when the concentration of NOCl is 0.15 *M*? The rate constant for this second-order reaction is 8.0×10^{-8} L mol^{-1} s^{-1}.

39. What is the half-life for the decomposition of O_3 when the concentration of O_3 is 2.35×10^{-6} *M*? The rate constant for this second-order reaction is 50.4 L mol^{-1} h^{-1}.

40. The reaction of compound *A* to give compounds *C* and *D* was found to be second-order in *A*. The rate constant for the reaction was determined to be 2.42 L mol^{-1} s^{-1}. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

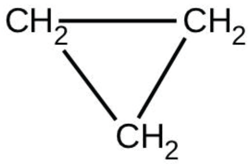
41. The half-life of a reaction of compound *A* to give compounds *D* and *E* is 8.50 min when the initial concentration of *A* is 0.150 M. How long will it take for the concentration to drop to 0.0300 M if the reaction is (a) first order with respect to *A* or (b) second order with respect to *A*?

42. Some bacteria are resistant to the antibiotic penicillin because they produce penicillinase, an enzyme with a molecular weight of 3×10^4 g/mol that converts penicillin into inactive molecules. Although the kinetics of enzyme-catalyzed reactions can be complex, at low concentrations this reaction can be described by a rate law that is first order in the catalyst (penicillinase) and that also involves the concentration of penicillin. From the following data: 1.0 L of a solution containing 0.15 µg (0.15×10^{-6} g) of penicillinase, determine the order of the reaction with respect to penicillin and the value of the rate constant.

[Penicillin] (*M*)	Rate (mol L^{-1} min^{-1})
2.0×10^{-6}	1.0×10^{-10}
3.0×10^{-6}	1.5×10^{-10}
4.0×10^{-6}	2.0×10^{-10}

43. Both technetium-99 and thallium-201 are used to image heart muscle in patients with suspected heart problems. The half-lives are 6 h and 73 h, respectively. What percent of the radioactivity would remain for each of the isotopes after 2 days (48 h)?

44. There are two molecules with the formula C_3H_6. Propene, $CH_3CH = CH_2$, is the monomer of the polymer polypropylene, which is used for indoor-outdoor carpets. Cyclopropane is used as an anesthetic:



When heated to 499 °C, cyclopropane rearranges (isomerizes) and forms propene with a rate constant of $5.95 \times 10^{-4}\ s^{-1}$. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

45. Fluorine-18 is a radioactive isotope that decays by positron emission to form oxygen-18 with a half-life of 109.7 min. (A positron is a particle with the mass of an electron and a single unit of positive charge; the equation is $^{18}_{9}F \longrightarrow {}^{8}_{18}O + {}^{0}_{+1}e$) Physicians use ^{18}F to study the brain by injecting a quantity of fluoro-substituted glucose into the blood of a patient. The glucose accumulates in the regions where the brain is active and needs nourishment.

(a) What is the rate constant for the decomposition of fluorine-18?

(b) If a sample of glucose containing radioactive fluorine-18 is injected into the blood, what percent of the radioactivity will remain after 5.59 h?

(c) How long does it take for 99.99% of the ^{18}F to decay?

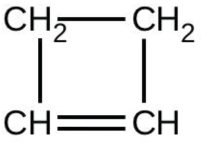
46. Suppose that the half-life of steroids taken by an athlete is 42 days. Assuming that the steroids biodegrade by a first-order process, how long would it take for $\frac{1}{64}$ of the initial dose to remain in the athlete's body?

47. Recently, the skeleton of King Richard III was found under a parking lot in England. If tissue samples from the skeleton contain about 93.79% of the carbon-14 expected in living tissue, what year did King Richard III die? The half-life for carbon-14 is 5730 years.

48. Nitroglycerine is an extremely sensitive explosive. In a series of carefully controlled experiments, samples of the explosive were heated to 160 °C and their first-order decomposition studied. Determine the average rate constants for each experiment using the following data:

Initial [$C_3H_5N_3O_9$] (*M*)	4.88	3.52	2.29	1.81	5.33	4.05	2.95	1.72
t (s)	300	300	300	300	180	180	180	180
% Decomposed	52.0	52.9	53.2	53.9	34.6	35.9	36.0	35.4

49. For the past 10 years, the unsaturated hydrocarbon 1,3-butadiene $(CH_2 = CH – CH = CH_2)$ has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. An isomer exists also as cyclobutene:



The isomerization of cyclobutene to butadiene is first-order and the rate constant has been measured as 2.0×10^{-4} s^{-1} at 150 °C in a 0.53-L flask. Determine the partial pressure of cyclobutene and its concentration after 30.0 minutes if an isomerization reaction is carried out at 150 °C with an initial pressure of 55 torr.

17.5 Collision Theory

50. Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

51. When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

52. What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

53. Account for the relationship between the rate of a reaction and its activation energy.

54. Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

55. How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

56. The rate of a certain reaction doubles for every 10 °C rise in temperature.

(a) How much faster does the reaction proceed at 45 °C than at 25 °C?

(b) How much faster does the reaction proceed at 95 °C than at 25 °C?

57. In an experiment, a sample of $NaClO_3$ was 90% decomposed in 48 min. Approximately how long would this decomposition have taken if the sample had been heated 20 °C higher? (Hint: Assume the rate doubles for each 10 °C rise in temperature.)

58. The rate constant at 325 °C for the decomposition reaction $C_4H_8 \longrightarrow 2C_2H_4$ is 6.1×10^{-8} s^{-1}, and the activation energy is 261 kJ per mole of C_4H_8. Determine the frequency factor for the reaction.

59. The rate constant for the decomposition of acetaldehyde, CH_3CHO, to methane, CH_4, and carbon monoxide, CO, in the gas phase is 1.1×10^{-2} L mol^{-1} s^{-1} at 703 K and 4.95 L mol^{-1} s^{-1} at 865 K. Determine the activation energy for this decomposition.

60. An elevated level of the enzyme alkaline phosphatase (ALP) in human serum is an indication of possible liver or bone disorder. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration can be determined by measuring the rate of one of these reactions under controlled conditions. One such reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy for the ALP–catalyzed conversion of PNPP to PNP and phosphate?

61. In terms of collision theory, to which of the following is the rate of a chemical reaction proportional?

(a) the change in free energy per second

(b) the change in temperature per second

(c) the number of collisions per second

(d) the number of product molecules

62. Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, H_2, and iodine, I_2. The value of the rate constant, *k*, for the reaction was measured at several different temperatures and the data are shown here:

Temperature (K)	*k* (L mol^{-1} s^{-1})
555	6.23×10^{-7}
575	2.42×10^{-6}
645	1.44×10^{-4}
700	2.01×10^{-3}

What is the value of the activation energy (in kJ/mol) for this reaction?

63. The element Co exists in two oxidation states, Co(II) and Co(III), and the ions form many complexes. The rate at which one of the complexes of Co(III) was reduced by Fe(II) in water was measured. Determine the activation energy of the reaction from the following data:

T (K)	*k* (s^{-1})
293	0.054
298	0.100

64. The hydrolysis of the sugar sucrose to the sugars glucose and fructose,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

follows a first-order rate law for the disappearance of sucrose: rate = $k[C_{12}H_{22}O_{11}]$ (The products of the reaction, glucose and fructose, have the same molecular formulas but differ in the arrangement of the atoms in their molecules.)

(a) In neutral solution, $k = 2.1 \times 10^{-11}$ s^{-1} at 27 °C and 8.5×10^{-11} s^{-1} at 37 °C. Determine the activation energy, the frequency factor, and the rate constant for this equation at 47 °C (assuming the kinetics remain consistent with the Arrhenius equation at this temperature).

(b) When a solution of sucrose with an initial concentration of 0.150 *M* reaches equilibrium, the concentration of sucrose is 1.65×10^{-7} *M*. How long will it take the solution to reach equilibrium at 27 °C in the absence of a catalyst? Because the concentration of sucrose at equilibrium is so low, assume that the reaction is irreversible.

(c) Why does assuming that the reaction is irreversible simplify the calculation in part (b)?

65. Use the **PhET Reactions & Rates interactive simulation (http://openstaxcollege.org/l/16PHETreaction)** to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “straight shot” default option, try launching the *A* atom with varying amounts of energy. What changes when the Total Energy line at launch is below the transition state of the Potential Energy line? Why? What happens when it is above the transition state? Why?

66. Use the **PhET Reactions & Rates interactive simulation (http://openstaxcollege.org/l/16PHETreaction)** to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “angled shot” option, try launching the *A* atom with varying angles, but with more Total energy than the transition state. What happens when the *A* atom hits the *BC* molecule from different directions? Why?

17.6 Reaction Mechanisms

67. Why are elementary reactions involving three or more reactants very uncommon?

68. In general, can we predict the effect of doubling the concentration of *A* on the rate of the overall reaction $A + B \longrightarrow C$? Can we predict the effect if the reaction is known to be an elementary reaction?

69. Define these terms:

(a) unimolecular reaction

(b) bimolecular reaction

(c) elementary reaction

(d) overall reaction

70. What is the rate law for the elementary termolecular reaction $A + 2B \longrightarrow \text{products}$? For $3A \longrightarrow \text{products}$?

71. Given the following reactions and the corresponding rate laws, in which of the reactions might the elementary reaction and the overall reaction be the same?

(a) $Cl_2 + CO \longrightarrow Cl_2CO$
rate $= k[Cl_2]^{3/2}[CO]$

(b) $PCl_3 + Cl_2 \longrightarrow PCl_5$
rate $= k[PCl_3][Cl_2]$

(c) $2NO + H_2 \longrightarrow N_2 + H_2O$
rate $= k[NO][H_2]$

(d) $2NO + O_2 \longrightarrow 2NO_2$
rate $= k[NO]^2[O_2]$

(e) $NO + O_3 \longrightarrow NO_2 + O_2$
rate $= k[NO][O_3]$

72. Write the rate law for each of the following elementary reactions:

(a) $O_3 \xrightarrow{\text{sunlight}} O_2 + O$

(b) $O_3 + Cl \longrightarrow O_2 + ClO$

(c) $ClO + O \longrightarrow Cl + O_2$

(d) $O_3 + NO \longrightarrow NO_2 + O_2$

(e) $NO_2 + O \longrightarrow NO + O_2$

73. Nitrogen monoxide, NO, reacts with hydrogen, H_2, according to the following equation:
$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$

What would the rate law be if the mechanism for this reaction were:
$2NO + H_2 \longrightarrow N_2 + H_2O_2$ (slow)
$H_2O_2 + H_2 \longrightarrow 2H_2O$ (fast)

74. Experiments were conducted to study the rate of the reaction represented by this equation.[3]

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

Initial concentrations and rates of reaction are given here.

Experiment	Initial Concentration [NO] (mol L^{-1})	Initial Concentration, [H_2] (mol L^{-1} min^{-1})	Initial Rate of Formation of N_2 (mol L^{-1} min^{-1})
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

Consider the following questions:

(a) Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.

(b) Write the overall rate law for the reaction.

(c) Calculate the value of the rate constant, *k*, for the reaction. Include units.

(d) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 had been consumed.

(e) The following sequence of elementary steps is a proposed mechanism for the reaction.

Step 1: $NO + NO \rightleftharpoons N_2O_2$

Step 2: $N_2O_2 + H_2 \rightleftharpoons H_2O + N_2O$

Step 3: $N_2O + H_2 \rightleftharpoons N_2 + H_2O$

Based on the data presented, which of these is the rate determining step? Show that the mechanism is consistent with the observed rate law for the reaction and the overall stoichiometry of the reaction.

75. The reaction of CO with Cl_2 gives phosgene ($COCl_2$), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:

$Cl_2(g) \rightleftharpoons 2Cl(g)$ (fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)
$CO(g) + Cl(g) \longrightarrow COCl(g)$ (slow, k_2 the rate constant)
$COCl(g) + Cl(g) \longrightarrow COCl_2(g)$ (fast, k_3 the rate constant)

(a) Write the overall reaction.

(b) Identify all intermediates.

(c) Write the rate law for each elementary reaction.

(d) Write the overall rate law expression.

17.7 Catalysis

76. Account for the increase in reaction rate brought about by a catalyst.

77. Compare the functions of homogeneous and heterogeneous catalysts.

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[3] This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

78. Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as CCl_2F_2, catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:

$$O_3 \xrightarrow{\text{sunlight}} O_2 + O$$

$$O_3 + Cl \longrightarrow O_2 + ClO$$
$$ClO + O \longrightarrow Cl + O_2$$

(a) Explain why chlorine atoms are catalysts in the gas-phase transformation:
$2O_3 \longrightarrow 3O_2$

(b) Nitric oxide is also involved in the decomposition of ozone by the mechanism:

$$O_3 \xrightarrow{\text{sunlight}} O_2 + O$$

$$O_3 + NO \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$

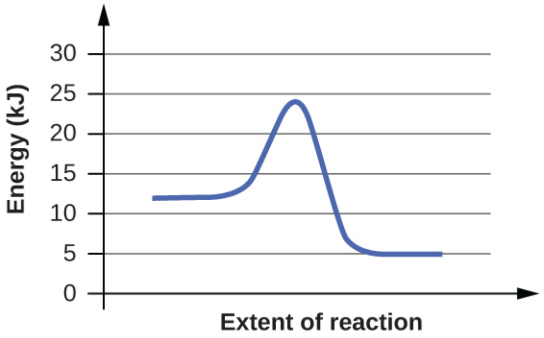
Is NO a catalyst for the decomposition? Explain your answer.

79. Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction: $H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$. Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

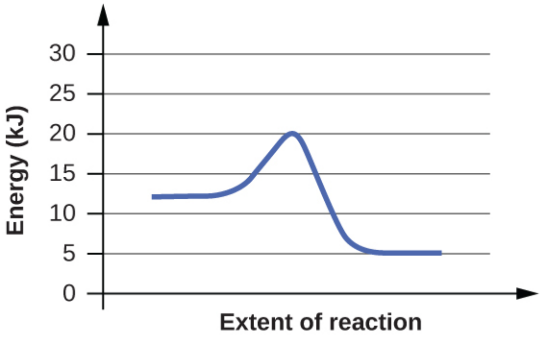
80. Nitrogen and oxygen react at high temperatures. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?

81. For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

(a)

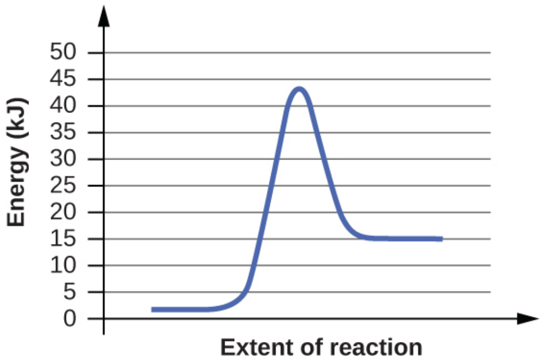


(a)

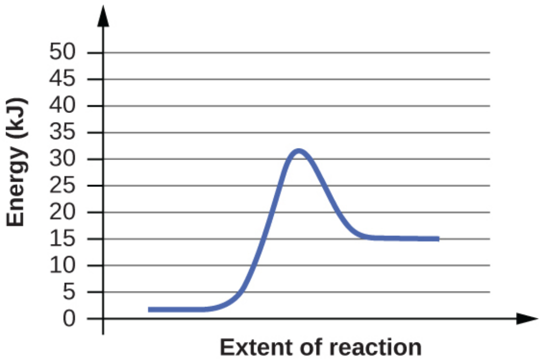


(b)

(b)



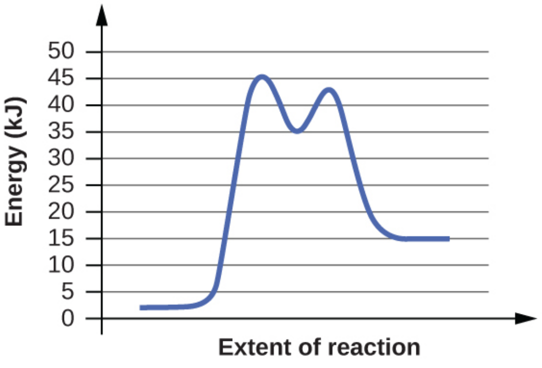
(a)



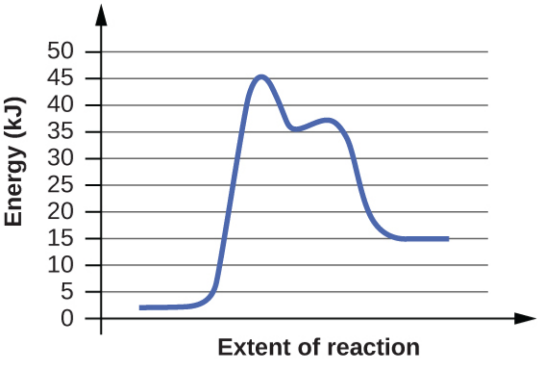
(b)

82. For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

(a)

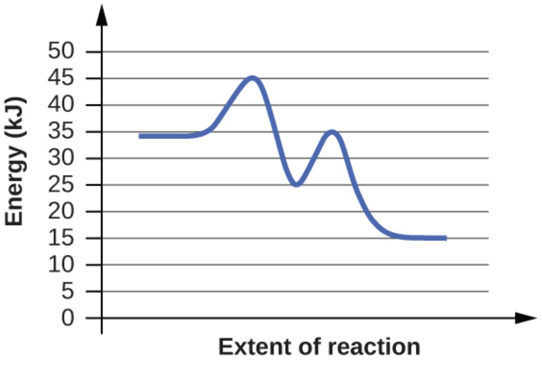


(a)

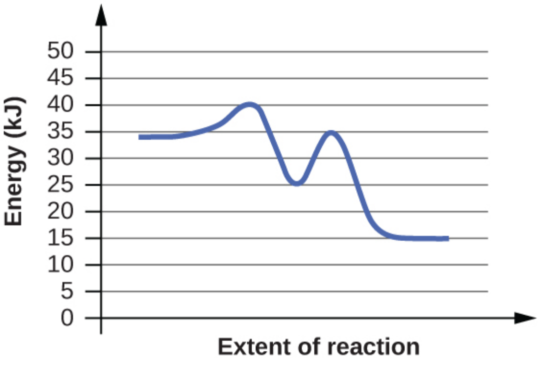


(b)

(b)



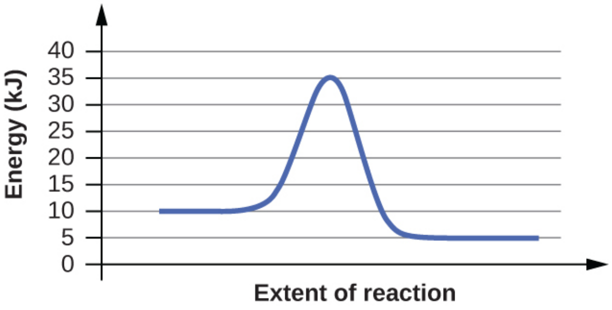
(a)



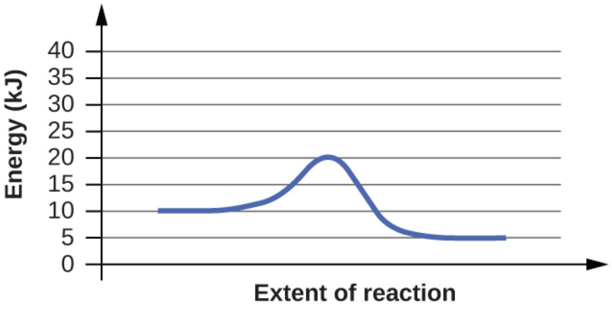
(b)

83. For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)

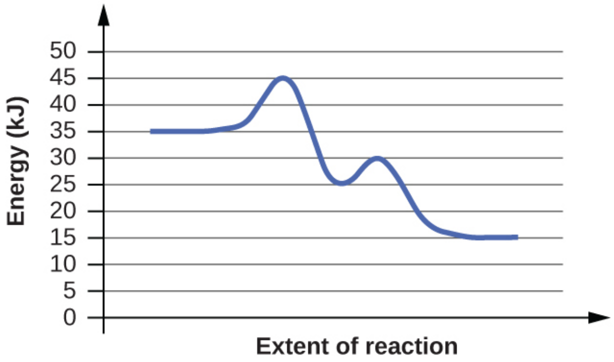


(b)

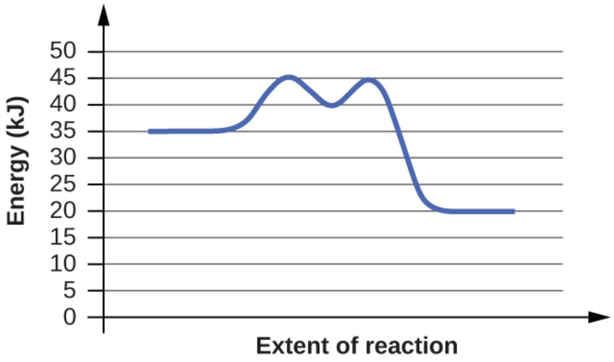


84. For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)



85. Assuming the diagrams in **Exercise 17.83** represent different mechanisms for the same reaction, which of the reactions has the faster rate?

86. Consider the similarities and differences in the two reaction diagrams shown in **Exercise 17.84**. Do these diagrams represent two different overall reactions, or do they represent the same overall reaction taking place by two different mechanisms? Explain your answer.

Chapter 18

Representative Metals, Metalloids, and Nonmetals

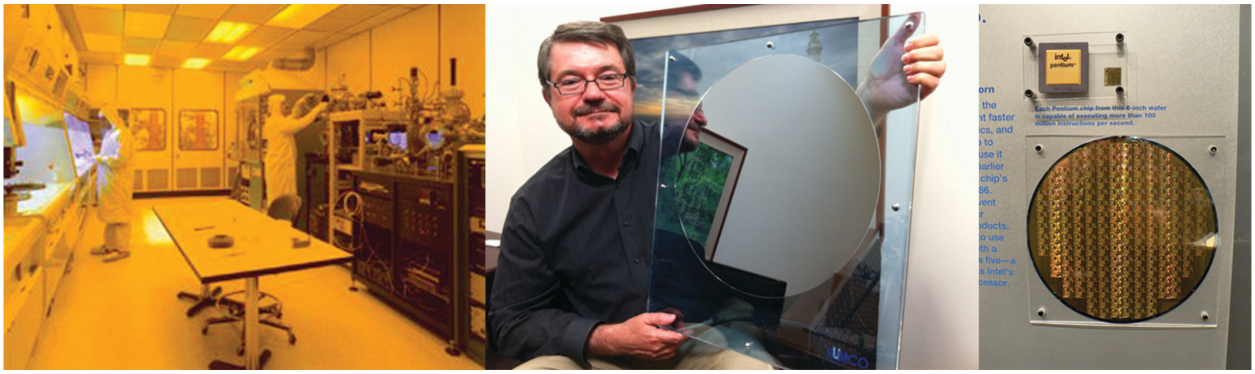


Figure 18.1 Purity is extremely important when preparing silicon wafers. Technicians in a cleanroom prepare silicon without impurities (left). The CEO of VLSI Research, Don Hutcheson, shows off a pure silicon wafer (center). A silicon wafer covered in Pentium chips is an enlarged version of the silicon wafers found in many electronics used today (right). (credit middle: modification of work by “Intel Free Press”/Flickr; credit right: modification of work by Naotake Murayama)

Chapter Outline

Introduction

The development of the periodic table in the mid-1800s came from observations that there was a periodic relationship between the properties of the elements. Chemists, who have an understanding of the variations of these properties, have been able to use this knowledge to solve a wide variety of technical challenges. For example, silicon and other semiconductors form the backbone of modern electronics because of our ability to fine-tune the electrical properties of these materials. This chapter explores important properties of representative metals, metalloids, and nonmetals in the periodic table.

18.1 Periodicity

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

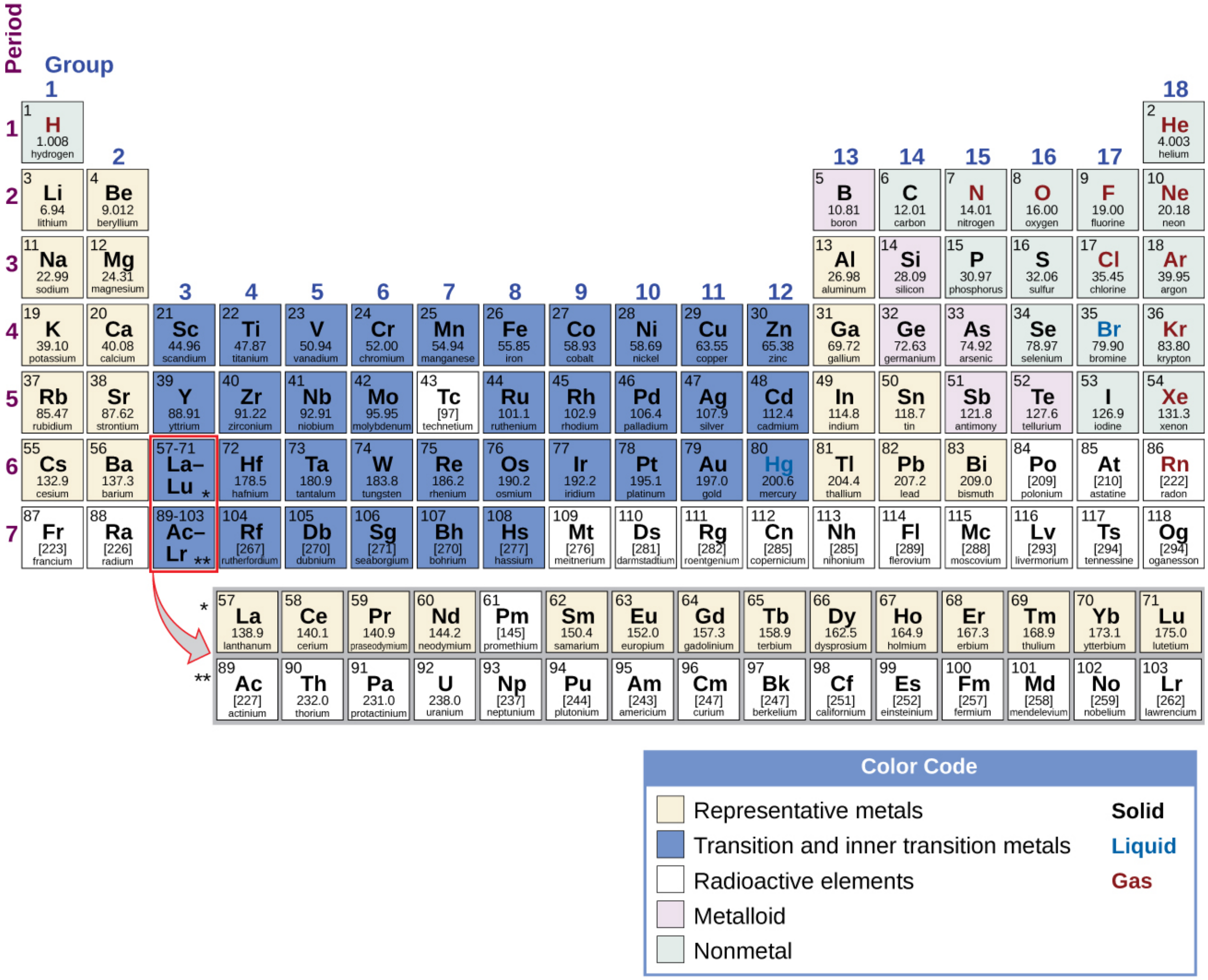
- Classify elements
- Make predictions about the periodicity properties of the representative elements

We begin this section by examining the behaviors of representative metals in relation to their positions in the periodic table. The primary focus of this section will be the application of periodicity to the representative metals.

It is possible to divide elements into groups according to their electron configurations. The **representative elements** are elements where the *s* and *p* orbitals are filling. The transition elements are elements where the *d* orbitals (groups 3–11 on the periodic table) are filling, and the inner transition metals are the elements where the *f* orbitals are filling. The *d* orbitals fill with the elements in group 11; therefore, the elements in group 12 qualify as representative elements because the last electron enters an *s* orbital. Metals among the representative elements are the **representative metals**. Metallic character results from an element's ability to lose its outer valence electrons and results in high thermal and electrical conductivity, among other physical and chemical properties. There are 20 nonradioactive representative metals in groups 1, 2, 3, 12, 13, 14, and 15 of the periodic table (the elements shaded in yellow in **Figure 18.2**). The radioactive elements copernicium, flerovium, polonium, and livermorium are also metals but are beyond the scope of this chapter.

In addition to the representative metals, some of the representative elements are metalloids. A **metalloid** is an element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors.

The remaining representative elements are nonmetals. Unlike **metals**, which typically form cations and ionic compounds (containing ionic bonds), nonmetals tend to form anions or molecular compounds. In general, the combination of a metal and a nonmetal produces a salt. A salt is an ionic compound consisting of cations and anions.



Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008 hydrogen																	2 He 4.003 helium
2	3 Li 6.94 lithium	4 Be 9.012 beryllium											5 B 10.81 boron	6 C 12.01 carbon	7 N 14.01 nitrogen	8 O 16.00 oxygen	9 F 19.00 fluorine	10 Ne 20.18 neon
3	11 Na 22.99 sodium	12 Mg 24.31 magnesium											13 Al 26.98 aluminum	14 Si 28.09 silicon	15 P 30.97 phosphorus	16 S 32.06 sulfur	17 Cl 35.45 chlorine	18 Ar 39.95 argon
4	19 K 39.10 potassium	20 Ca 40.08 calcium	21 Sc 44.96 scandium	22 Ti 47.87 titanium	23 V 50.94 vanadium	24 Cr 52.00 chromium	25 Mn 54.94 manganese	26 Fe 55.85 iron	27 Co 58.93 cobalt	28 Ni 58.69 nickel	29 Cu 63.55 copper	30 Zn 65.38 zinc	31 Ga 69.72 gallium	32 Ge 72.63 germanium	33 As 74.92 arsenic	34 Se 78.97 selenium	35 Br 79.90 bromine	36 Kr 83.80 krypton
5	37 Rb 85.47 rubidium	38 Sr 87.62 strontium	39 Y 88.91 yttrium	40 Zr 91.22 zirconium	41 Nb 92.91 niobium	42 Mo 95.95 molybdenum	43 Tc [97] technetium	44 Ru 101.1 ruthenium	45 Rh 102.9 rhodium	46 Pd 106.4 palladium	47 Ag 107.9 silver	48 Cd 112.4 cadmium	49 In 114.8 indium	50 Sn 118.7 tin	51 Sb 121.8 antimony	52 Te 127.6 tellurium	53 I 126.9 iodine	54 Xe 131.3 xenon
6	55 Cs 132.9 cesium	56 Ba 137.3 barium	57-71 La–Lu *	72 Hf 178.5 hafnium	73 Ta 180.9 tantalum	74 W 183.8 tungsten	75 Re 186.2 rhenium	76 Os 190.2 osmium	77 Ir 192.2 iridium	78 Pt 195.1 platinum	79 Au 197.0 gold	80 Hg 200.6 mercury	81 Tl 204.4 thallium	82 Pb 207.2 lead	83 Bi 209.0 bismuth	84 Po [209] polonium	85 At [210] astatine	86 Rn [222] radon
7	87 Fr [223] francium	88 Ra [226] radium	89-103 Ac–Lr **	104 Rf [267] rutherfordium	105 Db [270] dubnium	106 Sg [271] seaborgium	107 Bh [270] bohrium	108 Hs [277] hassium	109 Mt [276] meitnerium	110 Ds [281] darmstadtium	111 Rg [282] roentgenium	112 Cn [285] copernicium	113 Nh [285] nihonium	114 Fl [289] flerovium	115 Mc [288] moscovium	116 Lv [293] livermorium	117 Ts [294] tennessine	118 Og [294] oganesson

*	57 La 138.9 lanthanum	58 Ce 140.1 cerium	59 Pr 140.9 praseodymium	60 Nd 144.2 neodymium	61 Pm [145] promethium	62 Sm 150.4 samarium	63 Eu 152.0 europium	64 Gd 157.3 gadolinium	65 Tb 158.9 terbium	66 Dy 162.5 dysprosium	67 Ho 164.9 holmium	68 Er 167.3 erbium	69 Tm 168.9 thulium	70 Yb 173.1 ytterbium	71 Lu 175.0 lutetium
**	89 Ac [227] actinium	90 Th 232.0 thorium	91 Pa 231.0 protactinium	92 U 238.0 uranium	93 Np [237] neptunium	94 Pu [244] plutonium	95 Am [243] americium	96 Cm [247] curium	97 Bk [247] berkelium	98 Cf [251] californium	99 Es [252] einsteinium	100 Fm [257] fermium	101 Md [258] mendelevium	102 No [259] nobelium	103 Lr [262] lawrencium

Color Code		
🟨	Representative metals	Solid
🟦	Transition and inner transition metals	Liquid
⬜	Radioactive elements	Gas
🟪	Metalloid	
🟩	Nonmetal	

Figure 18.2 The location of the representative metals is shown in the periodic table. Nonmetals are shown in green, metalloids in purple, and the transition metals and inner transition metals in blue.

Most of the representative metals do not occur naturally in an uncombined state because they readily react with water and oxygen in the air. However, it is possible to isolate elemental beryllium, magnesium, zinc, cadmium, mercury, aluminum, tin, and lead from their naturally occurring minerals and use them because they react very slowly with air. Part of the reason why these elements react slowly is that these elements react with air to form a protective coating. The formation of this protective coating is **passivation**. The coating is a nonreactive film of oxide or some other compound. Elemental magnesium, aluminum, zinc, and tin are important in the fabrication of many familiar items, including wire, cookware, foil, and many household and personal objects. Although beryllium, cadmium, mercury, and lead are readily available, there are limitations in their use because of their toxicity.

Group 1: The Alkali Metals

The alkali metals lithium, sodium, potassium, rubidium, cesium, and francium constitute group 1 of the periodic table. Although hydrogen is in group 1 (and also in group 17), it is a nonmetal and deserves separate consideration later in this chapter. The name alkali metal is in reference to the fact that these metals and their oxides react with water to form very basic (alkaline) solutions.

The properties of the alkali metals are similar to each other as expected for elements in the same family. The alkali metals have the largest atomic radii and the lowest first ionization energy in their periods. This combination makes it very easy to remove the single electron in the outermost (valence) shell of each. The easy loss of this valence electron means that these metals readily form stable cations with a charge of 1+. Their reactivity increases with increasing atomic number due to the ease of losing the lone valence electron (decreasing ionization energy). Since oxidation is so easy, the reverse, reduction, is difficult, which explains why it is hard to isolate the elements. The solid alkali metals are very soft; lithium, shown in **Figure 18.3**, has the lowest density of any metal (0.5 g/cm^3).

The alkali metals all react vigorously with water to form hydrogen gas and a basic solution of the metal hydroxide. This means they are easier to oxidize than is hydrogen. As an example, the reaction of lithium with water is:

$$2\text{Li}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{LiOH}(aq) + \text{H}_2(g)$$

Figure 18.3 Lithium floats in paraffin oil because its density is less than the density of paraffin oil.

Alkali metals react directly with all the nonmetals (except the noble gases) to yield binary ionic compounds containing 1+ metal ions. These metals are so reactive that it is necessary to avoid contact with both moisture and oxygen in the air. Therefore, they are stored in sealed containers under mineral oil, as shown in **Figure 18.4**, to prevent contact with air and moisture. The pure metals never exist free (uncombined) in nature due to their high reactivity. In addition, this high reactivity makes it necessary to prepare the metals by electrolysis of alkali metal compounds.

Figure 18.4 To prevent contact with air and water, potassium for laboratory use comes as sticks or beads stored under kerosene or mineral oil, or in sealed containers. (credit: http://images-of-elements.com/potassium.php)

Unlike many other metals, the reactivity and softness of the alkali metals make these metals unsuitable for structural applications. However, there are applications where the reactivity of the alkali metals is an advantage. For example, the production of metals such as titanium and zirconium relies, in part, on the ability of sodium to reduce compounds of these metals. The manufacture of many organic compounds, including certain dyes, drugs, and perfumes, utilizes reduction by lithium or sodium.

Sodium and its compounds impart a bright yellow color to a flame, as seen in **Figure 18.5**. Passing an electrical discharge through sodium vapor also produces this color. In both cases, this is an example of an emission spectrum as discussed in the chapter on electronic structure. Streetlights sometime employ sodium vapor lights because the sodium vapor penetrates fog better than most other light. This is because the fog does not scatter yellow light as much as it scatters white light. The other alkali metals and their salts also impart color to a flame. Lithium creates a bright, crimson color, whereas the others create a pale, violet color.

Figure 18.5 Dipping a wire into a solution of a sodium salt and then heating the wire causes emission of a bright yellow light, characteristic of sodium.

Link to Learning

This video (http://openstaxcollege.org/l/16alkalih2o) demonstrates the reactions of the alkali metals with water.

Group 2: The Alkaline Earth Metals

The **alkaline earth metals** (beryllium, magnesium, calcium, strontium, barium, and radium) constitute group 2 of the periodic table. The name alkaline metal comes from the fact that the oxides of the heavier members of the group react with water to form alkaline solutions. The nuclear charge increases when going from group 1 to group 2. Because of this charge increase, the atoms of the alkaline earth metals are smaller and have higher first ionization energies than the alkali metals within the same period. The higher ionization energy makes the alkaline earth metals less reactive than the alkali metals; however, they are still very reactive elements. Their reactivity increases, as expected, with increasing size and decreasing ionization energy. In chemical reactions, these metals readily lose both valence electrons to form compounds in which they exhibit an oxidation state of 2+. Due to their high reactivity, it is common to produce the alkaline earth metals, like the alkali metals, by electrolysis. Even though the ionization energies are low, the two metals with the highest ionization energies (beryllium and magnesium) do form compounds that exhibit some covalent characters. Like the alkali metals, the heavier alkaline earth metals impart color to a flame. As in the case of the alkali metals, this is part of the emission spectrum of these elements. Calcium and strontium produce shades of red, whereas barium produces a green color.

Magnesium is a silver-white metal that is malleable and ductile at high temperatures. Passivation decreases the reactivity of magnesium metal. Upon exposure to air, a tightly adhering layer of magnesium oxycarbonate forms on the surface of the metal and inhibits further reaction. (The carbonate comes from the reaction of carbon dioxide in the atmosphere.) Magnesium is the lightest of the widely used structural metals, which is why most magnesium production is for lightweight alloys.

Magnesium (shown in **Figure 18.6**), calcium, strontium, and barium react with water and air. At room temperature, barium shows the most vigorous reaction. The products of the reaction with water are hydrogen and the metal hydroxide. The formation of hydrogen gas indicates that the heavier alkaline earth metals are better reducing agents (more easily oxidized) than is hydrogen. As expected, these metals react with both acids and nonmetals to form ionic compounds. Unlike most salts of the alkali metals, many of the common salts of the alkaline earth metals are insoluble in water because of the high lattice energies of these compounds, containing a divalent metal ion.

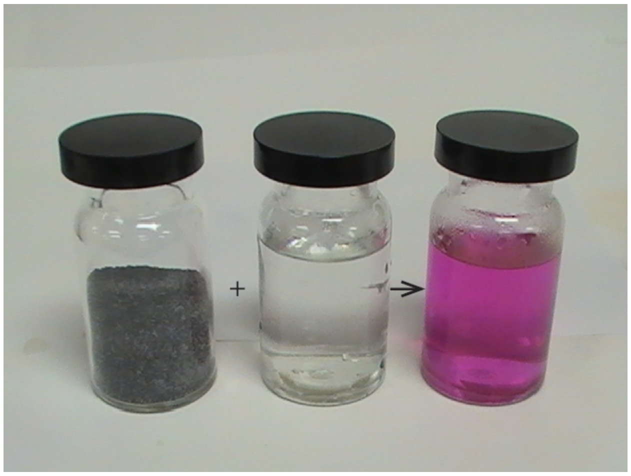


Figure 18.6 From left to right: Mg(*s*), warm water at pH 7, and the resulting solution with a pH greater than 7, as indicated by the pink color of the phenolphthalein indicator. (credit: modification of work by Sahar Atwa)

The potent reducing power of hot magnesium is useful in preparing some metals from their oxides. Indeed, magnesium's affinity for oxygen is so great that burning magnesium reacts with carbon dioxide, producing elemental carbon:

$$2\text{Mg}(s) + \text{CO}_2(g) \longrightarrow 2\text{MgO}(s) + \text{C}(s)$$

For this reason, a CO_2 fire extinguisher will not extinguish a magnesium fire. Additionally, the brilliant white light emitted by burning magnesium makes it useful in flares and fireworks.

Group 12

The elements in group 12 are transition elements; however, the last electron added is not a *d* electron, but an *s* electron. Since the last electron added is an *s* electron, these elements qualify as representative metals, or post-transition metals. The group 12 elements behave more like the alkaline earth metals than transition metals. Group 12 contains the four elements zinc, cadmium, mercury, and copernicium. Each of these elements has two electrons in its outer shell (ns^2). When atoms of these metals form cations with a charge of 2+, where the two outer electrons are lost, they have pseudo-noble gas electron configurations. Mercury is sometimes an exception because it also exhibits an oxidation state of 1+ in compounds that contain a diatomic $\text{Hg}_2{}^{2+}$ ion. In their elemental forms and in compounds, cadmium and mercury are both toxic.

Zinc is the most reactive in group 12, and mercury is the least reactive. (This is the reverse of the reactivity trend of the metals of groups 1 and 2, in which reactivity increases down a group. The increase in reactivity with increasing atomic number only occurs for the metals in groups 1 and 2.) The decreasing reactivity is due to the formation of ions with a pseudo-noble gas configuration and to other factors that are beyond the scope of this discussion. The chemical behaviors of zinc and cadmium are quite similar to each other but differ from that of mercury.

Zinc and cadmium have lower reduction potentials than hydrogen, and, like the alkali metals and alkaline earth metals, they will produce hydrogen gas when they react with acids. The reaction of zinc with hydrochloric acid, shown in **Figure 18.7**, is:

$$\text{Zn}(s) + 2\text{H}_3\text{O}^+(aq) + 2\text{Cl}^-(aq) \longrightarrow \text{H}_2(g) + \text{Zn}^{2+}(aq) + 2\text{Cl}^-(aq) + 2\text{H}_2\text{O}(l)$$

Figure 18.7 Zinc is an active metal. It dissolves in hydrochloric acid, forming a solution of colorless Zn^{2+} ions, Cl^- ions, and hydrogen gas.

Zinc is a silvery metal that quickly tarnishes to a blue-gray appearance. This change in color is due to an adherent coating of a basic carbonate, $\text{Zn}_2(\text{OH})_2\text{CO}_3$, which passivates the metal to inhibit further corrosion. Dry cell and alkaline batteries contain a zinc anode. Brass (Cu and Zn) and some bronze (Cu, Sn, and sometimes Zn) are important zinc alloys. About half of zinc production serves to protect iron and other metals from corrosion. This protection may take the form of a sacrificial anode (also known as a galvanic anode, which is a means of providing cathodic protection for various metals) or as a thin coating on the protected metal. Galvanized steel is steel with a protective coating of zinc.

Chemistry in Everyday Life

Sacrificial Anodes

A sacrificial anode, or galvanic anode, is a means of providing cathodic protection of various metals. Cathodic protection refers to the prevention of corrosion by converting the corroding metal into a cathode. As a cathode, the metal resists corrosion, which is an oxidation process. Corrosion occurs at the sacrificial anode instead of at the cathode.

The construction of such a system begins with the attachment of a more active metal (more negative reduction potential) to the metal needing protection. Attachment may be direct or via a wire. To complete the circuit, a *salt bridge* is necessary. This salt bridge is often seawater or ground water. Once the circuit is complete, oxidation (corrosion) occurs at the anode and not the cathode.

The commonly used sacrificial anodes are magnesium, aluminum, and zinc. Magnesium has the most negative reduction potential of the three and serves best when the salt bridge is less efficient due to a low electrolyte concentration such as in freshwater. Zinc and aluminum work better in saltwater than does magnesium. Aluminum is lighter than zinc and has a higher capacity; however, an oxide coating may passivate the aluminum. In special cases, other materials are useful. For example, iron will protect copper.

Mercury is very different from zinc and cadmium. Mercury is the only metal that is liquid at 25 °C. Many metals dissolve in mercury, forming solutions called amalgams (see the feature on Amalgams), which are alloys of mercury with one or more other metals. Mercury, shown in **Figure 18.8**, is a nonreactive element that is more difficult to oxidize than hydrogen. Thus, it does not displace hydrogen from acids; however, it will react with strong oxidizing acids, such as nitric acid:

$$\mathrm{Hg}(l) + \mathrm{HCl}(aq) \longrightarrow \text{no reaction}$$
$$3\mathrm{Hg}(l) + 8\mathrm{HNO}_3(aq) \longrightarrow 3\mathrm{Hg(NO}_3)_2(aq) + 4\mathrm{H}_2\mathrm{O}(l) + 2\mathrm{NO}(g)$$

The clear NO initially formed quickly undergoes further oxidation to the reddish brown NO_2.

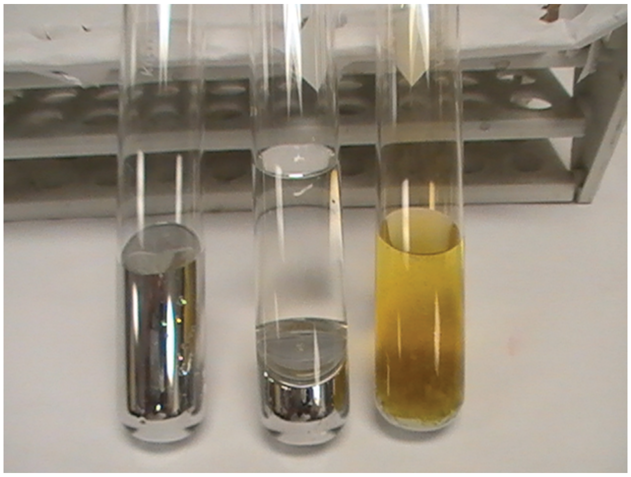


Figure 18.8 From left to right: Hg(*l*), Hg + concentrated HCl, Hg + concentrated HNO_3. (credit: Sahar Atwa)

Most mercury compounds decompose when heated. Most mercury compounds contain mercury with a 2+-oxidation state. When there is a large excess of mercury, it is possible to form compounds containing the $\mathrm{Hg_2}^{2+}$ ion. All mercury compounds are toxic, and it is necessary to exercise great care in their synthesis.

Chemistry in Everyday Life

Amalgams

An amalgam is an alloy of mercury with one or more other metals. This is similar to considering steel to be an alloy of iron with other metals. Most metals will form an amalgam with mercury, with the main exceptions being iron, platinum, tungsten, and tantalum.

Due to toxicity issues with mercury, there has been a significant decrease in the use of amalgams. Historically, amalgams were important in electrolytic cells and in the extraction of gold. Amalgams of the alkali metals still find use because they are strong reducing agents and easier to handle than the pure alkali metals.

Prospectors had a problem when they found finely divided gold. They learned that adding mercury to their pans collected the gold into the mercury to form an amalgam for easier collection. Unfortunately, losses of small amounts of mercury over the years left many streams in California polluted with mercury.

Dentists use amalgams containing silver and other metals to fill cavities. There are several reasons to use an amalgam including low cost, ease of manipulation, and longevity compared to alternate materials. Dental amalgams are approximately 50% mercury by weight, which, in recent years, has become a concern due to the toxicity of mercury.

After reviewing the best available data, the Food and Drug Administration (FDA) considers amalgam-based fillings to be safe for adults and children over six years of age. Even with multiple fillings, the mercury levels in the patients remain far below the lowest levels associated with harm. Clinical studies have found no link between dental amalgams and health problems. Health issues may not be the same in cases of children under six or pregnant women. The FDA conclusions are in line with the opinions of the Environmental Protection Agency (EPA) and Centers for Disease Control (CDC). The only health consideration noted is that some people are allergic to the amalgam or one of its components.

Group 13

Group 13 contains the metalloid boron and the metals aluminum, gallium, indium, and thallium. The lightest element, boron, is semiconducting, and its binary compounds tend to be covalent and not ionic. The remaining elements of the group are metals, but their oxides and hydroxides change characters. The oxides and hydroxides of aluminum and gallium exhibit both acidic and basic behaviors. A substance, such as these two, that will react with both acids and bases is amphoteric. This characteristic illustrates the combination of nonmetallic and metallic behaviors of these two elements. Indium and thallium oxides and hydroxides exhibit only basic behavior, in accordance with the clearly metallic character of these two elements. The melting point of gallium is unusually low (about 30 °C) and will melt in your hand.

Aluminum is amphoteric because it will react with both acids and bases. A typical reaction with an acid is:

$$2\text{Al}(s) + 6\text{HCl}(aq) \longrightarrow 2\text{AlCl}_3(aq) + 3\text{H}_2(g)$$

The products of the reaction of aluminum with a base depend upon the reaction conditions, with the following being one possibility:

$$2\text{Al}(s) + 2\text{NaOH}(aq) + 6\text{H}_2\text{O}(l) \longrightarrow 2\text{Na}\big[\text{Al(OH)}_4\big](aq) + 3\text{H}_2(g)$$

With both acids and bases, the reaction with aluminum generates hydrogen gas.

The group 13 elements have a valence shell electron configuration of ns^2np^1. Aluminum normally uses all of its valence electrons when it reacts, giving compounds in which it has an oxidation state of 3+. Although many of these compounds are covalent, others, such as AlF_3 and $\text{Al}_2(\text{SO}_4)_3$, are ionic. Aqueous solutions of aluminum salts contain the cation $\big[\text{Al(H}_2\text{O)}_6\big]^{3+},$ abbreviated as $\text{Al}^{3+}(aq)$. Gallium, indium, and thallium also form ionic compounds containing M^{3+} ions. These three elements exhibit not only the expected oxidation state of 3+ from the three valence electrons but also an oxidation state (in this case, 1+) that is two below the expected value. This phenomenon, the inert pair effect, refers to the formation of a stable ion with an oxidation state two lower than expected for the group. The pair of electrons is the valence *s* orbital for those elements. In general, the inert pair effect is important for the lower *p*-block elements. In an aqueous solution, the $\text{Tl}^{+}(aq)$ ion is more stable than is $\text{Tl}^{3+}(aq)$. In general, these metals will react with air and water to form 3+ ions; however, thallium reacts to give thallium(I) derivatives. The metals of group 13 all react directly with nonmetals such as sulfur, phosphorus, and the halogens, forming binary compounds.

The metals of group 13 (Al, Ga, In, and Tl) are all reactive. However, passivation occurs as a tough, hard, thin film of the metal oxide forms upon exposure to air. Disruption of this film may counter the passivation, allowing the metal to react. One way to disrupt the film is to expose the passivated metal to mercury. Some of the metal dissolves in the mercury to form an amalgam, which sheds the protective oxide layer to expose the metal to further reaction. The formation of an amalgam allows the metal to react with air and water.

Link to Learning

Although easily oxidized, the passivation of aluminum makes it very useful as a strong, lightweight building material. Because of the formation of an amalgam, mercury is corrosive to structural materials made of aluminum. This **video (http://openstaxcollege.org/l/16aluminumhg)** demonstrates how the integrity of an aluminum beam can be destroyed by the addition of a small amount of elemental mercury.

The most important uses of aluminum are in the construction and transportation industries, and in the manufacture of aluminum cans and aluminum foil. These uses depend on the lightness, toughness, and strength of the metal, as well as its resistance to corrosion. Because aluminum is an excellent conductor of heat and resists corrosion, it is useful in the manufacture of cooking utensils.

Aluminum is a very good reducing agent and may replace other reducing agents in the isolation of certain metals from their oxides. Although more expensive than reduction by carbon, aluminum is important in the isolation of Mo, W, and Cr from their oxides.

Group 14

The metallic members of group 14 are tin, lead, and flerovium. Carbon is a typical nonmetal. The remaining elements of the group, silicon and germanium, are examples of semimetals or metalloids. Tin and lead form the stable divalent cations, Sn^{2+} and Pb^{2+}, with oxidation states two below the group oxidation state of 4+. The stability of this oxidation state is a consequence of the inert pair effect. Tin and lead also form covalent compounds with a formal 4+-oxidation state. For example, $SnCl_4$ and $PbCl_4$ are low-boiling covalent liquids.


(a) (b)

Figure 18.9 (a) Tin(II) chloride is an ionic solid; (b) tin(IV) chloride is a covalent liquid.

Tin reacts readily with nonmetals and acids to form tin(II) compounds (indicating that it is more easily oxidized than hydrogen) and with nonmetals to form either tin(II) or tin(IV) compounds (shown in **Figure 18.9**), depending on the stoichiometry and reaction conditions. Lead is less reactive. It is only slightly easier to oxidize than hydrogen, and oxidation normally requires a hot concentrated acid.

Many of these elements exist as allotropes. **Allotropes** are two or more forms of the same element in the same physical state with different chemical and physical properties. There are two common allotropes of tin. These allotropes are grey (brittle) tin and white tin. As with other allotropes, the difference between these forms of tin is in the arrangement of the atoms. White tin is stable above 13.2 °C and is malleable like other metals. At low temperatures, gray tin is the more stable form. Gray tin is brittle and tends to break down to a powder. Consequently, articles made of tin will disintegrate in cold weather, particularly if the cold spell is lengthy. The change progresses slowly from the spot of origin, and the gray tin that is first formed catalyzes further change. In a way, this effect is similar to the spread of an infection in a plant or animal body, leading people to call this process tin disease or tin pest.

The principal use of tin is in the coating of steel to form tin plate-sheet iron, which constitutes the tin in tin cans. Important tin alloys are bronze (Cu and Sn) and solder (Sn and Pb). Lead is important in the lead storage batteries in automobiles.

Group 15

Bismuth, the heaviest member of group 15, is a less reactive metal than the other representative metals. It readily gives up three of its five valence electrons to active nonmetals to form the tri-positive ion, Bi^{3+}. It forms compounds with the group oxidation state of 5+ only when treated with strong oxidizing agents. The stability of the 3+-oxidation state is another example of the inert pair effect.

18.2 Occurrence and Preparation of the Representative Metals

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

- Identify natural sources of representative metals
- Describe electrolytic and chemical reduction processes used to prepare these elements from natural sources

Because of their reactivity, we do not find most representative metals as free elements in nature. However, compounds that contain ions of most representative metals are abundant. In this section, we will consider the two common techniques used to isolate the metals from these compounds—electrolysis and chemical reduction.

These metals primarily occur in minerals, with lithium found in silicate or phosphate minerals, and sodium and potassium found in salt deposits from evaporation of ancient seas and in silicates. The alkaline earth metals occur as silicates and, with the exception of beryllium, as carbonates and sulfates. Beryllium occurs as the mineral beryl, $Be_3Al_2Si_6O_{18}$, which, with certain impurities, may be either the gemstone emerald or aquamarine. Magnesium is in seawater and, along with the heavier alkaline earth metals, occurs as silicates, carbonates, and sulfates. Aluminum occurs abundantly in many types of clay and in bauxite, an impure aluminum oxide hydroxide. The principle tin ore is the oxide cassiterite, SnO_2, and the principle lead and thallium ores are the sulfides or the products of weathering of the sulfides. The remaining representative metals occur as impurities in zinc or aluminum ores.

Electrolysis

Ions of metals in of groups 1 and 2, along with aluminum, are very difficult to reduce; therefore, it is necessary to prepare these elements by electrolysis, an important process discussed in the chapter on electrochemistry. Briefly, electrolysis involves using electrical energy to drive unfavorable chemical reactions to completion; it is useful in the isolation of reactive metals in their pure forms. Sodium, aluminum, and magnesium are typical examples.

The Preparation of Sodium

The most important method for the production of sodium is the electrolysis of molten sodium chloride; the set-up is a **Downs cell**, shown in Figure 18.10. The reaction involved in this process is:

$$2\text{NaCl}(l) \xrightarrow[600\,°\text{C}]{\text{electrolysis}} 2\text{Na}(l) + \text{Cl}_2(g)$$

The electrolysis cell contains molten sodium chloride (melting point 801 °C), to which calcium chloride has been added to lower the melting point to 600 °C (a colligative effect). The passage of a direct current through the cell causes the sodium ions to migrate to the negatively charged cathode and pick up electrons, reducing the ions to sodium metal. Chloride ions migrate to the positively charged anode, lose electrons, and undergo oxidation to chlorine gas. The overall cell reaction comes from adding the following reactions:

$$\begin{aligned}&\text{at the cathode: } 2\text{Na}^+ + 2\text{e}^- \longrightarrow 2\text{Na}(l)\\&\text{at the anode: } 2\text{Cl}^- \longrightarrow \text{Cl}_2(g) + 2\text{e}^-\\&\text{overall change: } 2\text{Na}^+ + 2\text{Cl}^- \longrightarrow 2\text{Na}(l) + \text{Cl}_2(g)\end{aligned}$$

Separation of the molten sodium and chlorine prevents recombination. The liquid sodium, which is less dense than molten sodium chloride, floats to the surface and flows into a collector. The gaseous chlorine goes to storage tanks. Chlorine is also a valuable product.

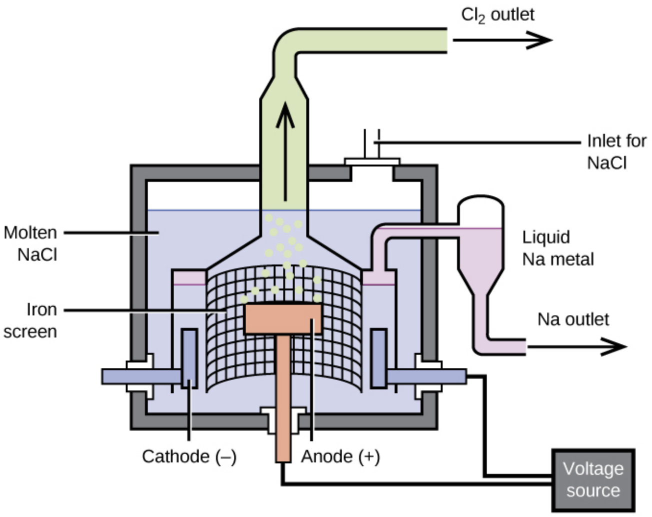


Figure 18.10 Pure sodium metal is isolated by electrolysis of molten sodium chloride using a Downs cell. It is not possible to isolate sodium by electrolysis of aqueous solutions of sodium salts because hydrogen ions are more easily reduced than are sodium ions; as a result, hydrogen gas forms at the cathode instead of the desired sodium metal. The high temperature required to melt NaCl means that liquid sodium metal forms.

The Preparation of Aluminum

The preparation of aluminum utilizes a process invented in 1886 by Charles M. Hall, who began to work on the problem while a student at Oberlin College in Ohio. Paul L. T. Héroult discovered the process independently a month or two later in France. In honor to the two inventors, this electrolysis cell is known as the **Hall–Héroult cell**. The Hall–Héroult cell is an electrolysis cell for the production of aluminum. **Figure 18.11** illustrates the Hall–Héroult cell.

The production of aluminum begins with the purification of bauxite, the most common source of aluminum. The reaction of bauxite, AlO(OH), with hot sodium hydroxide forms soluble sodium aluminate, while clay and other impurities remain undissolved:

$$\text{AlO(OH)}(s) + \text{NaOH}(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{Na[Al(OH)}_4](aq)$$

After the removal of the impurities by filtration, the addition of acid to the aluminate leads to the reprecipitation of aluminum hydroxide:

$$\text{Na[Al(OH)}_4](aq) + \text{H}_3\text{O}^+(aq) \longrightarrow \text{Al(OH)}_3(s) + \text{Na}^+(aq) + 2\text{H}_2\text{O}(l)$$

The next step is to remove the precipitated aluminum hydroxide by filtration. Heating the hydroxide produces aluminum oxide, Al_2O_3, which dissolves in a molten mixture of cryolite, Na_3AlF_6, and calcium fluoride, CaF_2. Electrolysis of this solution takes place in a cell like that shown in **Figure 18.11**. Reduction of aluminum ions to the metal occurs at the cathode, while oxygen, carbon monoxide, and carbon dioxide form at the anode.

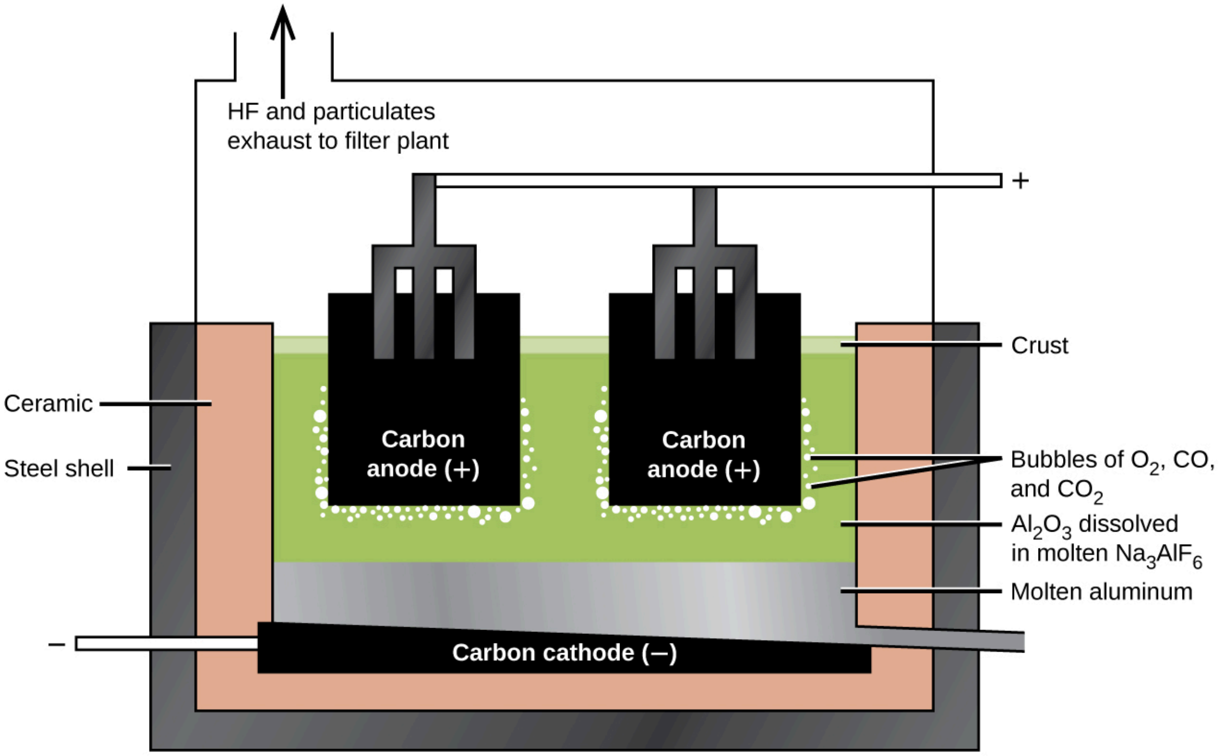


Figure 18.11 An electrolytic cell is used for the production of aluminum. The electrolysis of a solution of cryolite and calcium fluoride results in aluminum metal at the cathode, and oxygen, carbon monoxide, and carbon dioxide at the anode.

The Preparation of Magnesium

Magnesium is the other metal that is isolated in large quantities by electrolysis. Seawater, which contains approximately 0.5% magnesium chloride, serves as the major source of magnesium. Addition of calcium hydroxide to seawater precipitates magnesium hydroxide. The addition of hydrochloric acid to magnesium hydroxide, followed by evaporation of the resultant aqueous solution, leaves pure magnesium chloride. The electrolysis of molten magnesium chloride forms liquid magnesium and chlorine gas:

$$\begin{gathered}\mathrm{MgCl_2}(aq) + \mathrm{Ca(OH)_2}(aq) \longrightarrow \mathrm{Mg(OH)_2}(s) + \mathrm{CaCl_2}(aq) \\ \mathrm{Mg(OH)_2}(s) + 2\mathrm{HCl}(aq) \longrightarrow \mathrm{MgCl_2}(aq) + 2\mathrm{H_2O}(l) \\ \mathrm{MgCl_2}(l) \longrightarrow \mathrm{Mg}(l) + \mathrm{Cl_2}(g)\end{gathered}$$

Some production facilities have moved away from electrolysis completely. In the next section, we will see how the Pidgeon process leads to the chemical reduction of magnesium.

Chemical Reduction

It is possible to isolate many of the representative metals by **chemical reduction** using other elements as reducing agents. In general, chemical reduction is much less expensive than electrolysis, and for this reason, chemical reduction is the method of choice for the isolation of these elements. For example, it is possible to produce potassium, rubidium, and cesium by chemical reduction, as it is possible to reduce the molten chlorides of these metals with sodium metal. This may be surprising given that these metals are more reactive than sodium; however, the metals formed are more volatile than sodium and can be distilled for collection. The removal of the metal vapor leads to a shift in the equilibrium to produce more metal (see how reactions can be driven in the discussions of Le Châtelier's principle in the chapter on fundamental equilibrium concepts).

The production of magnesium, zinc, and tin provide additional examples of chemical reduction.

The Preparation of Magnesium

The **Pidgeon process** involves the reaction of magnesium oxide with elemental silicon at high temperatures to form pure magnesium:

$$\mathrm{Si}(s) + 2\mathrm{MgO}(s) \xrightarrow{\Delta} \mathrm{SiO}_2(s) + 2\mathrm{Mg}(g)$$

Although this reaction is unfavorable in terms of thermodynamics, the removal of the magnesium vapor produced takes advantage of Le Châtelier's principle to continue the forward progress of the reaction. Over 75% of the world's production of magnesium, primarily in China, comes from this process.

The Preparation of Zinc

Zinc ores usually contain zinc sulfide, zinc oxide, or zinc carbonate. After separation of these compounds from the ores, heating in air converts the ore to zinc oxide by one of the following reactions:

$$2\mathrm{ZnS}(s) + 3\mathrm{O}_2(g) \xrightarrow{\Delta} 2\mathrm{ZnO}(s) + 2\mathrm{SO}_2(g)$$
$$\mathrm{ZnCO}_3(s) \xrightarrow{\Delta} \mathrm{ZnO}(s) + \mathrm{CO}_2(g)$$

Carbon, in the form of coal, reduces the zinc oxide to form zinc vapor:

$$\mathrm{ZnO}(s) + \mathrm{C}(s) \longrightarrow \mathrm{Zn}(g) + \mathrm{CO}(g)$$

The zinc can be distilled (boiling point 907 °C) and condensed. This zinc contains impurities of cadmium (767 °C), iron (2862 °C), lead (1750 °C), and arsenic (613 °C). Careful redistillation produces pure zinc. Arsenic and cadmium are distilled from the zinc because they have lower boiling points. At higher temperatures, the zinc is distilled from the other impurities, mainly lead and iron.

The Preparation of Tin

The ready reduction of tin(IV) oxide by the hot coals of a campfire accounts for the knowledge of tin in the ancient world. In the modern process, the roasting of tin ores containing SnO_2 removes contaminants such as arsenic and sulfur as volatile oxides. Treatment of the remaining material with hydrochloric acid removes the oxides of other metals. Heating the purified ore with carbon at temperature above 1000 °C produces tin:

$$\mathrm{SnO}_2(s) + 2\mathrm{C}(s) \xrightarrow{\Delta} \mathrm{Sn}(s) + 2\mathrm{CO}(g)$$

The molten tin collects at the bottom of the furnace and is drawn off and cast into blocks.

18.3 Structure and General Properties of the Metalloids

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

- Describe the general preparation, properties, and uses of the metalloids
- Describe the preparation, properties, and compounds of boron and silicon

A series of six elements called the metalloids separate the metals from the nonmetals in the periodic table. The metalloids are boron, silicon, germanium, arsenic, antimony, and tellurium. These elements look metallic; however, they do not conduct electricity as well as metals so they are semiconductors. They are semiconductors because their electrons are more tightly bound to their nuclei than are those of metallic conductors. Their chemical behavior falls between that of metals and nonmetals. For example, the pure metalloids form covalent crystals like the nonmetals, but like the metals, they generally do not form monatomic anions. This intermediate behavior is in part due to their intermediate electronegativity values. In this section, we will briefly discuss the chemical behavior of metalloids and deal with two of these elements—boron and silicon—in more detail.

The metalloid boron exhibits many similarities to its neighbor carbon and its diagonal neighbor silicon. All three elements form covalent compounds. However, boron has one distinct difference in that its $2s^2 2p^1$ outer electron structure gives it one less valence electron than it has valence orbitals. Although boron exhibits an oxidation state of 3+ in most of its stable compounds, this electron deficiency provides boron with the ability to form other, sometimes fractional, oxidation states, which occur, for example, in the boron hydrides.

Silicon has the valence shell electron configuration $3s^2 3p^2$, and it commonly forms tetrahedral structures in which it is sp^3 hybridized with a formal oxidation state of 4+. The major differences between the chemistry of carbon and silicon result from the relative strength of the carbon-carbon bond, carbon's ability to form stable bonds to itself, and the presence of the empty 3*d* valence-shell orbitals in silicon. Silicon's empty *d* orbitals and boron's empty *p* orbital enable tetrahedral silicon compounds and trigonal planar boron compounds to act as Lewis acids. Carbon, on the other hand, has no available valence shell orbitals; tetrahedral carbon compounds cannot act as Lewis acids. Germanium is very similar to silicon in its chemical behavior.

Arsenic and antimony generally form compounds in which an oxidation state of 3+ or 5+ is exhibited; however, arsenic can form arsenides with an oxidation state of 3−. These elements tarnish only slightly in dry air but readily oxidize when warmed.

Tellurium combines directly with most elements. The most stable tellurium compounds are the tellurides—salts of Te^{2-} formed with active metals and lanthanides—and compounds with oxygen, fluorine, and chlorine, in which tellurium normally exhibits an oxidation state 2+ or 4+. Although tellurium(VI) compounds are known (for example, TeF_6), there is a marked resistance to oxidation to this maximum group oxidation state.

Structures of the Metalloids

Covalent bonding is the key to the crystal structures of the metalloids. In this regard, these elements resemble nonmetals in their behavior.

Elemental silicon, germanium, arsenic, antimony, and tellurium are lustrous, metallic-looking solids. Silicon and germanium crystallize with a diamond structure. Each atom within the crystal has covalent bonds to four neighboring atoms at the corners of a regular tetrahedron. Single crystals of silicon and germanium are giant, three-dimensional molecules. There are several allotropes of arsenic with the most stable being layer like and containing puckered sheets of arsenic atoms. Each arsenic atom forms covalent bonds to three other atoms within the sheet. The crystal structure of antimony is similar to that of arsenic, both shown in **Figure 18.12**. The structures of arsenic and antimony are similar to the structure of graphite, covered later in this chapter. Tellurium forms crystals that contain infinite spiral chains of tellurium atoms. Each atom in the chain bonds to two other atoms.

Link to Learning

Explore a **cubic diamond (http://openstaxcollege.org/l/16crystal)** crystal structure.

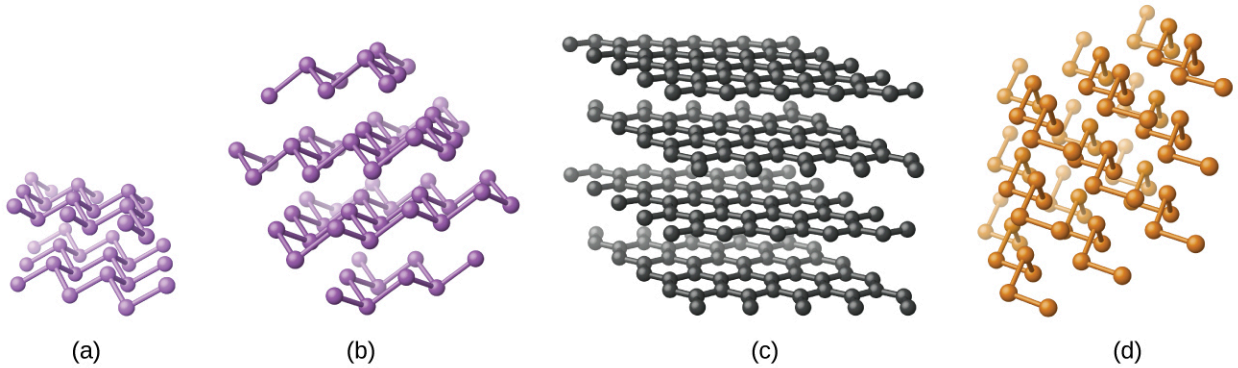


Figure 18.12 (a) Arsenic and (b) antimony have a layered structure similar to that of (c) graphite, except that the layers are puckered rather than planar. (d) Elemental tellurium forms spiral chains.

Pure crystalline boron is transparent. The crystals consist of icosahedra, as shown in **Figure 18.13**, with a boron atom at each corner. In the most common form of boron, the icosahedra pack together in a manner similar to the cubic closest packing of spheres. All boron-boron bonds within each icosahedron are identical and are approximately 176 pm in length. In the different forms of boron, there are different arrangements and connections between the icosahedra.

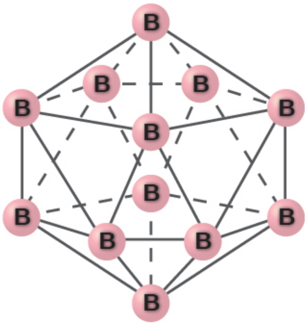


Figure 18.13 An icosahedron is a symmetrical, solid shape with 20 faces, each of which is an equilateral triangle. The faces meet at 12 corners.

The name silicon is derived from the Latin word for flint, *silex*. The metalloid silicon readily forms compounds containing Si-O-Si bonds, which are of prime importance in the mineral world. This bonding capability is in contrast to the nonmetal carbon, whose ability to form carbon-carbon bonds gives it prime importance in the plant and animal worlds.

Occurrence, Preparation, and Compounds of Boron and Silicon

Boron constitutes less than 0.001% by weight of the earth’s crust. In nature, it only occurs in compounds with oxygen. Boron is widely distributed in volcanic regions as boric acid, $B(OH)_3$, and in dry lake regions, including the desert areas of California, as borates and salts of boron oxyacids, such as borax, $Na_2B_4O_7{\cdot}10H_2O$.

Elemental boron is chemically inert at room temperature, reacting with only fluorine and oxygen to form boron trifluoride, BF_3, and boric oxide, B_2O_3, respectively. At higher temperatures, boron reacts with all nonmetals, except tellurium and the noble gases, and with nearly all metals; it oxidizes to B_2O_3 when heated with concentrated nitric or sulfuric acid. Boron does not react with nonoxidizing acids. Many boron compounds react readily with water to give boric acid, $B(OH)_3$ (sometimes written as H_3BO_3).

Reduction of boric oxide with magnesium powder forms boron (95–98.5% pure) as a brown, amorphous powder:

$$B_2O_3(s) + 3Mg(s) \longrightarrow 2B(s) + 3MgO(s)$$

An **amorphous** substance is a material that appears to be a solid, but does not have a long-range order like a true solid. Treatment with hydrochloric acid removes the magnesium oxide. Further purification of the boron begins with conversion of the impure boron into boron trichloride. The next step is to heat a mixture of boron trichloride and hydrogen:

$$2BCl_3(g) + 3H_2(g) \xrightarrow{1500\ °C} 2B(s) + 6HCl(g) \qquad \Delta H° = 253.7\ \text{kJ}$$

Silicon makes up nearly one-fourth of the mass of the earth's crust—second in abundance only to oxygen. The crust is composed almost entirely of minerals in which the silicon atoms are at the center of the silicon-oxygen tetrahedron, which connect in a variety of ways to produce, among other things, chains, layers, and three-dimensional frameworks. These minerals constitute the bulk of most common rocks, soil, and clays. In addition, materials such as bricks, ceramics, and glasses contain silicon compounds.

It is possible to produce silicon by the high-temperature reduction of silicon dioxide with strong reducing agents, such as carbon and magnesium:

$$SiO_2(s) + 2C(s) \xrightarrow{\Delta} Si(s) + 2CO(g)$$
$$SiO_2(s) + 2Mg(s) \xrightarrow{\Delta} Si(s) + 2MgO(s)$$

Extremely pure silicon is necessary for the manufacture of semiconductor electronic devices. This process begins with the conversion of impure silicon into silicon tetrahalides, or silane (SiH_4), followed by decomposition at high temperatures. Zone refining, illustrated in **Figure 18.14**, completes the purification. In this method, a rod of silicon is heated at one end by a heat source that produces a thin cross-section of molten silicon. Slowly lowering the rod through the heat source moves the molten zone from one end of the rod to other. As this thin, molten region moves, impurities in the silicon dissolve in the liquid silicon and move with the molten region. Ultimately, the impurities move to one end of the rod, which is then cut off.

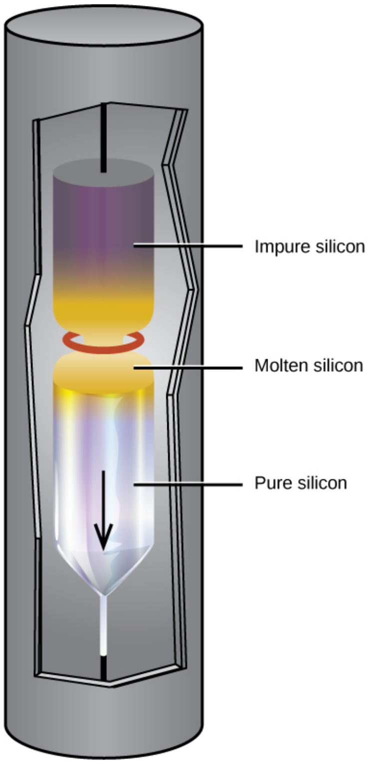


Figure 18.14 A zone-refining apparatus used to purify silicon.

This highly purified silicon, containing no more than one part impurity per million parts of silicon, is the most important element in the computer industry. Pure silicon is necessary in semiconductor electronic devices such as transistors, computer chips, and solar cells.

Like some metals, passivation of silicon occurs due the formation of a very thin film of oxide (primarily silicon dioxide, SiO_2). Silicon dioxide is soluble in hot aqueous base; thus, strong bases destroy the passivation. Removal of the passivation layer allows the base to dissolve the silicon, forming hydrogen gas and silicate anions. For example:

$$\text{Si}(s) + 4\text{OH}^-(aq) \longrightarrow \text{SiO}_4{}^{4-}(aq) + 2\text{H}_2(g)$$

Silicon reacts with halogens at high temperatures, forming volatile tetrahalides, such as SiF_4.

Unlike carbon, silicon does not readily form double or triple bonds. Silicon compounds of the general formula SiX_4, where X is a highly electronegative group, can act as Lewis acids to form six-coordinate silicon. For example, silicon tetrafluoride, SiF_4, reacts with sodium fluoride to yield $Na_2[SiF_6]$, which contains the octahedral $[\text{SiF}_6]^{2-}$ ion in which silicon is sp^3d^2 hybridized:

$$2\text{NaF}(s) + \text{SiF}_4(g) \longrightarrow \text{Na}_2\text{SiF}_6(s)$$

Antimony reacts readily with stoichiometric amounts of fluorine, chlorine, bromine, or iodine, yielding trihalides or, with excess fluorine or chlorine, forming the pentahalides SbF_5 and $SbCl_5$. Depending on the stoichiometry, it forms antimony(III) sulfide, Sb_2S_3, or antimony(V) sulfide when heated with sulfur. As expected, the metallic nature of the element is greater than that of arsenic, which lies immediately above it in group 15.

Boron and Silicon Halides

Boron trihalides—BF_3, BCl_3, BBr_3, and BI_3—can be prepared by the direct reaction of the elements. These nonpolar molecules contain boron with sp^2 hybridization and a trigonal planar molecular geometry. The fluoride and chloride compounds are colorless gasses, the bromide is a liquid, and the iodide is a white crystalline solid.

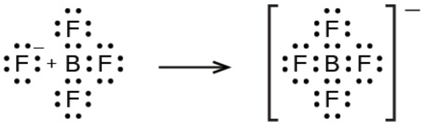
Except for boron trifluoride, the boron trihalides readily hydrolyze in water to form boric acid and the corresponding hydrohalic acid. Boron trichloride reacts according to the equation:

$$\mathrm{BCl_3}(g) + 3\mathrm{H_2O}(l) \longrightarrow \mathrm{B(OH)_3}(aq) + 3\mathrm{HCl}(aq)$$

Boron trifluoride reacts with hydrofluoric acid, to yield a solution of fluoroboric acid, HBF_4:

$$\mathrm{BF_3}(aq) + \mathrm{HF}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{BF_4{}^-}(aq)$$

In this reaction, the BF_3 molecule acts as the Lewis acid (electron pair acceptor) and accepts a pair of electrons from a fluoride ion:



All the tetrahalides of silicon, SiX_4, have been prepared. Silicon tetrachloride can be prepared by direct chlorination at elevated temperatures or by heating silicon dioxide with chlorine and carbon:

$$\mathrm{SiO_2}(s) + 2\mathrm{C}(s) + 2\mathrm{Cl_2}(g) \xrightarrow{\Delta} \mathrm{SiCl_4}(g) + 2\mathrm{CO}(g)$$

Silicon tetrachloride is a covalent tetrahedral molecule, which is a nonpolar, low-boiling (57 °C), colorless liquid.

It is possible to prepare silicon tetrafluoride by the reaction of silicon dioxide with hydrofluoric acid:

$$\mathrm{SiO_2}(s) + 4\mathrm{HF}(g) \longrightarrow \mathrm{SiF_4}(g) + 2\mathrm{H_2O}(l) \qquad \Delta H^\circ = -191.2\ \mathrm{kJ}$$

Hydrofluoric acid is the only common acid that will react with silicon dioxide or silicates. This reaction occurs because the silicon-fluorine bond is the only bond that silicon forms that is stronger than the silicon-oxygen bond. For this reason, it is possible to store all common acids, other than hydrofluoric acid, in glass containers.

Except for silicon tetrafluoride, silicon halides are extremely sensitive to water. Upon exposure to water, $SiCl_4$ reacts rapidly with hydroxide groups, replacing all four chlorine atoms to produce unstable orthosilicic acid, $Si(OH)_4$ or H_4SiO_4, which slowly decomposes into SiO_2.

Boron and Silicon Oxides and Derivatives

Boron burns at 700 °C in oxygen, forming boric oxide, B_2O_3. Boric oxide is necessary for the production of heat-resistant borosilicate glass, like that shown in **Figure 18.15** and certain optical glasses. Boric oxide dissolves in hot water to form boric acid, $B(OH)_3$:

$$B_2O_3(s) + 3H_2O(l) \longrightarrow 2B(OH)_3(aq)$$

Figure 18.15 Laboratory glassware, such as Pyrex and Kimax, is made of borosilicate glass because it does not break when heated. The inclusion of borates in the glass helps to mediate the effects of thermal expansion and contraction. This reduces the likelihood of thermal shock, which causes silicate glass to crack upon rapid heating or cooling. (credit: “Tweenk”/Wikimedia Commons)

The boron atom in $B(OH)_3$ is sp^2 hybridized and is located at the center of an equilateral triangle with oxygen atoms at the corners. In solid $B(OH)_3$, hydrogen bonding holds these triangular units together. Boric acid, shown in **Figure 18.16**, is a very weak acid that does not act as a proton donor but rather as a Lewis acid, accepting an unshared pair of electrons from the Lewis base OH^-:

$$B(OH)_3(aq) + 2H_2O(l) \rightleftharpoons B(OH)_4{}^-(aq) + H_3O^+(aq) \qquad K_a = 5.8 \times 10^{-10}$$

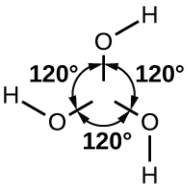


Figure 18.16 Boric acid has a planar structure with three –OH groups spread out equally at 120° angles from each other.

Heating boric acid to 100 °C causes molecules of water to split out between pairs of adjacent –OH groups to form metaboric acid, HBO_2. At about 150 °C, additional B-O-B linkages form, connecting the BO_3 groups together with shared oxygen atoms to form tetraboric acid, $H_2B_4O_7$. Complete water loss, at still higher temperatures, results in boric oxide.

Borates are salts of the oxyacids of boron. Borates result from the reactions of a base with an oxyacid or from the fusion of boric acid or boric oxide with a metal oxide or hydroxide. Borate anions range from the simple trigonal planar $BO_3{}^{3-}$ ion to complex species containing chains and rings of three- and four-coordinated boron atoms. The structures of the anions found in CaB_2O_4, $K[B_5O_6(OH)_4]·2H_2O$ (commonly written $KB_5O_8·4H_2O$) and $Na_2[B_4O_5(OH)_4]·8H_2O$ (commonly written $Na_2B_4O_7·10H_2O$) are shown in **Figure 18.17**. Commercially, the most important borate is borax, $Na_2[B_4O_5(OH)_4]·8H_2O$, which is an important component of some laundry detergents. Most of the supply of borax comes directly from dry lakes, such as Searles Lake in California, or is prepared from kernite, $Na_2B_4O_7·4H_2O$.

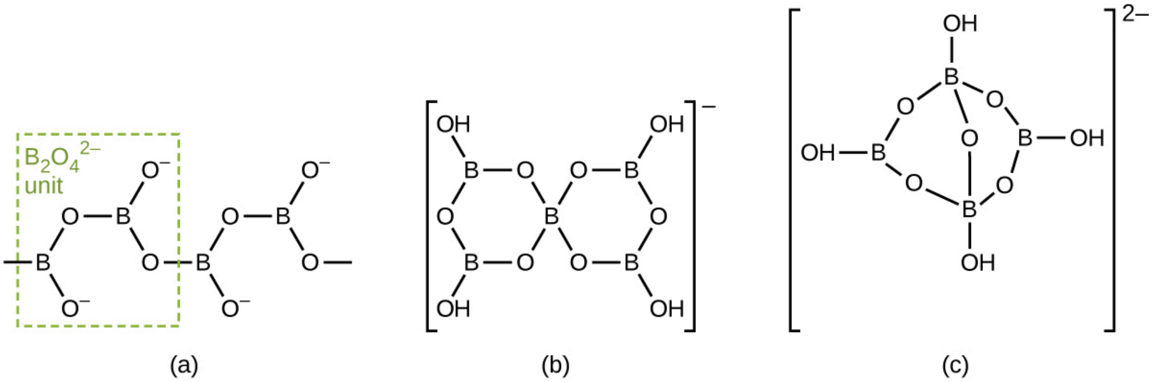


Figure 18.17 The borate anions are (a) CaB_2O_4, (b) $KB_5O_8{\cdot}4H_2O$, and (c) $Na_2B_4O_7{\cdot}10H_2O$. The anion in CaB_2O_4 is an “infinite” chain.

Silicon dioxide, silica, occurs in both crystalline and amorphous forms. The usual crystalline form of silicon dioxide is quartz, a hard, brittle, clear, colorless solid. It is useful in many ways—for architectural decorations, semiprecious jewels, and frequency control in radio transmitters. Silica takes many crystalline forms, or **polymorphs**, in nature. Trace amounts of Fe^{3+} in quartz give amethyst its characteristic purple color. The term *quartz* is also used for articles such as tubing and lenses that are manufactured from amorphous silica. Opal is a naturally occurring form of amorphous silica.

The contrast in structure and physical properties between silicon dioxide and carbon dioxide is interesting, as illustrated in **Figure 18.18**. Solid carbon dioxide (dry ice) contains single CO_2 molecules with each of the two oxygen atoms attached to the carbon atom by double bonds. Very weak intermolecular forces hold the molecules together in the crystal. The volatility of dry ice reflect these weak forces between molecules. In contrast, silicon dioxide is a covalent network solid. In silicon dioxide, each silicon atom links to four oxygen atoms by single bonds directed toward the corners of a regular tetrahedron, and SiO_4 tetrahedra share oxygen atoms. This arrangement gives a three dimensional, continuous, silicon-oxygen network. A quartz crystal is a macromolecule of silicon dioxide. The difference between these two compounds is the ability of the group 14 elements to form strong π bonds. Second-period elements, such as carbon, form very strong π bonds, which is why carbon dioxide forms small molecules with strong double bonds. Elements below the second period, such as silicon, do not form π bonds as readily as second-period elements, and when they do form, the π bonds are weaker than those formed by second-period elements. For this reason, silicon dioxide does not contain π bonds but only σ bonds.

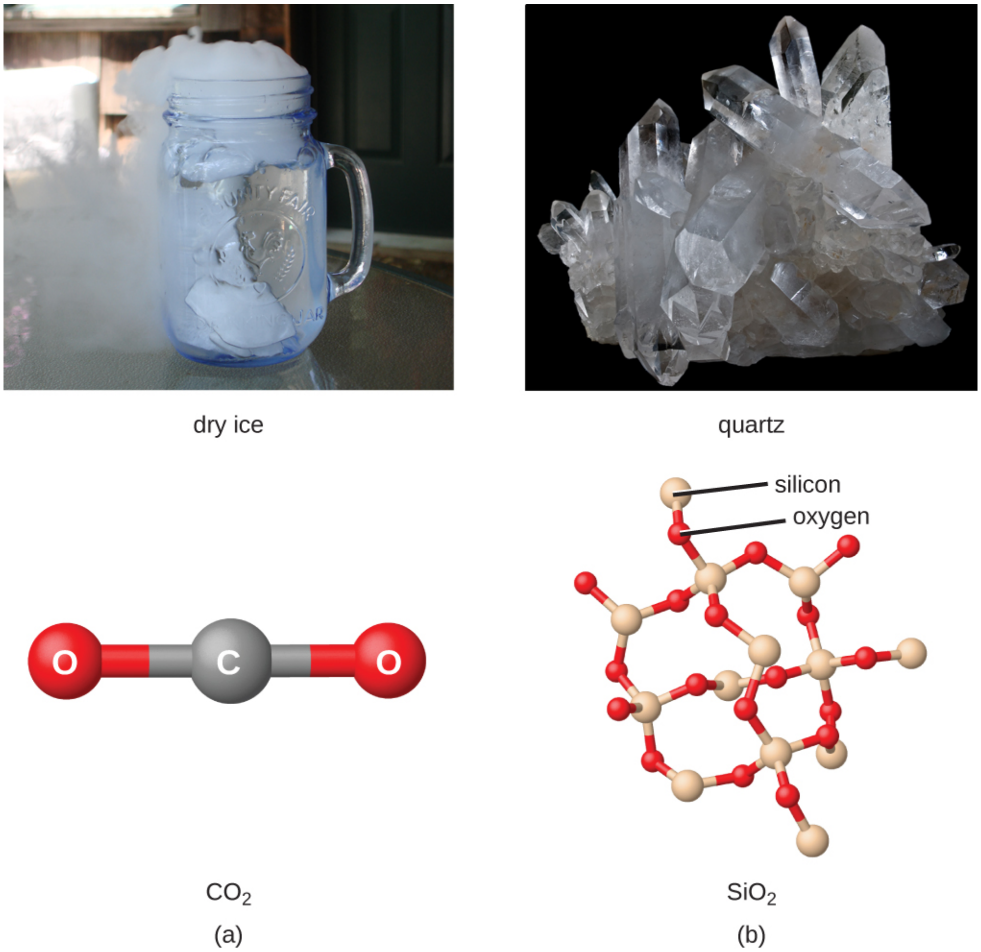


Figure 18.18 Because carbon tends to form double and triple bonds and silicon does not, (a) carbon dioxide is a discrete molecule with two C=O double bonds and (b) silicon dioxide is an infinite network of oxygen atoms bridging between silicon atoms with each silicon atom possessing four Si-O single bonds. (credit a photo: modification of work by Erica Gerdes; credit b photo: modification of work by Didier Descouens)

At 1600 °C, quartz melts to yield a viscous liquid. When the liquid cools, it does not crystallize readily but usually supercools and forms a glass, also called silica. The SiO_4 tetrahedra in glassy silica have a random arrangement characteristic of supercooled liquids, and the glass has some very useful properties. Silica is highly transparent to both visible and ultraviolet light. For this reason, it is important in the manufacture of lamps that give radiation rich in ultraviolet light and in certain optical instruments that operate with ultraviolet light. The coefficient of expansion of silica glass is very low; therefore, rapid temperature changes do not cause it to fracture. CorningWare and other ceramic cookware contain amorphous silica.

Silicates are salts containing anions composed of silicon and oxygen. In nearly all silicates, sp^3-hybridized silicon atoms occur at the centers of tetrahedra with oxygen at the corners. There is a variation in the silicon-to-oxygen ratio that occurs because silicon-oxygen tetrahedra may exist as discrete, independent units or may share oxygen atoms at corners in a variety of ways. In addition, the presence of a variety of cations gives rise to the large number of silicate minerals.

Many ceramics are composed of silicates. By including small amounts of other compounds, it is possible to modify the physical properties of the silicate materials to produce ceramics with useful characteristics.

18.4 Structure and General Properties of the Nonmetals

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

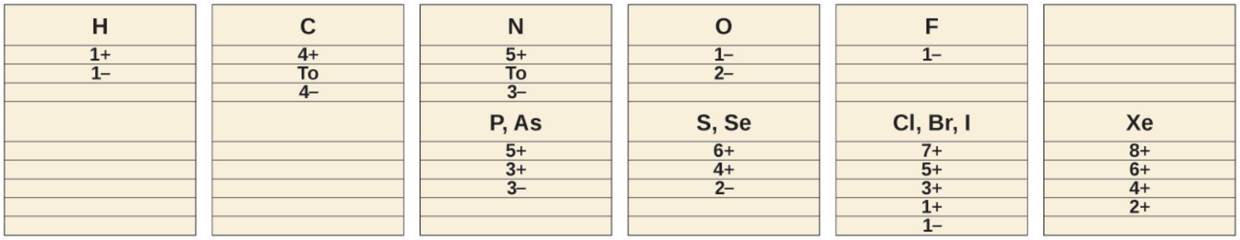
- Describe structure and properties of nonmetals

The nonmetals are elements located in the upper right portion of the periodic table. Their properties and behavior are quite different from those of metals on the left side. Under normal conditions, more than half of the nonmetals are gases, one is a liquid, and the rest include some of the softest and hardest of solids. The nonmetals exhibit a rich variety of chemical behaviors. They include the most reactive and least reactive of elements, and they form many different ionic and covalent compounds. This section presents an overview of the properties and chemical behaviors of the nonmetals, as well as the chemistry of specific elements. Many of these nonmetals are important in biological systems.

In many cases, trends in electronegativity enable us to predict the type of bonding and the physical states in compounds involving the nonmetals. We know that electronegativity decreases as we move down a given group and increases as we move from left to right across a period. The nonmetals have higher electronegativities than do metals, and compounds formed between metals and nonmetals are generally ionic in nature because of the large differences in electronegativity between them. The metals form cations, the nonmetals form anions, and the resulting compounds are solids under normal conditions. On the other hand, compounds formed between two or more nonmetals have small differences in electronegativity between the atoms, and covalent bonding—sharing of electrons—results. These substances tend to be molecular in nature and are gases, liquids, or volatile solids at room temperature and pressure.

In normal chemical processes, nonmetals do not form monatomic positive ions (cations) because their ionization energies are too high. All monatomic nonmetal ions are anions; examples include the chloride ion, Cl^-, the nitride ion, N^{3-}, and the selenide ion, Se^{2-}.

The common oxidation states that the nonmetals exhibit in their ionic and covalent compounds are shown in **Figure 18.19**. Remember that an element exhibits a positive oxidation state when combined with a more electronegative element and that it exhibits a negative oxidation state when combined with a less electronegative element.



H	C	N	O	F	
1+	4+	5+	1–	1–	
1–	To	To	2–		
	4–	3–			
		P, As	S, Se	Cl, Br, I	Xe
		5+	6+	7+	8+
		3+	4+	5+	6+
		3–	2–	3+	4+
				1+	2+
				1–	

Figure 18.19 Nonmetals exhibit these common oxidation states in ionic and covalent compounds.

The first member of each nonmetal group exhibits different behaviors, in many respects, from the other group members. The reasons for this include smaller size, greater ionization energy, and (most important) the fact that the first member of each group has only four valence orbitals (one 2*s* and three 2*p*) available for bonding, whereas other group members have empty *d* orbitals in their valence shells, making possible five, six, or even more bonds around the central atom. For example, nitrogen forms only NF_3, whereas phosphorus forms both PF_3 and PF_5.

Another difference between the first group member and subsequent members is the greater ability of the first member to form π bonds. This is primarily a function of the smaller size of the first member of each group, which allows better overlap of atomic orbitals. Nonmetals, other than the first member of each group, rarely form π bonds to nonmetals that are the first member of a group. For example, sulfur-oxygen π bonds are well known, whereas sulfur does not normally form stable π bonds to itself.

The variety of oxidation states displayed by most of the nonmetals means that many of their chemical reactions involve changes in oxidation state through oxidation-reduction reactions. There are five general aspects of the oxidation-reduction chemistry:

1. Nonmetals oxidize most metals. The oxidation state of the metal becomes positive as it undergoes oxidation and that of the nonmetal becomes negative as it undergoes reduction. For example:

$$\begin{array}{llll} 4\text{Fe}(s) + & 3\text{O}_2(g) & \longrightarrow & 2\text{Fe}_2\text{O}_3(s) \\ \;\;0 & \;\;0 & & \;\;+3\;\;-2 \end{array}$$

2. With the exception of nitrogen and carbon, which are poor oxidizing agents, a more electronegative nonmetal oxidizes a less electronegative nonmetal or the anion of the nonmetal:

$$\begin{array}{llll} \text{S}(s) + & \text{O}_2(g) & \longrightarrow & 2\text{SO}_2(s) \\ 0 & 0 & & \;\;+4\;\;\;-2 \end{array}$$

$$\begin{array}{llll} \text{Cl}_2(g) + & 2\text{I}^-(aq) & \longrightarrow & \text{I}_2(s) + 2\text{Cl}^-(aq) \\ 0 & & & 0 \end{array}$$

3. Fluorine and oxygen are the strongest oxidizing agents within their respective groups; each oxidizes all the elements that lie below it in the group. Within any period, the strongest oxidizing agent is in group 17. A nonmetal often oxidizes an element that lies to its left in the same period. For example:

$$\begin{array}{llll} 2\text{As}(s) + & 3\text{Br}_2(l) & \longrightarrow & 2\text{AsBr}_3(s) \\ 0 & 0 & & +3\;-1 \end{array}$$

4. The stronger a nonmetal is as an oxidizing agent, the more difficult it is to oxidize the anion formed by the nonmetal. This means that the most stable negative ions are formed by elements at the top of the group or in group 17 of the period.

5. Fluorine and oxygen are the strongest oxidizing elements known. Fluorine does not form compounds in which it exhibits positive oxidation states; oxygen exhibits a positive oxidation state only when combined with fluorine. For example:

$$\begin{array}{llll} 2\text{F}_2(g) + & 2\text{OH}^-(aq) & \longrightarrow & \text{OF}_2(g) + 2\text{F}^-(aq) + \text{H}_2\text{O}(l) \\ 0 & & & +2 \qquad\;\; -1 \end{array}$$

With the exception of most of the noble gases, all nonmetals form compounds with oxygen, yielding covalent oxides. Most of these oxides are acidic, that is, they react with water to form oxyacids. Recall from the acid-base chapter that an oxyacid is an acid consisting of hydrogen, oxygen, and some other element. Notable exceptions are carbon monoxide, CO, nitrous oxide, N_2O, and nitric oxide, NO. There are three characteristics of these acidic oxides:

1. Oxides such as SO_2 and N_2O_5, in which the nonmetal exhibits one of its common oxidation states, are **acid anhydrides** and react with water to form acids with no change in oxidation state. The product is an oxyacid. For example:

$$\text{SO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{SO}_3(aq)$$

$$\text{N}_2\text{O}_5(s) + \text{H}_2\text{O}(l) \longrightarrow 2\text{HNO}_3(aq)$$

2. Those oxides such as NO_2 and ClO_2, in which the nonmetal does not exhibit one of its common oxidation states, also react with water. In these reactions, the nonmetal is both oxidized and reduced. For example:

$$\begin{array}{lllll} 3\text{NO}_2(g) + & \text{H}_2\text{O}(l) & \longrightarrow & 2\text{HNO}_3(aq) + & \text{NO}(g) \\ +4 & & & +5 & +2 \end{array}$$

   Reactions in which the same element is both oxidized and reduced are called **disproportionation reactions**.

3. The acid strength increases as the electronegativity of the central atom increases. To learn more, see the discussion in the chapter on acid-base chemistry.

The binary hydrogen compounds of the nonmetals also exhibit an acidic behavior in water, although only HCl, HBr, and HI are strong acids. The acid strength of the nonmetal hydrogen compounds increases from left to right across a period and down a group. For example, ammonia, NH_3, is a weaker acid than is water, H_2O, which is weaker than is hydrogen fluoride, HF. Water, H_2O, is also a weaker acid than is hydrogen sulfide, H_2S, which is weaker than is hydrogen selenide, H_2Se. Weaker acidic character implies greater basic character.

Structures of the Nonmetals

The structures of the nonmetals differ dramatically from those of metals. Metals crystallize in closely packed arrays that do not contain molecules or covalent bonds. Nonmetal structures contain covalent bonds, and many nonmetals consist of individual molecules. The electrons in nonmetals are localized in covalent bonds, whereas in a metal, there is delocalization of the electrons throughout the solid.

The noble gases are all monatomic, whereas the other nonmetal gases—hydrogen, nitrogen, oxygen, fluorine, and chlorine—normally exist as the diatomic molecules H_2, N_2, O_2, F_2, and Cl_2. The other halogens are also diatomic; Br_2 is a liquid and I_2 exists as a solid under normal conditions. The changes in state as one moves down the halogen family offer excellent examples of the increasing strength of intermolecular London forces with increasing molecular mass and increasing polarizability.

Oxygen has two allotropes: O_2, dioxygen, and O_3, ozone. Phosphorus has three common allotropes, commonly referred to by their colors: white, red, and black. Sulfur has several allotropes. There are also many carbon allotropes. Most people know of diamond, graphite, and charcoal, but fewer people know of the recent discovery of fullerenes, carbon nanotubes, and graphene.

Descriptions of the physical properties of three nonmetals that are characteristic of molecular solids follow.

Carbon

Carbon occurs in the uncombined (elemental) state in many forms, such as diamond, graphite, charcoal, coke, carbon black, graphene, and fullerene.

Diamond, shown in **Figure 18.20**, is a very hard crystalline material that is colorless and transparent when pure. Each atom forms four single bonds to four other atoms at the corners of a tetrahedron (sp^3 hybridization); this makes the diamond a giant molecule. Carbon-carbon single bonds are very strong, and, because they extend throughout the crystal to form a three-dimensional network, the crystals are very hard and have high melting points (~4400 °C).

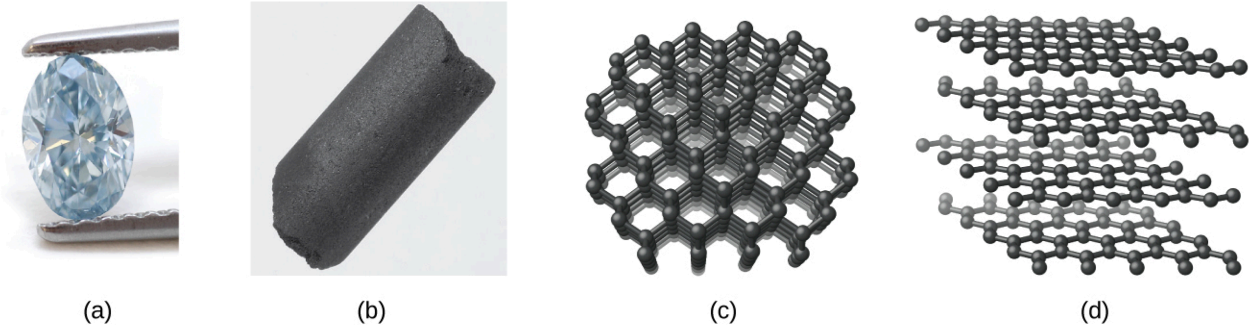


Figure 18.20 (a) Diamond and (b) graphite are two forms of carbon. (c) In the crystal structure of diamond, the covalent bonds form three-dimensional tetrahedrons. (d) In the crystal structure of graphite, each planar layer is composed of six-membered rings. (credit a: modification of work by “Fancy Diamonds”/Flickr; credit b: modification of work from http://images-of-elements.com/carbon.php)

Graphite, also shown in **Figure 18.20**, is a soft, slippery, grayish-black solid that conducts electricity. These properties relate to its structure, which consists of layers of carbon atoms, with each atom surrounded by three other carbon atoms in a trigonal planar arrangement. Each carbon atom in graphite forms three σ bonds, one to each of its nearest neighbors, by means of sp^2-hybrid orbitals. The unhybridized p orbital on each carbon atom will overlap unhybridized orbitals on adjacent carbon atoms in the same layer to form π bonds. Many resonance forms are necessary to describe the electronic structure of a graphite layer; **Figure 18.21** illustrates two of these forms.

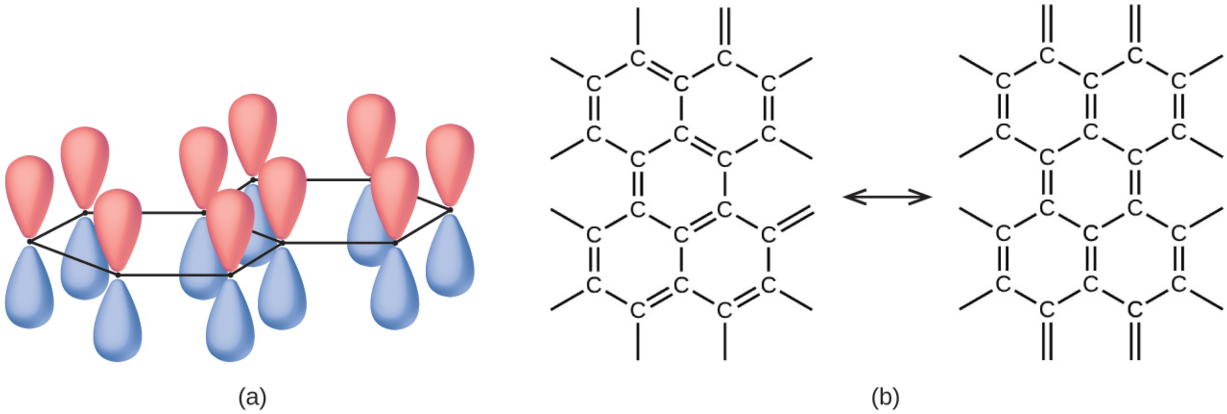


Figure 18.21 (a) Carbon atoms in graphite have unhybridized *p* orbitals. Each *p* orbital is perpendicular to the plane of carbon atoms. (b) These are two of the many resonance forms of graphite necessary to describe its electronic structure as a resonance hybrid.

Atoms within a graphite layer are bonded together tightly by the σ and π bonds; however, the forces between layers are weak. London dispersion forces hold the layers together. To learn more, see the discussion of these weak forces in the chapter on liquids and solids. The weak forces between layers give graphite the soft, flaky character that makes it useful as the so-called "lead" in pencils and the slippery character that makes it useful as a lubricant. The loosely held electrons in the resonating π bonds can move throughout the solid and are responsible for the electrical conductivity of graphite.

Other forms of elemental carbon include carbon black, charcoal, and coke. Carbon black is an amorphous form of carbon prepared by the incomplete combustion of natural gas, CH_4. It is possible to produce charcoal and coke by heating wood and coal, respectively, at high temperatures in the absence of air.

Recently, new forms of elemental carbon molecules have been identified in the soot generated by a smoky flame and in the vapor produced when graphite is heated to very high temperatures in a vacuum or in helium. One of these new forms, first isolated by Professor Richard Smalley and coworkers at Rice University, consists of icosahedral (soccer-ball-shaped) molecules that contain 60 carbon atoms, C_{60}. This is buckminsterfullerene (often called bucky balls) after the architect Buckminster Fuller, who designed domed structures, which have a similar appearance (**Figure 18.22**).

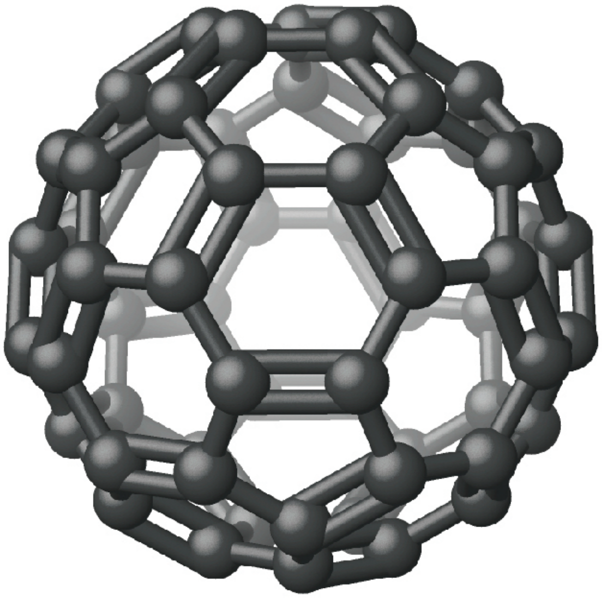


Figure 18.22 The molecular structure of C_{60}, buckminsterfullerene, is icosahedral.

Chemistry in Everyday Life

Nanotubes and Graphene

Graphene and carbon nanotubes are two recently discovered allotropes of carbon. Both of the forms bear some relationship to graphite. Graphene is a single layer of graphite (one atom thick), as illustrated in **Figure 18.23**, whereas carbon nanotubes roll the layer into a small tube, as illustrated in **Figure 18.23**.

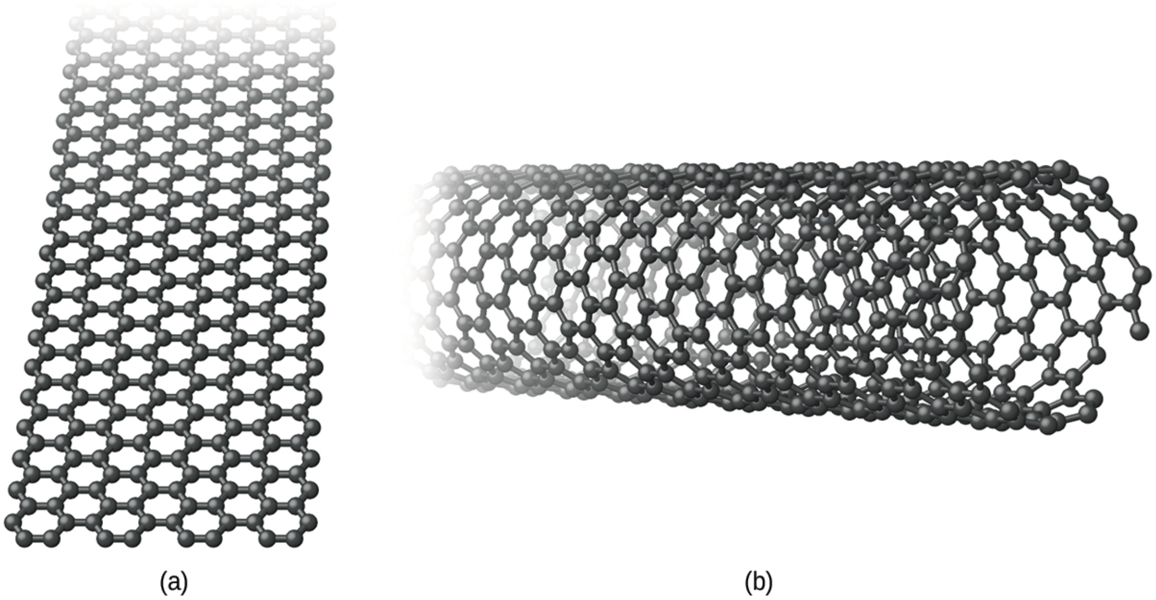


Figure 18.23 (a) Graphene and (b) carbon nanotubes are both allotropes of carbon.

Graphene is a very strong, lightweight, and efficient conductor of heat and electricity discovered in 2003. As in graphite, the carbon atoms form a layer of six-membered rings with sp^2-hybridized carbon atoms at the corners. Resonance stabilizes the system and leads to its conductivity. Unlike graphite, there is no stacking of the layers to give a three-dimensional structure. Andre Geim and Kostya Novoselov at the University of Manchester won the 2010 Nobel Prize in Physics for their pioneering work characterizing graphene.

The simplest procedure for preparing graphene is to use a piece of adhesive tape to remove a single layer of graphene from the surface of a piece of graphite. This method works because there are only weak London dispersion forces between the layers in graphite. Alternative methods are to deposit a single layer of carbon atoms on the surface of some other material (ruthenium, iridium, or copper) or to synthesize it at the surface of silicon carbide via the sublimation of silicon.

There currently are no commercial applications of graphene. However, its unusual properties, such as high electron mobility and thermal conductivity, should make it suitable for the manufacture of many advanced electronic devices and for thermal management applications.

Carbon nanotubes are carbon allotropes, which have a cylindrical structure. Like graphite and graphene, nanotubes consist of rings of sp^2-hybridized carbon atoms. Unlike graphite and graphene, which occur in layers, the layers wrap into a tube and bond together to produce a stable structure. The walls of the tube may be one atom or multiple atoms thick.

Carbon nanotubes are extremely strong materials that are harder than diamond. Depending upon the shape of the nanotube, it may be a conductor or semiconductor. For some applications, the conducting form is preferable, whereas other applications utilize the semiconducting form.

The basis for the synthesis of carbon nanotubes is the generation of carbon atoms in a vacuum. It is possible to produce carbon atoms by an electrical discharge through graphite, vaporization of graphite with a laser, and the decomposition of a carbon compound.

The strength of carbon nanotubes will eventually lead to some of their most exciting applications, as a thread produced from several nanotubes will support enormous weight. However, the current applications only employ bulk nanotubes. The addition of nanotubes to polymers improves the mechanical, thermal, and electrical properties of the bulk material. There are currently nanotubes in some bicycle parts, skis, baseball bats, fishing rods, and surfboards.

Phosphorus

The name *phosphorus* comes from the Greek words meaning *light bringing.* When phosphorus was first isolated, scientists noted that it glowed in the dark and burned when exposed to air. Phosphorus is the only member of its group that does not occur in the uncombined state in nature; it exists in many allotropic forms. We will consider two of those forms: white phosphorus and red phosphorus.

White phosphorus is a white, waxy solid that melts at 44.2 °C and boils at 280 °C. It is insoluble in water (in which it is stored—see **Figure 18.24**), is very soluble in carbon disulfide, and bursts into flame in air. As a solid, as a liquid, as a gas, and in solution, white phosphorus exists as P_4 molecules with four phosphorus atoms at the corners of a regular tetrahedron, as illustrated in **Figure 18.24**. Each phosphorus atom covalently bonds to the other three atoms in the molecule by single covalent bonds. White phosphorus is the most reactive allotrope and is very toxic.

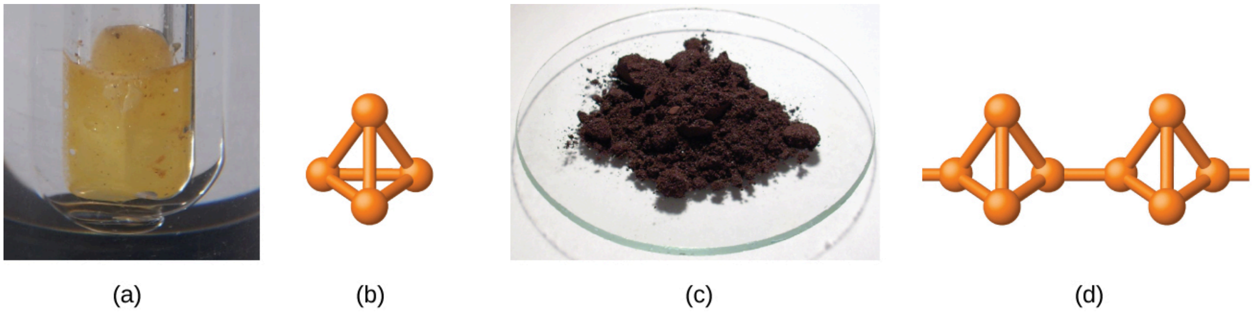


Figure 18.24 (a) Because white phosphorus bursts into flame in air, it is stored in water. (b) The structure of white phosphorus consists of P_4 molecules arranged in a tetrahedron. (c) Red phosphorus is much less reactive than is white phosphorus. (d) The structure of red phosphorus consists of networks of P_4 tetrahedra joined by P-P single bonds. (credit a: modification of work from http://images-of-elements.com/phosphorus.php)

Heating white phosphorus to 270–300 °C in the absence of air yields red phosphorus. Red phosphorus (shown in **Figure 18.24**) is denser, has a higher melting point (~600 °C), is much less reactive, is essentially nontoxic, and is easier and safer to handle than is white phosphorus. Its structure is highly polymeric and appears to contain three-dimensional networks of P_4 tetrahedra joined by P-P single bonds. Red phosphorus is insoluble in solvents that dissolve white phosphorus. When red phosphorus is heated, P_4 molecules sublime from the solid.

Sulfur

The allotropy of sulfur is far greater and more complex than that of any other element. Sulfur is the brimstone referred to in the Bible and other places, and references to sulfur occur throughout recorded history—right up to the relatively recent discovery that it is a component of the atmospheres of Venus and of Io, a moon of Jupiter. The most common and most stable allotrope of sulfur is yellow, rhombic sulfur, so named because of the shape of its crystals. Rhombic sulfur is the form to which all other allotropes revert at room temperature. Crystals of rhombic sulfur melt at 113 °C. Cooling this liquid gives long needles of monoclinic sulfur. This form is stable from 96 °C to the melting point, 119 °C. At room temperature, it gradually reverts to the rhombic form.

Both rhombic sulfur and monoclinic sulfur contain S_8 molecules in which atoms form eight-membered, puckered rings that resemble crowns, as illustrated in **Figure 18.25**. Each sulfur atom is bonded to each of its two neighbors in the ring by covalent S-S single bonds.

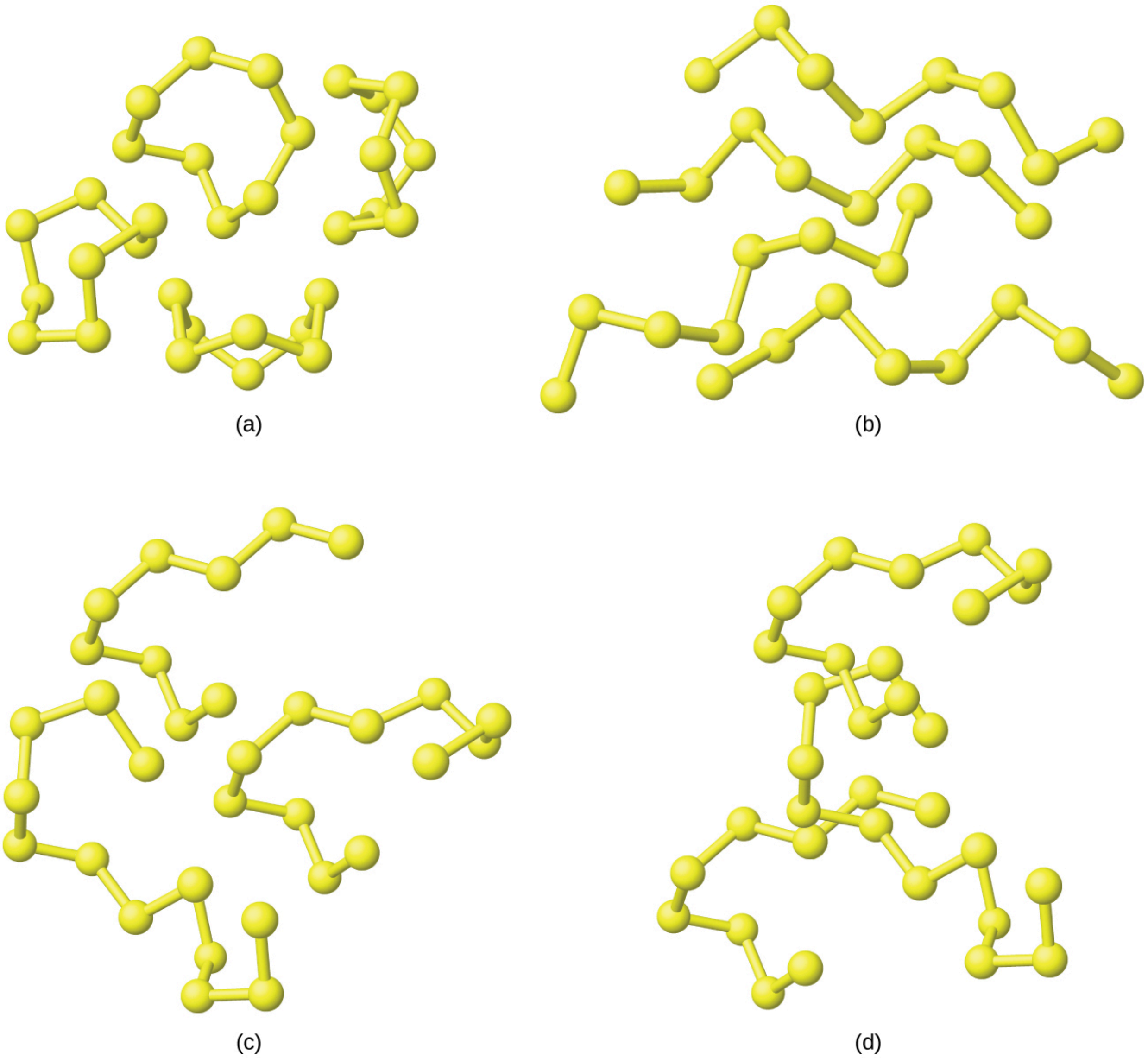


Figure 18.25 These four sulfur allotropes show eight-membered, puckered rings. Each sulfur atom bonds to each of its two neighbors in the ring by covalent S-S single bonds. Here are (a) individual S_8 rings, (b) S_8 chains formed when the rings open, (c) longer chains formed by adding sulfur atoms to S_8 chains, and (d) part of the very long sulfur chains formed at higher temperatures.

When rhombic sulfur melts, the straw-colored liquid is quite mobile; its viscosity is low because S_8 molecules are essentially spherical and offer relatively little resistance as they move past each other. As the temperature rises, S-S bonds in the rings break, and polymeric chains of sulfur atoms result. These chains combine end to end, forming still longer chains that tangle with one another. The liquid gradually darkens in color and becomes so viscous that finally (at about 230 °C) it does not pour easily. The dangling atoms at the ends of the chains of sulfur atoms are responsible for the dark red color because their electronic structure differs from those of sulfur atoms that have bonds to two adjacent sulfur atoms. This causes them to absorb light differently and results in a different visible color. Cooling the liquid rapidly produces a rubberlike amorphous mass, called plastic sulfur.

Sulfur boils at 445 °C and forms a vapor consisting of S_2, S_6, and S_8 molecules; at about 1000 °C, the vapor density corresponds to the formula S_2, which is a paramagnetic molecule like O_2 with a similar electronic structure and a weak sulfur-sulfur double bond.

As seen in this discussion, an important feature of the structural behavior of the nonmetals is that the elements usually occur with eight electrons in their valence shells. If necessary, the elements form enough covalent bonds to supplement the electrons already present to possess an octet. For example, members of group 15 have five valence electrons and require only three additional electrons to fill their valence shells. These elements form three covalent bonds in their free state: triple bonds in the N_2 molecule or single bonds to three different atoms in arsenic and phosphorus. The elements of group 16 require only two additional electrons. Oxygen forms a double bond in the O_2 molecule, and sulfur, selenium, and tellurium form two single bonds in various rings and chains. The halogens form diatomic molecules in which each atom is involved in only one bond. This provides the electron required necessary to complete the octet on the halogen atom. The noble gases do not form covalent bonds to other noble gas atoms because they already have a filled outer shell.

18.5 Occurrence, Preparation, and Compounds of Hydrogen

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

- Describe the properties, preparation, and compounds of hydrogen

Hydrogen is the most abundant element in the universe. The sun and other stars are composed largely of hydrogen. Astronomers estimate that 90% of the atoms in the universe are hydrogen atoms. Hydrogen is a component of more compounds than any other element. Water is the most abundant compound of hydrogen found on earth. Hydrogen is an important part of petroleum, many minerals, cellulose and starch, sugar, fats, oils, alcohols, acids, and thousands of other substances.

At ordinary temperatures, hydrogen is a colorless, odorless, tasteless, and nonpoisonous gas consisting of the diatomic molecule H_2. Hydrogen is composed of three isotopes, and unlike other elements, these isotopes have different names and chemical symbols: protium, ^1H, deuterium, ^2H (or “D”), and tritium ^3H (or “T”). In a naturally occurring sample of hydrogen, there is one atom of deuterium for every 7000 H atoms and one atom of radioactive tritium for every 10^{18} H atoms. The chemical properties of the different isotopes are very similar because they have identical electron structures, but they differ in some physical properties because of their differing atomic masses. Elemental deuterium and tritium have lower vapor pressure than ordinary hydrogen. Consequently, when liquid hydrogen evaporates, the heavier isotopes are concentrated in the last portions to evaporate. Electrolysis of heavy water, D_2O, yields deuterium. Most tritium originates from nuclear reactions.

Preparation of Hydrogen

Elemental hydrogen must be prepared from compounds by breaking chemical bonds. The most common methods of preparing hydrogen follow.

From Steam and Carbon or Hydrocarbons

Water is the cheapest and most abundant source of hydrogen. Passing steam over coke (an impure form of elemental carbon) at 1000 °C produces a mixture of carbon monoxide and hydrogen known as water gas:

$$\mathrm{C}(s) + \mathrm{H_2O}(g) \xrightarrow{1000\ ^\circ\mathrm{C}} \underbrace{\mathrm{CO}(g) + \mathrm{H_2}(g)}_{\text{water gas}}$$

Water gas is as an industrial fuel. It is possible to produce additional hydrogen by mixing the water gas with steam in the presence of a catalyst to convert the CO to CO_2. This reaction is the water gas shift reaction.

It is also possible to prepare a mixture of hydrogen and carbon monoxide by passing hydrocarbons from natural gas or petroleum and steam over a nickel-based catalyst. Propane is an example of a hydrocarbon reactant:

$$C_3H_8(g) + 3H_2O(g) \xrightarrow[\text{catalyst}]{900\ °\text{C}} 3CO(g) + 7H_2(g)$$

Electrolysis

Hydrogen forms when direct current electricity passes through water containing an electrolyte such as H_2SO_4, as illustrated in **Figure 18.26**. Bubbles of hydrogen form at the cathode, and oxygen evolves at the anode. The net reaction is:

$$2H_2O(l) + \text{electrical energy} \longrightarrow 2H_2(g) + O_2(g)$$

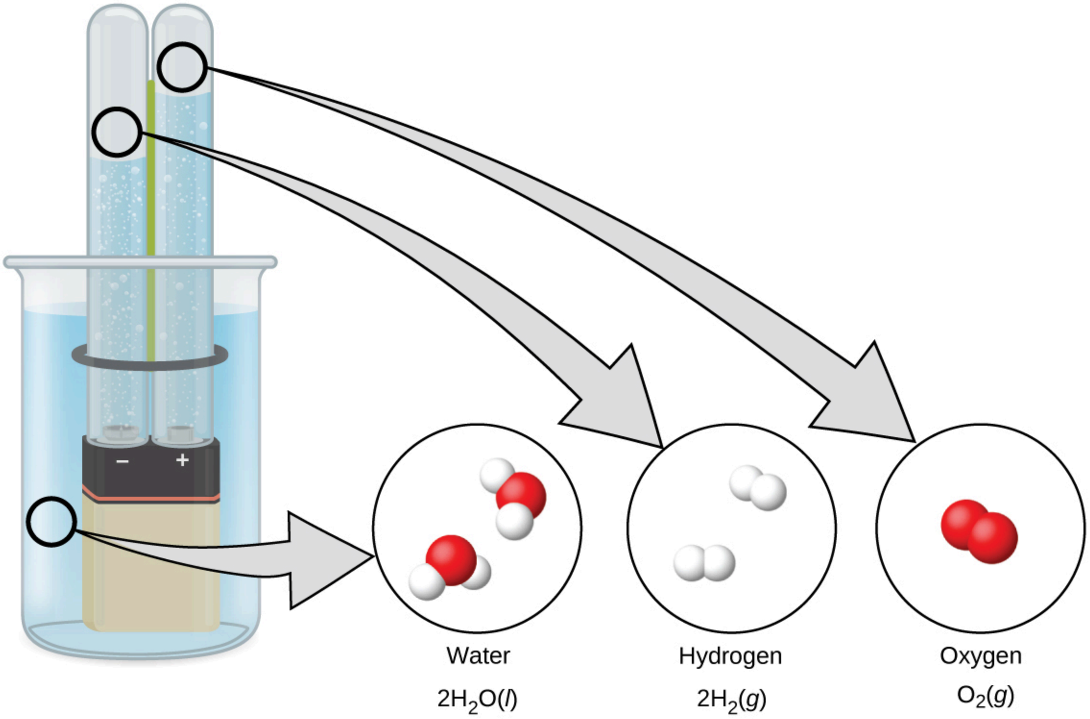


Figure 18.26 The electrolysis of water produces hydrogen and oxygen. Because there are twice as many hydrogen atoms as oxygen atoms and both elements are diatomic, there is twice the volume of hydrogen produced at the cathode as there is oxygen produced at the anode.

Reaction of Metals with Acids

This is the most convenient laboratory method of producing hydrogen. Metals with lower reduction potentials reduce the hydrogen ion in dilute acids to produce hydrogen gas and metal salts. For example, as shown in **Figure 18.27**, iron in dilute hydrochloric acid produces hydrogen gas and iron(II) chloride:

$$\mathrm{Fe}(s) + 2\mathrm{H_3O^+}(aq) + 2\mathrm{Cl^-}(aq) \longrightarrow \mathrm{Fe^{2+}}(aq) + 2\mathrm{Cl^-}(aq) + \mathrm{H_2}(g) + 2\mathrm{H_2O}(l)$$

Figure 18.27 The reaction of iron with an acid produces hydrogen. Here, iron reacts with hydrochloric acid. (credit: Mark Ott)

Reaction of Ionic Metal Hydrides with Water

It is possible to produce hydrogen from the reaction of hydrides of the active metals, which contain the very strongly basic H^- anion, with water:

$$\mathrm{CaH_2}(s) + 2\mathrm{H_2O}(l) \longrightarrow \mathrm{Ca^{2+}}(aq) + 2\mathrm{OH^-}(aq) + 2\mathrm{H_2}(g)$$

Metal hydrides are expensive but convenient sources of hydrogen, especially where space and weight are important factors. They are important in the inflation of life jackets, life rafts, and military balloons.

Reactions

Under normal conditions, hydrogen is relatively inactive chemically, but when heated, it enters into many chemical reactions.

Two thirds of the world's hydrogen production is devoted to the manufacture of ammonia, which is a fertilizer and used in the manufacture of nitric acid. Large quantities of hydrogen are also important in the process of **hydrogenation**, discussed in the chapter on organic chemistry.

It is possible to use hydrogen as a nonpolluting fuel. The reaction of hydrogen with oxygen is a very exothermic reaction, releasing 286 kJ of energy per mole of water formed. Hydrogen burns without explosion under controlled conditions. The oxygen-hydrogen torch, because of the high heat of combustion of hydrogen, can achieve temperatures up to 2800 °C. The hot flame of this torch is useful in cutting thick sheets of many metals. Liquid hydrogen is also an important rocket fuel (**Figure 18.28**).

Figure 18.28 Before the fleet's retirement in 2011, liquid hydrogen and liquid oxygen were used in the three main engines of a space shuttle. Two compartments in the large tank held these liquids until the shuttle was launched. (credit: "reynermedia"/Flickr)

An uncombined hydrogen atom consists of a nucleus and one valence electron in the 1*s* orbital. The $n = 1$ valence shell has a capacity for two electrons, and hydrogen can rightfully occupy two locations in the periodic table. It is possible to consider hydrogen a group 1 element because hydrogen can lose an electron to form the cation, H^+. It is also possible to consider hydrogen to be a group 17 element because it needs only one electron to fill its valence orbital to form a hydride ion, H^-, or it can share an electron to form a single, covalent bond. In reality, hydrogen is a unique element that almost deserves its own location in the periodic table.

Reactions with Elements

When heated, hydrogen reacts with the metals of group 1 and with Ca, Sr, and Ba (the more active metals in group 2). The compounds formed are crystalline, ionic hydrides that contain the hydride anion, H^-, a strong reducing agent and a strong base, which reacts vigorously with water and other acids to form hydrogen gas.

The reactions of hydrogen with nonmetals generally produce *acidic* hydrogen compounds with hydrogen in the 1+ oxidation state. The reactions become more exothermic and vigorous as the electronegativity of the nonmetal increases. Hydrogen reacts with nitrogen and sulfur only when heated, but it reacts explosively with fluorine (forming HF) and, under some conditions, with chlorine (forming HCl). A mixture of hydrogen and oxygen explodes if ignited. Because of the explosive nature of the reaction, it is necessary to exercise caution when handling hydrogen (or any other combustible gas) to avoid the formation of an explosive mixture in a confined space. Although most hydrides of the nonmetals are acidic, ammonia and phosphine (PH_3) are very, very weak acids and generally function as bases. There is a summary of these reactions of hydrogen with the elements in **Table 18.1**.

Chemical Reactions of Hydrogen with Other Elements

General Equation	Comments
$MH \text{ or } MH_2 \longrightarrow MOH \text{ or } M(OH)_2 + H_2$	ionic hydrides with group 1 and Ca, Sr, and Ba
$H_2 + C \longrightarrow \text{(no reaction)}$	
$3H_2 + N_2 \longrightarrow 2NH_3$	requires high pressure and temperature; low yield
$2H_2 + O_2 \longrightarrow 2H_2O$	exothermic and potentially explosive
$H_2 + S \longrightarrow H_2S$	requires heating; low yield

Table 18.1

Chemical Reactions of Hydrogen with Other Elements

General Equation	Comments
$H_2 + X_2 \longrightarrow 2HX$	X = F, Cl, Br, and I; explosive with F_2; low yield with I_2

Table 18.1

Reaction with Compounds

Hydrogen reduces the heated oxides of many metals, with the formation of the metal and water vapor. For example, passing hydrogen over heated CuO forms copper and water.

Hydrogen may also reduce the metal ions in some metal oxides to lower oxidation states:

$$H_2(g) + MnO_2(s) \xrightarrow{\Delta} MnO(s) + H_2O(g)$$

Hydrogen Compounds

Other than the noble gases, each of the nonmetals forms compounds with hydrogen. For brevity, we will discuss only a few hydrogen compounds of the nonmetals here.

Nitrogen Hydrogen Compounds

Ammonia, NH_3, forms naturally when any nitrogen-containing organic material decomposes in the absence of air. The laboratory preparation of ammonia is by the reaction of an ammonium salt with a strong base such as sodium hydroxide. The acid-base reaction with the weakly acidic ammonium ion gives ammonia, illustrated in **Figure 18.29**. Ammonia also forms when ionic nitrides react with water. The nitride ion is a much stronger base than the hydroxide ion:

$$Mg_3N_2(s) + 6H_2O(l) \longrightarrow 3Mg(OH)_2(s) + 2NH_3(g)$$

The commercial production of ammonia is by the direct combination of the elements in the **Haber process**:

$$N_2(g) + 3H_2(g) \overset{\text{catalyst}}{\rightleftharpoons} 2NH_3(g) \qquad \Delta H° = -92 \text{ kJ}$$

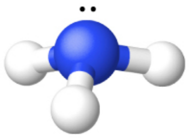


Figure 18.29 The structure of ammonia is shown with a central nitrogen atom and three hydrogen atoms.

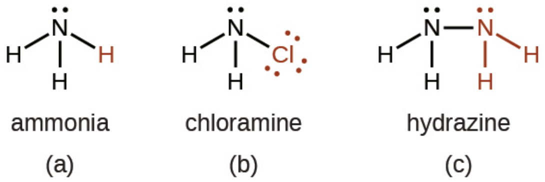
Ammonia is a colorless gas with a sharp, pungent odor. Smelling salts utilize this powerful odor. Gaseous ammonia readily liquefies to give a colorless liquid that boils at −33 °C. Due to intermolecular hydrogen bonding, the enthalpy of vaporization of liquid ammonia is higher than that of any other liquid except water, so ammonia is useful as a refrigerant. Ammonia is quite soluble in water (658 L at STP dissolves in 1 L H_2O).

The chemical properties of ammonia are as follows:

1. Ammonia acts as a Brønsted base, as discussed in the chapter on acid-base chemistry. The ammonium ion is similar in size to the potassium ion; compounds of the two ions exhibit many similarities in their structures and solubilities.
2. Ammonia can display acidic behavior, although it is a much weaker acid than water. Like other acids, ammonia reacts with metals, although it is so weak that high temperatures are necessary. Hydrogen and

(depending on the stoichiometry) amides (salts of $NH_2{}^-$), imides (salts of NH^{2-}), or nitrides (salts of N^{3-}) form.

3. The nitrogen atom in ammonia has its lowest possible oxidation state (3−) and thus is not susceptible to reduction. However, it can be oxidized. Ammonia burns in air, giving NO and water. Hot ammonia and the ammonium ion are active reducing agents. Of particular interest are the oxidations of ammonium ion by nitrite ion, $NO_2{}^-$, to yield pure nitrogen and by nitrate ion to yield nitrous oxide, N_2O.
4. There are a number of compounds that we can consider derivatives of ammonia through the replacement of one or more hydrogen atoms with some other atom or group of atoms. Inorganic derivations include chloramine, NH_2Cl, and hydrazine, N_2H_4:



Chloramine, NH_2Cl, results from the reaction of sodium hypochlorite, NaOCl, with ammonia in basic solution. In the presence of a large excess of ammonia at low temperature, the chloramine reacts further to produce hydrazine, N_2H_4:

$$NH_3(aq) + OCl^-(aq) \longrightarrow NH_2Cl(aq) + OH^-(aq)$$
$$NH_2Cl(aq) + NH_3(aq) + OH^-(aq) \longrightarrow N_2H_4(aq) + Cl^-(aq) + H_2O(l)$$

Anhydrous hydrazine is relatively stable in spite of its positive free energy of formation:

$$N_2(g) + 2H_2(g) \longrightarrow N_2H_4(l) \qquad \Delta G_f^\circ = 149.2 \text{ kJ mol}^{-1}$$

Hydrazine is a fuming, colorless liquid that has some physical properties remarkably similar to those of H_2O (it melts at 2 °C, boils at 113.5 °C, and has a density at 25 °C of 1.00 g/mL). It burns rapidly and completely in air with substantial evolution of heat:

$$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -621.5 \text{ kJ mol}^{-1}$$

Like ammonia, hydrazine is both a Brønsted base and a Lewis base, although it is weaker than ammonia. It reacts with strong acids and forms two series of salts that contain the $N_2H_5{}^+$ and $N_2H_6{}^{2+}$ ions, respectively. Some rockets use hydrazine as a fuel.

Phosphorus Hydrogen Compounds

The most important hydride of phosphorus is phosphine, PH_3, a gaseous analog of ammonia in terms of both formula and structure. Unlike ammonia, it is not possible to form phosphine by direct union of the elements. There are two methods for the preparation of phosphine. One method is by the action of an acid on an ionic phosphide. The other method is the disproportionation of white phosphorus with hot concentrated base to produce phosphine and the hydrogen phosphite ion:

$$AlP(s) + 3H_3O^+(aq) \longrightarrow PH_3(g) + Al^{3+}(aq) + 3H_2O(l)$$
$$P_4(s) + 4OH^-(aq) + 2H_2O(l) \longrightarrow 2HPO_3{}^{2-}(aq) + 2PH_3(g)$$

Phosphine is a colorless, very poisonous gas, which has an odor like that of decaying fish. Heat easily decomposes phosphine ($4PH_3 \longrightarrow P_4 + 6H_2$), and the compound burns in air. The major uses of phosphine are as a fumigant for grains and in semiconductor processing. Like ammonia, gaseous phosphine unites with gaseous hydrogen halides, forming phosphonium compounds like PH_4Cl and PH_4I. Phosphine is a much weaker base than ammonia; therefore, these compounds decompose in water, and the insoluble PH_3 escapes from solution.

Sulfur Hydrogen Compounds

Hydrogen sulfide, H_2S, is a colorless gas that is responsible for the offensive odor of rotten eggs and of many hot springs. Hydrogen sulfide is as toxic as hydrogen cyanide; therefore, it is necessary to exercise great care in handling it. Hydrogen sulfide is particularly deceptive because it paralyzes the olfactory nerves; after a short exposure, one does not smell it.

The production of hydrogen sulfide by the direct reaction of the elements (H_2 + S) is unsatisfactory because the yield is low. A more effective preparation method is the reaction of a metal sulfide with a dilute acid. For example:

$$\text{FeS}(s) + 2\text{H}_3\text{O}^+(aq) \longrightarrow \text{Fe}^{2+}(aq) + \text{H}_2\text{S}(g) + 2\text{H}_2\text{O}(l)$$

It is easy to oxidize the sulfur in metal sulfides and in hydrogen sulfide, making metal sulfides and H_2S good reducing agents. In acidic solutions, hydrogen sulfide reduces Fe^{3+} to Fe^{2+}, $\text{MnO}_4{}^-$ to Mn^{2+}, $\text{Cr}_2\text{O}_7{}^{2-}$ to Cr^{3+}, and HNO_3 to NO_2. The sulfur in H_2S usually oxidizes to elemental sulfur, unless a large excess of the oxidizing agent is present. In which case, the sulfide may oxidize to $\text{SO}_3{}^{2-}$ or $\text{SO}_4{}^{2-}$ (or to SO_2 or SO_3 in the absence of water):

$$2\text{H}_2\text{S}(g) + \text{O}_2(g) \longrightarrow 2\text{S}(s) + 2\text{H}_2\text{O}(l)$$

This oxidation process leads to the removal of the hydrogen sulfide found in many sources of natural gas. The deposits of sulfur in volcanic regions may be the result of the oxidation of H_2S present in volcanic gases.

Hydrogen sulfide is a weak diprotic acid that dissolves in water to form hydrosulfuric acid. The acid ionizes in two stages, yielding hydrogen sulfide ions, HS^-, in the first stage and sulfide ions, S^{2-}, in the second. Since hydrogen sulfide is a weak acid, aqueous solutions of soluble sulfides and hydrogen sulfides are basic:

$$\begin{aligned}\text{S}^{2-}(aq) + \text{H}_2\text{O}(l) &\rightleftharpoons \text{HS}^-(aq) + \text{OH}^-(aq)\\ \text{HS}^-(aq) + \text{H}_2\text{O}(l) &\rightleftharpoons \text{H}_2\text{S}(g) + \text{OH}^-(aq)\end{aligned}$$

Halogen Hydrogen Compounds

Binary compounds containing only hydrogen and a halogen are **hydrogen halides**. At room temperature, the pure hydrogen halides HF, HCl, HBr, and HI are gases.

In general, it is possible to prepare the halides by the general techniques used to prepare other acids. Fluorine, chlorine, and bromine react directly with hydrogen to form the respective hydrogen halide. This is a commercially important reaction for preparing hydrogen chloride and hydrogen bromide.

The acid-base reaction between a nonvolatile strong acid and a metal halide will yield a hydrogen halide. The escape of the gaseous hydrogen halide drives the reaction to completion. For example, the usual method of preparing hydrogen fluoride is by heating a mixture of calcium fluoride, CaF_2, and concentrated sulfuric acid:

$$\text{CaF}_2(s) + \text{H}_2\text{SO}_4(aq) \longrightarrow \text{CaSO}_4(s) + 2\text{HF}(g)$$

Gaseous hydrogen fluoride is also a by-product in the preparation of phosphate fertilizers by the reaction of fluoroapatite, $Ca_5(PO_4)_3F$, with sulfuric acid. The reaction of concentrated sulfuric acid with a chloride salt produces hydrogen chloride both commercially and in the laboratory.

In most cases, sodium chloride is the chloride of choice because it is the least expensive chloride. Hydrogen bromide and hydrogen iodide cannot be prepared using sulfuric acid because this acid is an oxidizing agent capable of oxidizing both bromide and iodide. However, it is possible to prepare both hydrogen bromide and hydrogen iodide using an acid such as phosphoric acid because it is a weaker oxidizing agent. For example:

$$\text{H}_3\text{PO}_4(l) + \text{Br}^-(aq) \longrightarrow \text{HBr}(g) + \text{H}_2\text{PO}_4{}^-(aq)$$

All of the hydrogen halides are very soluble in water, forming hydrohalic acids. With the exception of hydrogen fluoride, which has a strong hydrogen-fluoride bond, they are strong acids. Reactions of hydrohalic acids with metals, metal hydroxides, oxides, or carbonates produce salts of the halides. Most chloride salts are soluble in water. AgCl, $PbCl_2$, and Hg_2Cl_2 are the commonly encountered exceptions.

The halide ions give the substances the properties associated with $X^-(aq)$. The heavier halide ions (Cl^-, Br^-, and I^-) can act as reducing agents, and the lighter halogens or other oxidizing agents will oxidize them:

$$\begin{aligned} Cl_2(aq) + 2e^- &\longrightarrow 2Cl^-(aq) & E° &= 1.36\text{ V} \\ Br_2(aq) + 2e^- &\longrightarrow 2Br^-(aq) & E° &= 1.09\text{ V} \\ I_2(aq) + 2e^- &\longrightarrow 2I^-(aq) & E° &= 0.54\text{ V} \end{aligned}$$

For example, bromine oxidizes iodine:

$$Br_2(aq) + 2HI(aq) \longrightarrow 2HBr(aq) + I_2(aq) \qquad E° = 0.55\text{ V}$$

Hydrofluoric acid is unique in its reactions with sand (silicon dioxide) and with glass, which is a mixture of silicates:

$$SiO_2(s) + 4HF(aq) \longrightarrow SiF_4(g) + 2H_2O(l)$$
$$CaSiO_3(s) + 6HF(aq) \longrightarrow CaF_2(s) + SiF_4(g) + 3H_2O(l)$$

The volatile silicon tetrafluoride escapes from these reactions. Because hydrogen fluoride attacks glass, it can frost or etch glass and is used to etch markings on thermometers, burets, and other glassware.

The largest use for hydrogen fluoride is in production of hydrochlorofluorocarbons for refrigerants, in plastics, and in propellants. The second largest use is in the manufacture of cryolite, Na_3AlF_6, which is important in the production of aluminum. The acid is also important in the production of other inorganic fluorides (such as BF_3), which serve as catalysts in the industrial synthesis of certain organic compounds.

Hydrochloric acid is relatively inexpensive. It is an important and versatile acid in industry and is important for the manufacture of metal chlorides, dyes, glue, glucose, and various other chemicals. A considerable amount is also important for the activation of oil wells and as pickle liquor—an acid used to remove oxide coating from iron or steel that is to be galvanized, tinned, or enameled. The amounts of hydrobromic acid and hydroiodic acid used commercially are insignificant by comparison.

18.6 Occurrence, Preparation, and Properties of Carbonates

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

- Describe the preparation, properties, and uses of some representative metal carbonates

The chemistry of carbon is extensive; however, most of this chemistry is not relevant to this chapter. The other aspects of the chemistry of carbon will appear in the chapter covering organic chemistry. In this chapter, we will focus on the carbonate ion and related substances. The metals of groups 1 and 2, as well as zinc, cadmium, mercury, and lead(II), form ionic **carbonates**—compounds that contain the carbonate anions, $CO_3{}^{2-}$. The metals of group 1, magnesium, calcium, strontium, and barium also form **hydrogen carbonates**—compounds that contain the hydrogen carbonate anion, $HCO_3{}^-$, also known as the **bicarbonate anion**.

With the exception of magnesium carbonate, it is possible to prepare carbonates of the metals of groups 1 and 2 by the reaction of carbon dioxide with the respective oxide or hydroxide. Examples of such reactions include:

$$Na_2O(s) + CO_2(g) \longrightarrow Na_2CO_3(s)$$
$$Ca(OH)_2(s) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l)$$

The carbonates of the alkaline earth metals of group 12 and lead(II) are not soluble. These carbonates precipitate upon mixing a solution of soluble alkali metal carbonate with a solution of soluble salts of these metals. Examples of net ionic equations for the reactions are:

$$Ca^{2+}(aq) + CO_3{}^{2-}(aq) \longrightarrow CaCO_3(s)$$
$$Pb^{2+}(aq) + CO_3{}^{2-}(aq) \longrightarrow PbCO_3(s)$$

Pearls and the shells of most mollusks are calcium carbonate. Tin(II) or one of the trivalent or tetravalent ions such as Al^{3+} or Sn^{4+} behave differently in this reaction as carbon dioxide and the corresponding oxide form instead of the carbonate.

Alkali metal hydrogen carbonates such as $NaHCO_3$ and $CsHCO_3$ form by saturating a solution of the hydroxides with carbon dioxide. The net ionic reaction involves hydroxide ion and carbon dioxide:

$$\text{OH}^-(aq) + \text{CO}_2(aq) \longrightarrow \text{HCO}_3{}^-(aq)$$

It is possible to isolate the solids by evaporation of the water from the solution.

Although they are insoluble in pure water, alkaline earth carbonates dissolve readily in water containing carbon dioxide because hydrogen carbonate salts form. For example, caves and sinkholes form in limestone when $CaCO_3$ dissolves in water containing dissolved carbon dioxide:

$$\text{CaCO}_3(s) + \text{CO}_2(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{Ca}^{2+}(aq) + 2\text{HCO}_3{}^-(aq)$$

Hydrogen carbonates of the alkaline earth metals remain stable only in solution; evaporation of the solution produces the carbonate. Stalactites and stalagmites, like those shown in **Figure 18.30**, form in caves when drops of water containing dissolved calcium hydrogen carbonate evaporate to leave a deposit of calcium carbonate.

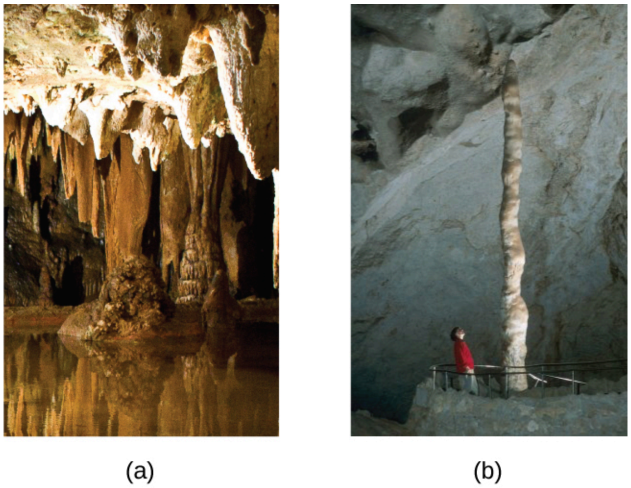

(a) (b)

Figure 18.30 (a) Stalactites and (b) stalagmites are cave formations of calcium carbonate. (credit a: modification of work by Arvind Govindaraj; credit b: modification of work by the National Park Service.)

The two carbonates used commercially in the largest quantities are sodium carbonate and calcium carbonate. In the United States, sodium carbonate is extracted from the mineral trona, $Na_3(CO_3)(HCO_3)(H_2O)_2$. Following recrystallization to remove clay and other impurities, heating the recrystallized trona produces Na_2CO_3:

$$2\text{Na}_3(\text{CO}_3)(\text{HCO}_3)(\text{H}_2\text{O})_2(s) \longrightarrow 3\text{Na}_2\text{CO}_3(s) + 5\text{H}_2\text{O}(l) + \text{CO}_2(g)$$

Carbonates are moderately strong bases. Aqueous solutions are basic because the carbonate ion accepts hydrogen ion from water in this reversible reaction:

$$\text{CO}_3{}^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3{}^-(aq) + \text{OH}^-(aq)$$

Carbonates react with acids to form salts of the metal, gaseous carbon dioxide, and water. The reaction of calcium carbonate, the active ingredient of the antacid Tums, with hydrochloric acid (stomach acid), as shown in **Figure 18.31**, illustrates the reaction:

$$\mathrm{CaCO_3}(s) + 2\mathrm{HCl}(aq) \longrightarrow \mathrm{CaCl_2}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$$

Figure 18.31 The reaction of calcium carbonate with hydrochloric acid is shown. (credit: Mark Ott)

Other applications of carbonates include glass making—where carbonate ions serve as a source of oxide ions—and synthesis of oxides.

Hydrogen carbonates are amphoteric because they act as both weak acids and weak bases. Hydrogen carbonate ions act as acids and react with solutions of soluble hydroxides to form a carbonate and water:

$$\mathrm{KHCO_3}(aq) + \mathrm{KOH}(aq) \longrightarrow \mathrm{K_2CO_3}(aq) + \mathrm{H_2O}(l)$$

With acids, hydrogen carbonates form a salt, carbon dioxide, and water. Baking soda (bicarbonate of soda or sodium bicarbonate) is sodium hydrogen carbonate. Baking powder contains baking soda and a solid acid such as potassium hydrogen tartrate (cream of tartar), $\mathrm{KHC_4H_4O_6}$. As long as the powder is dry, no reaction occurs; immediately after the addition of water, the acid reacts with the hydrogen carbonate ions to form carbon dioxide:

$$\mathrm{HC_4H_4O_6}^{-}(aq) + \mathrm{HCO_3}^{-}(aq) \longrightarrow \mathrm{C_4H_4O_6}^{2-}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$$

Dough will trap the carbon dioxide, causing it to expand during baking, producing the characteristic texture of baked goods.

18.7 Occurrence, Preparation, and Properties of Nitrogen

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

- Describe the properties, preparation, and uses of nitrogen

Most pure nitrogen comes from the fractional distillation of liquid air. The atmosphere consists of 78% nitrogen by volume. This means there are more than 20 million tons of nitrogen over every square mile of the earth’s surface. Nitrogen is a component of proteins and of the genetic material (DNA/RNA) of all plants and animals.

Under ordinary conditions, nitrogen is a colorless, odorless, and tasteless gas. It boils at 77 K and freezes at 63 K. Liquid nitrogen is a useful coolant because it is inexpensive and has a low boiling point. Nitrogen is very unreactive because of the very strong triple bond between the nitrogen atoms. The only common reactions at room temperature occur with lithium to form $\mathrm{Li_3N}$, with certain transition metal complexes, and with hydrogen or oxygen in nitrogen-fixing bacteria. The general lack of reactivity of nitrogen makes the remarkable ability of some bacteria to synthesize nitrogen compounds using atmospheric nitrogen gas as the source one of the most exciting chemical events on our planet. This process is one type of **nitrogen fixation**. In this case, nitrogen fixation is the process where organisms convert atmospheric nitrogen into biologically useful chemicals. Nitrogen fixation also occurs when lightning passes through air, causing molecular nitrogen to react with oxygen to form nitrogen oxides, which are then carried down to the soil.

Chemistry in Everyday Life

Nitrogen Fixation

All living organisms require nitrogen compounds for survival. Unfortunately, most of these organisms cannot absorb nitrogen from its most abundant source—the atmosphere. Atmospheric nitrogen consists of N_2 molecules, which are very unreactive due to the strong nitrogen-nitrogen triple bond. However, a few organisms can overcome this problem through a process known as nitrogen fixation, illustrated in **Figure 18.32**.

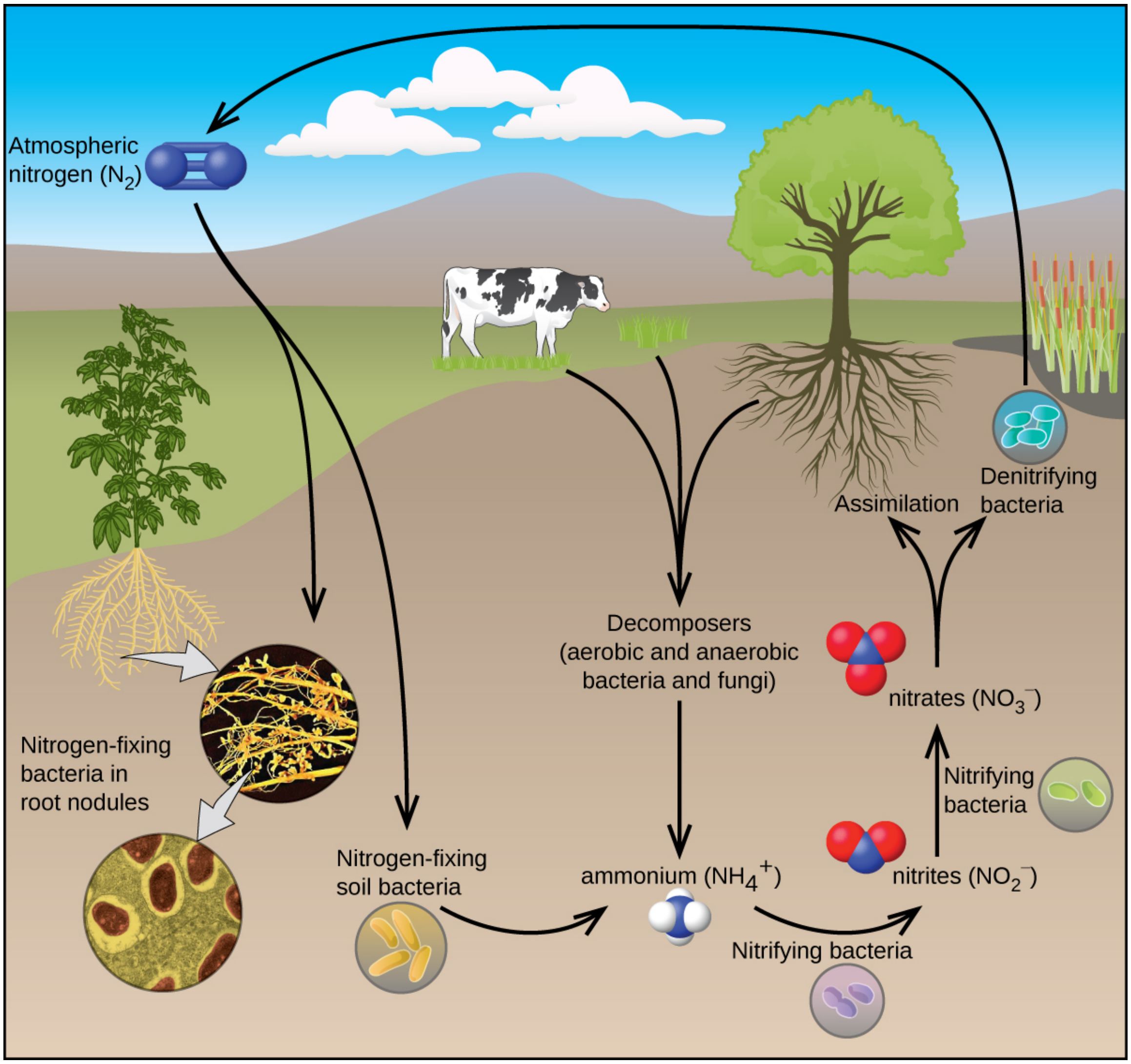


Figure 18.32 All living organisms require nitrogen. A few microorganisms are able to process atmospheric nitrogen using nitrogen fixation. (credit "roots": modification of work by the United States Department of Agriculture; credit "root nodules": modification of work by Louisa Howard)

Nitrogen fixation is the process where organisms convert atmospheric nitrogen into biologically useful chemicals. To date, the only known kind of biological organisms capable of nitrogen fixation are microorganisms. These organisms employ enzymes called nitrogenases, which contain iron and molybdenum. Many of these microorganisms live in a symbiotic relationship with plants, with the best-known example being the presence of rhizobia in the root nodules of legumes.

Large volumes of atmospheric nitrogen are necessary for making ammonia—the principal starting material used for preparation of large quantities of other nitrogen-containing compounds. Most other uses for elemental nitrogen depend on its inactivity. It is helpful when a chemical process requires an inert atmosphere. Canned foods and luncheon meats cannot oxidize in a pure nitrogen atmosphere, so they retain a better flavor and color, and spoil less rapidly, when sealed in nitrogen instead of air. This technology allows fresh produce to be available year-round, regardless of growing season.

There are compounds with nitrogen in all of its oxidation states from 3− to 5+. Much of the chemistry of nitrogen involves oxidation-reduction reactions. Some active metals (such as alkali metals and alkaline earth metals) can reduce nitrogen to form metal nitrides. In the remainder of this section, we will examine nitrogen-oxygen chemistry.

There are well-characterized nitrogen oxides in which nitrogen exhibits each of its positive oxidation numbers from 1+ to 5+. When ammonium nitrate is carefully heated, nitrous oxide (dinitrogen oxide) and water vapor form. Stronger heating generates nitrogen gas, oxygen gas, and water vapor. No one should ever attempt this reaction—it can be very explosive. In 1947, there was a major ammonium nitrate explosion in Texas City, Texas, and, in 2013, there was another major explosion in West, Texas. In the last 100 years, there were nearly 30 similar disasters worldwide, resulting in the loss of numerous lives. In this oxidation-reduction reaction, the nitrogen in the nitrate ion oxidizes the nitrogen in the ammonium ion. Nitrous oxide, shown in **Figure 18.33**, is a colorless gas possessing a mild, pleasing odor and a sweet taste. It finds application as an anesthetic for minor operations, especially in dentistry, under the name “laughing gas.”

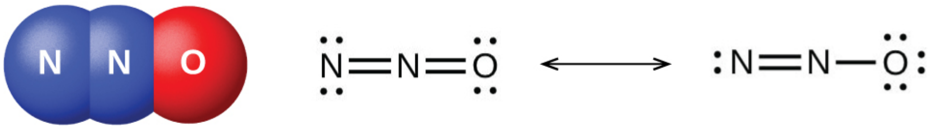


Figure 18.33 Nitrous oxide, N_2O, is an anesthetic that has these molecular (left) and resonance (right) structures.

Low yields of nitric oxide, NO, form when heating nitrogen and oxygen together. NO also forms when lightning passes through air during thunderstorms. Burning ammonia is the commercial method of preparing nitric oxide. In the laboratory, the reduction of nitric acid is the best method for preparing nitric oxide. When copper reacts with dilute nitric acid, nitric oxide is the principal reduction product:

$$3\text{Cu}(s) + 8\text{HNO}_3(aq) \longrightarrow 2\text{NO}(g) + 3\text{Cu}(\text{NO}_3)_2(aq) + 4\text{H}_2\text{O}(l)$$

Gaseous nitric oxide is the most thermally stable of the nitrogen oxides and is the simplest known thermally stable molecule with an unpaired electron. It is one of the air pollutants generated by internal combustion engines, resulting from the reaction of atmospheric nitrogen and oxygen during the combustion process.

At room temperature, nitric oxide is a colorless gas consisting of diatomic molecules. As is often the case with molecules that contain an unpaired electron, two molecules combine to form a dimer by pairing their unpaired electrons to form a bond. Liquid and solid NO both contain N_2O_2 dimers, like that shown in **Figure 18.34**. Most substances with unpaired electrons exhibit color by absorbing visible light; however, NO is colorless because the absorption of light is not in the visible region of the spectrum.

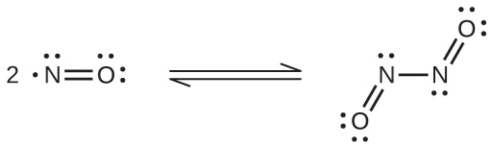


Figure 18.34 This shows the equilibrium between NO and N_2O_2. The molecule, N_2O_2, absorbs light.

Cooling a mixture of equal parts nitric oxide and nitrogen dioxide to −21 °C produces dinitrogen trioxide, a blue liquid consisting of N_2O_3 molecules (shown in **Figure 18.35**). Dinitrogen trioxide exists only in the liquid and solid states. When heated, it reverts to a mixture of NO and NO_2.

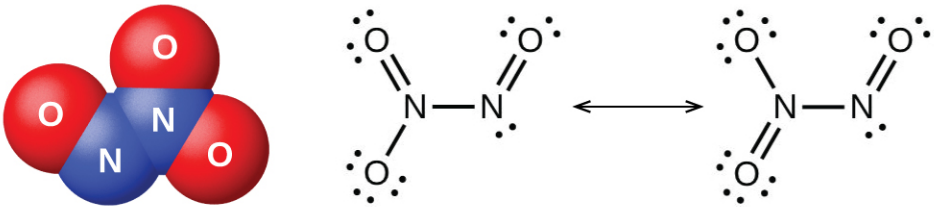


Figure 18.35 Dinitrogen trioxide, N_2O_3, only exists in liquid or solid states and has these molecular (left) and resonance (right) structures.

It is possible to prepare nitrogen dioxide in the laboratory by heating the nitrate of a heavy metal, or by the reduction of concentrated nitric acid with copper metal, as shown in **Figure 18.36**. Commercially, it is possible to prepare nitrogen dioxide by oxidizing nitric oxide with air.

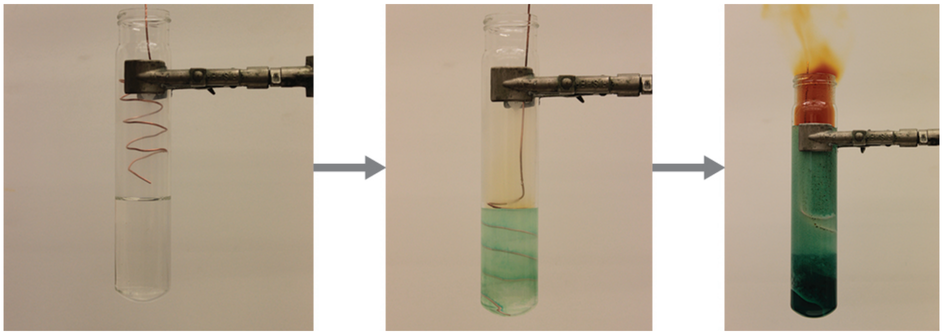


Figure 18.36 The reaction of copper metal with concentrated HNO_3 produces a solution of $Cu(NO_3)_2$ and brown fumes of NO_2. (credit: modification of work by Mark Ott)

The nitrogen dioxide molecule (illustrated in **Figure 18.37**) contains an unpaired electron, which is responsible for its color and paramagnetism. It is also responsible for the dimerization of NO_2. At low pressures or at high temperatures, nitrogen dioxide has a deep brown color that is due to the presence of the NO_2 molecule. At low temperatures, the color almost entirely disappears as dinitrogen tetraoxide, N_2O_4, forms. At room temperature, an equilibrium exists:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_P = 6.86$$

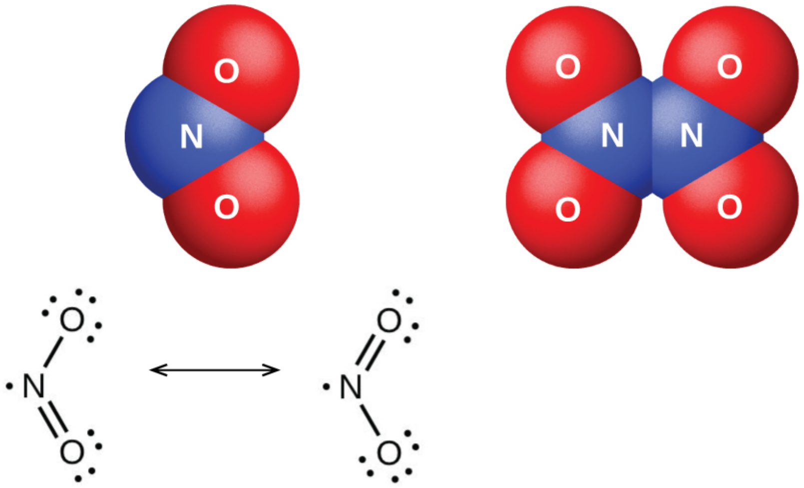


Figure 18.37 The molecular and resonance structures for nitrogen dioxide (NO_2, left) and dinitrogen tetraoxide (N_2O_4, right) are shown.

Dinitrogen pentaoxide, N_2O_5 (illustrated in **Figure 18.38**), is a white solid that is formed by the dehydration of nitric acid by phosphorus(V) oxide (tetraphosphorus decoxide):

$$P_4O_{10}(s) + 4HNO_3(l) \longrightarrow 4HPO_3(s) + 2N_2O_5(s)$$

It is unstable above room temperature, decomposing to N_2O_4 and O_2.

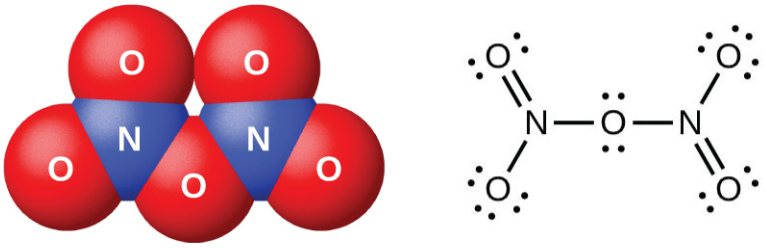


Figure 18.38 This image shows the molecular structure and one resonance structure of a molecule of dinitrogen pentaoxide, N_2O_5.

The oxides of nitrogen(III), nitrogen(IV), and nitrogen(V) react with water and form nitrogen-containing oxyacids. Nitrogen(III) oxide, N_2O_3, is the anhydride of nitrous acid; HNO_2 forms when N_2O_3 reacts with water. There are no stable oxyacids containing nitrogen with an oxidation state of 4+; therefore, nitrogen(IV) oxide, NO_2, disproportionates in one of two ways when it reacts with water. In cold water, a mixture of HNO_2 and HNO_3 forms. At higher temperatures, HNO_3 and NO will form. Nitrogen(V) oxide, N_2O_5, is the anhydride of nitric acid; HNO_3 is produced when N_2O_5 reacts with water:

$$N_2O_5(s) + H_2O(l) \longrightarrow 2HNO_3(aq)$$

The nitrogen oxides exhibit extensive oxidation-reduction behavior. Nitrous oxide resembles oxygen in its behavior when heated with combustible substances. N_2O is a strong oxidizing agent that decomposes when heated to form nitrogen and oxygen. Because one-third of the gas liberated is oxygen, nitrous oxide supports combustion better than air (one-fifth oxygen). A glowing splinter bursts into flame when thrust into a bottle of this gas. Nitric oxide acts both as an oxidizing agent and as a reducing agent. For example:

$$\text{oxidizing agent: } P_4(s) + 6NO(g) \longrightarrow P_4O_6(s) + 3N_2(g)$$
$$\text{reducing agent: } Cl_2(g) + 2NO(g) \longrightarrow 2ClNO(g)$$

Nitrogen dioxide (or dinitrogen tetraoxide) is a good oxidizing agent. For example:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$
$$NO_2(g) + 2HCl(aq) \longrightarrow NO(g) + Cl_2(g) + H_2O(l)$$

18.8 Occurrence, Preparation, and Properties of Phosphorus

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

- Describe the properties, preparation, and uses of phosphorus

The industrial preparation of phosphorus is by heating calcium phosphate, obtained from phosphate rock, with sand and coke:

$$2Ca_3(PO_4)_2(s) + 6SiO_2(s) + 10C(s) \xrightarrow{\Delta} 6CaSiO_3(l) + 10CO(g) + P_4(g)$$

The phosphorus distills out of the furnace and is condensed into a solid or burned to form P_4O_{10}. The preparation of many other phosphorus compounds begins with P_4O_{10}. The acids and phosphates are useful as fertilizers and in the chemical industry. Other uses are in the manufacture of special alloys such as ferrophosphorus and phosphor bronze. Phosphorus is important in making pesticides, matches, and some plastics. Phosphorus is an active nonmetal. In compounds, phosphorus usually occurs in oxidation states of 3−, 3+, and 5+. Phosphorus exhibits oxidation numbers that are unusual for a group 15 element in compounds that contain phosphorus-phosphorus bonds; examples include diphosphorus tetrahydride, $H_2P\text{-}PH_2$, and tetraphosphorus trisulfide, P_4S_3, illustrated in **Figure 18.39**.

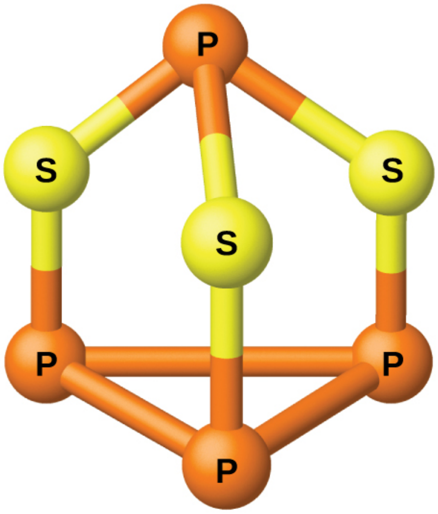


Figure 18.39 P_4S_3 is a component of the heads of strike-anywhere matches.

Phosphorus Oxygen Compounds

Phosphorus forms two common oxides, phosphorus(III) oxide (or tetraphosphorus hexaoxide), P_4O_6, and phosphorus(V) oxide (or tetraphosphorus decaoxide), P_4O_{10}, both shown in **Figure 18.40**. Phosphorus(III) oxide is a white crystalline solid with a garlic-like odor. Its vapor is very poisonous. It oxidizes slowly in air and inflames when heated to 70 °C, forming P_4O_{10}. Phosphorus(III) oxide dissolves slowly in cold water to form phosphorous acid, H_3PO_3.

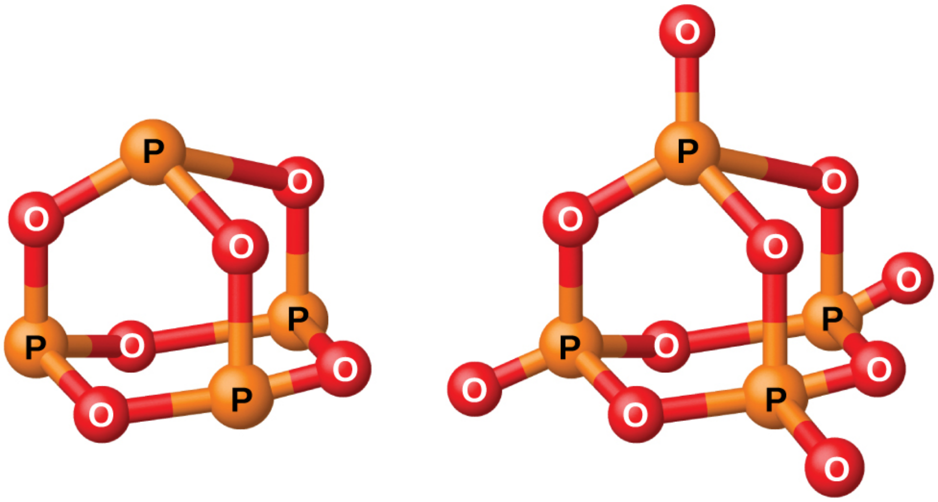


Figure 18.40 This image shows the molecular structures of P_4O_6 (left) and P_4O_{10} (right).

Phosphorus(V) oxide, P_4O_{10}, is a white powder that is prepared by burning phosphorus in excess oxygen. Its enthalpy of formation is very high (−2984 kJ), and it is quite stable and a very poor oxidizing agent. Dropping P_4O_{10} into water produces a hissing sound, heat, and orthophosphoric acid:

$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$$

Because of its great affinity for water, phosphorus(V) oxide is an excellent drying agent for gases and solvents, and for removing water from many compounds.

Phosphorus Halogen Compounds

Phosphorus will react directly with the halogens, forming trihalides, PX_3, and pentahalides, PX_5. The trihalides are much more stable than the corresponding nitrogen trihalides; nitrogen pentahalides do not form because of nitrogen's inability to form more than four bonds.

The chlorides PCl_3 and PCl_5, both shown in **Figure 18.41**, are the most important halides of phosphorus. Phosphorus trichloride is a colorless liquid that is prepared by passing chlorine over molten phosphorus. Phosphorus pentachloride is an off-white solid that is prepared by oxidizing the trichloride with excess chlorine. The pentachloride sublimes when warmed and forms an equilibrium with the trichloride and chlorine when heated.

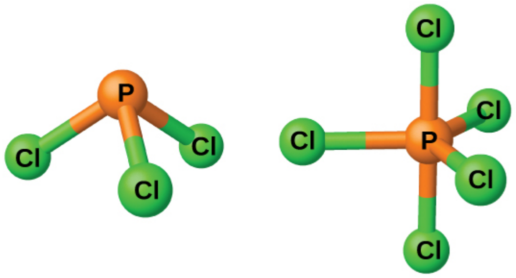


Figure 18.41 This image shows the molecular structure of PCl_3 (left) and PCl_5 (right) in the gas phase.

Like most other nonmetal halides, both phosphorus chlorides react with an excess of water and yield hydrogen chloride and an oxyacid: PCl_3 yields phosphorous acid H_3PO_3 and PCl_5 yields phosphoric acid, H_3PO_4.

The pentahalides of phosphorus are Lewis acids because of the empty valence *d* orbitals of phosphorus. These compounds readily react with halide ions (Lewis bases) to give the anion $PX_6{}^-$. Whereas phosphorus pentafluoride is a molecular compound in all states, X-ray studies show that solid phosphorus pentachloride is an ionic compound, $[PCl_4{}^+][PCl_6{}^-]$, as are phosphorus pentabromide, $[PBr_4{}^+][Br^-]$, and phosphorus pentaiodide, $[PI_4{}^+][I^-]$.

18.9 Occurrence, Preparation, and Compounds of Oxygen

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

- Describe the properties, preparation, and compounds of oxygen
- Describe the preparation, properties, and uses of some representative metal oxides, peroxides, and hydroxides

Oxygen is the most abundant element on the earth's crust. The earth's surface is composed of the crust, atmosphere, and hydrosphere. About 50% of the mass of the earth's crust consists of oxygen (combined with other elements, principally silicon). Oxygen occurs as O_2 molecules and, to a limited extent, as O_3 (ozone) molecules in air. It forms about 20% of the mass of the air. About 89% of water by mass consists of combined oxygen. In combination with carbon, hydrogen, and nitrogen, oxygen is a large part of plants and animals.

Oxygen is a colorless, odorless, and tasteless gas at ordinary temperatures. It is slightly denser than air. Although it is only slightly soluble in water (49 mL of gas dissolves in 1 L at STP), oxygen's solubility is very important to aquatic life.

Most of the oxygen isolated commercially comes from air and the remainder from the electrolysis of water. The separation of oxygen from air begins with cooling and compressing the air until it liquefies. As liquid air warms, oxygen with its higher boiling point (90 K) separates from nitrogen, which has a lower boiling point (77 K). It is possible to separate the other components of air at the same time based on differences in their boiling points.

Oxygen is essential in combustion processes such as the burning of fuels. Plants and animals use the oxygen from the air in respiration. The administration of oxygen-enriched air is an important medical practice when a patient is receiving an inadequate supply of oxygen because of shock, pneumonia, or some other illness.

The chemical industry employs oxygen for oxidizing many substances. A significant amount of oxygen produced commercially is important in the removal of carbon from iron during steel production. Large quantities of pure oxygen are also necessary in metal fabrication and in the cutting and welding of metals with oxyhydrogen and oxyacetylene torches.

Liquid oxygen is important to the space industry. It is an oxidizing agent in rocket engines. It is also the source of gaseous oxygen for life support in space.

As we know, oxygen is very important to life. The energy required for the maintenance of normal body functions in human beings and in other organisms comes from the slow oxidation of chemical compounds. Oxygen is the final oxidizing agent in these reactions. In humans, oxygen passes from the lungs into the blood, where it combines with hemoglobin, producing oxyhemoglobin. In this form, blood transports the oxygen to tissues, where it is transferred to the tissues. The ultimate products are carbon dioxide and water. The blood carries the carbon dioxide through the veins to the lungs, where the blood releases the carbon dioxide and collects another supply of oxygen. Digestion and assimilation of food regenerate the materials consumed by oxidation in the body; the energy liberated is the same as if the food burned outside the body.

Green plants continually replenish the oxygen in the atmosphere by a process called **photosynthesis**. The products of photosynthesis may vary, but, in general, the process converts carbon dioxide and water into glucose (a sugar) and oxygen using the energy of light:

$$\underset{\text{carbon dioxide}}{6CO_2(g)} + \underset{\text{water}}{6H_2O(l)} \xrightarrow[\text{light}]{\text{chlorophyll}} \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{oxygen}}{6O_2(g)}$$

Thus, the oxygen that became carbon dioxide and water by the metabolic processes in plants and animals returns to the atmosphere by photosynthesis.

When dry oxygen is passed between two electrically charged plates, **ozone** (O_3, illustrated in Figure 18.42), an allotrope of oxygen possessing a distinctive odor, forms. The formation of ozone from oxygen is an endothermic reaction, in which the energy comes from an electrical discharge, heat, or ultraviolet light:

$$3O_2(g) \xrightarrow{\text{electric discharge}} 2O_3(g) \qquad \Delta H° = 287 \text{ kJ}$$

The sharp odor associated with sparking electrical equipment is due, in part, to ozone.

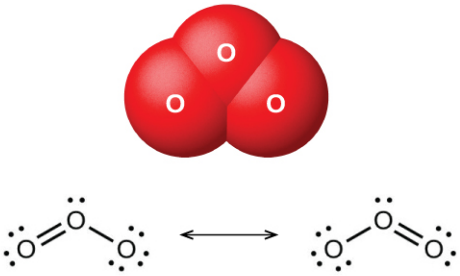


Figure 18.42 The image shows the bent ozone (O_3) molecule and the resonance structures necessary to describe its bonding.

Ozone forms naturally in the upper atmosphere by the action of ultraviolet light from the sun on the oxygen there. Most atmospheric ozone occurs in the stratosphere, a layer of the atmosphere extending from about 10 to 50 kilometers above the earth's surface. This ozone acts as a barrier to harmful ultraviolet light from the sun by absorbing it via a chemical decomposition reaction:

$$O_3(g) \xrightarrow{\text{ultraviolet light}} O(g) + O_2(g)$$

The reactive oxygen atoms recombine with molecular oxygen to complete the ozone cycle. The presence of stratospheric ozone decreases the frequency of skin cancer and other damaging effects of ultraviolet radiation. It has been clearly demonstrated that chlorofluorocarbons, CFCs (known commercially as Freons), which were present as aerosol propellants in spray cans and as refrigerants, caused depletion of ozone in the stratosphere. This occurred because ultraviolet light also causes CFCs to decompose, producing atomic chlorine. The chlorine atoms react with ozone molecules, resulting in a net removal of O_3 molecules from stratosphere. This process is explored in detail in our coverage of chemical kinetics. There is a worldwide effort to reduce the amount of CFCs used commercially, and the ozone hole is already beginning to decrease in size as atmospheric concentrations of atomic chlorine decrease. While ozone in the stratosphere helps protect us, ozone in the troposphere is a problem. This ozone is a toxic component of photochemical smog.

The uses of ozone depend on its reactivity with other substances. It can be used as a bleaching agent for oils, waxes, fabrics, and starch: It oxidizes the colored compounds in these substances to colorless compounds. It is an alternative to chlorine as a disinfectant for water.

Reactions

Elemental oxygen is a strong oxidizing agent. It reacts with most other elements and many compounds.

Reaction with Elements

Oxygen reacts directly at room temperature or at elevated temperatures with all other elements except the noble gases, the halogens, and few second- and third-row transition metals of low reactivity (those with higher reduction potentials than copper). Rust is an example of the reaction of oxygen with iron. The more active metals form peroxides or superoxides. Less active metals and the nonmetals give oxides. Two examples of these reactions are:

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$
$$P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$$

The oxides of halogens, at least one of the noble gases, and metals with higher reduction potentials than copper do not form by the direct action of the elements with oxygen.

Reaction with Compounds

Elemental oxygen also reacts with some compounds. If it is possible to oxidize any of the elements in a given compound, further oxidation by oxygen can occur. For example, hydrogen sulfide, H_2S, contains sulfur with an oxidation state of 2−. Because the sulfur does not exhibit its maximum oxidation state, we would expect H_2S to react with oxygen. It does, yielding water and sulfur dioxide. The reaction is:

$$2H_2S(g) + 3O_2(g) \longrightarrow 2H_2O(l) + 2SO_2(g)$$

It is also possible to oxidize oxides such as CO and P_4O_6 that contain an element with a lower oxidation state. The ease with which elemental oxygen picks up electrons is mirrored by the difficulty of removing electrons from oxygen in most oxides. Of the elements, only the very reactive fluorine can oxidize oxides to form oxygen gas.

Oxides, Peroxides, and Hydroxides

Compounds of the representative metals with oxygen fall into three categories: (1) **oxides**, containing oxide ions, O^{2-}; (2) **peroxides**, containing peroxides ions, $O_2{}^{2-}$, with oxygen-oxygen covalent single bonds and a very limited number of **superoxides**, containing superoxide ions, $O_2{}^{-}$, with oxygen-oxygen covalent bonds that have a bond order of $1\frac{1}{2}$. In addition, there are (3) **hydroxides**, containing hydroxide ions, OH^-. All representative metals form oxides. Some of the metals of group 2 also form peroxides, MO_2, and the metals of group 1 also form peroxides, M_2O_2, and superoxides, MO_2.

Oxides

It is possible to produce the oxides of most representative metals by heating the corresponding hydroxides (forming the oxide and gaseous water) or carbonates (forming the oxide and gaseous CO_2). Equations for example reactions are:

$$2Al(OH)_3(s) \xrightarrow{\Delta} Al_2O_3(s) + 3H_2O(g)$$
$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

However, alkali metal salts generally are very stable and do not decompose easily when heated. Alkali metal oxides result from the oxidation-reduction reactions created by heating nitrates or hydroxides with the metals. Equations for sample reactions are:

$$2KNO_3(s) + 10K(s) \xrightarrow{\Delta} 6K_2O(s) + N_2(g)$$
$$2LiOH(s) + 2Li(s) \xrightarrow{\Delta} 2Li_2O(s) + H_2(g)$$

With the exception of mercury(II) oxide, it is possible to produce the oxides of the metals of groups 2–15 by burning the corresponding metal in air. The heaviest member of each group, the member for which the inert pair effect is most pronounced, forms an oxide in which the oxidation state of the metal ion is two less than the group oxidation state (inert pair effect). Thus, Tl_2O, PbO, and Bi_2O_3 form when burning thallium, lead, and bismuth, respectively.

The oxides of the lighter members of each group exhibit the group oxidation state. For example, SnO_2 forms from burning tin. Mercury(II) oxide, HgO, forms slowly when mercury is warmed below 500 °C; it decomposes at higher temperatures.

Burning the members of groups 1 and 2 in air is not a suitable way to form the oxides of these elements. These metals are reactive enough to combine with nitrogen in the air, so they form mixtures of oxides and ionic nitrides. Several also form peroxides or superoxides when heated in air.

Ionic oxides all contain the oxide ion, a very powerful hydrogen ion acceptor. With the exception of the very insoluble aluminum oxide, Al_2O_3, tin(IV), SnO_2, and lead(IV), PbO_2, the oxides of the representative metals react with acids to form salts. Some equations for these reactions are:

$$\begin{gathered}\mathrm{Na_2O + 2HNO_3}(aq) \longrightarrow \mathrm{2NaNO_3}(aq) + \mathrm{H_2O}(l) \\ \mathrm{CaO}(s) + \mathrm{2HCL}(aq) \longrightarrow \mathrm{CaCl_2}(aq) + \mathrm{H_2O}(l) \\ \mathrm{SnO}(s) + \mathrm{2HClO_4}(aq) \longrightarrow \mathrm{Sn(ClO_4)_2}(aq) + \mathrm{H_2O}(l)\end{gathered}$$

The oxides of the metals of groups 1 and 2 and of thallium(I) oxide react with water and form hydroxides. Examples of such reactions are:

$$\begin{gathered}\mathrm{Na_2O}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{NaOH}(aq) \\ \mathrm{CaO}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(aq) \\ \mathrm{Tl_2O}(s) + \mathrm{H_2O}(aq) \longrightarrow \mathrm{2TlOH}(aq)\end{gathered}$$

The oxides of the alkali metals have little industrial utility, unlike magnesium oxide, calcium oxide, and aluminum oxide. Magnesium oxide is important in making firebrick, crucibles, furnace linings, and thermal insulation—applications that require chemical and thermal stability. Calcium oxide, sometimes called *quicklime* or lime in the industrial market, is very reactive, and its principal uses reflect its reactivity. Pure calcium oxide emits an intense white light when heated to a high temperature (as illustrated in **Figure 18.43**). Blocks of calcium oxide heated by gas flames were the stage lights in theaters before electricity was available. This is the source of the phrase "in the limelight."

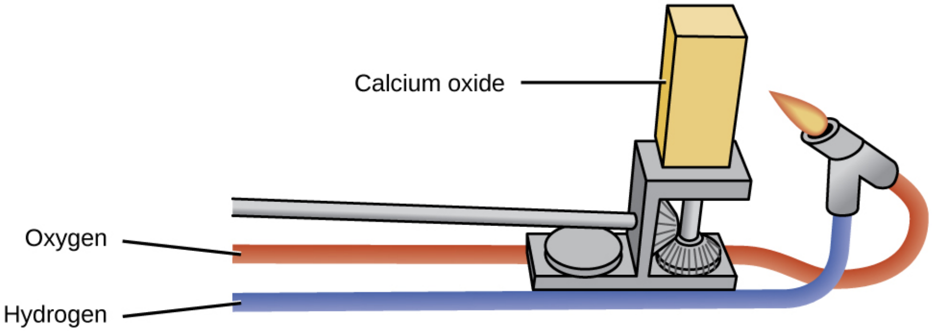


Figure 18.43 Calcium oxide has many industrial uses. When it is heated at high temperatures, it emits an intense white light.

Calcium oxide and calcium hydroxide are inexpensive bases used extensively in chemical processing, although most of the useful products prepared from them do not contain calcium. Calcium oxide, CaO, is made by heating calcium carbonate, $CaCO_3$, which is widely and inexpensively available as limestone or oyster shells:

$$\mathrm{CaCO_3}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

Although this decomposition reaction is reversible, it is possible to obtain a 100% yield of CaO by allowing the CO_2 to escape. It is possible to prepare calcium hydroxide by the familiar acid-base reaction of a soluble metal oxide with water:

$$\text{CaO}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{Ca(OH)}_2(s)$$

Both CaO and $Ca(OH)_2$ are useful as bases; they accept protons and neutralize acids.

Alumina (Al_2O_3) occurs in nature as the mineral corundum, a very hard substance used as an abrasive for grinding and polishing. Corundum is important to the jewelry trade as ruby and sapphire. The color of ruby is due to the presence of a small amount of chromium; other impurities produce the wide variety of colors possible for sapphires. Artificial rubies and sapphires are now manufactured by melting aluminum oxide (melting point = 2050 °C) with small amounts of oxides to produce the desired colors and cooling the melt in such a way as to produce large crystals. Ruby lasers use synthetic ruby crystals.

Zinc oxide, ZnO, was a useful white paint pigment; however, pollutants tend to discolor the compound. The compound is also important in the manufacture of automobile tires and other rubber goods, and in the preparation of medicinal ointments. For example, zinc-oxide-based sunscreens, as shown in **Figure 18.44**, help prevent sunburn. The zinc oxide in these sunscreens is present in the form of very small grains known as nanoparticles. Lead dioxide is a constituent of charged lead storage batteries. Lead(IV) tends to revert to the more stable lead(II) ion by gaining two electrons, so lead dioxide is a powerful oxidizing agent.

Figure 18.44 Zinc oxide protects exposed skin from sunburn. (credit: modification of work by "osseous"/Flickr)

Peroxides and Superoxides

Peroxides and superoxides are strong oxidizers and are important in chemical processes. Hydrogen peroxide, H_2O_2, prepared from metal peroxides, is an important bleach and disinfectant. Peroxides and superoxides form when the metal or metal oxides of groups 1 and 2 react with pure oxygen at elevated temperatures. Sodium peroxide and the peroxides of calcium, strontium, and barium form by heating the corresponding metal or metal oxide in pure oxygen:

$$2\text{Na}(s) + \text{O}_2(g) \xrightarrow{\Delta} \text{Na}_2\text{O}_2(s)$$
$$2\text{Na}_2\text{O}(s) + \text{O}_2(g) \xrightarrow{\Delta} 2\text{Na}_2\text{O}_2(s)$$
$$2\text{SrO}(s) + \text{O}_2(g) \xrightarrow{\Delta} 2\text{SrO}_2(s)$$

The peroxides of potassium, rubidium, and cesium can be prepared by heating the metal or its oxide in a carefully controlled amount of oxygen:

$$2\text{K}(s) + \text{O}_2(g) \longrightarrow \text{K}_2\text{O}_2(s) \qquad (2\text{ mol K per mol O}_2)$$

With an excess of oxygen, the superoxides KO_2, RbO_2, and CsO_2 form. For example:

$$\text{K}(s) + \text{O}_2(g) \longrightarrow \text{KO}_2(s) \qquad (1\text{ mol K per mol O}_2)$$

The stability of the peroxides and superoxides of the alkali metals increases as the size of the cation increases.

Hydroxides

Hydroxides are compounds that contain the OH^- ion. It is possible to prepare these compounds by two general types of reactions. Soluble metal hydroxides can be produced by the reaction of the metal or metal oxide with water.

Insoluble metal hydroxides form when a solution of a soluble salt of the metal combines with a solution containing hydroxide ions.

With the exception of beryllium and magnesium, the metals of groups 1 and 2 react with water to form hydroxides and hydrogen gas. Examples of such reactions include:

$$\begin{gathered}2\mathrm{Li}(s) + 2\mathrm{H_2O}(l) \longrightarrow 2\mathrm{LiOH}(aq) + \mathrm{H_2}(g)\\ \mathrm{Ca}(s) + 2\mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(aq) + \mathrm{H_2}(g)\end{gathered}$$

However, these reactions can be violent and dangerous; therefore, it is preferable to produce soluble metal hydroxides by the reaction of the respective oxide with water:

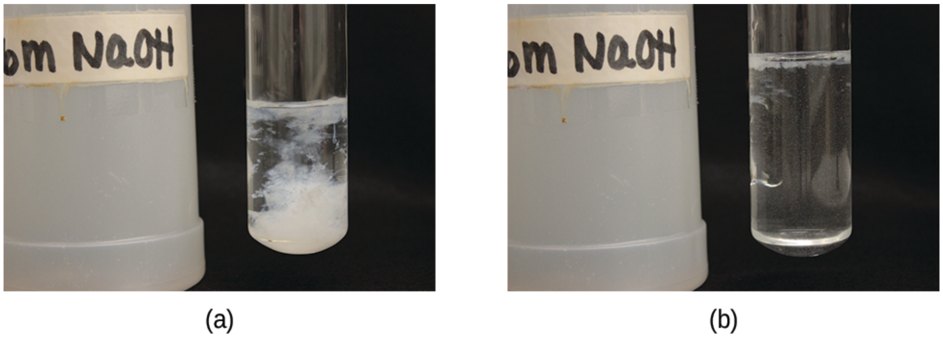
$$\begin{gathered}\mathrm{Li_2O}(s) + \mathrm{H_2O}(l) \longrightarrow 2\mathrm{LiOH}(aq)\\ \mathrm{CaO}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(aq)\end{gathered}$$

Most metal oxides are **base anhydrides**. This is obvious for the soluble oxides because they form metal hydroxides. Most other metal oxides are insoluble and do not form hydroxides in water; however, they are still base anhydrides because they will react with acids.

It is possible to prepare the insoluble hydroxides of beryllium, magnesium, and other representative metals by the addition of sodium hydroxide to a solution of a salt of the respective metal. The net ionic equations for the reactions involving a magnesium salt, an aluminum salt, and a zinc salt are:

$$\begin{gathered}\mathrm{Mg^{2+}}(aq) + 2\mathrm{OH^-}(aq) \longrightarrow \mathrm{Mg(OH)_2}(s)\\ \mathrm{Al^{3+}}(aq) + 3\mathrm{OH^-}(aq) \longrightarrow \mathrm{Al(OH)_3}(s)\\ \mathrm{Zn^{2+}}(aq) + 2\mathrm{OH^-}(aq) \longrightarrow \mathrm{Zn(OH)_2}(s)\end{gathered}$$

An excess of hydroxide must be avoided when preparing aluminum, gallium, zinc, and tin(II) hydroxides, or the hydroxides will dissolve with the formation of the corresponding complex ions: $\mathrm{Al(OH)_4}^-$, $\mathrm{Ga(OH)_4}^-$, $\mathrm{Zn(OH)_4}^{2-}$, and $\mathrm{Sn(OH)_3}^-$ (see **Figure 18.45**). The important aspect of complex ions for this chapter is that they form by a Lewis acid-base reaction with the metal being the Lewis acid.



(a) (b)

Figure 18.45 (a) Mixing solutions of NaOH and $\mathrm{Zn(NO_3)_2}$ produces a white precipitate of $\mathrm{Zn(OH)_2}$. (b) Addition of an excess of NaOH results in dissolution of the precipitate. (credit: modification of work by Mark Ott)

Industry uses large quantities of sodium hydroxide as a cheap, strong base. Sodium chloride is the starting material for the production of NaOH because NaCl is a less expensive starting material than the oxide. Sodium hydroxide is among the top 10 chemicals in production in the United States, and this production was almost entirely by electrolysis of solutions of sodium chloride. This process is the **chlor-alkali process**, and it is the primary method for producing chlorine.

Sodium hydroxide is an ionic compound and melts without decomposition. It is very soluble in water, giving off a great deal of heat and forming very basic solutions: 40 grams of sodium hydroxide dissolves in only 60 grams of water at 25 °C. Sodium hydroxide is employed in the production of other sodium compounds and is used to neutralize acidic solutions during the production of other chemicals such as petrochemicals and polymers.

Many of the applications of hydroxides are for the neutralization of acids (such as the antacid shown in **Figure 18.46**) and for the preparation of oxides by thermal decomposition. An aqueous suspension of magnesium hydroxide constitutes the antacid milk of magnesia. Because of its ready availability (from the reaction of water with calcium oxide prepared by the decomposition of limestone, $CaCO_3$), low cost, and activity, calcium hydroxide is used extensively in commercial applications needing a cheap, strong base. The reaction of hydroxides with appropriate acids is also used to prepare salts.

Figure 18.46 Calcium carbonate, $CaCO_3$, can be consumed in the form of an antacid to neutralize the effects of acid in your stomach. (credit: "Midnightcomm"/Wikimedia Commons)

Chemistry in Everyday Life

The Chlor-Alkali Process

Although they are very different chemically, there is a link between chlorine and sodium hydroxide because there is an important electrochemical process that produces the two chemicals simultaneously. The process known as the chlor-alkali process, utilizes sodium chloride, which occurs in large deposits in many parts of the world. This is an electrochemical process to oxidize chloride ion to chlorine and generate sodium hydroxide.

Passing a direct current of electricity through a solution of NaCl causes the chloride ions to migrate to the positive electrode where oxidation to gaseous chlorine occurs when the ion gives up an electron to the electrode:

$$2\text{Cl}^-(aq) \longrightarrow \text{Cl}_2(g) + 2\text{e}^- \qquad \text{(at the positive electrode)}$$

The electrons produced travel through the outside electrical circuit to the negative electrode. Although the positive sodium ions migrate toward this negative electrode, metallic sodium does not form because sodium ions are too difficult to reduce under the conditions used. (Recall that metallic sodium is active enough to react with water and hence, even if produced, would immediately react with water to produce sodium ions again.) Instead, water molecules pick up electrons from the electrode and undergo reduction to form hydrogen gas and hydroxide ions:

$$2H_2O(l) + 2e^- \ \text{(from the negative electrode)} \longrightarrow H_2(g) + 2OH^-(aq)$$

The overall result is the conversion of the aqueous solution of NaCl to an aqueous solution of NaOH, gaseous Cl_2, and gaseous H_2:

$$2Na^+(aq) + 2Cl^-(aq) + 2H_2O(l) \xrightarrow{\text{electrolysis}} 2Na^+(aq) + 2OH^-(aq) + Cl_2(g) + H_2(g)$$

Nonmetal Oxygen Compounds

Most nonmetals react with oxygen to form nonmetal oxides. Depending on the available oxidation states for the element, a variety of oxides might form. Fluorine will combine with oxygen to form fluorides such as OF_2, where the oxygen has a 2+-oxidation state.

Sulfur Oxygen Compounds

The two common oxides of sulfur are sulfur dioxide, SO_2, and sulfur trioxide, SO_3. The odor of burning sulfur comes from sulfur dioxide. Sulfur dioxide, shown in **Figure 18.47**, occurs in volcanic gases and in the atmosphere near industrial plants that burn fuel containing sulfur compounds.

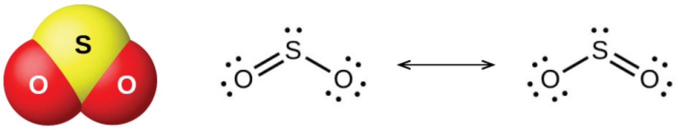


Figure 18.47 This image shows the molecular structure (left) and resonance forms (right) of sulfur dioxide.

Commercial production of sulfur dioxide is from either burning sulfur or roasting sulfide ores such as ZnS, FeS_2, and Cu_2S in air. (Roasting, which forms the metal oxide, is the first step in the separation of many metals from their ores.) A convenient method for preparing sulfur dioxide in the laboratory is by the action of a strong acid on either sulfite salts containing the $SO_3{}^{2-}$ ion or hydrogen sulfite salts containing $HSO_3{}^-$. Sulfurous acid, H_2SO_3, forms first, but quickly decomposes into sulfur dioxide and water. Sulfur dioxide also forms when many reducing agents react with hot, concentrated sulfuric acid. Sulfur trioxide forms slowly when heating sulfur dioxide and oxygen together, and the reaction is exothermic:

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \qquad \Delta H° = -197.8 \text{ kJ}$$

Sulfur dioxide is a gas at room temperature, and the SO_2 molecule is bent. Sulfur trioxide melts at 17 °C and boils at 43 °C. In the vapor state, its molecules are single SO_3 units (shown in **Figure 18.48**), but in the solid state, SO_3 exists in several polymeric forms.

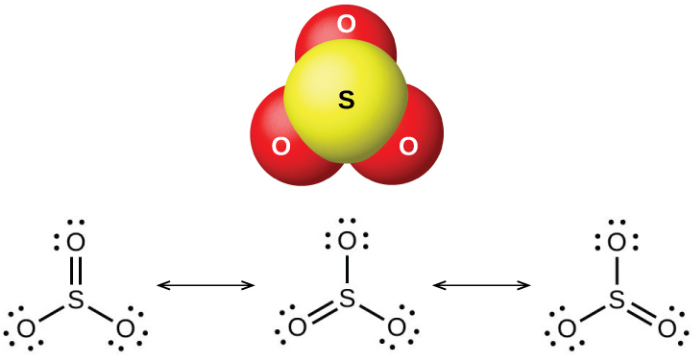


Figure 18.48 This image shows the structure (top) of sulfur trioxide in the gas phase and its resonance forms (bottom).

The sulfur oxides react as Lewis acids with many oxides and hydroxides in Lewis acid-base reactions, with the formation of **sulfites** or **hydrogen sulfites**, and **sulfates** or **hydrogen sulfates**, respectively.

Halogen Oxygen Compounds

The halogens do not react directly with oxygen, but it is possible to prepare binary oxygen-halogen compounds by the reactions of the halogens with oxygen-containing compounds. Oxygen compounds with chlorine, bromine, and iodine are oxides because oxygen is the more electronegative element in these compounds. On the other hand, fluorine compounds with oxygen are fluorides because fluorine is the more electronegative element.

As a class, the oxides are extremely reactive and unstable, and their chemistry has little practical importance. Dichlorine oxide, formally called dichlorine monoxide, and chlorine dioxide, both shown in **Figure 18.49**, are the only commercially important compounds. They are important as bleaching agents (for use with pulp and flour) and for water treatment.

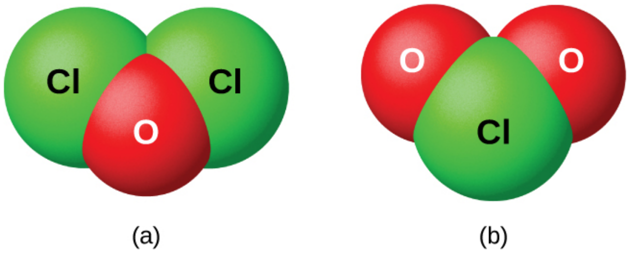


Figure 18.49 This image shows the structures of the (a) Cl_2O and (b) ClO_2 molecules.

Nonmetal Oxyacids and Their Salts

Nonmetal oxides form acids when allowed to react with water; these are acid anhydrides. The resulting oxyanions can form salts with various metal ions.

Nitrogen Oxyacids and Salts

Nitrogen pentaoxide, N_2O_5, and NO_2 react with water to form nitric acid, HNO_3. Alchemists, as early as the eighth century, knew nitric acid (shown in **Figure 18.50**) as *aqua fortis* (meaning "strong water"). The acid was useful in the separation of gold from silver because it dissolves silver but not gold. Traces of nitric acid occur in the atmosphere after thunderstorms, and its salts are widely distributed in nature. There are tremendous deposits of Chile saltpeter,

$NaNO_3$, in the desert region near the boundary of Chile and Peru. Bengal saltpeter, KNO_3, occurs in India and in other countries of the Far East.

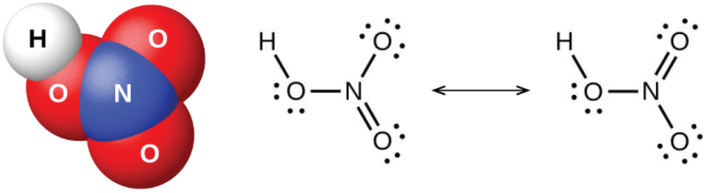


Figure 18.50 This image shows the molecular structure (left) of nitric acid, HNO_3 and its resonance forms (right).

In the laboratory, it is possible to produce nitric acid by heating a nitrate salt (such as sodium or potassium nitrate) with concentrated sulfuric acid:

$$NaNO_3(s) + H_2SO_4(l) \xrightarrow{\Delta} NaHSO_4(s) + HNO_3(g)$$

The **Ostwald process** is the commercial method for producing nitric acid. This process involves the oxidation of ammonia to nitric oxide, NO; oxidation of nitric oxide to nitrogen dioxide, NO_2; and further oxidation and hydration of nitrogen dioxide to form nitric acid:

$$\begin{gathered}4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g) \\ 2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \\ 3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)\end{gathered}$$

Or

$$4NO_2(g) + O_2(g) + 2H_2O(g) \longrightarrow 4HNO_3(l)$$

Pure nitric acid is a colorless liquid. However, it is often yellow or brown in color because NO_2 forms as the acid decomposes. Nitric acid is stable in aqueous solution; solutions containing 68% of the acid are commercially available concentrated nitric acid. It is both a strong oxidizing agent and a strong acid.

The action of nitric acid on a metal rarely produces H_2 (by reduction of H^+) in more than small amounts. Instead, the reduction of nitrogen occurs. The products formed depend on the concentration of the acid, the activity of the metal, and the temperature. Normally, a mixture of nitrates, nitrogen oxides, and various reduction products form. Less active metals such as copper, silver, and lead reduce concentrated nitric acid primarily to nitrogen dioxide. The reaction of dilute nitric acid with copper produces NO. In each case, the nitrate salts of the metals crystallize upon evaporation of the resultant solutions.

Nonmetallic elements, such as sulfur, carbon, iodine, and phosphorus, undergo oxidation by concentrated nitric acid to their oxides or oxyacids, with the formation of NO_2:

$$\begin{gathered}S(s) + 6HNO_3(aq) \longrightarrow H_2SO_4(aq) + 6NO_2(g) + 2H_2O(l) \\ C(s) + 4HNO_3(aq) \longrightarrow CO_2(g) + 4NO_2(g) + 2H_2O(l)\end{gathered}$$

Nitric acid oxidizes many compounds; for example, concentrated nitric acid readily oxidizes hydrochloric acid to chlorine and chlorine dioxide. A mixture of one part concentrated nitric acid and three parts concentrated hydrochloric acid (called *aqua regia*, which means royal water) reacts vigorously with metals. This mixture is particularly useful in dissolving gold, platinum, and other metals that are more difficult to oxidize than hydrogen. A simplified equation to represent the action of *aqua regia* on gold is:

$$\text{Au}(s) + 4\text{HCl}(aq) + 3\text{HNO}_3(aq) \longrightarrow \text{HAuCl}_4(aq) + 3\text{NO}_2(g) + 3\text{H}_2\text{O}(l)$$

Link to Learning

Although gold is generally unreactive, you can watch a **video (http://openstaxcollege.org/l/16gold)** of the complex mixture of compounds present in *aqua regia* dissolving it into solution.

Nitrates, salts of nitric acid, form when metals, oxides, hydroxides, or carbonates react with nitric acid. Most nitrates are soluble in water; indeed, one of the significant uses of nitric acid is to prepare soluble metal nitrates.

Nitric acid finds extensive use in the laboratory and in chemical industries as a strong acid and strong oxidizing agent. It is important in the manufacture of explosives, dyes, plastics, and drugs. Salts of nitric acid (nitrates) are valuable as fertilizers. Gunpowder is a mixture of potassium nitrate, sulfur, and charcoal.

The reaction of N_2O_3 with water gives a pale blue solution of nitrous acid, HNO_2. However, HNO_2 (shown in **Figure 18.51**) is easier to prepare by the addition of an acid to a solution of nitrite; nitrous acid is a weak acid, so the nitrite ion is basic in aqueous solution:

$$\text{NO}_2{}^-(aq) + \text{H}_3\text{O}^+(aq) \longrightarrow \text{HNO}_2(aq) + \text{H}_2\text{O}(l)$$

Nitrous acid is very unstable and exists only in solution. It disproportionates slowly at room temperature (rapidly when heated) into nitric acid and nitric oxide. Nitrous acid is an active oxidizing agent with strong reducing agents, and strong oxidizing agents oxidize it to nitric acid.

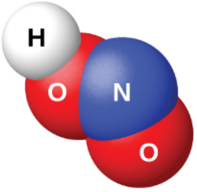


Figure 18.51 This image shows the molecular structure of a molecule of nitrous acid, HNO_2.

Sodium nitrite, $NaNO_2$, is an additive to meats such as hot dogs and cold cuts. The nitrite ion has two functions. It limits the growth of bacteria that can cause food poisoning, and it prolongs the meat's retention of its red color. The addition of sodium nitrite to meat products is controversial because nitrous acid reacts with certain organic compounds to form a class of compounds known as nitrosamines. Nitrosamines produce cancer in laboratory animals. This has prompted the FDA to limit the amount of $NaNO_2$ in foods.

The nitrites are much more stable than the acid, but nitrites, like nitrates, can explode. Nitrites, like nitrates, are also soluble in water ($AgNO_2$ is only slightly soluble).

Phosphorus Oxyacids and Salts

Pure orthophosphoric acid, H_3PO_4 (shown in **Figure 18.52**), forms colorless, deliquescent crystals that melt at 42 °C. The common name of this compound is phosphoric acid, and is commercially available as a viscous 82% solution known as syrupy phosphoric acid. One use of phosphoric acid is as an additive to many soft drinks.

One commercial method of preparing orthophosphoric acid is to treat calcium phosphate rock with concentrated sulfuric acid:

$$\text{Ca}_3(\text{PO}_4)_2(s) + 3\text{H}_2\text{SO}_4(aq) \longrightarrow 2\text{H}_3\text{PO}_4(aq) + 3\text{CaSO}_4(s)$$

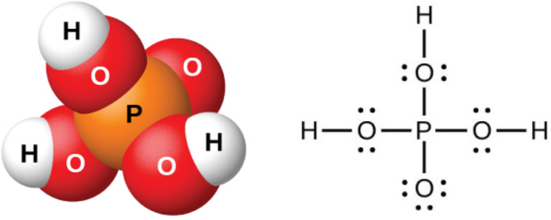


Figure 18.52 Orthophosphoric acid, H_3PO_4, is colorless when pure and has this molecular (left) and Lewis structure (right).

Dilution of the products with water, followed by filtration to remove calcium sulfate, gives a dilute acid solution contaminated with calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$, and other compounds associated with calcium phosphate rock. It is possible to prepare pure orthophosphoric acid by dissolving P_4O_{10} in water.

The action of water on P_4O_6, PCl_3, PBr_3, or PI_3 forms phosphorous acid, H_3PO_3 (shown in **Figure 18.53**). The best method for preparing pure phosphorous acid is by hydrolyzing phosphorus trichloride:

$$\text{PCl}_3(l) + 3\text{H}_2\text{O}(l) \longrightarrow \text{H}_3\text{PO}_3(aq) + 3\text{HCl}(g)$$

Heating the resulting solution expels the hydrogen chloride and leads to the evaporation of water. When sufficient water evaporates, white crystals of phosphorous acid will appear upon cooling. The crystals are deliquescent, very soluble in water, and have an odor like that of garlic. The solid melts at 70.1 °C and decomposes at about 200 °C by disproportionation into phosphine and orthophosphoric acid:

$$4\text{H}_3\text{PO}_3(l) \longrightarrow \text{PH}_3(g) + 3\text{H}_3\text{PO}_4(l)$$

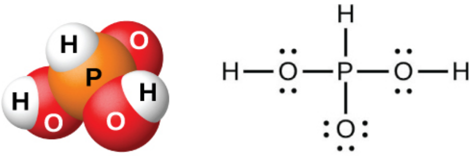


Figure 18.53 In a molecule of phosphorous acid, H_3PO_3, only the two hydrogen atoms bonded to an oxygen atom are acidic.

Phosphorous acid forms only two series of salts, which contain the dihydrogen phosphite ion, $\text{H}_2\text{PO}_3{}^-$, or the hydrogen phosphate ion, $\text{HPO}_3{}^{2-}$, respectively. It is not possible to replace the third atom of hydrogen because it is not very acidic, as it is not easy to ionize the P-H bond.

Sulfur Oxyacids and Salts

The preparation of sulfuric acid, H_2SO_4 (shown in **Figure 18.54**), begins with the oxidation of sulfur to sulfur trioxide and then converting the trioxide to sulfuric acid. Pure sulfuric acid is a colorless, oily liquid that freezes at 10.5 °C. It fumes when heated because the acid decomposes to water and sulfur trioxide. The heating process causes the loss of more sulfur trioxide than water, until reaching a concentration of 98.33% acid. Acid of this concentration boils at 338 °C without further change in concentration (a constant boiling solution) and is commercially concentrated H_2SO_4. The amount of sulfuric acid used in industry exceeds that of any other manufactured compound.

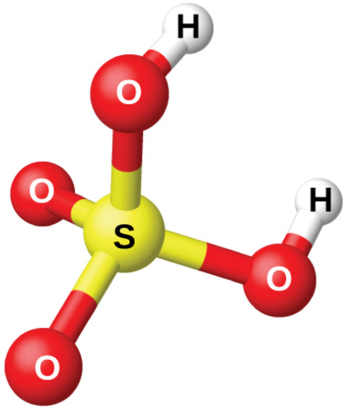


Figure 18.54 Sulfuric acid has a tetrahedral molecular structure.

The strong affinity of concentrated sulfuric acid for water makes it a good dehydrating agent. It is possible to dry gases and immiscible liquids that do not react with the acid by passing them through the acid.

Sulfuric acid is a strong diprotic acid that ionizes in two stages. In aqueous solution, the first stage is essentially complete. The secondary ionization is not nearly so complete, and $HSO_4{}^-$ is a moderately strong acid (about 25% ionized in solution of a $HSO_4{}^-$ salt: $K_a = 1.2 \times 10^{-2}$).

Being a diprotic acid, sulfuric acid forms both sulfates, such as Na_2SO_4, and hydrogen sulfates, such as $NaHSO_4$. Most sulfates are soluble in water; however, the sulfates of barium, strontium, calcium, and lead are only slightly soluble in water.

Among the important sulfates are $Na_2SO_4{\cdot}10H_2O$ and Epsom salts, $MgSO_4{\cdot}7H_2O$. Because the $HSO_4{}^-$ ion is an acid, hydrogen sulfates, such as $NaHSO_4$, exhibit acidic behavior, and this compound is the primary ingredient in some household cleansers.

Hot, concentrated sulfuric acid is an oxidizing agent. Depending on its concentration, the temperature, and the strength of the reducing agent, sulfuric acid oxidizes many compounds and, in the process, undergoes reduction to SO_2, $HSO_3{}^-$, $SO_3{}^{2-}$, S, H_2S, or S^{2-}.

Sulfur dioxide dissolves in water to form a solution of sulfurous acid, as expected for the oxide of a nonmetal. Sulfurous acid is unstable, and it is not possible to isolate anhydrous H_2SO_3. Heating a solution of sulfurous acid expels the sulfur dioxide. Like other diprotic acids, sulfurous acid ionizes in two steps: The hydrogen sulfite ion, $HSO_3{}^-$, and the sulfite ion, $SO_3{}^{2-}$, form. Sulfurous acid is a moderately strong acid. Ionization is about 25% in the first stage, but it is much less in the second ($K_{a1} = 1.2 \times 10^{-2}$ and $K_{a2} = 6.2 \times 10^{-8}$).

In order to prepare solid sulfite and hydrogen sulfite salts, it is necessary to add a stoichiometric amount of a base to a sulfurous acid solution and then evaporate the water. These salts also form from the reaction of SO_2 with oxides and hydroxides. Heating solid sodium hydrogen sulfite forms sodium sulfite, sulfur dioxide, and water:

$$2NaHSO_3(s) \xrightarrow{\Delta} Na_2SO_3(s) + SO_2(g) + H_2O(l)$$

Strong oxidizing agents can oxidize sulfurous acid. Oxygen in the air oxidizes it slowly to the more stable sulfuric acid:

$$2H_2SO_3(aq) + O_2(g) + 2H_2O(l) \xrightarrow{\Delta} 2H_3O^+(aq) + 2HSO_4{}^-(aq)$$

Solutions of sulfites are also very susceptible to air oxidation to produce sulfates. Thus, solutions of sulfites always contain sulfates after exposure to air.

Halogen Oxyacids and Their Salts

The compounds HXO, HXO_2, HXO_3, and HXO_4, where X represents Cl, Br, or I, are the hypohalous, halous, halic, and perhalic acids, respectively. The strengths of these acids increase from the hypohalous acids, which are very weak acids, to the perhalic acids, which are very strong. **Table 18.2** lists the known acids, and, where known, their pK_a values are given in parentheses.

Oxyacids of the Halogens

Name	Fluorine	Chlorine	Bromine	Iodine
hypohalous	HOF	HOCl (7.5)	HOBr (8.7)	HOI (11)
halous		$HClO_2$ (2.0)		
halic		$HClO_3$	$HBrO_3$	HIO_3 (0.8)
perhalic		$HClO_4$	$HBrO_4$	HIO_4 (1.6)
paraperhalic				H_5IO_6 (1.6)

Table 18.2

The only known oxyacid of fluorine is the very unstable hypofluorous acid, HOF, which is prepared by the reaction of gaseous fluorine with ice:

$$F_2(g) + H_2O(s) \longrightarrow HOF(g) + HF(g)$$

The compound is very unstable and decomposes above −40 °C. This compound does not ionize in water, and there are no known salts. It is uncertain whether the name hypofluorous acid is even appropriate for HOF; a more appropriate name might be hydrogen hypofluorite.

The reactions of chlorine and bromine with water are analogous to that of fluorine with ice, but these reactions do not go to completion, and mixtures of the halogen and the respective hypohalous and hydrohalic acids result. Other than HOF, the hypohalous acids only exist in solution. The hypohalous acids are all very weak acids; however, HOCl is a stronger acid than HOBr, which, in turn, is stronger than HOI.

The addition of base to solutions of the hypohalous acids produces solutions of salts containing the basic hypohalite ions, OX^-. It is possible to isolate these salts as solids. All of the hypohalites are unstable with respect to disproportionation in solution, but the reaction is slow for hypochlorite. Hypobromite and hypoiodite disproportionate rapidly, even in the cold:

$$3XO^-(aq) \longrightarrow 2X^-(aq) + XO_3^{\ -}(aq)$$

Sodium hypochlorite is an inexpensive bleach (Clorox) and germicide. The commercial preparation involves the electrolysis of cold, dilute, aqueous sodium chloride solutions under conditions where the resulting chlorine and hydroxide ion can react. The net reaction is:

$$Cl^-(aq) + H_2O(l) \xrightarrow{\text{electrical energy}} ClO^-(aq) + H_2(g)$$

The only definitely known halous acid is chlorous acid, $HClO_2$, obtained by the reaction of barium chlorite with dilute sulfuric acid:

$$Ba(ClO_2)_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + 2HClO_2(aq)$$

Filtering the insoluble barium sulfate leaves a solution of $HClO_2$. Chlorous acid is not stable; it slowly decomposes in solution to yield chlorine dioxide, hydrochloric acid, and water. Chlorous acid reacts with bases to give salts containing the chlorite ion (shown in **Figure 18.55**). Sodium chlorite finds an extensive application in the bleaching of paper because it is a strong oxidizing agent and does not damage the paper.

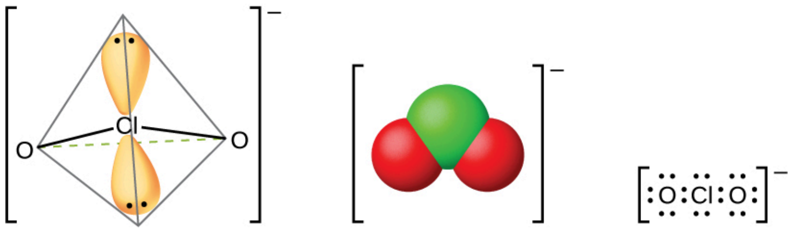


Figure 18.55 Chlorite ions, $ClO_2{}^-$, are produced when chlorous acid reacts with bases.

Chloric acid, $HClO_3$, and bromic acid, $HBrO_3$, are stable only in solution. The reaction of iodine with concentrated nitric acid produces stable white iodic acid, HIO_3:

$$I_2(s) + 10HNO_3(aq) \longrightarrow 2HIO_3(s) + 10NO_2(g) + 4H_2O(l)$$

It is possible to obtain the lighter halic acids from their barium salts by reaction with dilute sulfuric acid. The reaction is analogous to that used to prepare chlorous acid. All of the halic acids are strong acids and very active oxidizing agents. The acids react with bases to form salts containing chlorate ions (shown in **Figure 18.56**). Another preparative method is the electrochemical oxidation of a hot solution of a metal halide to form the appropriate metal chlorates. Sodium chlorate is a weed killer; potassium chlorate is used as an oxidizing agent.

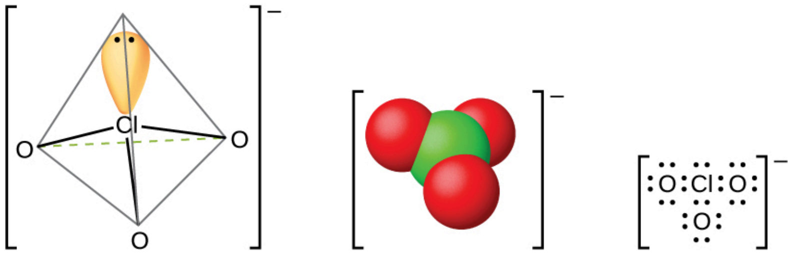


Figure 18.56 Chlorate ions, $ClO_3{}^-$, are produced when halic acids react with bases.

Perchloric acid, $HClO_4$, forms when treating a perchlorate, such as potassium perchlorate, with sulfuric acid under reduced pressure. The $HClO_4$ can be distilled from the mixture:

$$KClO_4(s) + H_2SO_4(aq) \longrightarrow HClO_4(g) + KHSO_4(s)$$

Dilute aqueous solutions of perchloric acid are quite stable thermally, but concentrations above 60% are unstable and dangerous. Perchloric acid and its salts are powerful oxidizing agents, as the very electronegative chlorine is more stable in a lower oxidation state than 7+. Serious explosions have occurred when heating concentrated solutions with easily oxidized substances. However, its reactions as an oxidizing agent are slow when perchloric acid is cold and dilute. The acid is among the strongest of all acids. Most salts containing the perchlorate ion (shown in **Figure 18.57**) are soluble. It is possible to prepare them from reactions of bases with perchloric acid and, commercially, by the electrolysis of hot solutions of their chlorides.

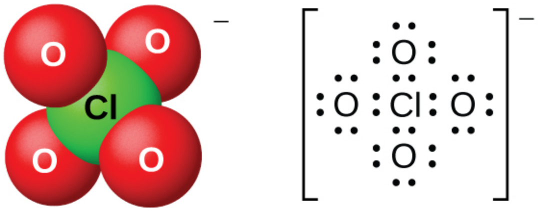


Figure 18.57 Perchlorate ions, $ClO_4{}^-$, can be produced when perchloric acid reacts with a base or by electrolysis of hot solutions of their chlorides.

Perbromate salts are difficult to prepare, and the best syntheses currently involve the oxidation of bromates in basic solution with fluorine gas followed by acidification. There are few, if any, commercial uses of this acid or its salts.

There are several different acids containing iodine in the 7+-oxidation state; they include metaperiodic acid, HIO_4, and paraperiodic acid, H_5IO_6. These acids are strong oxidizing agents and react with bases to form the appropriate salts.

18.10 Occurrence, Preparation, and Properties of Sulfur

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

- Describe the properties, preparation, and uses of sulfur

Sulfur exists in nature as elemental deposits as well as sulfides of iron, zinc, lead, and copper, and sulfates of sodium, calcium, barium, and magnesium. Hydrogen sulfide is often a component of natural gas and occurs in many volcanic gases, like those shown in **Figure 18.58**. Sulfur is a constituent of many proteins and is essential for life.

Figure 18.58 Volcanic gases contain hydrogen sulfide. (credit: Daniel Julie/Wikimedia Commons)

The **Frasch process**, illustrated in **Figure 18.59**, is important in the mining of free sulfur from enormous underground deposits in Texas and Louisiana. Superheated water (170 °C and 10 atm pressure) is forced down the outermost of three concentric pipes to the underground deposit. The hot water melts the sulfur. The innermost pipe conducts compressed air into the liquid sulfur. The air forces the liquid sulfur, mixed with air, to flow up through the outlet pipe. Transferring the mixture to large settling vats allows the solid sulfur to separate upon cooling. This sulfur is 99.5% to 99.9% pure and requires no purification for most uses.

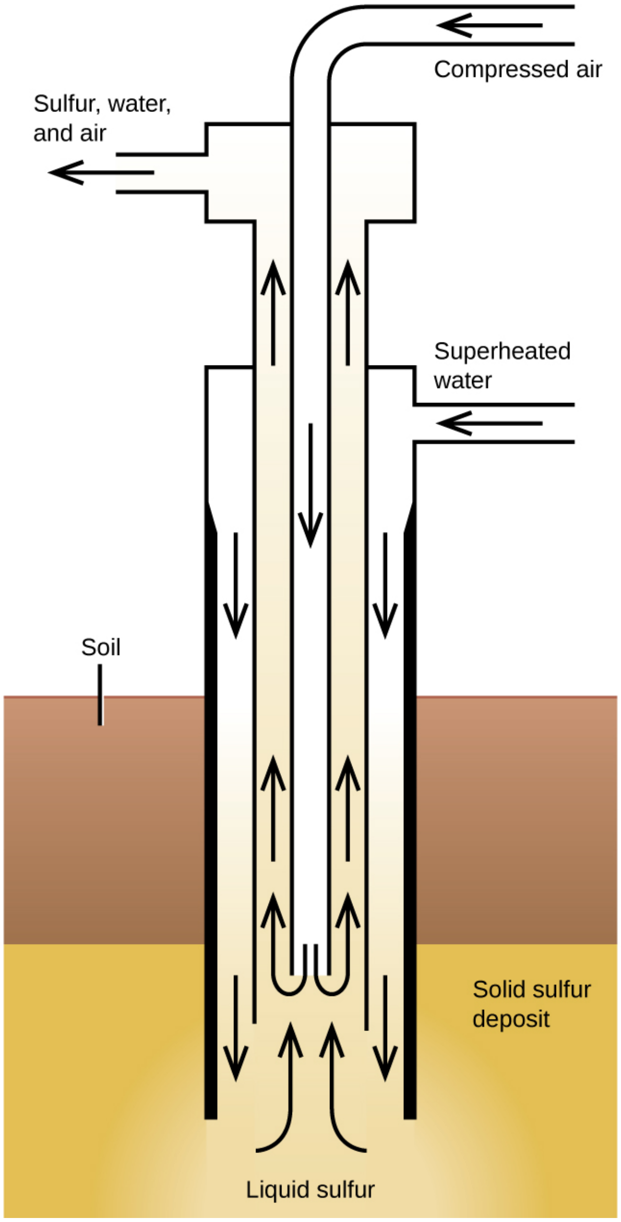


Figure 18.59 The Frasch process is used to mine sulfur from underground deposits.

Larger amounts of sulfur also come from hydrogen sulfide recovered during the purification of natural gas.

Sulfur exists in several allotropic forms. The stable form at room temperature contains eight-membered rings, and so the true formula is S_8. However, chemists commonly use S to simplify the coefficients in chemical equations; we will follow this practice in this book.

Like oxygen, which is also a member of group 16, sulfur exhibits a distinctly nonmetallic behavior. It oxidizes metals, giving a variety of binary sulfides in which sulfur exhibits a negative oxidation state (2−). Elemental sulfur oxidizes less electronegative nonmetals, and more electronegative nonmetals, such as oxygen and the halogens, will oxidize it. Other strong oxidizing agents also oxidize sulfur. For example, concentrated nitric acid oxidizes sulfur to the sulfate ion, with the concurrent formation of nitrogen(IV) oxide:

$$\mathrm{S}(s) + 6\mathrm{HNO_3}(aq) \longrightarrow 2\mathrm{H_3O^+}(aq) + \mathrm{SO_4{}^{2-}}(aq) + 6\mathrm{NO_2}(g)$$

The chemistry of sulfur with an oxidation state of 2− is similar to that of oxygen. Unlike oxygen, however, sulfur forms many compounds in which it exhibits positive oxidation states.

18.11 Occurrence, Preparation, and Properties of Halogens

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

- Describe the preparation, properties, and uses of halogens
- Describe the properties, preparation, and uses of halogen compounds

The elements in group 17 are the halogens. These are the elements fluorine, chlorine, bromine, iodine, and astatine. These elements are too reactive to occur freely in nature, but their compounds are widely distributed. Chlorides are the most abundant; although fluorides, bromides, and iodides are less common, they are reasonably available. In this section, we will examine the occurrence, preparation, and properties of halogens. Next, we will examine halogen compounds with the representative metals followed by an examination of the interhalogens. This section will conclude with some applications of halogens.

Occurrence and Preparation

All of the halogens occur in seawater as halide ions. The concentration of the chloride ion is 0.54 *M*; that of the other halides is less than 10^{-4} *M*. Fluoride also occurs in minerals such as $\mathrm{CaF_2}$, $\mathrm{Ca(PO_4)_3F}$, and $\mathrm{Na_3AlF_6}$. Chloride also occurs in the Great Salt Lake and the Dead Sea, and in extensive salt beds that contain NaCl, KCl, or $\mathrm{MgCl_2}$. Part of the chlorine in your body is present as hydrochloric acid, which is a component of stomach acid. Bromine compounds occur in the Dead Sea and underground brines. Iodine compounds are found in small quantities in Chile saltpeter, underground brines, and sea kelp. Iodine is essential to the function of the thyroid gland.

The best sources of halogens (except iodine) are halide salts. It is possible to oxidize the halide ions to free diatomic halogen molecules by various methods, depending on the ease of oxidation of the halide ion. Fluoride is the most difficult to oxidize, whereas iodide is the easiest.

The major method for preparing fluorine is electrolytic oxidation. The most common electrolysis procedure is to use a molten mixture of potassium hydrogen fluoride, $\mathrm{KHF_2}$, and anhydrous hydrogen fluoride. Electrolysis causes HF to decompose, forming fluorine gas at the anode and hydrogen at the cathode. It is necessary to keep the two gases separated to prevent their explosive recombination to reform hydrogen fluoride.

Most commercial chlorine comes from the electrolysis of the chloride ion in aqueous solutions of sodium chloride; this is the chlor-alkali process discussed previously. Chlorine is also a product of the electrolytic production of metals such as sodium, calcium, and magnesium from their fused chlorides. It is also possible to prepare chlorine by the chemical oxidation of the chloride ion in acid solution with strong oxidizing agents such as manganese dioxide ($\mathrm{MnO_2}$) or sodium dichromate ($\mathrm{Na_2Cr_2O_7}$). The reaction with manganese dioxide is:

$$\mathrm{MnO_2}(s) + 2\mathrm{Cl^-}(aq) + 4\mathrm{H_3O^+}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{Cl_2}(g) + 6\mathrm{H_2O}(l)$$

The commercial preparation of bromine involves the oxidation of bromide ion by chlorine:

$$2\text{Br}^-(aq) + \text{Cl}_2(g) \longrightarrow \text{Br}_2(l) + 2\text{Cl}^-(aq)$$

Chlorine is a stronger oxidizing agent than bromine. This method is important for the production of essentially all domestic bromine.

Some iodine comes from the oxidation of iodine chloride, ICl, or iodic acid, HIO_3. The commercial preparation of iodine utilizes the reduction of sodium iodate, $NaIO_3$, an impurity in deposits of Chile saltpeter, with sodium hydrogen sulfite:

$$2\text{IO}_3{}^-(aq) + 5\text{HSO}_3{}^-(aq) \longrightarrow 3\text{HSO}_4{}^-(aq) + 2\text{SO}_4{}^{2-}(aq) + \text{H}_2\text{O}(l) + \text{I}_2(s)$$

Properties of the Halogens

Fluorine is a pale yellow gas, chlorine is a greenish-yellow gas, bromine is a deep reddish-brown liquid, and iodine is a grayish-black crystalline solid. Liquid bromine has a high vapor pressure, and the reddish vapor is readily visible in **Figure 18.60**. Iodine crystals have a noticeable vapor pressure. When gently heated, these crystals sublime and form a beautiful deep violet vapor.

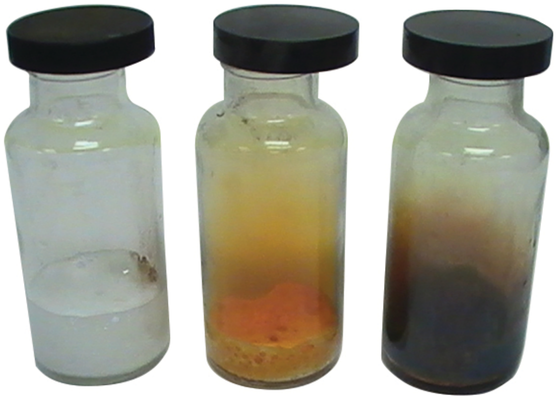


Figure 18.60 Chlorine is a pale yellow-green gas (left), gaseous bromine is deep orange (center), and gaseous iodine is purple (right). (Fluorine is so reactive that it is too dangerous to handle.) (credit: Sahar Atwa)

Bromine is only slightly soluble in water, but it is miscible in all proportions in less polar (or nonpolar) solvents such as chloroform, carbon tetrachloride, and carbon disulfide, forming solutions that vary from yellow to reddish-brown, depending on the concentration.

Iodine is soluble in chloroform, carbon tetrachloride, carbon disulfide, and many hydrocarbons, giving violet solutions of I_2 molecules. Iodine dissolves only slightly in water, giving brown solutions. It is quite soluble in aqueous solutions of iodides, with which it forms brown solutions. These brown solutions result because iodine molecules have empty valence *d* orbitals and can act as weak Lewis acids towards the iodide ion. The equation for the reversible reaction of iodine (Lewis acid) with the iodide ion (Lewis base) to form triiodide ion, $I_3{}^-$, is:

$$\text{I}_2(s) + \text{I}^-(aq) \longrightarrow \text{I}_3{}^-(aq)$$

The easier it is to oxidize the halide ion, the more difficult it is for the halogen to act as an oxidizing agent. Fluorine generally oxidizes an element to its highest oxidation state, whereas the heavier halogens may not. For example, when excess fluorine reacts with sulfur, SF_6 forms. Chlorine gives SCl_2 and bromine, S_2Br_2. Iodine does not react with sulfur.

Fluorine is the most powerful oxidizing agent of the known elements. It spontaneously oxidizes most other elements; therefore, the reverse reaction, the oxidation of fluorides, is very difficult to accomplish. Fluorine reacts directly and forms binary fluorides with all of the elements except the lighter noble gases (He, Ne, and Ar). Fluorine is such a strong oxidizing agent that many substances ignite on contact with it. Drops of water inflame in fluorine and form

O_2, OF_2, H_2O_2, O_3, and HF. Wood and asbestos ignite and burn in fluorine gas. Most hot metals burn vigorously in fluorine. However, it is possible to handle fluorine in copper, iron, or nickel containers because an adherent film of the fluoride salt passivates their surfaces. Fluorine is the only element that reacts directly with the noble gas xenon.

Although it is a strong oxidizing agent, chlorine is less active than fluorine. Mixing chlorine and hydrogen in the dark makes the reaction between them to be imperceptibly slow. Exposure of the mixture to light causes the two to react explosively. Chlorine is also less active towards metals than fluorine, and oxidation reactions usually require higher temperatures. Molten sodium ignites in chlorine. Chlorine attacks most nonmetals (C, N_2, and O_2 are notable exceptions), forming covalent molecular compounds. Chlorine generally reacts with compounds that contain only carbon and hydrogen (hydrocarbons) by adding to multiple bonds or by substitution.

In cold water, chlorine undergoes a disproportionation reaction:

$$\text{Cl}_2(aq) + 2\text{H}_2\text{O}(l) \longrightarrow \text{HOCl}(aq) + \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)$$

Half the chlorine atoms oxidize to the 1+ oxidation state (hypochlorous acid), and the other half reduce to the 1− oxidation state (chloride ion). This disproportionation is incomplete, so chlorine water is an equilibrium mixture of chlorine molecules, hypochlorous acid molecules, hydronium ions, and chloride ions. When exposed to light, this solution undergoes a photochemical decomposition:

$$2\text{HOCl}(aq) + 2\text{H}_2\text{O}(l) \xrightarrow{\text{sunlight}} 2\text{H}_3\text{O}^+(aq) + 2\text{Cl}^-(aq) + \text{O}_2(g)$$

The nonmetal chlorine is more electronegative than any other element except fluorine, oxygen, and nitrogen. In general, very electronegative elements are good oxidizing agents; therefore, we would expect elemental chlorine to oxidize all of the other elements except for these three (and the nonreactive noble gases). Its oxidizing property, in fact, is responsible for its principal use. For example, phosphorus(V) chloride, an important intermediate in the preparation of insecticides and chemical weapons, is manufactured by oxidizing the phosphorus with chlorine:

$$\text{P}_4(s) + 10\text{Cl}_2(g) \longrightarrow 4\text{PCl}_5(l)$$

A great deal of chlorine is also used to oxidize, and thus to destroy, organic or biological materials in water purification and in bleaching.

The chemical properties of bromine are similar to those of chlorine, although bromine is the weaker oxidizing agent and its reactivity is less than that of chlorine.

Iodine is the least reactive of the halogens. It is the weakest oxidizing agent, and the iodide ion is the most easily oxidized halide ion. Iodine reacts with metals, but heating is often required. It does not oxidize other halide ions.

Compared with the other halogens, iodine reacts only slightly with water. Traces of iodine in water react with a mixture of starch and iodide ion, forming a deep blue color. This reaction is a very sensitive test for the presence of iodine in water.

Halides of the Representative Metals

Thousands of salts of the representative metals have been prepared. The binary halides are an important subclass of salts. A salt is an ionic compound composed of cations and anions, other than hydroxide or oxide ions. In general, it is possible to prepare these salts from the metals or from oxides, hydroxides, or carbonates. We will illustrate the general types of reactions for preparing salts through reactions used to prepare binary halides.

The binary compounds of a metal with the halogens are the **halides**. Most binary halides are ionic. However, mercury, the elements of group 13 with oxidation states of 3+, tin(IV), and lead(IV) form covalent binary halides.

The direct reaction of a metal and a halogen produce the halide of the metal. Examples of these oxidation-reduction reactions include:

$$\mathrm{Cd}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{CdCl_2}(s)$$
$$\mathrm{2Ga}(l) + \mathrm{3Br_2}(l) \longrightarrow \mathrm{2GaBr_3}(s)$$

Link to Learning

Reactions of the alkali metals with elemental halogens are very exothermic and often quite violent. Under controlled conditions, they provide exciting demonstrations for budding students of chemistry. You can view the **initial heating (http://openstaxcollege.org/l/16sodium)** of the sodium that removes the coating of sodium hydroxide, sodium peroxide, and residual mineral oil to expose the reactive surface. The reaction with chlorine gas then proceeds very nicely.

If a metal can exhibit two oxidation states, it may be necessary to control the stoichiometry in order to obtain the halide with the lower oxidation state. For example, preparation of tin(II) chloride requires a 1:1 ratio of Sn to $\mathrm{Cl_2}$, whereas preparation of tin(IV) chloride requires a 1:2 ratio:

$$\mathrm{Sn}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{SnCl_2}(s)$$
$$\mathrm{Sn}(s) + \mathrm{2Cl_2}(g) \longrightarrow \mathrm{SnCl_4}(l)$$

The active representative metals—those that are easier to oxidize than hydrogen—react with gaseous hydrogen halides to produce metal halides and hydrogen. The reaction of zinc with hydrogen fluoride is:

$$\mathrm{Zn}(s) + \mathrm{2HF}(g) \longrightarrow \mathrm{ZnF_2}(s) + \mathrm{H_2}(g)$$

The active representative metals also react with solutions of hydrogen halides to form hydrogen and solutions of the corresponding halides. Examples of such reactions include:

$$\mathrm{Cd}(s) + \mathrm{2HBr}(aq) \longrightarrow \mathrm{CdBr_2}(aq) + \mathrm{H_2}(g)$$
$$\mathrm{Sn}(s) + \mathrm{2HI}(aq) \longrightarrow \mathrm{SnI_2}(aq) + \mathrm{H_2}(g)$$

Hydroxides, carbonates, and some oxides react with solutions of the hydrogen halides to form solutions of halide salts. It is possible to prepare additional salts by the reaction of these hydroxides, carbonates, and oxides with aqueous solution of other acids:

$$\mathrm{CaCo_3}(s) + \mathrm{2HCl}(aq) \longrightarrow \mathrm{CaCl_2}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$$
$$\mathrm{TlOH}(aq) + \mathrm{HF}(aq) \longrightarrow \mathrm{TlF}(aq) + \mathrm{H_2O}(l)$$

A few halides and many of the other salts of the representative metals are insoluble. It is possible to prepare these soluble salts by metathesis reactions that occur when solutions of soluble salts are mixed (see **Figure 18.61**). Metathesis reactions are examined in the chapter on the stoichiometry of chemical reactions.

Figure 18.61 Solid HgI_2 forms when solutions of KI and $Hg(NO_3)_2$ are mixed. (credit: Sahar Atwa)

Several halides occur in large quantities in nature. The ocean and underground brines contain many halides. For example, magnesium chloride in the ocean is the source of magnesium ions used in the production of magnesium. Large underground deposits of sodium chloride, like the salt mine shown in **Figure 18.62**, occur in many parts of the world. These deposits serve as the source of sodium and chlorine in almost all other compounds containing these elements. The chlor-alkali process is one example.

Figure 18.62 Underground deposits of sodium chloride are found throughout the world and are often mined. This is a tunnel in the Kłodawa salt mine in Poland. (credit: Jarek Zok)

Interhalogens

Compounds formed from two or more different halogens are **interhalogens**. Interhalogen molecules consist of one atom of the heavier halogen bonded by single bonds to an odd number of atoms of the lighter halogen. The structures of IF_3, IF_5, and IF_7 are illustrated in **Figure 18.63**. Formulas for other interhalogens, each of which comes from the reaction of the respective halogens, are in **Table 18.3**.

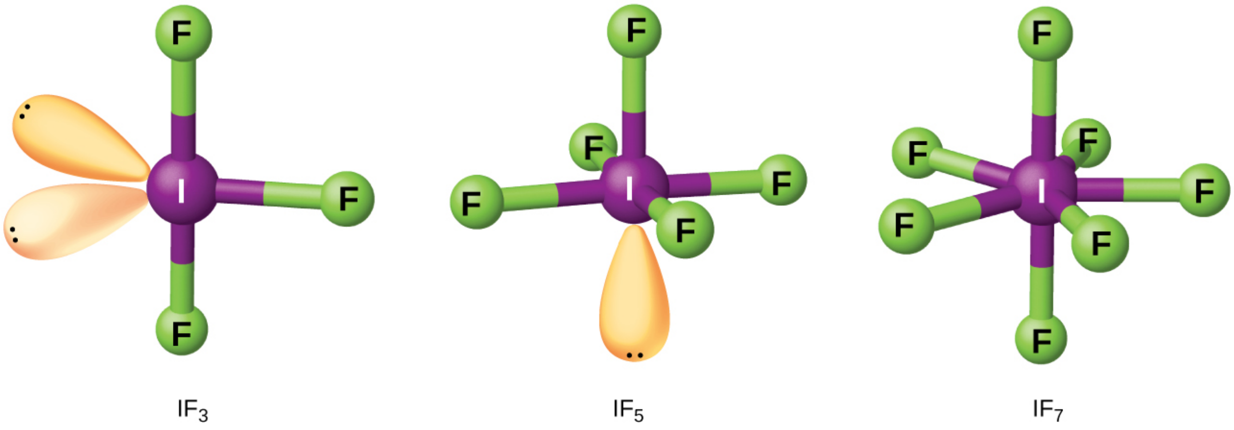


Figure 18.63 The structure of IF_3 is T-shaped (left), IF_5 is square pyramidal (center), and IF_7 is pentagonal bipyramidal (right).

Note from **Table 18.3** that fluorine is able to oxidize iodine to its maximum oxidation state, 7+, whereas bromine and chlorine, which are more difficult to oxidize, achieve only the 5+-oxidation state. A 7+-oxidation state is the limit for the halogens. Because smaller halogens are grouped about a larger one, the maximum number of smaller atoms possible increases as the radius of the larger atom increases. Many of these compounds are unstable, and most are extremely reactive. The interhalogens react like their component halides; halogen fluorides, for example, are stronger oxidizing agents than are halogen chlorides.

The ionic polyhalides of the alkali metals, such as KI_3, $KICl_2$, $KICl_4$, $CsIBr_2$, and $CsBrCl_2$, which contain an anion composed of at least three halogen atoms, are closely related to the interhalogens. As seen previously, the formation of the polyhalide anion $I_3{}^-$ is responsible for the solubility of iodine in aqueous solutions containing an iodide ion.

Interhalogens

YX	YX_3	YX_5	YX_7
ClF(*g*)	ClF_3(*g*)	ClF_5(*g*)	
BrF(*g*)	BrF_3(*l*)	BrF_5(*l*)	
BrCl(*g*)			
IF(*s*)	IF_3(*s*)	IF_5(*l*)	IF_7(*g*)
ICl(*l*)	ICl_3(*s*)		
IBr(*s*)			

Table 18.3

Applications

The fluoride ion and fluorine compounds have many important uses. Compounds of carbon, hydrogen, and fluorine are replacing Freons (compounds of carbon, chlorine, and fluorine) as refrigerants. Teflon is a polymer composed of $–CF_2CF_2–$ units. Fluoride ion is added to water supplies and to some toothpastes as SnF_2 or NaF to fight tooth decay. Fluoride partially converts teeth from $Ca_5(PO_4)_3(OH)$ into $Ca_5(PO_4)_3F$.

Chlorine is important to bleach wood pulp and cotton cloth. The chlorine reacts with water to form hypochlorous acid, which oxidizes colored substances to colorless ones. Large quantities of chlorine are important in chlorinating hydrocarbons (replacing hydrogen with chlorine) to produce compounds such as tetrachloride (CCl_4), chloroform ($CHCl_3$), and ethyl chloride (C_2H_5Cl), and in the production of polyvinyl chloride (PVC) and other polymers. Chlorine is also important to kill the bacteria in community water supplies.

Bromine is important in the production of certain dyes, and sodium and potassium bromides are used as sedatives. At one time, light-sensitive silver bromide was a component of photographic film.

Iodine in alcohol solution with potassium iodide is an antiseptic (tincture of iodine). Iodide salts are essential for the proper functioning of the thyroid gland; an iodine deficiency may lead to the development of a goiter. Iodized table salt contains 0.023% potassium iodide. Silver iodide is useful in the seeding of clouds to induce rain; it was important in the production of photographic film and iodoform, CHI_3, is an antiseptic.

18.12 Occurrence, Preparation, and Properties of the Noble Gases

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

- Describe the properties, preparation, and uses of the noble gases

The elements in group 18 are the noble gases (helium, neon, argon, krypton, xenon, and radon). They earned the name “noble” because they were assumed to be nonreactive since they have filled valence shells. In 1962, Dr. Neil Bartlett at the University of British Columbia proved this assumption to be false.

These elements are present in the atmosphere in small amounts. Some natural gas contains 1–2% helium by mass. Helium is isolated from natural gas by liquefying the condensable components, leaving only helium as a gas. The United States possesses most of the world’s commercial supply of this element in its helium-bearing gas fields. Argon, neon, krypton, and xenon come from the fractional distillation of liquid air. Radon comes from other radioactive elements. More recently, it was observed that this radioactive gas is present in very small amounts in soils and minerals. Its accumulation in well-insulated, tightly sealed buildings, however, constitutes a health hazard, primarily lung cancer.

The boiling points and melting points of the noble gases are extremely low relative to those of other substances of comparable atomic or molecular masses. This is because only weak London dispersion forces are present, and these forces can hold the atoms together only when molecular motion is very slight, as it is at very low temperatures. Helium is the only substance known that does not solidify on cooling at normal pressure. It remains liquid close to absolute zero (0.001 K) at ordinary pressures, but it solidifies under elevated pressure.

Helium is used for filling balloons and lighter-than-air craft because it does not burn, making it safer to use than hydrogen. Helium at high pressures is not a narcotic like nitrogen. Thus, mixtures of oxygen and helium are important for divers working under high pressures. Using a helium-oxygen mixture avoids the disoriented mental state known as nitrogen narcosis, the so-called rapture of the deep. Helium is important as an inert atmosphere for the melting and welding of easily oxidizable metals and for many chemical processes that are sensitive to air.

Liquid helium (boiling point, 4.2 K) is an important coolant to reach the low temperatures necessary for cryogenic research, and it is essential for achieving the low temperatures necessary to produce superconduction in traditional superconducting materials used in powerful magnets and other devices. This cooling ability is necessary for the magnets used for magnetic resonance imaging, a common medical diagnostic procedure. The other common coolant is liquid nitrogen (boiling point, 77 K), which is significantly cheaper.

Neon is a component of neon lamps and signs. Passing an electric spark through a tube containing neon at low pressure generates the familiar red glow of neon. It is possible to change the color of the light by mixing argon or mercury vapor with the neon or by utilizing glass tubes of a special color.

Argon was useful in the manufacture of gas-filled electric light bulbs, where its lower heat conductivity and chemical inertness made it preferable to nitrogen for inhibiting the vaporization of the tungsten filament and prolonging the life of the bulb. Fluorescent tubes commonly contain a mixture of argon and mercury vapor. Argon is the third most abundant gas in dry air.

Krypton-xenon flash tubes are used to take high-speed photographs. An electric discharge through such a tube gives a very intense light that lasts only $\frac{1}{50{,}000}$ of a second. Krypton forms a difluoride, KrF_2, which is thermally unstable at room temperature.

Stable compounds of xenon form when xenon reacts with fluorine. Xenon difluoride, XeF_2, forms after heating an excess of xenon gas with fluorine gas and then cooling. The material forms colorless crystals, which are stable at room temperature in a dry atmosphere. Xenon tetrafluoride, XeF_4, and xenon hexafluoride, XeF_6, are prepared in an analogous manner, with a stoichiometric amount of fluorine and an excess of fluorine, respectively. Compounds with oxygen are prepared by replacing fluorine atoms in the xenon fluorides with oxygen.

When XeF_6 reacts with water, a solution of XeO_3 results and the xenon remains in the 6+-oxidation state:

$$\text{XeF}_6(s) + 3\text{H}_2\text{O}(l) \longrightarrow \text{XeO}_3(aq) + 6\text{HF}(aq)$$

Dry, solid xenon trioxide, XeO_3, is extremely explosive—it will spontaneously detonate. Both XeF_6 and XeO_3 disproportionate in basic solution, producing xenon, oxygen, and salts of the perxenate ion, $\text{XeO}_6{}^{4-}$, in which xenon reaches its maximum oxidation sate of 8+.

Radon apparently forms RnF_2—evidence of this compound comes from radiochemical tracer techniques.

Unstable compounds of argon form at low temperatures, but stable compounds of helium and neon are not known.

Key Terms

acid anhydride compound that reacts with water to form an acid or acidic solution

alkaline earth metal any of the metals (beryllium, magnesium, calcium, strontium, barium, and radium) occupying group 2 of the periodic table; they are reactive, divalent metals that form basic oxides

allotropes two or more forms of the same element, in the same physical state, with different chemical structures

amorphous solid material such as a glass that does not have a regular repeating component to its three-dimensional structure; a solid but not a crystal

base anhydride metal oxide that behaves as a base towards acids

bicarbonate anion salt of the hydrogen carbonate ion, $HCO_3{}^-$

bismuth heaviest member of group 15; a less reactive metal than other representative metals

borate compound containing boron-oxygen bonds, typically with clusters or chains as a part of the chemical structure

carbonate salt of the anion $CO_3{}^{2-}$; often formed by the reaction of carbon dioxide with bases

chemical reduction method of preparing a representative metal using a reducing agent

chlor-alkali process electrolysis process for the synthesis of chlorine and sodium hydroxide

disproportionation reaction chemical reaction where a single reactant is simultaneously reduced and oxidized; it is both the reducing agent and the oxidizing agent

Downs cell electrochemical cell used for the commercial preparation of metallic sodium (and chlorine) from molten sodium chloride

Frasch process important in the mining of free sulfur from enormous underground deposits

Haber process main industrial process used to produce ammonia from nitrogen and hydrogen; involves the use of an iron catalyst and elevated temperatures and pressures

halide compound containing an anion of a group 17 element in the 1− oxidation state (fluoride, F^-; chloride, Cl^-; bromide, Br^-; and iodide, I^-)

Hall–Héroult cell electrolysis apparatus used to isolate pure aluminum metal from a solution of alumina in molten cryolite

hydrogen carbonate salt of carbonic acid, H_2CO_3 (containing the anion $HCO_3{}^-$) in which one hydrogen atom has been replaced; an acid carbonate; also known as *bicarbonate ion*

hydrogen halide binary compound formed between hydrogen and the halogens: HF, HCl, HBr, and HI

hydrogen sulfate $HSO_4{}^-$ ion

hydrogen sulfite $HSO_3{}^-$ ion

hydrogenation addition of hydrogen (H_2) to reduce a compound

hydroxide compound of a metal with the hydroxide ion OH^- or the group −OH

interhalogen compound formed from two or more different halogens

metal (representative) atoms of the metallic elements of groups 1, 2, 12, 13, 14, 15, and 16, which form ionic compounds by losing electrons from their outer *s* or *p* orbitals

metalloid element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors

nitrate $NO_3{}^-$ ion; salt of nitric acid

nitrogen fixation formation of nitrogen compounds from molecular nitrogen

Ostwald process industrial process used to convert ammonia into nitric acid

oxide binary compound of oxygen with another element or group, typically containing O^{2-} ions or the group –O– or =O

ozone allotrope of oxygen; O_3

passivation metals with a protective nonreactive film of oxide or other compound that creates a barrier for chemical reactions; physical or chemical removal of the passivating film allows the metals to demonstrate their expected chemical reactivity

peroxide molecule containing two oxygen atoms bonded together or as the anion, $O_2{}^{2-}$

photosynthesis process whereby light energy promotes the reaction of water and carbon dioxide to form carbohydrates and oxygen; this allows photosynthetic organisms to store energy

Pidgeon process chemical reduction process used to produce magnesium through the thermal reaction of magnesium oxide with silicon

polymorph variation in crystalline structure that results in different physical properties for the resulting compound

representative element element where the *s* and *p* orbitals are filling

representative metal metal among the representative elements

silicate compound containing silicon-oxygen bonds, with silicate tetrahedra connected in rings, sheets, or three-dimensional networks, depending on the other elements involved in the formation of the compounds

sulfate $SO_4{}^{2-}$ ion

sulfite $SO_3{}^{2-}$ ion

superoxide oxide containing the anion $O_2{}^-$

Summary

18.1 Periodicity

This section focuses on the periodicity of the representative elements. These are the elements where the electrons are entering the *s* and *p* orbitals. The representative elements occur in groups 1, 2, and 12–18. These elements are representative metals, metalloids, and nonmetals. The alkali metals (group 1) are very reactive, readily form ions with a charge of 1+ to form ionic compounds that are usually soluble in water, and react vigorously with water to form hydrogen gas and a basic solution of the metal hydroxide. The outermost electrons of the alkaline earth metals (group 2) are more difficult to remove than the outer electron of the alkali metals, leading to the group 2 metals being less reactive than those in group 1. These elements easily form compounds in which the metals exhibit an oxidation state of 2+. Zinc, cadmium, and mercury (group 12) commonly exhibit the group oxidation state of 2+ (although mercury also exhibits an oxidation state of 1+ in compounds that contain $\text{Hg}_2{}^{2+}$). Aluminum, gallium, indium, and thallium (group 13) are easier to oxidize than is hydrogen. Aluminum, gallium, and indium occur with an oxidation state 3+ (however, thallium also commonly occurs as the Tl^+ ion). Tin and lead form stable divalent cations and covalent compounds in which the metals exhibit the 4+-oxidation state.

18.2 Occurrence and Preparation of the Representative Metals

Because of their chemical reactivity, it is necessary to produce the representative metals in their pure forms by reduction from naturally occurring compounds. Electrolysis is important in the production of sodium, potassium, and aluminum. Chemical reduction is the primary method for the isolation of magnesium, zinc, and tin. Similar procedures are important for the other representative metals.

18.3 Structure and General Properties of the Metalloids

The elements boron, silicon, germanium, arsenic, antimony, and tellurium separate the metals from the nonmetals in the periodic table. These elements, called metalloids or sometimes semimetals, exhibit properties characteristic of both metals and nonmetals. The structures of these elements are similar in many ways to those of nonmetals, but the elements are electrical semiconductors.

18.4 Structure and General Properties of the Nonmetals

Nonmetals have structures that are very different from those of the metals, primarily because they have greater electronegativity and electrons that are more tightly bound to individual atoms. Most nonmetal oxides are acid anhydrides, meaning that they react with water to form acidic solutions. Molecular structures are common for most of the nonmetals, and several have multiple allotropes with varying physical properties.

18.5 Occurrence, Preparation, and Compounds of Hydrogen

Hydrogen is the most abundant element in the universe and its chemistry is truly unique. Although it has some chemical reactivity that is similar to that of the alkali metals, hydrogen has many of the same chemical properties of a nonmetal with a relatively low electronegativity. It forms ionic hydrides with active metals, covalent compounds in which it has an oxidation state of 1− with less electronegative elements, and covalent compounds in which it has an oxidation state of 1+ with more electronegative nonmetals. It reacts explosively with oxygen, fluorine, and chlorine, less readily with bromine, and much less readily with iodine, sulfur, and nitrogen. Hydrogen reduces the oxides of metals with lower reduction potentials than chromium to form the metal and water. The hydrogen halides are all acidic when dissolved in water.

18.6 Occurrence, Preparation, and Properties of Carbonates

The usual method for the preparation of the carbonates of the alkali and alkaline earth metals is by reaction of an oxide or hydroxide with carbon dioxide. Other carbonates form by precipitation. Metal carbonates or hydrogen carbonates such as limestone (CaCO_3), the antacid Tums (CaCO_3), and baking soda (NaHCO_3) are common examples. Carbonates and hydrogen carbonates decompose in the presence of acids and most decompose on heating.

18.7 Occurrence, Preparation, and Properties of Nitrogen

Nitrogen exhibits oxidation states ranging from 3− to 5+. Because of the stability of the N≡N triple bond, it requires a great deal of energy to make compounds from molecular nitrogen. Active metals such as the alkali metals and alkaline earth metals can reduce nitrogen to form metal nitrides. Nitrogen oxides and nitrogen hydrides are also important substances.

18.8 Occurrence, Preparation, and Properties of Phosphorus

Phosphorus (group 15) commonly exhibits oxidation states of 3− with active metals and of 3+ and 5+ with more electronegative nonmetals. The halogens and oxygen will oxidize phosphorus. The oxides are phosphorus(V) oxide, P_4O_{10}, and phosphorus(III) oxide, P_4O_6. The two common methods for preparing orthophosphoric acid, H_3PO_4, are either the reaction of a phosphate with sulfuric acid or the reaction of water with phosphorus(V) oxide. Orthophosphoric acid is a triprotic acid that forms three types of salts.

18.9 Occurrence, Preparation, and Compounds of Oxygen

Oxygen is one of the most reactive elements. This reactivity, coupled with its abundance, makes the chemistry of oxygen very rich and well understood.

Compounds of the representative metals with oxygen exist in three categories (1) oxides, (2) peroxides and superoxides, and (3) hydroxides. Heating the corresponding hydroxides, nitrates, or carbonates is the most common method for producing oxides. Heating the metal or metal oxide in oxygen may lead to the formation of peroxides and superoxides. The soluble oxides dissolve in water to form solutions of hydroxides. Most metals oxides are base anhydrides and react with acids. The hydroxides of the representative metals react with acids in acid-base reactions to form salts and water. The hydroxides have many commercial uses.

All nonmetals except fluorine form multiple oxides. Nearly all of the nonmetal oxides are acid anhydrides. The acidity of oxyacids requires that the hydrogen atoms bond to the oxygen atoms in the molecule rather than to the other nonmetal atom. Generally, the strength of the oxyacid increases with the number of oxygen atoms bonded to the nonmetal atom and not to a hydrogen.

18.10 Occurrence, Preparation, and Properties of Sulfur

Sulfur (group 16) reacts with almost all metals and readily forms the sulfide ion, S^{2-}, in which it has as oxidation state of 2−. Sulfur reacts with most nonmetals.

18.11 Occurrence, Preparation, and Properties of Halogens

The halogens form halides with less electronegative elements. Halides of the metals vary from ionic to covalent; halides of nonmetals are covalent. Interhalogens form by the combination of two or more different halogens.

All of the representative metals react directly with elemental halogens or with solutions of the hydrohalic acids (HF, HCl, HBr, and HI) to produce representative metal halides. Other laboratory preparations involve the addition of aqueous hydrohalic acids to compounds that contain such basic anions, such as hydroxides, oxides, or carbonates.

18.12 Occurrence, Preparation, and Properties of the Noble Gases

The most significant property of the noble gases (group 18) is their inactivity. They occur in low concentrations in the atmosphere. They find uses as inert atmospheres, neon signs, and as coolants. The three heaviest noble gases react with fluorine to form fluorides. The xenon fluorides are the best characterized as the starting materials for a few other noble gas compounds.

Exercises

18.1 Periodicity

1. How do alkali metals differ from alkaline earth metals in atomic structure and general properties?

2. Why does the reactivity of the alkali metals decrease from cesium to lithium?

3. Predict the formulas for the nine compounds that may form when each species in column 1 of **Table 18.3** reacts with each species in column 2.

1	2
Na	I
Sr	Se
Al	O

4. Predict the best choice in each of the following. You may wish to review the chapter on electronic structure for relevant examples.

(a) the most metallic of the elements Al, Be, and Ba

(b) the most covalent of the compounds NaCl, $CaCl_2$, and $BeCl_2$

(c) the lowest first ionization energy among the elements Rb, K, and Li

(d) the smallest among Al, Al^+, and Al^{3+}

(e) the largest among Cs^+, Ba^{2+}, and Xe

5. Sodium chloride and strontium chloride are both white solids. How could you distinguish one from the other?

6. The reaction of quicklime, CaO, with water produces slaked lime, $Ca(OH)_2$, which is widely used in the construction industry to make mortar and plaster. The reaction of quicklime and water is highly exothermic:

$$\text{CaO}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{Ca(OH)}_2(s) \qquad \Delta H = -350 \text{ kJ mol}^{-1}$$

(a) What is the enthalpy of reaction per gram of quicklime that reacts?

(b) How much heat, in kilojoules, is associated with the production of 1 ton of slaked lime?

7. Write a balanced equation for the reaction of elemental strontium with each of the following:

(a) oxygen

(b) hydrogen bromide

(c) hydrogen

(d) phosphorus

(e) water

8. How many moles of ionic species are present in 1.0 L of a solution marked 1.0 *M* mercury(I) nitrate?

9. What is the mass of fish, in kilograms, that one would have to consume to obtain a fatal dose of mercury, if the fish contains 30 parts per million of mercury by weight? (Assume that all the mercury from the fish ends up as mercury(II) chloride in the body and that a fatal dose is 0.20 g of $HgCl_2$.) How many pounds of fish is this?

10. The elements sodium, aluminum, and chlorine are in the same period.

(a) Which has the greatest electronegativity?

(b) Which of the atoms is smallest?

(c) Write the Lewis structure for the simplest covalent compound that can form between aluminum and chlorine.

(d) Will the oxide of each element be acidic, basic, or amphoteric?

11. Does metallic tin react with HCl?

12. What is tin pest, also known as tin disease?

13. Compare the nature of the bonds in $PbCl_2$ to that of the bonds in $PbCl_4$.

14. Is the reaction of rubidium with water more or less vigorous than that of sodium? How does the rate of reaction of magnesium compare?

18.2 Occurrence and Preparation of the Representative Metals

15. Write an equation for the reduction of cesium chloride by elemental calcium at high temperature.

16. Why is it necessary to keep the chlorine and sodium, resulting from the electrolysis of sodium chloride, separate during the production of sodium metal?

17. Give balanced equations for the overall reaction in the electrolysis of molten lithium chloride and for the reactions occurring at the electrodes. You may wish to review the chapter on electrochemistry for relevant examples.

18. The electrolysis of molten sodium chloride or of aqueous sodium chloride produces chlorine.

Calculate the mass of chlorine produced from 3.00 kg sodium chloride in each case. You may wish to review the chapter on electrochemistry for relevant examples.

19. What mass, in grams, of hydrogen gas forms during the complete reaction of 10.01 g of calcium with water?

20. How many grams of oxygen gas are necessary to react completely with 3.01×10^{21} atoms of magnesium to yield magnesium oxide?

21. Magnesium is an active metal; it burns in the form of powder, ribbons, and filaments to provide flashes of brilliant light. Why is it possible to use magnesium in construction?

22. Why is it possible for an active metal like aluminum to be useful as a structural metal?

23. Describe the production of metallic aluminum by electrolytic reduction.

24. What is the common ore of tin and how is tin separated from it?

25. A chemist dissolves a 1.497-g sample of a type of metal (an alloy of Sn, Pb, Sb, and Cu) in nitric acid, and metastannic acid, H_2SnO_3, is precipitated. She heats the precipitate to drive off the water, which leaves 0.4909 g of tin(IV) oxide. What was the percentage of tin in the original sample?

26. Consider the production of 100 kg of sodium metal using a current of 50,000 A, assuming a 100% yield.

(a) How long will it take to produce the 100 kg of sodium metal?

(b) What volume of chlorine at 25 °C and 1.00 atm forms?

27. What mass of magnesium forms when 100,000 A is passed through a $MgCl_2$ melt for 1.00 h if the yield of magnesium is 85% of the theoretical yield?

18.3 Structure and General Properties of the Metalloids

28. Give the hybridization of the metalloid and the molecular geometry for each of the following compounds or ions. You may wish to review the chapters on chemical bonding and advanced covalent bonding for relevant examples.

(a) GeH_4

(b) SbF_3

(c) $Te(OH)_6$

(d) H_2Te

(e) GeF_2

(f) $TeCl_4$

(g) $SiF_6{}^{2-}$

(h) $SbCl_5$

(i) TeF_6

29. Write a Lewis structure for each of the following molecules or ions. You may wish to review the chapter on chemical bonding.

(a) H_3BPH_3

(b) $BF_4{}^{-}$

(c) BBr_3

(d) $B(CH_3)_3$

(e) $B(OH)_3$

30. Describe the hybridization of boron and the molecular structure about the boron in each of the following:

(a) H_3BPH_3

(b) $BF_4{}^-$

(c) BBr_3

(d) $B(CH_3)_3$

(e) $B(OH)_3$

31. Using only the periodic table, write the complete electron configuration for silicon, including any empty orbitals in the valence shell. You may wish to review the chapter on electronic structure.

32. Write a Lewis structure for each of the following molecules and ions:

(a) $(CH_3)_3SiH$

(b) $SiO_4{}^{4-}$

(c) Si_2H_6

(d) $Si(OH)_4$

(e) $SiF_6{}^{2-}$

33. Describe the hybridization of silicon and the molecular structure of the following molecules and ions:

(a) $(CH_3)_3SiH$

(b) $SiO_4{}^{4-}$

(c) Si_2H_6

(d) $Si(OH)_4$

(e) $SiF_6{}^{2-}$

34. Describe the hybridization and the bonding of a silicon atom in elemental silicon.

35. Classify each of the following molecules as polar or nonpolar. You may wish to review the chapter on chemical bonding.

(a) SiH_4

(b) Si_2H_6

(c) $SiCl_3H$

(d) SiF_4

(e) $SiCl_2F_2$

36. Silicon reacts with sulfur at elevated temperatures. If 0.0923 g of silicon reacts with sulfur to give 0.3030 g of silicon sulfide, determine the empirical formula of silicon sulfide.

37. Name each of the following compounds:

(a) TeO_2

(b) Sb_2S_3

(c) GeF_4

(d) SiH_4

(e) GeH_4

38. Write a balanced equation for the reaction of elemental boron with each of the following (most of these reactions require high temperature):

(a) F_2

(b) O_2

(c) S

(d) Se

(e) Br_2

39. Why is boron limited to a maximum coordination number of four in its compounds?

40. Write a formula for each of the following compounds:

(a) silicon dioxide

(b) silicon tetraiodide

(c) silane

(d) silicon carbide

(e) magnesium silicide

41. From the data given in **Appendix I** , determine the standard enthalpy change and the standard free energy change for each of the following reactions:

(a) $BF_3(g) + 3H_2O(l) \longrightarrow B(OH)_3(s) + 3HF(g)$

(b) $BCl_3(g) + 3H_2O(l) \longrightarrow B(OH)_3(s) + 3HCl(g)$

(c) $B_2H_6(g) + 6H_2O(l) \longrightarrow 2B(OH)_3(s) + 6H_2(g)$

42. A hydride of silicon prepared by the reaction of Mg_2Si with acid exerted a pressure of 306 torr at 26 °C in a bulb with a volume of 57.0 mL. If the mass of the hydride was 0.0861 g, what is its molecular mass? What is the molecular formula for the hydride?

43. Suppose you discovered a diamond completely encased in a silicate rock. How would you chemically free the diamond without harming it?

18.4 Structure and General Properties of the Nonmetals

44. Carbon forms a number of allotropes, two of which are graphite and diamond. Silicon has a diamond structure. Why is there no allotrope of silicon with a graphite structure?

45. Nitrogen in the atmosphere exists as very stable diatomic molecules. Why does phosphorus form less stable P_4 molecules instead of P_2 molecules?

46. Write balanced chemical equations for the reaction of the following acid anhydrides with water:

(a) SO_3

(b) N_2O_3

(c) Cl_2O_7

(d) P_4O_{10}

(e) NO_2

47. Determine the oxidation number of each element in each of the following compounds:

(a) HCN

(b) OF_2

(c) $AsCl_3$

48. Determine the oxidation state of sulfur in each of the following:

(a) SO_3

(b) SO_2

(c) $SO_3{}^{2-}$

49. Arrange the following in order of increasing electronegativity: F; Cl; O; and S.

50. Why does white phosphorus consist of tetrahedral P_4 molecules while nitrogen consists of diatomic N_2 molecules?

18.5 Occurrence, Preparation, and Compounds of Hydrogen

51. Why does hydrogen not exhibit an oxidation state of 1− when bonded to nonmetals?

52. The reaction of calcium hydride, CaH_2, with water can be characterized as a Lewis acid-base reaction:
$CaH_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + 2H_2(g)$

Identify the Lewis acid and the Lewis base among the reactants. The reaction is also an oxidation-reduction reaction. Identify the oxidizing agent, the reducing agent, and the changes in oxidation number that occur in the reaction.

53. In drawing Lewis structures, we learn that a hydrogen atom forms only one bond in a covalent compound. Why?

54. What mass of CaH_2 is necessary to react with water to provide enough hydrogen gas to fill a balloon at 20 °C and 0.8 atm pressure with a volume of 4.5 L? The balanced equation is:
$CaH_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + 2H_2(g)$

55. What mass of hydrogen gas results from the reaction of 8.5 g of KH with water?
$KH + H_2O \longrightarrow KOH + H_2$

18.6 Occurrence, Preparation, and Properties of Carbonates

56. Carbon forms the $CO_3{}^{2-}$ ion, yet silicon does not form an analogous $SiO_3{}^{2-}$ ion. Why?

57. Complete and balance the following chemical equations:

(a) hardening of plaster containing slaked lime
$Ca(OH)_2 + CO_2 \longrightarrow$

(b) removal of sulfur dioxide from the flue gas of power plants
$CaO + SO_2 \longrightarrow$

(c) the reaction of baking powder that produces carbon dioxide gas and causes bread to rise
$NaHCO_3 + NaH_2PO_4 \longrightarrow$

58. Heating a sample of $Na_2CO_3{\cdot}xH_2O$ weighing 4.640 g until the removal of the water of hydration leaves 1.720 g of anhydrous Na_2CO_3. What is the formula of the hydrated compound?

18.7 Occurrence, Preparation, and Properties of Nitrogen

59. Write the Lewis structures for each of the following:

(a) NH^{2-}

(b) N_2F_4

(c) $NH_2{}^{-}$

(d) NF_3

(e) $N_3{}^{-}$

60. For each of the following, indicate the hybridization of the nitrogen atom (for $N_3{}^-$, the central nitrogen).

(a) N_2F_4

(b) $NH_2{}^-$

(c) NF_3

(d) $N_3{}^-$

61. Explain how ammonia can function both as a Brønsted base and as a Lewis base.

62. Determine the oxidation state of nitrogen in each of the following. You may wish to review the chapter on chemical bonding for relevant examples.

(a) NCl_3

(b) ClNO

(c) N_2O_5

(d) N_2O_3

(e) $NO_2{}^-$

(f) N_2O_4

(g) N_2O

(h) $NO_3{}^-$

(i) HNO_2

(j) HNO_3

63. For each of the following, draw the Lewis structure, predict the ONO bond angle, and give the hybridization of the nitrogen. You may wish to review the chapters on chemical bonding and advanced theories of covalent bonding for relevant examples.

(a) NO_2

(b) $NO_2{}^-$

(c) $NO_2{}^+$

64. How many grams of gaseous ammonia will the reaction of 3.0 g hydrogen gas and 3.0 g of nitrogen gas produce?

65. Although PF_5 and AsF_5 are stable, nitrogen does not form NF_5 molecules. Explain this difference among members of the same group.

66. The equivalence point for the titration of a 25.00-mL sample of CsOH solution with 0.1062 *M* HNO_3 is at 35.27 mL. What is the concentration of the CsOH solution?

18.8 Occurrence, Preparation, and Properties of Phosphorus

67. Write the Lewis structure for each of the following. You may wish to review the chapter on chemical bonding and molecular geometry.

(a) PH_3

(b) $PH_4{}^+$

(c) P_2H_4

(d) $PO_4{}^{3-}$

(e) PF_5

68. Describe the molecular structure of each of the following molecules or ions listed. You may wish to review the chapter on chemical bonding and molecular geometry.

(a) PH_3

(b) $PH_4{}^+$

(c) P_2H_4

(d) $PO_4{}^{3-}$

69. Complete and balance each of the following chemical equations. (In some cases, there may be more than one correct answer.)

(a) $P_4 + Al \longrightarrow$

(b) $P_4 + Na \longrightarrow$

(c) $P_4 + F_2 \longrightarrow$

(d) $P_4 + Cl_2 \longrightarrow$

(e) $P_4 + O_2 \longrightarrow$

(f) $P_4O_6 + O_2 \longrightarrow$

70. Describe the hybridization of phosphorus in each of the following compounds: P_4O_{10}, P_4O_6, PH_4I (an ionic compound), PBr_3, H_3PO_4, H_3PO_3, PH_3, and P_2H_4. You may wish to review the chapter on advanced theories of covalent bonding.

71. What volume of 0.200 *M* NaOH is necessary to neutralize the solution produced by dissolving 2.00 g of PCl_3 is an excess of water? Note that when H_3PO_3 is titrated under these conditions, only one proton of the acid molecule reacts.

72. How much $POCl_3$ can form from 25.0 g of PCl_5 and the appropriate amount of H_2O?

73. How many tons of $Ca_3(PO_4)_2$ are necessary to prepare 5.0 tons of phosphorus if the yield is 90%?

74. Write equations showing the stepwise ionization of phosphorous acid.

75. Draw the Lewis structures and describe the geometry for the following:

(a) $PF_4{}^+$

(b) PF_5

(c) $PF_6{}^-$

(d) POF_3

76. Why does phosphorous acid form only two series of salts, even though the molecule contains three hydrogen atoms?

77. Assign an oxidation state to phosphorus in each of the following:

(a) NaH_2PO_3

(b) PF_5

(c) P_4O_6

(d) K_3PO_4

(e) Na_3P

(f) $Na_4P_2O_7$

78. Phosphoric acid, one of the acids used in some cola drinks, is produced by the reaction of phosphorus(V) oxide, an acidic oxide, with water. Phosphorus(V) oxide is prepared by the combustion of phosphorus.

(a) Write the empirical formula of phosphorus(V) oxide.

(b) What is the molecular formula of phosphorus(V) oxide if the molar mass is about 280.

(c) Write balanced equations for the production of phosphorus(V) oxide and phosphoric acid.

(d) Determine the mass of phosphorus required to make 1.00×10^4 kg of phosphoric acid, assuming a yield of 98.85%.

18.9 Occurrence, Preparation, and Compounds of Oxygen

79. Predict the product of burning francium in air.

80. Using equations, describe the reaction of water with potassium and with potassium oxide.

81. Write balanced chemical equations for the following reactions:

(a) zinc metal heated in a stream of oxygen gas

(b) zinc carbonate heated until loss of mass stops

(c) zinc carbonate added to a solution of acetic acid, CH_3CO_2H

(d) zinc added to a solution of hydrobromic acid

82. Write balanced chemical equations for the following reactions:

(a) cadmium burned in air

(b) elemental cadmium added to a solution of hydrochloric acid

(c) cadmium hydroxide added to a solution of acetic acid, CH_3CO_2H

83. Illustrate the amphoteric nature of aluminum hydroxide by citing suitable equations.

84. Write balanced chemical equations for the following reactions:

(a) metallic aluminum burned in air

(b) elemental aluminum heated in an atmosphere of chlorine

(c) aluminum heated in hydrogen bromide gas

(d) aluminum hydroxide added to a solution of nitric acid

85. Write balanced chemical equations for the following reactions:

(a) sodium oxide added to water

(b) cesium carbonate added to an excess of an aqueous solution of HF

(c) aluminum oxide added to an aqueous solution of $HClO_4$

(d) a solution of sodium carbonate added to solution of barium nitrate

(e) titanium metal produced from the reaction of titanium tetrachloride with elemental sodium

86. What volume of 0.250 M H_2SO_4 solution is required to neutralize a solution that contains 5.00 g of $CaCO_3$?

87. Which is the stronger acid, $HClO_4$ or $HBrO_4$? Why?

88. Write a balanced chemical equation for the reaction of an excess of oxygen with each of the following. Remember that oxygen is a strong oxidizing agent and tends to oxidize an element to its maximum oxidation state.

(a) Mg

(b) Rb

(c) Ga

(d) C_2H_2

(e) CO

89. Which is the stronger acid, H_2SO_4 or H_2SeO_4? Why? You may wish to review the chapter on acid-base equilibria.

18.10 Occurrence, Preparation, and Properties of Sulfur

90. Explain why hydrogen sulfide is a gas at room temperature, whereas water, which has a lower molecular mass, is a liquid.

91. Give the hybridization and oxidation state for sulfur in SO_2, in SO_3, and in H_2SO_4.

92. Which is the stronger acid, $NaHSO_3$ or $NaHSO_4$?

93. Determine the oxidation state of sulfur in SF_6, SO_2F_2, and KHS.

94. Which is a stronger acid, sulfurous acid or sulfuric acid? Why?

95. Oxygen forms double bonds in O_2, but sulfur forms single bonds in S_8. Why?

96. Give the Lewis structure of each of the following:

(a) SF_4

(b) K_2SO_4

(c) SO_2Cl_2

(d) H_2SO_3

(e) SO_3

97. Write two balanced chemical equations in which sulfuric acid acts as an oxidizing agent.

98. Explain why sulfuric acid, H_2SO_4, which is a covalent molecule, dissolves in water and produces a solution that contains ions.

99. How many grams of Epsom salts ($MgSO_4 \cdot 7H_2O$) will form from 5.0 kg of magnesium?

18.11 Occurrence, Preparation, and Properties of Halogens

100. What does it mean to say that mercury(II) halides are weak electrolytes?

101. Why is $SnCl_4$ not classified as a salt?

102. The following reactions are all similar to those of the industrial chemicals. Complete and balance the equations for these reactions:

(a) reaction of a weak base and a strong acid

$$\mathrm{NH_3 + HClO_4} \longrightarrow$$

(b) preparation of a soluble silver salt for silver plating

$$\mathrm{Ag_2CO_3 + HNO_3} \longrightarrow$$

(c) preparation of strontium hydroxide by electrolysis of a solution of strontium chloride

$$\mathrm{SrCl_2}(aq) + \mathrm{H_2O}(l) \xrightarrow{\text{electrolysis}}$$

103. Which is the stronger acid, $HClO_3$ or $HBrO_3$? Why?

104. What is the hybridization of iodine in IF_3 and IF_5?

105. Predict the molecular geometries and draw Lewis structures for each of the following. You may wish to review the chapter on chemical bonding and molecular geometry.

(a) IF_5

(b) $I_3{}^-$

(c) PCl_5

(d) SeF_4

(e) ClF_3

106. Which halogen has the highest ionization energy? Is this what you would predict based on what you have learned about periodic properties?

107. Name each of the following compounds:

(a) BrF_3

(b) $NaBrO_3$

(c) PBr_5

(d) $NaClO_4$

(e) KClO

108. Explain why, at room temperature, fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid.

109. What is the oxidation state of the halogen in each of the following?

(a) H_5IO_6

(b) $IO_4{}^-$

(c) ClO_2

(d) ICl_3

(e) F_2

110. Physiological saline concentration—that is, the sodium chloride concentration in our bodies—is approximately 0.16 *M*. A saline solution for contact lenses is prepared to match the physiological concentration. If you purchase 25 mL of contact lens saline solution, how many grams of sodium chloride have you bought?

18.12 Occurrence, Preparation, and Properties of the Noble Gases

111. Give the hybridization of xenon in each of the following. You may wish to review the chapter on the advanced theories of covalent bonding.

(a) XeF_2

(b) XeF_4

(c) XeO_3

(d) XeO_4

(e) $XeOF_4$

112. What is the molecular structure of each of the following molecules? You may wish to review the chapter on chemical bonding and molecular geometry.

(a) XeF_2

(b) XeF_4

(c) XeO_3

(d) XeO_4

(e) $XeOF_4$

113. Indicate whether each of the following molecules is polar or nonpolar. You may wish to review the chapter on chemical bonding and molecular geometry.

(a) XeF_2

(b) XeF_4

(c) XeO_3

(d) XeO_4

(e) $XeOF_4$

114. What is the oxidation state of the noble gas in each of the following? You may wish to review the chapter on chemical bonding and molecular geometry.

(a) XeO_2F_2

(b) KrF_2

(c) $XeF_3{}^+$

(d) $XeO_6{}^{4-}$

(e) XeO_3

115. A mixture of xenon and fluorine was heated. A sample of the white solid that formed reacted with hydrogen to yield 81 mL of xenon (at STP) and hydrogen fluoride, which was collected in water, giving a solution of hydrofluoric acid. The hydrofluoric acid solution was titrated, and 68.43 mL of 0.3172 *M* sodium hydroxide was required to reach the equivalence point. Determine the empirical formula for the white solid and write balanced chemical equations for the reactions involving xenon.

116. Basic solutions of Na_4XeO_6 are powerful oxidants. What mass of $Mn(NO_3)_2 \cdot 6H_2O$ reacts with 125.0 mL of a 0.1717 *M* basic solution of Na_4XeO_6 that contains an excess of sodium hydroxide if the products include Xe and solution of sodium permanganate?

Chapter 19

Transition Metals and Coordination Chemistry

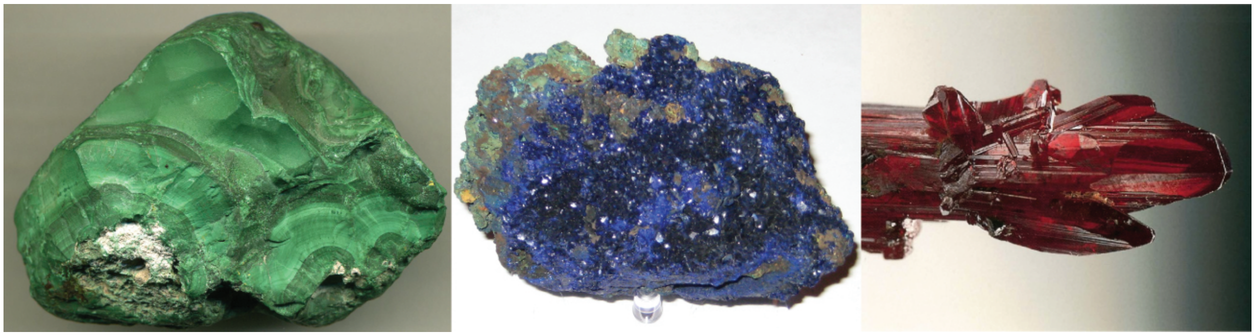


Figure 19.1 Transition metals often form vibrantly colored complexes. The minerals malachite (green), azurite (blue), and proustite (red) are some examples. (credit left: modification of work by James St. John; credit middle: modification of work by Stephanie Clifford; credit right: modification of work by Terry Wallace)

Chapter Outline

Introduction

We have daily contact with many transition metals. Iron occurs everywhere—from the rings in your spiral notebook and the cutlery in your kitchen to automobiles, ships, buildings, and in the hemoglobin in your blood. Titanium is useful in the manufacture of lightweight, durable products such as bicycle frames, artificial hips, and jewelry. Chromium is useful as a protective plating on plumbing fixtures and automotive detailing.

In addition to being used in their pure elemental forms, many compounds containing transition metals have numerous other applications. Silver nitrate is used to create mirrors, zirconium silicate provides friction in automotive brakes, and many important cancer-fighting agents, like the drug cisplatin and related species, are platinum compounds.

The variety of properties exhibited by transition metals is due to their complex valence shells. Unlike most main group metals where one oxidation state is normally observed, the valence shell structure of transition metals means that they usually occur in several different stable oxidation states. In addition, electron transitions in these elements can correspond with absorption of photons in the visible electromagnetic spectrum, leading to colored compounds. Because of these behaviors, transition metals exhibit a rich and fascinating chemistry.

19.1 Occurrence, Preparation, and Properties of Transition Metals and Their Compounds

Transition metals are defined as those elements that have (or readily form) partially filled *d* orbitals. As shown in **Figure 19.2**, the ***d*-block elements** in groups 3–11 are transition elements. The ***f*-block elements**, also called *inner transition metals* (the lanthanides and actinides), also meet this criterion because the *d* orbital is partially occupied before the *f* orbitals. The *d* orbitals fill with the copper family (group 11); for this reason, the next family (group

12) are technically not transition elements. However, the group 12 elements do display some of the same chemical properties and are commonly included in discussions of transition metals. Some chemists do treat the group 12 elements as transition metals.

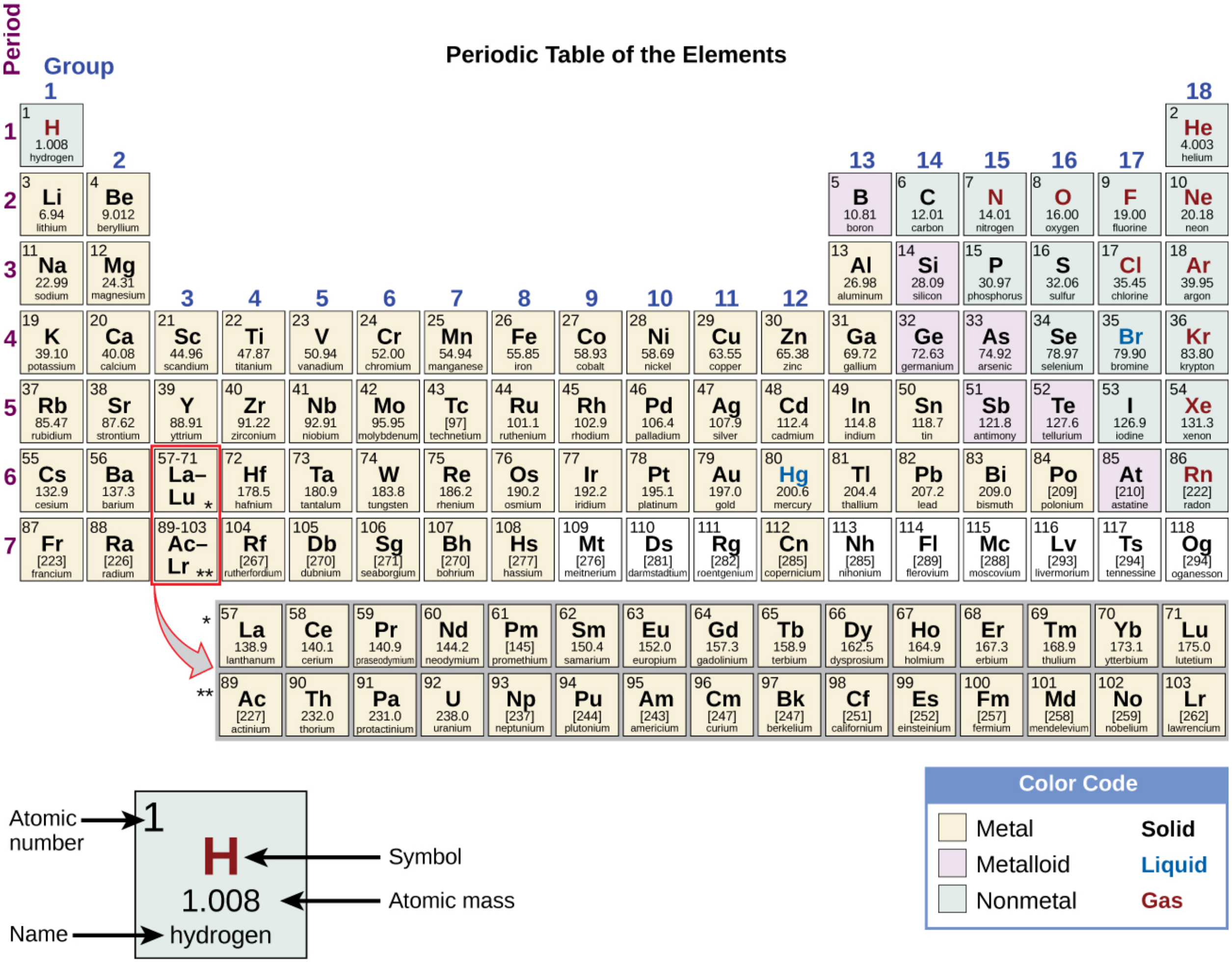


Figure 19.2 The transition metals are located in groups 3–11 of the periodic table. The inner transition metals are in the two rows below the body of the table.

The *d*-block elements are divided into the **first transition series** (the elements Sc through Cu), the **second transition series** (the elements Y through Ag), and the **third transition series** (the element La and the elements Hf through Au). Actinium, Ac, is the first member of the **fourth transition series**, which also includes Rf through Rg.

The *f*-block elements are the elements Ce through Lu, which constitute the **lanthanide series** (or **lanthanoid series**), and the elements Th through Lr, which constitute the **actinide series** (or **actinoid series**). Because lanthanum behaves very much like the lanthanide elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third transition series. Similarly, the behavior of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series.

Example 19.1

Valence Electrons in Transition Metals

Review how to write electron configurations, covered in the chapter on electronic structure and periodic properties of elements. Recall that for the transition and inner transition metals, it is necessary to remove the *s* electrons before the *d* or *f* electrons. Then, for each ion, give the electron configuration:

(a) cerium(III)

(b) lead(II)

(c) Ti^{2+}

(d) Am^{3+}

(e) Pd^{2+}

For the examples that are transition metals, determine to which series they belong.

Solution

For ions, the *s*-valence electrons are lost prior to the *d* or *f* electrons.

(a) $Ce^{3+}[Xe]4f^1$; Ce^{3+} is an inner transition element in the lanthanide series.

(b) $Pb^{2+}[Xe]6s^25d^{10}4f^{14}$; the electrons are lost from the *p* orbital. This is a main group element.

(c) titanium(II) $[Ar]3d^2$; first transition series

(d) americium(III) $[Rn]5f^6$; actinide

(e) palladium(II) $[Kr]4d^8$; second transition series

Check Your Learning

Give an example of an ion from the first transition series with no *d* electrons.

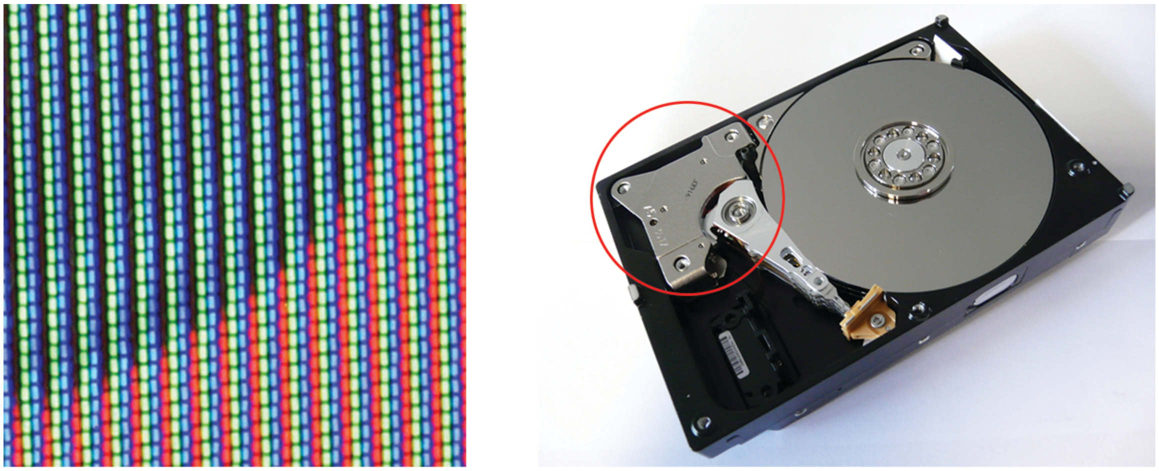
Answer: V^{5+} is one possibility. Other examples include Sc^{3+}, Ti^{4+}, Cr^{6+}, and Mn^{7+}.

Chemistry in Everyday Life

Uses of Lanthanides in Devices

Lanthanides (elements 57–71) are fairly abundant in the earth's crust, despite their historic characterization as **rare earth elements**. Thulium, the rarest naturally occurring lanthanoid, is more common in the earth's crust than silver (4.5×10^{-5}% versus 0.79×10^{-5}% by mass). There are 17 rare earth elements, consisting of the 15 lanthanoids plus scandium and yttrium. They are called rare because they were once difficult to extract economically, so it was rare to have a pure sample; due to similar chemical properties, it is difficult to separate any one lanthanide from the others. However, newer separation methods, such as ion exchange resins similar to those found in home water softeners, make the separation of these elements easier and more economical. Most ores that contain these elements have low concentrations of all the rare earth elements mixed together.

The commercial applications of lanthanides are growing rapidly. For example, europium is important in flat screen displays found in computer monitors, cell phones, and televisions. Neodymium is useful in laptop hard drives and in the processes that convert crude oil into gasoline (**Figure 19.3**). Holmium is found in dental and medical equipment. In addition, many alternative energy technologies rely heavily on lanthanoids. Neodymium and dysprosium are key components of hybrid vehicle engines and the magnets used in wind turbines.



(a) (b)

Figure 19.3 (a) Europium is used in display screens for televisions, computer monitors, and cell phones. (b) Neodymium magnets are commonly found in computer hard drives. (credit b: modification of work by “KUERT Datenrettung”/Flickr)

As the demand for lanthanide materials has increased faster than supply, prices have also increased. In 2008, dysprosium cost $110/kg; by 2014, the price had increased to $470/kg. Increasing the supply of lanthanoid elements is one of the most significant challenges facing the industries that rely on the optical and magnetic properties of these materials.

The transition elements have many properties in common with other metals. They are almost all hard, high-melting solids that conduct heat and electricity well. They readily form alloys and lose electrons to form stable cations. In addition, transition metals form a wide variety of stable **coordination compounds**, in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons. Many different molecules and ions can donate lone pairs to the metal center, serving as Lewis bases. In this chapter, we shall focus primarily on the chemical behavior of the elements of the first transition series.

Properties of the Transition Elements

Transition metals demonstrate a wide range of chemical behaviors. As can be seen from their reduction potentials (see **Appendix H**), some transition metals are strong reducing agents, whereas others have very low reactivity. For example, the lanthanides all form stable 3+ aqueous cations. The driving force for such oxidations is similar to that of alkaline earth metals such as Be or Mg, forming Be^{2+} and Mg^{2+}. On the other hand, materials like platinum and gold have much higher reduction potentials. Their ability to resist oxidation makes them useful materials for constructing circuits and jewelry.

Ions of the lighter *d*-block elements, such as Cr^{3+}, Fe^{3+}, and Co^{2+}, form colorful hydrated ions that are stable in water. However, ions in the period just below these (Mo^{3+}, Ru^{3+}, and Ir^{2+}) are unstable and react readily with oxygen from the air. The majority of simple, water-stable ions formed by the heavier *d*-block elements are oxyanions such as $MoO_4{}^{2-}$ and $ReO_4{}^{-}$.

Ruthenium, osmium, rhodium, iridium, palladium, and platinum are the **platinum metals**. With difficulty, they form simple cations that are stable in water, and, unlike the earlier elements in the second and third transition series, they do not form stable oxyanions.

Both the *d*- and *f*-block elements react with nonmetals to form binary compounds; heating is often required. These elements react with halogens to form a variety of halides ranging in oxidation state from 1+ to 6+. On heating, oxygen reacts with all of the transition elements except palladium, platinum, silver, and gold. The oxides of these latter metals can be formed using other reactants, but they decompose upon heating. The *f*-block elements, the elements of group 3, and the elements of the first transition series except copper react with aqueous solutions of acids, forming hydrogen gas and solutions of the corresponding salts.

Transition metals can form compounds with a wide range of oxidation states. Some of the observed oxidation states of the elements of the first transition series are shown in **Figure 19.4**. As we move from left to right across the first transition series, we see that the number of common oxidation states increases at first to a maximum towards the middle of the table, then decreases. The values in the table are typical values; there are other known values, and it is possible to synthesize new additions. For example, in 2014, researchers were successful in synthesizing a new oxidation state of iridium (9+).

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
								1+	
		2+	2+	2+	2+	2+	2+	2+	2+
3+	3+	3+	3+	3+	3+	3+	3+	3+	
	4+	4+	4+	4+					
		5+							
			6+	6+	6+				
				7+					

Figure 19.4 Transition metals of the first transition series can form compounds with varying oxidation states.

For the elements scandium through manganese (the first half of the first transition series), the highest oxidation state corresponds to the loss of all of the electrons in both the *s* and *d* orbitals of their valence shells. The titanium(IV) ion, for example, is formed when the titanium atom loses its two 3*d* and two 4*s* electrons. These highest oxidation states are the most stable forms of scandium, titanium, and vanadium. However, it is not possible to continue to remove all of the valence electrons from metals as we continue through the series. Iron is known to form oxidation states from 2+ to 6+, with iron(II) and iron(III) being the most common. Most of the elements of the first transition series form ions with a charge of 2+ or 3+ that are stable in water, although those of the early members of the series can be readily oxidized by air.

The elements of the second and third transition series generally are more stable in higher oxidation states than are the elements of the first series. In general, the atomic radius increases down a group, which leads to the ions of the second and third series being larger than are those in the first series. Removing electrons from orbitals that are located farther from the nucleus is easier than removing electrons close to the nucleus. For example, molybdenum and tungsten, members of group 6, are limited mostly to an oxidation state of 6+ in aqueous solution. Chromium, the lightest member of the group, forms stable Cr^{3+} ions in water and, in the absence of air, less stable Cr^{2+} ions. The sulfide with the highest oxidation state for chromium is Cr_2S_3, which contains the Cr^{3+} ion. Molybdenum and tungsten form sulfides in which the metals exhibit oxidation states of 4+ and 6+.

Example 19.2

Activity of the Transition Metals

Which is the strongest oxidizing agent in acidic solution: dichromate ion, which contains chromium(VI), permanganate ion, which contains manganese(VII), or titanium dioxide, which contains titanium(IV)?

Solution

First, we need to look up the reduction half reactions (in **Appendix L**) for each oxide in the specified oxidation state:

$$\begin{aligned}
&Cr_2O_7{}^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O && +1.33\text{ V}\\
&MnO_4{}^{-} + 8H^+ + 5e^- \longrightarrow Mn^{2+} + H_2O && +1.51\text{ V}\\
&TiO_2 + 4H^+ + 2e^- \longrightarrow Ti^{2+} + 2H_2O && -0.50\text{ V}
\end{aligned}$$

A larger reduction potential means that it is easier to reduce the reactant. Permanganate, with the largest reduction potential, is the strongest oxidizer under these conditions. Dichromate is next, followed by titanium dioxide as the weakest oxidizing agent (the hardest to reduce) of this set.

Check Your Learning

Predict what reaction (if any) will occur between HCl and Co(*s*), and between HBr and Pt(*s*). You will need to use the standard reduction potentials from **Appendix L**.

Answer: $Co(s) + 2HCl \longrightarrow H_2 + CoCl_2(aq)$; no reaction because Pt(*s*) will not be oxidized by H^+

Preparation of the Transition Elements

Ancient civilizations knew about iron, copper, silver, and gold. The time periods in human history known as the Bronze Age and Iron Age mark the advancements in which societies learned to isolate certain metals and use them to make tools and goods. Naturally occurring ores of copper, silver, and gold can contain high concentrations of these metals in elemental form (**Figure 19.5**). Iron, on the other hand, occurs on earth almost exclusively in oxidized forms, such as rust (Fe_2O_3). The earliest known iron implements were made from iron meteorites. Surviving iron artifacts dating from approximately 4000 to 2500 BC are rare, but all known examples contain specific alloys of iron and nickel that occur only in extraterrestrial objects, not on earth. It took thousands of years of technological advances before civilizations developed iron **smelting**, the ability to extract a pure element from its naturally occurring ores and for iron tools to become common.

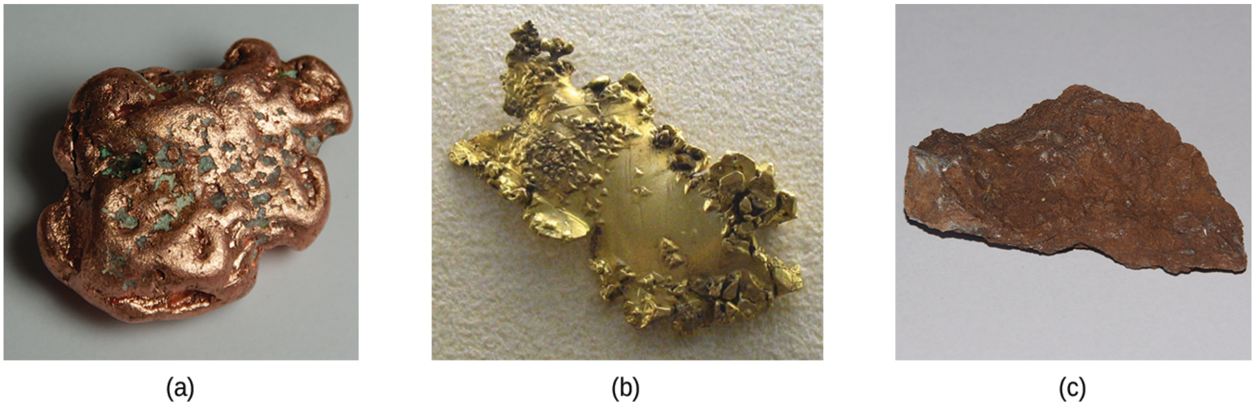


Figure 19.5 Transition metals occur in nature in various forms. Examples include (a) a nugget of copper, (b) a deposit of gold, and (c) an ore containing oxidized iron. (credit a: modification of work by http://images-of-elements.com/copper-2.jpg; credit c: modification of work by http://images-of-elements.com/iron-ore.jpg)

Generally, the transition elements are extracted from minerals found in a variety of ores. However, the ease of their recovery varies widely, depending on the concentration of the element in the ore, the identity of the other elements present, and the difficulty of reducing the element to the free metal.

In general, it is not difficult to reduce ions of the *d*-block elements to the free element. Carbon is a sufficiently strong reducing agent in most cases. However, like the ions of the more active main group metals, ions of the *f*-block elements must be isolated by electrolysis or by reduction with an active metal such as calcium.

We shall discuss the processes used for the isolation of iron, copper, and silver because these three processes illustrate the principal means of isolating most of the *d*-block metals. In general, each of these processes involves three principal steps: preliminary treatment, smelting, and refining.

1. Preliminary treatment. In general, there is an initial treatment of the ores to make them suitable for the extraction of the metals. This usually involves crushing or grinding the ore, concentrating the metal-bearing components, and sometimes treating these substances chemically to convert them into compounds that are easier to reduce to the metal.
2. Smelting. The next step is the extraction of the metal in the molten state, a process called smelting, which includes reduction of the metallic compound to the metal. Impurities may be removed by the addition of a compound that forms a slag—a substance with a low melting point that can be readily separated from the molten metal.
3. Refining. The final step in the recovery of a metal is refining the metal. Low boiling metals such as zinc and mercury can be refined by distillation. When fused on an inclined table, low melting metals like tin flow away from higher-melting impurities. Electrolysis is another common method for refining metals.

Isolation of Iron

The early application of iron to the manufacture of tools and weapons was possible because of the wide distribution of iron ores and the ease with which iron compounds in the ores could be reduced by carbon. For a long time, charcoal was the form of carbon used in the reduction process. The production and use of iron became much more widespread about 1620, when coke was introduced as the reducing agent. Coke is a form of carbon formed by heating coal in the absence of air to remove impurities.

The first step in the metallurgy of iron is usually roasting the ore (heating the ore in air) to remove water, decomposing carbonates into oxides, and converting sulfides into oxides. The oxides are then reduced in a blast furnace that is 80–100 feet high and about 25 feet in diameter (**Figure 19.6**) in which the roasted ore, coke, and limestone (impure $CaCO_3$) are introduced continuously into the top. Molten iron and slag are withdrawn at the bottom. The entire stock in a furnace may weigh several hundred tons.

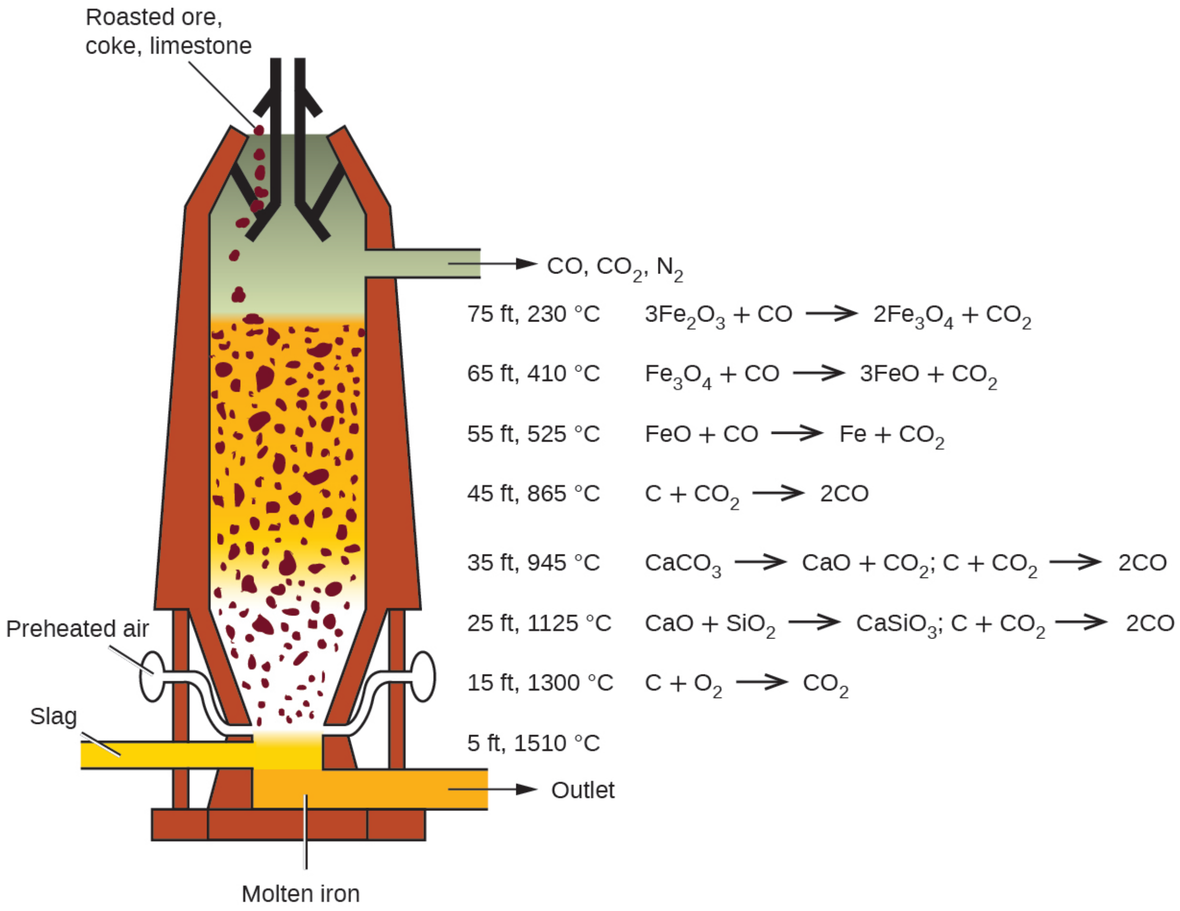


Figure 19.6 Within a blast furnace, different reactions occur in different temperature zones. Carbon monoxide is generated in the hotter bottom regions and rises upward to reduce the iron oxides to pure iron through a series of reactions that take place in the upper regions.

Near the bottom of a furnace are nozzles through which preheated air is blown into the furnace. As soon as the air enters, the coke in the region of the nozzles is oxidized to carbon dioxide with the liberation of a great deal of heat. The hot carbon dioxide passes upward through the overlying layer of white-hot coke, where it is reduced to carbon monoxide:

$$\mathrm{CO_2}(g) + \mathrm{C}(s) \longrightarrow 2\mathrm{CO}(g)$$

The carbon monoxide serves as the reducing agent in the upper regions of the furnace. The individual reactions are indicated in **Figure 19.6**.

The iron oxides are reduced in the upper region of the furnace. In the middle region, limestone (calcium carbonate) decomposes, and the resulting calcium oxide combines with silica and silicates in the ore to form slag. The slag is mostly calcium silicate and contains most of the commercially unimportant components of the ore:

$$\mathrm{CaO}(s) + \mathrm{SiO_2}(s) \longrightarrow \mathrm{CaSiO_3}(l)$$

Just below the middle of the furnace, the temperature is high enough to melt both the iron and the slag. They collect in layers at the bottom of the furnace; the less dense slag floats on the iron and protects it from oxidation. Several times a day, the slag and molten iron are withdrawn from the furnace. The iron is transferred to casting machines or to a steelmaking plant (**Figure 19.7**).

Figure 19.7 Molten iron is shown being cast as steel. (credit: Clint Budd)

Much of the iron produced is refined and converted into steel. **Steel** is made from iron by removing impurities and adding substances such as manganese, chromium, nickel, tungsten, molybdenum, and vanadium to produce alloys with properties that make the material suitable for specific uses. Most steels also contain small but definite percentages of carbon (0.04%–2.5%). However, a large part of the carbon contained in iron must be removed in the manufacture of steel; otherwise, the excess carbon would make the iron brittle.

Link to Learning

You can watch an animation of **steelmaking (http://openstaxcollege.org/l/16steelmaking)** that walks you through the process.

Isolation of Copper

The most important ores of copper contain copper sulfides (such as covellite, CuS), although copper oxides (such as tenorite, CuO) and copper hydroxycarbonates [such as malachite, $Cu_2(OH)_2CO_3$] are sometimes found. In the production of copper metal, the concentrated sulfide ore is roasted to remove part of the sulfur as sulfur dioxide. The remaining mixture, which consists of Cu_2S, FeS, FeO, and SiO_2, is mixed with limestone, which serves as a flux (a material that aids in the removal of impurities), and heated. Molten slag forms as the iron and silica are removed by Lewis acid-base reactions:

$$\mathrm{CaCO_3}(s) + \mathrm{SiO_2}(s) \longrightarrow \mathrm{CaSiO_3}(l) + \mathrm{CO_2}(g)$$

$$\mathrm{FeO}(s) + \mathrm{SiO_2}(s) \longrightarrow \mathrm{FeSiO_3}(l)$$

In these reactions, the silicon dioxide behaves as a Lewis acid, which accepts a pair of electrons from the Lewis base (the oxide ion).

Reduction of the Cu_2S that remains after smelting is accomplished by blowing air through the molten material. The air converts part of the Cu_2S into Cu_2O. As soon as copper(I) oxide is formed, it is reduced by the remaining copper(I) sulfide to metallic copper:

$$2\mathrm{Cu_2S}(l) + 3\mathrm{O_2}(g) \longrightarrow 2\mathrm{Cu_2O}(l) + 2\mathrm{SO_2}(g)$$
$$2\mathrm{Cu_2O}(l) + \mathrm{Cu_2S}(l) \longrightarrow 6\mathrm{Cu}(l) + \mathrm{SO_2}(g)$$

The copper obtained in this way is called blister copper because of its characteristic appearance, which is due to the air blisters it contains (**Figure 19.8**). This impure copper is cast into large plates, which are used as anodes in the electrolytic refining of the metal (which is described in the chapter on electrochemistry).

Figure 19.8 Blister copper is obtained during the conversion of copper-containing ore into pure copper. (credit: “Tortie tude”/Wikimedia Commons)

Isolation of Silver

Silver sometimes occurs in large nuggets (**Figure 19.9**) but more frequently in veins and related deposits. At one time, panning was an effective method of isolating both silver and gold nuggets. Due to their low reactivity, these metals, and a few others, occur in deposits as nuggets. The discovery of platinum was due to Spanish explorers in Central America mistaking platinum nuggets for silver. When the metal is not in the form of nuggets, it often useful to employ a process called **hydrometallurgy** to separate silver from its ores. Hydrology involves the separation of a metal from a mixture by first converting it into soluble ions and then extracting and reducing them to precipitate the pure metal. In the presence of air, alkali metal cyanides readily form the soluble dicyanoargentate(I) ion, $[\mathrm{Ag(CN)_2}]^-$, from silver metal or silver-containing compounds such as $\mathrm{Ag_2S}$ and AgCl. Representative equations are:

$$4\text{Ag}(s) + 8\text{CN}^-(aq) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \longrightarrow 4[\text{Ag(CN)}_2]^-(aq) + 4\text{OH}^-(aq)$$
$$2\text{Ag}_2\text{S}(s) + 8\text{CN}^-(aq) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \longrightarrow 4[\text{Ag(CN)}_2]^-(aq) + 2\text{S}(s) + 4\text{OH}^-(aq)$$
$$\text{AgCl}(s) + 2\text{CN}^-(aq) \longrightarrow [\text{Ag(CN)}_2]^-(aq) + \text{Cl}^-(aq)$$

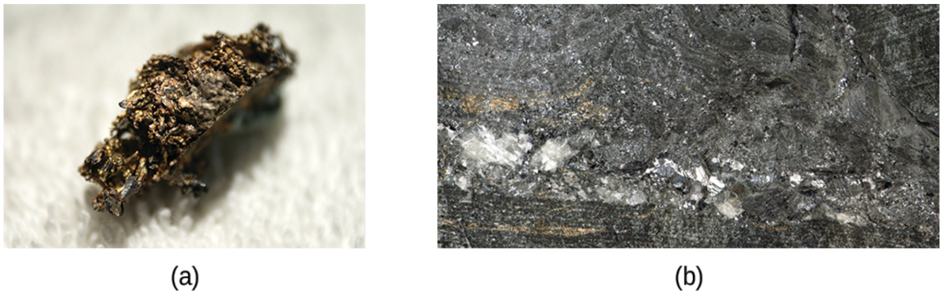

(a) (b)

Figure 19.9 Naturally occurring free silver may be found as nuggets (a) or in veins (b). (credit a: modification of work by “Teravolt”/Wikimedia Commons; credit b: modification of work by James St. John)

The silver is precipitated from the cyanide solution by the addition of either zinc or iron(II) ions, which serves as the reducing agent:

$$2[\text{Ag(CN)}_2]^-(aq) + \text{Zn}(s) \longrightarrow 2\text{Ag}(s) + [\text{Zn(CN)}_4]^{2-}(aq)$$

Example 19.3

Refining Redox

One of the steps for refining silver involves converting silver into dicyanoargenate(I) ions:

$$4\text{Ag}(s) + 8\text{CN}^-(aq) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \longrightarrow 4[\text{Ag(CN)}_2]^-(aq) + 4\text{OH}^-(aq)$$

Explain why oxygen must be present to carry out the reaction. Why does the reaction not occur as:

$$4\text{Ag}(s) + 8\text{CN}^-(aq) \longrightarrow 4[\text{Ag(CN)}_2]^-(aq)?$$

Solution

The charges, as well as the atoms, must balance in reactions. The silver atom is being oxidized from the 0 oxidation state to the 1+ state. Whenever something loses electrons, something must also gain electrons (be reduced) to balance the equation. Oxygen is a good oxidizing agent for these reactions because it can gain electrons to go from the 0 oxidation state to the 2− state.

Check Your Learning

During the refining of iron, carbon must be present in the blast furnace. Why is carbon necessary to convert iron oxide into iron?

Answer: The carbon is converted into CO, which is the reducing agent that accepts electrons so that iron(III) can be reduced to iron(0).

Transition Metal Compounds

The bonding in the simple compounds of the transition elements ranges from ionic to covalent. In their lower oxidation states, the transition elements form ionic compounds; in their higher oxidation states, they form covalent compounds or polyatomic ions. The variation in oxidation states exhibited by the transition elements gives these compounds a metal-based, oxidation-reduction chemistry. The chemistry of several classes of compounds containing elements of the transition series follows.

Halides

Anhydrous halides of each of the transition elements can be prepared by the direct reaction of the metal with halogens. For example:

$$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$$

Heating a metal halide with additional metal can be used to form a halide of the metal with a lower oxidation state:

$$Fe(s) + 2FeCl_3(s) \longrightarrow 3FeCl_2(s)$$

The stoichiometry of the metal halide that results from the reaction of the metal with a halogen is determined by the relative amounts of metal and halogen and by the strength of the halogen as an oxidizing agent. Generally, fluorine forms fluoride-containing metals in their highest oxidation states. The other halogens may not form analogous compounds.

In general, the preparation of stable water solutions of the halides of the metals of the first transition series is by the addition of a hydrohalic acid to carbonates, hydroxides, oxides, or other compounds that contain basic anions. Sample reactions are:

$$\begin{gathered} NiCO_3(s) + 2HF(aq) \longrightarrow NiF_2(aq) + H_2O(l) + CO_2(g) \\ Co(OH)_2(s) + 2HBr(aq) \longrightarrow CoBr_2(aq) + 2H_2O(l) \end{gathered}$$

Most of the first transition series metals also dissolve in acids, forming a solution of the salt and hydrogen gas. For example:

$$Cr(s) + 2HCl(aq) \longrightarrow CrCl_2(aq) + H_2(g)$$

The polarity of bonds with transition metals varies based not only upon the electronegativities of the atoms involved but also upon the oxidation state of the transition metal. Remember that bond polarity is a continuous spectrum with electrons being shared evenly (covalent bonds) at one extreme and electrons being transferred completely (ionic bonds) at the other. No bond is ever 100% ionic, and the degree to which the electrons are evenly distributed determines many properties of the compound. Transition metal halides with low oxidation numbers form more ionic bonds. For example, titanium(II) chloride and titanium(III) chloride ($TiCl_2$ and $TiCl_3$) have high melting points that are characteristic of ionic compounds, but titanium(IV) chloride ($TiCl_4$) is a volatile liquid, consistent with having covalent titanium-chlorine bonds. All halides of the heavier *d*-block elements have significant covalent characteristics.

The covalent behavior of the transition metals with higher oxidation states is exemplified by the reaction of the metal tetrahalides with water. Like covalent silicon tetrachloride, both the titanium and vanadium tetrahalides react with water to give solutions containing the corresponding hydrohalic acids and the metal oxides:

$$\begin{gathered} SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(aq) \\ TiCl_4(l) + 2H_2O(l) \longrightarrow TiO_2(s) + 4HCl(aq) \end{gathered}$$

Oxides

As with the halides, the nature of bonding in oxides of the transition elements is determined by the oxidation state of the metal. Oxides with low oxidation states tend to be more ionic, whereas those with higher oxidation states are more covalent. These variations in bonding are because the electronegativities of the elements are not fixed values. The electronegativity of an element increases with increasing oxidation state. Transition metals in low oxidation states have lower electronegativity values than oxygen; therefore, these metal oxides are ionic. Transition metals in very high oxidation states have electronegativity values close to that of oxygen, which leads to these oxides being covalent.

The oxides of the first transition series can be prepared by heating the metals in air. These oxides are Sc_2O_3, TiO_2, V_2O_5, Cr_2O_3, Mn_3O_4, Fe_3O_4, Co_3O_4, NiO, and CuO.

Alternatively, these oxides and other oxides (with the metals in different oxidation states) can be produced by heating the corresponding hydroxides, carbonates, or oxalates in an inert atmosphere. Iron(II) oxide can be prepared by heating iron(II) oxalate, and cobalt(II) oxide is produced by heating cobalt(II) hydroxide:

$$FeC_2O_4(s) \longrightarrow FeO(s) + CO(g) + CO_2(g)$$
$$Co(OH)_2(s) \longrightarrow CoO(s) + H_2O(g)$$

With the exception of CrO_3 and Mn_2O_7, transition metal oxides are not soluble in water. They can react with acids and, in a few cases, with bases. Overall, oxides of transition metals with the lowest oxidation states are basic (and react with acids), the intermediate ones are amphoteric, and the highest oxidation states are primarily acidic. Basic metal oxides at a low oxidation state react with aqueous acids to form solutions of salts and water. Examples include the reaction of cobalt(II) oxide accepting protons from nitric acid, and scandium(III) oxide accepting protons from hydrochloric acid:

$$CoO(s) + 2HNO_3(aq) \longrightarrow Co(NO_3)_2(aq) + H_2O(l)$$
$$Sc_2O_3(s) + 6HCl(aq) \longrightarrow 2ScCl_3(aq) + 3H_2O(l)$$

The oxides of metals with oxidation states of 4+ are amphoteric, and most are not soluble in either acids or bases. Vanadium(V) oxide, chromium(VI) oxide, and manganese(VII) oxide are acidic. They react with solutions of hydroxides to form salts of the oxyanions $VO_4{}^{3-}$, $CrO_4{}^{2-}$, and $MnO_4{}^{-}$. For example, the complete ionic equation for the reaction of chromium(VI) oxide with a strong base is given by:

$$CrO_3(s) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow 2Na^+(aq) + CrO_4{}^{2-}(aq) + H_2O(l)$$

Chromium(VI) oxide and manganese(VII) oxide react with water to form the acids H_2CrO_4 and $HMnO_4$, respectively.

Hydroxides

When a soluble hydroxide is added to an aqueous solution of a salt of a transition metal of the first transition series, a gelatinous precipitate forms. For example, adding a solution of sodium hydroxide to a solution of cobalt sulfate produces a gelatinous pink or blue precipitate of cobalt(II) hydroxide. The net ionic equation is:

$$Co^{2+}(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s)$$

In this and many other cases, these precipitates are hydroxides containing the transition metal ion, hydroxide ions, and water coordinated to the transition metal. In other cases, the precipitates are hydrated oxides composed of the metal ion, oxide ions, and water of hydration:

$$4Fe^{3+}(aq) + 6OH^-(aq) + n\,H_2O(l) \longrightarrow 2Fe_2O_3\cdot(n+3)H_2O(s)$$

These substances do not contain hydroxide ions. However, both the hydroxides and the hydrated oxides react with acids to form salts and water. When precipitating a metal from solution, it is necessary to avoid an excess of hydroxide ion, as this may lead to complex ion formation as discussed later in this chapter. The precipitated metal hydroxides can be separated for further processing or for waste disposal.

Carbonates

Many of the elements of the first transition series form insoluble carbonates. It is possible to prepare these carbonates by the addition of a soluble carbonate salt to a solution of a transition metal salt. For example, nickel carbonate can be prepared from solutions of nickel nitrate and sodium carbonate according to the following net ionic equation:

$$Ni^{2+}(aq) + CO_3{}^{2-} \longrightarrow NiCO_3(s)$$

The reactions of the transition metal carbonates are similar to those of the active metal carbonates. They react with acids to form metals salts, carbon dioxide, and water. Upon heating, they decompose, forming the transition metal oxides.

Other Salts

In many respects, the chemical behavior of the elements of the first transition series is very similar to that of the main group metals. In particular, the same types of reactions that are used to prepare salts of the main group metals can be used to prepare simple ionic salts of these elements.

A variety of salts can be prepared from metals that are more active than hydrogen by reaction with the corresponding acids: Scandium metal reacts with hydrobromic acid to form a solution of scandium bromide:

$$2\text{Sc}(s) + 6\text{HBr}(aq) \longrightarrow 2\text{ScBr}_3(aq) + 3\text{H}_2(g)$$

The common compounds that we have just discussed can also be used to prepare salts. The reactions involved include the reactions of oxides, hydroxides, or carbonates with acids. For example:

$$\text{Ni(OH)}_2(s) + 2\text{H}_3\text{O}^+(aq) + 2\text{ClO}_4{}^-(aq) \longrightarrow \text{Ni}^{2+}(aq) + 2\text{ClO}_4{}^-(aq) + 4\text{H}_2\text{O}(l)$$

Substitution reactions involving soluble salts may be used to prepare insoluble salts. For example:

$$\text{Ba}^{2+}(aq) + 2\text{Cl}^-(aq) + 2\text{K}^+(aq) + \text{CrO}_4{}^{2-}(aq) \longrightarrow \text{BaCrO}_4(s) + 2\text{K}^+(aq) + 2\text{Cl}^-(aq)$$

In our discussion of oxides in this section, we have seen that reactions of the covalent oxides of the transition elements with hydroxides form salts that contain oxyanions of the transition elements.

How Sciences Interconnect

High Temperature Superconductors

A **superconductor** is a substance that conducts electricity with no resistance. This lack of resistance means that there is no energy loss during the transmission of electricity. This would lead to a significant reduction in the cost of electricity.

Most currently used, commercial superconducting materials, such as NbTi and Nb_3Sn, do not become superconducting until they are cooled below 23 K (−250 °C). This requires the use of liquid helium, which has a boiling temperature of 4 K and is expensive and difficult to handle. The cost of liquid helium has deterred the widespread application of superconductors.

One of the most exciting scientific discoveries of the 1980s was the characterization of compounds that exhibit superconductivity at temperatures above 90 K. (Compared to liquid helium, 90 K is a high temperature.) Typical among the high-temperature superconducting materials are oxides containing yttrium (or one of several rare earth elements), barium, and copper in a 1:2:3 ratio. The formula of the ionic yttrium compound is $\text{YBa}_2\text{Cu}_3\text{O}_7$.

The new materials become superconducting at temperatures close to 90 K (**Figure 19.10**), temperatures that can be reached by cooling with liquid nitrogen (boiling temperature of 77 K). Not only are liquid nitrogen-cooled materials easier to handle, but the cooling costs are also about 1000 times lower than for liquid helium.

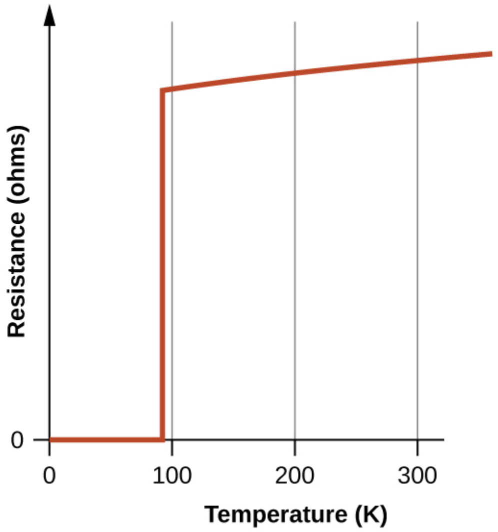


Figure 19.10 The resistance of the high-temperature superconductor $YBa_2Cu_3O_7$ varies with temperature. Note how the resistance falls to zero below 92 K, when the substance becomes superconducting.

Although the brittle, fragile nature of these materials presently hampers their commercial applications, they have tremendous potential that researchers are hard at work improving their processes to help realize. Superconducting transmission lines would carry current for hundreds of miles with no loss of power due to resistance in the wires. This could allow generating stations to be located in areas remote from population centers and near the natural resources necessary for power production. The first project demonstrating the viability of high-temperature superconductor power transmission was established in New York in 2008.

Researchers are also working on using this technology to develop other applications, such as smaller and more powerful microchips. In addition, high-temperature superconductors can be used to generate magnetic fields for applications such as medical devices, magnetic levitation trains, and containment fields for nuclear fusion reactors (**Figure 19.11**).

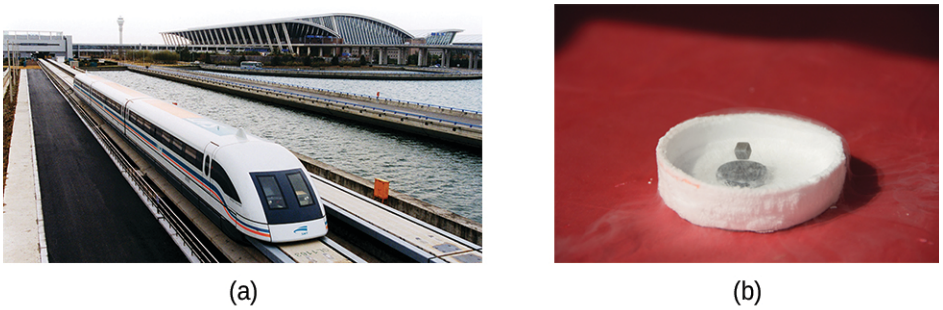


Figure 19.11 (a) This magnetic levitation train (or maglev) uses superconductor technology to move along its tracks. (b) A magnet can be levitated using a dish like this as a superconductor. (credit a: modification of work by Alex Needham; credit b: modification of work by Kevin Jarrett)

Link to Learning

Watch how a **high-temperature superconductor (http://openstaxcollege.org/l/16supercond)** levitates around a magnetic racetrack in the video.

19.2 Coordination Chemistry of Transition Metals

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

- List the defining traits of coordination compounds
- Describe the structures of complexes containing monodentate and polydentate ligands
- Use standard nomenclature rules to name coordination compounds
- Explain and provide examples of geometric and optical isomerism
- Identify several natural and technological occurrences of coordination compounds

The hemoglobin in your blood, the chlorophyll in green plants, vitamin B-12, and the catalyst used in the manufacture of polyethylene all contain coordination compounds. Ions of the metals, especially the transition metals, are likely to form complexes. Many of these compounds are highly colored (**Figure 19.12**). In the remainder of this chapter, we will consider the structure and bonding of these remarkable compounds.

Figure 19.12 Metal ions that contain partially filled *d* subshell usually form colored complex ions; ions with empty *d* subshell (d^0) or with filled *d* subshells (d^{10}) usually form colorless complexes. This figure shows, from left to right, solutions containing $[M(H_2O)_6]^{n+}$ ions with M = $Sc^{3+}(d^0)$, $Cr^{3+}(d^3)$, $Co^{2+}(d^7)$, $Ni^{2+}(d^8)$, $Cu^{2+}(d^9)$, and $Zn^{2+}(d^{10})$. (credit: Sahar Atwa)

Remember that in most main group element compounds, the valence electrons of the isolated atoms combine to form chemical bonds that satisfy the octet rule. For instance, the four valence electrons of carbon overlap with electrons from four hydrogen atoms to form CH_4. The one valence electron leaves sodium and adds to the seven valence electrons of chlorine to form the ionic formula unit NaCl (**Figure 19.13**). Transition metals do not normally bond in this fashion. They primarily form coordinate covalent bonds, a form of the Lewis acid-base interaction in which both of the electrons in the bond are contributed by a donor (Lewis base) to an electron acceptor (Lewis acid). The Lewis acid in coordination complexes, often called a **central metal** ion (or atom), is often a transition metal or inner transition metal, although main group elements can also form **coordination compounds**. The Lewis base donors, called **ligands**, can be a wide variety of chemicals—atoms, molecules, or ions. The only requirement is that they have one or more electron pairs, which can be donated to the central metal. Most often, this involves a **donor atom** with a lone pair of electrons that can form a coordinate bond to the metal.

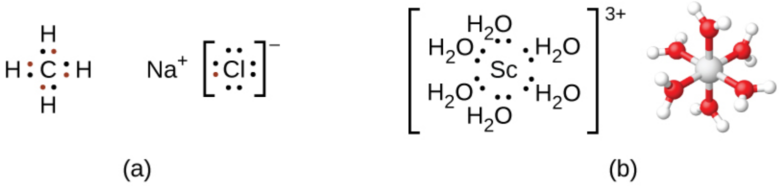


Figure 19.13 (a) Covalent bonds involve the sharing of electrons, and ionic bonds involve the transferring of electrons associated with each bonding atom, as indicated by the colored electrons. (b) However, coordinate covalent bonds involve electrons from a Lewis base being donated to a metal center. The lone pairs from six water molecules form bonds to the scandium ion to form an octahedral complex. (Only the donated pairs are shown.)

The **coordination sphere** consists of the central metal ion or atom plus its attached ligands. Brackets in a formula enclose the coordination sphere; species outside the brackets are not part of the coordination sphere. The **coordination number** of the central metal ion or atom is the number of donor atoms bonded to it. The coordination number for the silver ion in $[Ag(NH_3)_2]^+$ is two (**Figure 19.14**). For the copper(II) ion in $[CuCl_4]^{2-}$, the coordination number is four, whereas for the cobalt(II) ion in $[Co(H_2O)_6]^{2+}$ the coordination number is six. Each of these ligands is **monodentate**, from the Greek for “one toothed,” meaning that they connect with the central metal through only one atom. In this case, the number of ligands and the coordination number are equal.

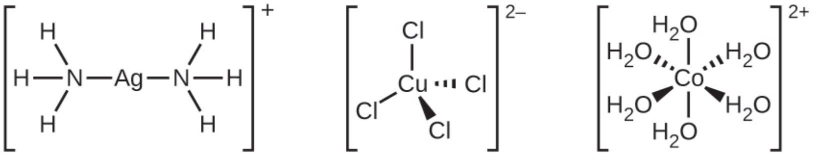


Figure 19.14 The complexes (a) $[Ag(NH_3)_2]^+$, (b) $[Cu(Cl)_4]^{2-}$, and (c) $[Co(H_2O)_6]^{2+}$ have coordination numbers of two, four, and six, respectively. The geometries of these complexes are the same as we have seen with VSEPR theory for main group elements: linear, tetrahedral, and octahedral.

Many other ligands coordinate to the metal in more complex fashions. **Bidentate ligands** are those in which two atoms coordinate to the metal center. For example, ethylenediamine (en, $H_2NCH_2CH_2NH_2$) contains two nitrogen atoms, each of which has a lone pair and can serve as a Lewis base (**Figure 19.15**). Both of the atoms can coordinate to a single metal center. In the complex $[Co(en)_3]^{3+}$, there are three bidentate en ligands, and the coordination number of the cobalt(III) ion is six. The most common coordination numbers are two, four, and six, but examples of all coordination numbers from 1 to 15 are known.

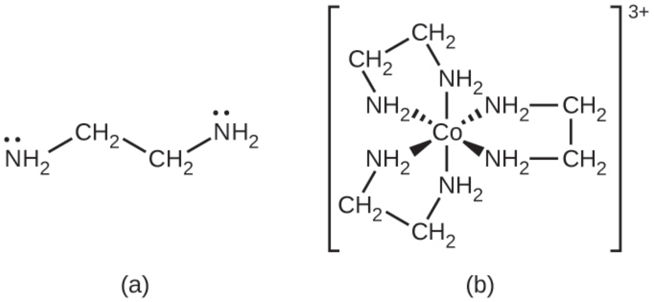


Figure 19.15 (a) The ethylenediamine (en) ligand contains two atoms with lone pairs that can coordinate to the metal center. (b) The cobalt(III) complex $[\text{Co(en)}_3]^{3+}$ contains three of these ligands, each forming two bonds to the cobalt ion.

Any ligand that bonds to a central metal ion by more than one donor atom is a **polydentate ligand** (or “many teeth”) because it can bite into the metal center with more than one bond. The term **chelate** (pronounced “KEY-late”) from the Greek for “claw” is also used to describe this type of interaction. Many polydentate ligands are **chelating ligands**, and a complex consisting of one or more of these ligands and a central metal is a chelate. A chelating ligand is also known as a chelating agent. A chelating ligand holds the metal ion rather like a crab’s claw would hold a marble. **Figure 19.15** showed one example of a chelate. The heme complex in hemoglobin is another important example (**Figure 19.16**). It contains a polydentate ligand with four donor atoms that coordinate to iron.

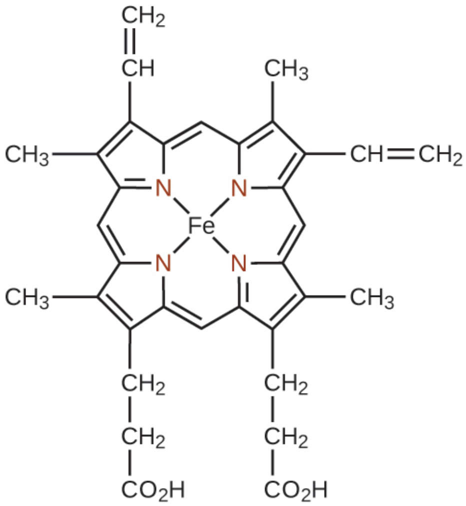


Figure 19.16 The single ligand heme contains four nitrogen atoms that coordinate to iron in hemoglobin to form a chelate.

Polydentate ligands are sometimes identified with prefixes that indicate the number of donor atoms in the ligand. As we have seen, ligands with one donor atom, such as NH_3, Cl^-, and H_2O, are monodentate ligands. Ligands with two donor groups are bidentate ligands. Ethylenediamine, $H_2NCH_2CH_2NH_2$, and the anion of the acid glycine, $NH_2CH_2CO_2{}^-$ (**Figure 19.17**) are examples of bidentate ligands. Tridentate ligands, tetradentate ligands, pentadentate ligands, and hexadentate ligands contain three, four, five, and six donor atoms, respectively. The ligand in heme (**Figure 19.16**) is a tetradentate ligand.

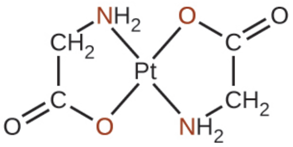


Figure 19.17 Each of the anionic ligands shown attaches in a bidentate fashion to platinum(II), with both a nitrogen and oxygen atom coordinating to the metal.

The Naming of Complexes

The nomenclature of the complexes is patterned after a system suggested by Alfred Werner, a Swiss chemist and Nobel laureate, whose outstanding work more than 100 years ago laid the foundation for a clearer understanding of these compounds. The following five rules are used for naming complexes:

1. If a coordination compound is ionic, name the cation first and the anion second, in accordance with the usual nomenclature.
2. Name the ligands first, followed by the central metal. Name the ligands alphabetically. Negative ligands (anions) have names formed by adding *-o* to the stem name of the group. For examples, see **Table 19.1**. For most neutral ligands, the name of the molecule is used. The four common exceptions are *aqua* (H_2O), *ammine* (NH_3), *carbonyl* (CO), and *nitrosyl* (NO). For example, name $[Pt(NH_3)_2Cl_4]$ as diamminetetrachloroplatinum(IV).

Examples of Anionic Ligands

Anionic Ligand	Name
F^-	fluoro
Cl^-	chloro
Br^-	bromo
I^-	iodo
CN^-	cyano
$NO_3{}^-$	nitrato
OH^-	hydroxo
O^{2-}	oxo
$C_2O_4{}^{2-}$	oxalato
$CO_2{}^{2-}$	carbonato

Table 19.1

3. If more than one ligand of a given type is present, the number is indicated by the prefixes *di-* (for two), *tri-* (for three), *tetra-* (for four), *penta-* (for five), and *hexa-* (for six). Sometimes, the prefixes *bis-* (for two), *tris-* (for three), and *tetrakis-* (for four) are used when the name of the ligand already includes *di-*, *tri-*, or *tetra-*, or when the ligand name begins with a vowel. For example, the ion bis(bipyridyl)osmium(II) uses bis- to signify that there are two ligands attached to Os, and each bipyridyl ligand contains two pyridine groups (C_5H_4N).

When the complex is either a cation or a neutral molecule, the name of the central metal atom is spelled exactly like the name of the element and is followed by a Roman numeral in parentheses to indicate its oxidation state (**Table 19.2** and **Table 19.3**). When the complex is an anion, the suffix -ate is added to the stem of the name of the metal, followed by the Roman numeral designation of its oxidation state (**Table 19.4**). Sometimes, the Latin name of the metal is used when the English name is clumsy. For example, *ferrate* is used instead of *ironate*, *plumbate* instead *leadate*, and *stannate* instead of *tinate*. The oxidation state of the metal is determined based on the charges of each ligand and the overall charge of the coordination compound. For example, in $[Cr(H_2O)_4Cl_2]Br$, the coordination sphere (in brackets) has a charge of 1+ to balance the bromide ion. The water ligands are neutral, and the chloride ligands are anionic with a charge of 1− each. To determine the oxidation state of the metal, we set the overall charge equal to the sum of the ligands and the metal: $+1 = -2 + x$, so the oxidation state (x) is equal to 3+.

Examples in Which the Complex Is a Cation

$[Co(NH_3)_6]Cl_3$	hexaamminecobalt(III) chloride
$[Pt(NH_3)_4Cl_2]^{2+}$	tetraamminedichloroplatinum(IV) ion
$[Ag(NH_3)_2]^{+}$	diamminesilver(I) ion
$[Cr(H_2O)_4Cl_2]Cl$	tetraaquadichlorochromium(III) chloride
$[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	tris(ethylenediamine)cobalt(III) sulfate

Table 19.2

Examples in Which the Complex Is Neutral

$[Pt(NH_3)_2Cl_4]$	diamminetetrachloroplatinum(IV)
$[Ni(H_2NCH_2CH_2NH_2)_2Cl_2]$	dichlorobis(ethylenediamine)nickel(II)

Table 19.3

Examples in Which the Complex Is an Anion

$[PtCl_6]^{2-}$	hexachloroplatinate(IV) ion
$Na_2[SnCl_6]$	sodium hexachlorostannate(IV)

Table 19.4

Link to Learning

Do you think you understand naming coordination complexes? You can look over more examples and test yourself with **online quizzes (http://openstaxcollege.org/l/16namingcomps)** at the University of Sydney's site.

Example 19.4

Coordination Numbers and Oxidation States

Determine the name of the following complexes and give the coordination number of the central metal atom.

(a) $Na_2[PtCl_6]$

(b) $K_3[Fe(C_2O_4)_3]$

(c) $[Co(NH_3)_5Cl]Cl_2$

Solution

(a) There are two Na^+ ions, so the coordination sphere has a negative two charge: $[PtCl_6]^{2-}$. There are six anionic chloride ligands, so $-2 = -6 + x$, and the oxidation state of the platinum is 4+. The name of the complex is sodium hexachloroplatinate(IV), and the coordination number is six. (b) The coordination sphere has a charge of 3− (based on the potassium) and the oxalate ligands each have a charge of 2−, so the metal oxidation state is given by $-3 = -6 + x$, and this is an iron(III) complex. The name is potassium trisoxalatoferrate(III) (note that tris is used instead of tri because the ligand name starts with a vowel). Because oxalate is a bidentate ligand, this complex has a coordination number of six. (c) In this example, the coordination sphere has a cationic charge of 2+. The NH_3 ligand is neutral, but the chloro ligand has a charge of 1−. The oxidation state is found by $+2 = -1 + x$ and is 3+, so the complex is pentaamminechlorocobalt(III) chloride and the coordination number is six.

Check Your Learning

The complex potassium dicyanoargenate(I) is used to make antiseptic compounds. Give the formula and coordination number.

Answer: $K[Ag(CN)_2]$; coordination number two

The Structures of Complexes

The most common structures of the complexes in coordination compounds are octahedral, tetrahedral, and square planar (see **Figure 19.18**). For transition metal complexes, the coordination number determines the geometry around the central metal ion. **Table 19.5** compares coordination numbers to the molecular geometry:

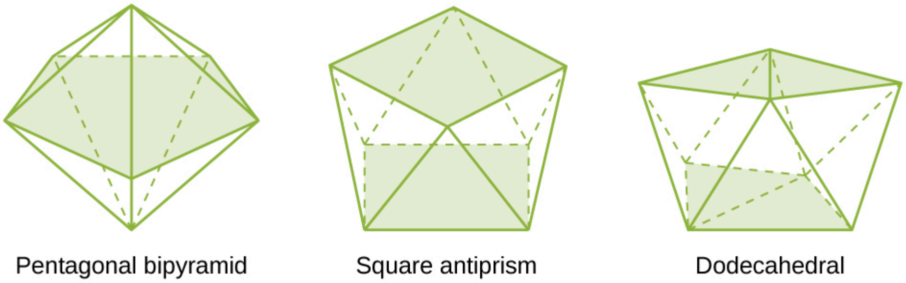


Figure 19.18 These are geometries of some complexes with coordination numbers of seven and eight.

Coordination Numbers and Molecular Geometry

Coordination Number	Molecular Geometry	Example
2	linear	$[Ag(NH_3)_2]^+$
3	trigonal planar	$[Cu(CN)_3]^{2-}$
4	tetrahedral(d^0 or d^{10}), low oxidation states for M	$[Ni(CO)_4]$
4	square planar (d^8)	$[NiCl_4]^{2-}$
5	trigonal bipyramidal	$[CoCl_5]^{2-}$

Table 19.5

Coordination Numbers and Molecular Geometry

Coordination Number	Molecular Geometry	Example
5	square pyramidal	$[VO(CN)_4]^{2-}$
6	octahedral	$[CoCl_6]^{3-}$
7	pentagonal bipyramid	$[ZrF_7]^{3-}$
8	square antiprism	$[ReF_8]^{2-}$
8	dodecahedron	$[Mo(CN)_8]^{4-}$
9 and above	more complicated structures	$[ReH_9]^{2-}$

Table 19.5

Unlike main group atoms in which both the bonding and nonbonding electrons determine the molecular shape, the nonbonding *d*-electrons do not change the arrangement of the ligands. Octahedral complexes have a coordination number of six, and the six donor atoms are arranged at the corners of an octahedron around the central metal ion. Examples are shown in **Figure 19.19**. The chloride and nitrate anions in $[Co(H_2O)_6]Cl_2$ and $[Cr(en)_3](NO_3)_3$, and the potassium cations in $K_2[PtCl_6]$, are outside the brackets and are not bonded to the metal ion.

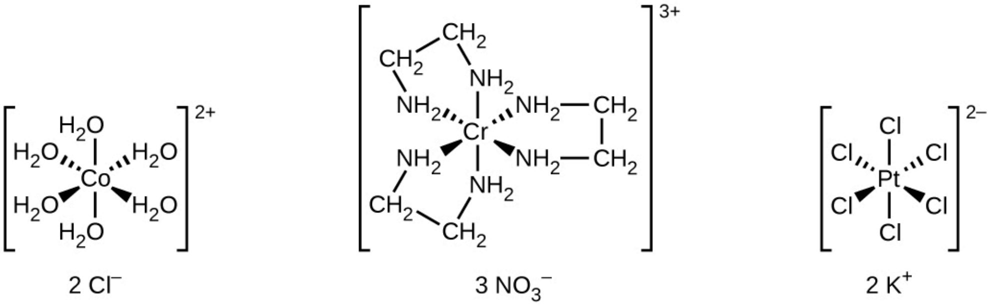


Figure 19.19 Many transition metal complexes adopt octahedral geometries, with six donor atoms forming bond angles of 90° about the central atom with adjacent ligands. Note that only ligands within the coordination sphere affect the geometry around the metal center.

For transition metals with a coordination number of four, two different geometries are possible: tetrahedral or square planar. Unlike main group elements, where these geometries can be predicted from VSEPR theory, a more detailed discussion of transition metal orbitals (discussed in the section on Crystal Field Theory) is required to predict which complexes will be tetrahedral and which will be square planar. In tetrahedral complexes such as $[Zn(CN)_4]^{2-}$ (**Figure 19.20**), each of the ligand pairs forms an angle of 109.5°. In square planar complexes, such as $[Pt(NH_3)_2Cl_2]$, each ligand has two other ligands at 90° angles (called the *cis* positions) and one additional ligand at an 180° angle, in the *trans* position.

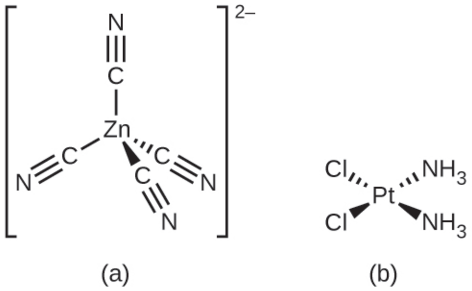


Figure 19.20 Transition metals with a coordination number of four can adopt a tetrahedral geometry (a) as in $K_2[Zn(CN)_4]$ or a square planar geometry (b) as shown in $[Pt(NH_3)_2Cl_2]$.

Isomerism in Complexes

Isomers are different chemical species that have the same chemical formula. Transition metals often form **geometric isomers**, in which the same atoms are connected through the same types of bonds but with differences in their orientation in space. Coordination complexes with two different ligands in the *cis* and *trans* positions from a ligand of interest form isomers. For example, the octahedral $[Co(NH_3)_4Cl_2]^+$ ion has two isomers. In the ***cis* configuration**, the two chloride ligands are adjacent to each other (**Figure 19.21**). The other isomer, the ***trans* configuration**, has the two chloride ligands directly across from one another.

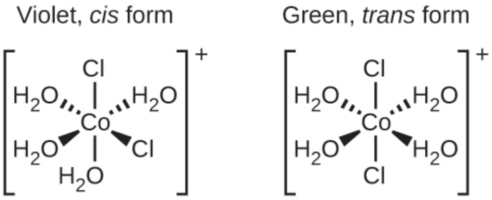


Figure 19.21 The *cis* and *trans* isomers of $[Co(H_2O)_4Cl_2]^+$ contain the same ligands attached to the same metal ion, but the spatial arrangement causes these two compounds to have very different properties.

Different geometric isomers of a substance are different chemical compounds. They exhibit different properties, even though they have the same formula. For example, the two isomers of $[Co(NH_3)_4Cl_2]NO_3$ differ in color; the *cis* form is violet, and the *trans* form is green. Furthermore, these isomers have different dipole moments, solubilities, and reactivities. As an example of how the arrangement in space can influence the molecular properties, consider the polarity of the two $[Co(NH_3)_4Cl_2]NO_3$ isomers. Remember that the polarity of a molecule or ion is determined by the bond dipoles (which are due to the difference in electronegativity of the bonding atoms) and their arrangement in space. In one isomer, *cis* chloride ligands cause more electron density on one side of the molecule than on the other, making it polar. For the *trans* isomer, each ligand is directly across from an identical ligand, so the bond dipoles cancel out, and the molecule is nonpolar.

Example 19.5

Geometric Isomers

Identify which geometric isomer of $[Pt(NH_3)_2Cl_2]$ is shown in **Figure 19.20**. Draw the other geometric isomer and give its full name.

Solution

In the **Figure 19.20**, the two chlorine ligands occupy *cis* positions. The other form is shown in **Figure 19.22**. When naming specific isomers, the descriptor is listed in front of the name. Therefore, this complex is *trans*-diamminedichloroplatinum(II).

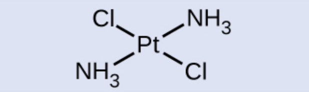
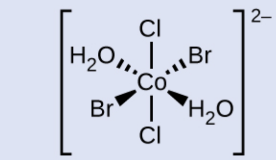


Figure 19.22 The *trans* isomer of [Pt(NH_3)$_2$$Cl_2$] has each ligand directly across from an adjacent ligand.

Check Your Learning

Draw the ion *trans*-diaqua-*trans*-dibromo-*trans*-dichlorocobalt(II).

Answer:



Another important type of isomers are **optical isomers**, or **enantiomers**, in which two objects are exact mirror images of each other but cannot be lined up so that all parts match. This means that optical isomers are nonsuperimposable mirror images. A classic example of this is a pair of hands, in which the right and left hand are mirror images of one another but cannot be superimposed. Optical isomers are very important in organic and biochemistry because living systems often incorporate one specific optical isomer and not the other. Unlike geometric isomers, pairs of optical isomers have identical properties (boiling point, polarity, solubility, etc.). Optical isomers differ only in the way they affect polarized light and how they react with other optical isomers. For coordination complexes, many coordination compounds such as $[M(en)_3]^{n+}$ [in which M^{n+} is a central metal ion such as iron(III) or cobalt(II)] form enantiomers, as shown in **Figure 19.23**. These two isomers will react differently with other optical isomers. For example, DNA helices are optical isomers, and the form that occurs in nature (right-handed DNA) will bind to only one isomer of $[M(en)_3]^{n+}$ and not the other.

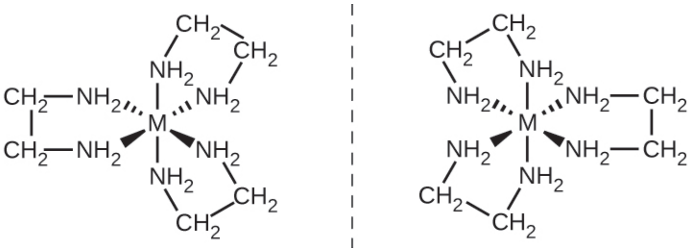


Figure 19.23 The complex $[M(en)_3]^{n+}$ (M^{n+} = a metal ion, en = ethylenediamine) has a nonsuperimposable mirror image.

The $[Co(en)_2Cl_2]^+$ ion exhibits geometric isomerism (*cis*/*trans*), and its *cis* isomer exists as a pair of optical isomers (**Figure 19.24**).

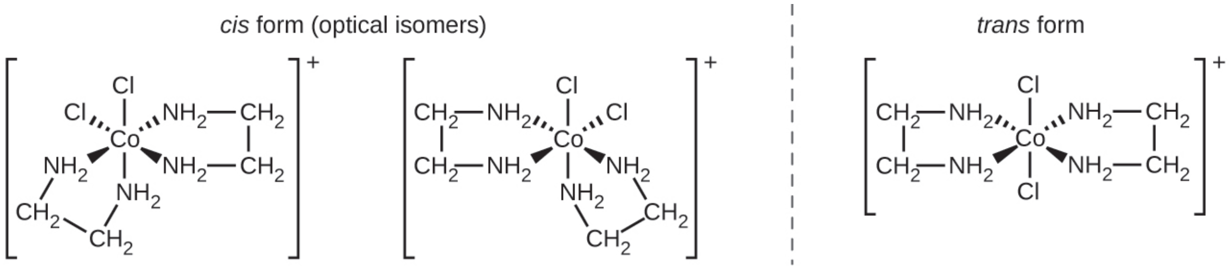


Figure 19.24 Three isomeric forms of $[Co(en)_2Cl_2]^+$ exist. The *trans* isomer, formed when the chlorines are positioned at a 180° angle, has very different properties from the *cis* isomers. The mirror images of the *cis* isomer form a pair of optical isomers, which have identical behavior except when reacting with other enantiomers.

Linkage isomers occur when the coordination compound contains a ligand that can bind to the transition metal center through two different atoms. For example, the CN ligand can bind through the carbon atom (cyano) or through the nitrogen atom (isocyano). Similarly, SCN− can be bound through the sulfur or nitrogen atom, affording two distinct compounds ($[Co(NH_3)_5SCN]^{2+}$ or $[Co(NH_3)_5NCS]^{2+}$).

Ionization isomers (or **coordination isomers**) occur when one anionic ligand in the inner coordination sphere is replaced with the counter ion from the outer coordination sphere. A simple example of two ionization isomers are $[CoCl_6][Br]$ and $[CoCl_5Br][Cl]$.

Coordination Complexes in Nature and Technology

Chlorophyll, the green pigment in plants, is a complex that contains magnesium (**Figure 19.25**). This is an example of a main group element in a coordination complex. Plants appear green because chlorophyll absorbs red and purple light; the reflected light consequently appears green. The energy resulting from the absorption of light is used in photosynthesis.

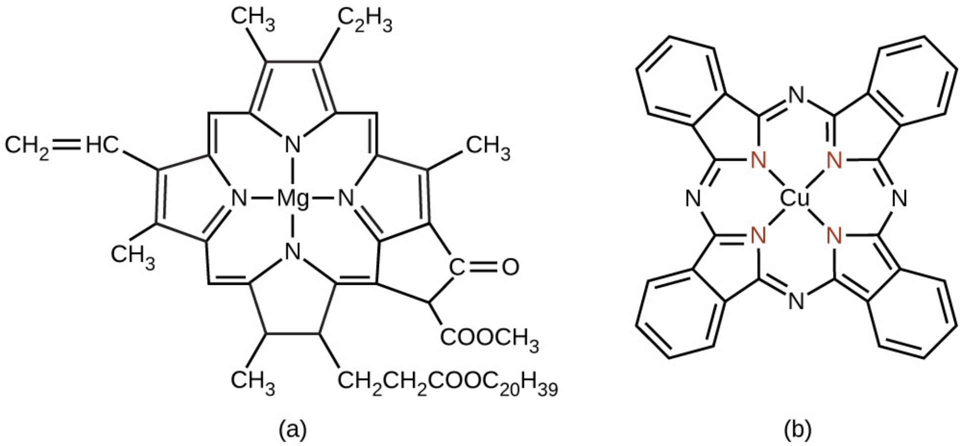


Figure 19.25 (a) Chlorophyll comes in several different forms, which all have the same basic structure around the magnesium center. (b) Copper phthalocyanine blue, a square planar copper complex, is present in some blue dyes.

Chemistry in Everyday Life

Transition Metal Catalysts

One of the most important applications of transition metals is as industrial catalysts. As you recall from the chapter on kinetics, a catalyst increases the rate of reaction by lowering the activation energy and is regenerated in the catalytic cycle. Over 90% of all manufactured products are made with the aid of one or more catalysts. The ability to bind ligands and change oxidation states makes transition metal catalysts well suited for catalytic applications. Vanadium oxide is used to produce 230,000,000 tons of sulfuric acid worldwide each year, which in turn is used to make everything from fertilizers to cans for food. Plastics are made with the aid of transition metal catalysts, along with detergents, fertilizers, paints, and more (see Figure 19.26). Very complicated pharmaceuticals are manufactured with catalysts that are selective, reacting with one specific bond out of a large number of possibilities. Catalysts allow processes to be more economical and more environmentally friendly. Developing new catalysts and better understanding of existing systems are important areas of current research.

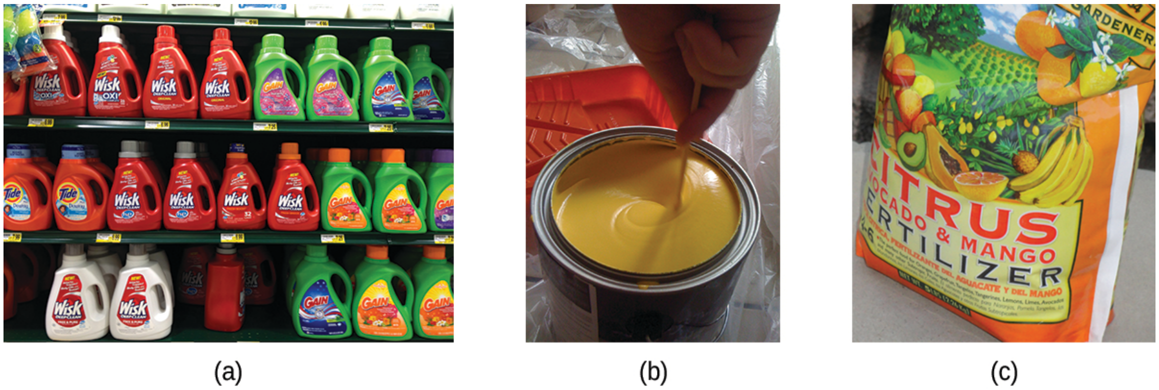


Figure 19.26 (a) Detergents, (b) paints, and (c) fertilizers are all made using transition metal catalysts. (credit a: modification of work by "Mr. Brian"/Flickr; credit b: modification of work by Ewen Roberts; credit c: modification of work by "osseous"/Flickr)

Portrait of a Chemist

Deanna D'Alessandro

Dr. Deanna D'Alessandro develops new metal-containing materials that demonstrate unique electronic, optical, and magnetic properties. Her research combines the fields of fundamental inorganic and physical chemistry with materials engineering. She is working on many different projects that rely on transition metals. For example, one type of compound she is developing captures carbon dioxide waste from power plants and catalytically converts it into useful products (see Figure 19.27).

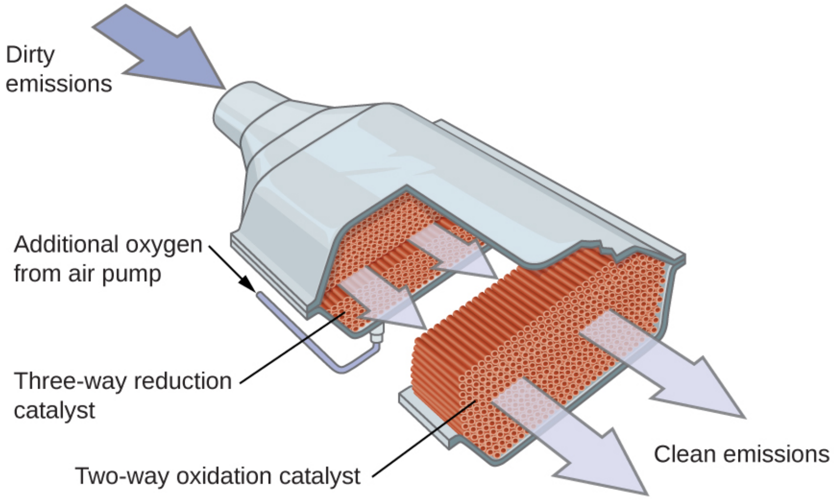


Figure 19.27 Catalytic converters change carbon dioxide emissions from power plants into useful products, and, like the one shown here, are also found in cars.

Another project involves the development of porous, sponge-like materials that are "photoactive." The absorption of light causes the pores of the sponge to change size, allowing gas diffusion to be controlled. This has many potential useful applications, from powering cars with hydrogen fuel cells to making better electronics components. Although not a complex, self-darkening sunglasses are an example of a photoactive substance.

Watch this **video (http://openstaxcollege.org/l/16DeannaD)** to learn more about this research and listen to Dr. D'Alessandro (shown in **Figure 19.28**) describe what it is like being a research chemist.

Figure 19.28 Dr. Deanna D'Alessandro is a functional materials researcher. Her work combines the inorganic and physical chemistry fields with engineering, working with transition metals to create new systems to power cars and convert energy (credit: image courtesy of Deanna D'Alessandro).

Many other coordination complexes are also brightly colored. The square planar copper(II) complex phthalocyanine blue (from **Figure 19.25**) is one of many complexes used as pigments or dyes. This complex is used in blue ink, blue jeans, and certain blue paints.

The structure of heme (**Figure 19.29**), the iron-containing complex in hemoglobin, is very similar to that in chlorophyll. In hemoglobin, the red heme complex is bonded to a large protein molecule (globin) by the attachment of the protein to the heme ligand. Oxygen molecules are transported by hemoglobin in the blood by being bound to the iron center. When the hemoglobin loses its oxygen, the color changes to a bluish red. Hemoglobin will only transport oxygen if the iron is Fe^{2+}; oxidation of the iron to Fe^{3+} prevents oxygen transport.

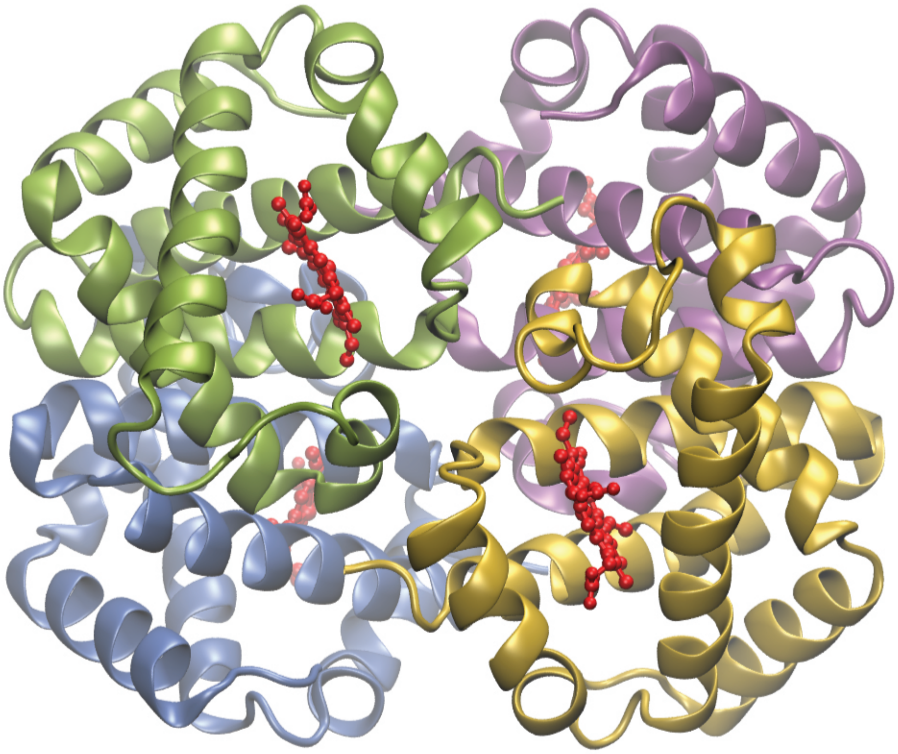


Figure 19.29 Hemoglobin contains four protein subunits, each of which has an iron center attached to a heme ligand (shown in red), which is coordinated to a globin protein. Each subunit is shown in a different color.

Complexing agents often are used for water softening because they tie up such ions as Ca^{2+}, Mg^{2+}, and Fe^{2+}, which make water hard. Many metal ions are also undesirable in food products because these ions can catalyze reactions that change the color of food. Coordination complexes are useful as preservatives. For example, the ligand EDTA, $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$, coordinates to metal ions through six donor atoms and prevents the metals from reacting (**Figure 19.30**). This ligand also is used to sequester metal ions in paper production, textiles, and detergents, and has pharmaceutical uses.

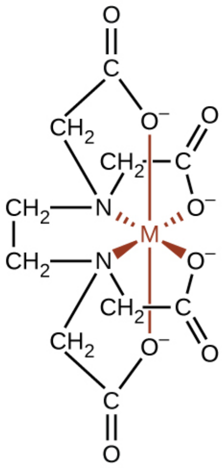


Figure 19.30 The ligand EDTA binds tightly to a variety of metal ions by forming hexadentate complexes.

Complexing agents that tie up metal ions are also used as drugs. British Anti-Lewisite (BAL), $HSCH_2CH(SH)CH_2OH$, is a drug developed during World War I as an antidote for the arsenic-based war gas Lewisite. BAL is now used to treat poisoning by heavy metals, such as arsenic, mercury, thallium, and chromium. The drug is a ligand and functions by making a water-soluble chelate of the metal; the kidneys eliminate this metal chelate (**Figure 19.31**). Another polydentate ligand, enterobactin, which is isolated from certain bacteria, is used to form complexes of iron and thereby to control the severe iron buildup found in patients suffering from blood diseases such as Cooley’s anemia, who require frequent transfusions. As the transfused blood breaks down, the usual metabolic processes that remove iron are overloaded, and excess iron can build up to fatal levels. Enterobactin forms a water-soluble complex with excess iron, and the body can safely eliminate this complex.

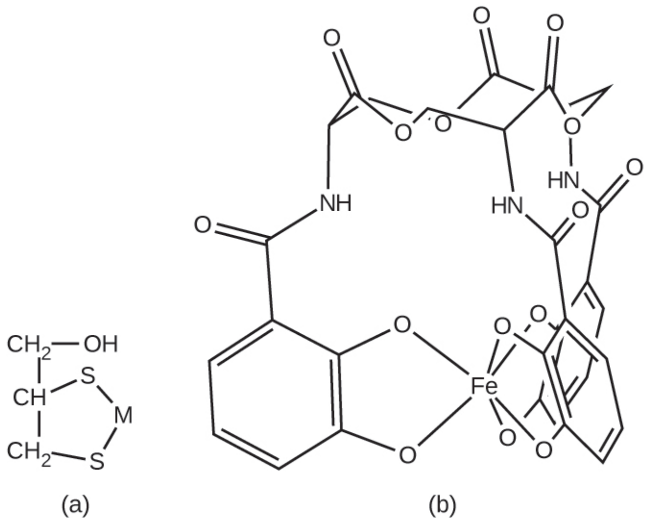


Figure 19.31 Coordination complexes are used as drugs. (a) British Anti-Lewisite is used to treat heavy metal poisoning by coordinating metals (M), and enterobactin (b) allows excess iron in the blood to be removed.

Example 19.6

Chelation Therapy

Ligands like BAL and enterobactin are important in medical treatments for heavy metal poisoning. However, chelation therapies can disrupt the normal concentration of ions in the body, leading to serious side effects, so researchers are searching for new chelation drugs. One drug that has been developed is dimercaptosuccinic acid (DMSA), shown in **Figure 19.32**. Identify which atoms in this molecule could act as donor atoms.

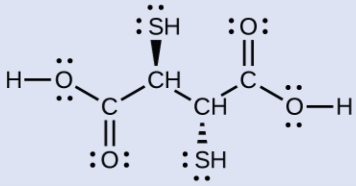


Figure 19.32 Dimercaptosuccinic acid is used to treat heavy metal poisoning.

Solution

All of the oxygen and sulfur atoms have lone pairs of electrons that can be used to coordinate to a metal center, so there are six possible donor atoms. Geometrically, only two of these atoms can be coordinated to a metal at once. The most common binding mode involves the coordination of one sulfur atom and one oxygen atom, forming a five-member ring with the metal.

Check Your Learning

Some alternative medicine practitioners recommend chelation treatments for ailments that are not clearly related to heavy metals, such as cancer and autism, although the practice is discouraged by many scientific organizations.[1] Identify at least two biologically important metals that could be disrupted by chelation therapy.

Answer: Ca, Fe, Zn, and Cu

Ligands are also used in the electroplating industry. When metal ions are reduced to produce thin metal coatings, metals can clump together to form clusters and nanoparticles. When metal coordination complexes are used, the ligands keep the metal atoms isolated from each other. It has been found that many metals plate out as a smoother, more uniform, better-looking, and more adherent surface when plated from a bath containing the metal as a complex ion. Thus, complexes such as $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ are used extensively in the electroplating industry.

In 1965, scientists at Michigan State University discovered that there was a platinum complex that inhibited cell division in certain microorganisms. Later work showed that the complex was *cis*-diamminedichloroplatinum(II), $[Pt(NH_3)_2(Cl)_2]$, and that the *trans* isomer was not effective. The inhibition of cell division indicated that this square planar compound could be an anticancer agent. In 1978, the US Food and Drug Administration approved this compound, known as cisplatin, for use in the treatment of certain forms of cancer. Since that time, many similar platinum compounds have been developed for the treatment of cancer. In all cases, these are the *cis* isomers and never the *trans* isomers. The diammine $(NH_3)_2$ portion is retained with other groups, replacing the dichloro $[(Cl)_2]$ portion. The newer drugs include carboplatin, oxaliplatin, and satraplatin.

19.3 Spectroscopic and Magnetic Properties of Coordination Compounds

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

- Outline the basic premise of crystal field theory (CFT)
- Identify molecular geometries associated with various d-orbital splitting patterns
- Predict electron configurations of split d orbitals for selected transition metal atoms or ions
- Explain spectral and magnetic properties in terms of CFT concepts

The behavior of coordination compounds cannot be adequately explained by the same theories used for main group element chemistry. The observed geometries of coordination complexes are not consistent with hybridized orbitals on the central metal overlapping with ligand orbitals, as would be predicted by valence bond theory. The observed colors indicate that the *d* orbitals often occur at different energy levels rather than all being degenerate, that is, of equal energy, as are the three *p* orbitals. To explain the stabilities, structures, colors, and magnetic properties of transition metal complexes, a different bonding model has been developed. Just as valence bond theory explains many aspects of bonding in main group chemistry, crystal field theory is useful in understanding and predicting the behavior of transition metal complexes.

Crystal Field Theory

To explain the observed behavior of transition metal complexes (such as how colors arise), a model involving electrostatic interactions between the electrons from the ligands and the electrons in the unhybridized *d* orbitals of the central metal atom has been developed. This electrostatic model is **crystal field theory** (CFT). It allows us to understand, interpret, and predict the colors, magnetic behavior, and some structures of coordination compounds of

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[1] National Council against Health Fraud, *NCAHF Policy Statement on Chelation Therapy*, (Peabody, MA, 2002).

transition metals.

CFT focuses on the nonbonding electrons on the central metal ion in coordination complexes not on the metal-ligand bonds. Like valence bond theory, CFT tells only part of the story of the behavior of complexes. However, it tells the part that valence bond theory does not. In its pure form, CFT ignores any covalent bonding between ligands and metal ions. Both the ligand and the metal are treated as infinitesimally small point charges.

All electrons are negative, so the electrons donated from the ligands will repel the electrons of the central metal. Let us consider the behavior of the electrons in the unhybridized *d* orbitals in an octahedral complex. The five *d* orbitals consist of lobe-shaped regions and are arranged in space, as shown in **Figure 19.33**. In an octahedral complex, the six ligands coordinate along the axes.

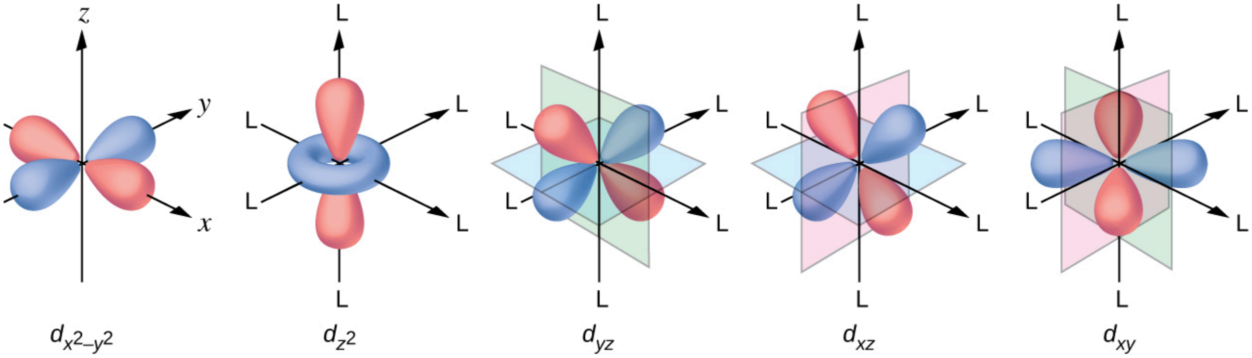


Figure 19.33 The directional characteristics of the five *d* orbitals are shown here. The shaded portions indicate the phase of the orbitals. The ligands (L) coordinate along the axes. For clarity, the ligands have been omitted from the $d_{x^2-y^2}$ orbital so that the axis labels could be shown.

In an uncomplexed metal ion in the gas phase, the electrons are distributed among the five *d* orbitals in accord with Hund's rule because the orbitals all have the same energy. However, when ligands coordinate to a metal ion, the energies of the *d* orbitals are no longer the same.

In octahedral complexes, the lobes in two of the five *d* orbitals, the d_{z^2} and $d_{x^2-y^2}$ orbitals, point toward the ligands (**Figure 19.33**). These two orbitals are called the **e_g orbitals** (the symbol actually refers to the symmetry of the orbitals, but we will use it as a convenient name for these two orbitals in an octahedral complex). The other three orbitals, the d_{xy}, d_{xz}, and d_{yz} orbitals, have lobes that point between the ligands and are called the **t_{2g} orbitals** (again, the symbol really refers to the symmetry of the orbitals). As six ligands approach the metal ion along the axes of the octahedron, their point charges repel the electrons in the *d* orbitals of the metal ion. However, the repulsions between the electrons in the e_g orbitals (the d_{z^2} and $d_{x^2-y^2}$ orbitals) and the ligands are greater than the repulsions between the electrons in the t_{2g} orbitals (the d_{zy}, d_{xz}, and d_{yz} orbitals) and the ligands. This is because the lobes of the e_g orbitals point directly at the ligands, whereas the lobes of the t_{2g} orbitals point between them. Thus, electrons in the e_g orbitals of the metal ion in an octahedral complex have higher potential energies than those of electrons in the t_{2g} orbitals. The difference in energy may be represented as shown in **Figure 19.34**.

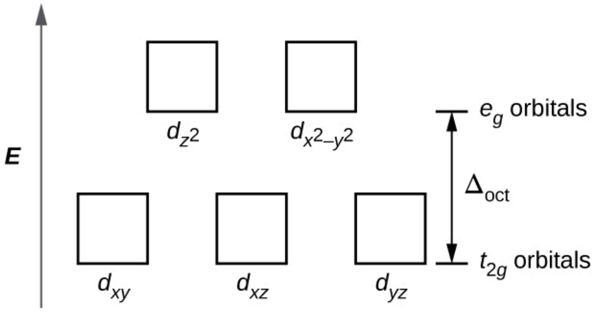


Figure 19.34 In octahedral complexes, the e_g orbitals are destabilized (higher in energy) compared to the t_{2g} orbitals because the ligands interact more strongly with the *d* orbitals at which they are pointed directly.

The difference in energy between the e_g and the t_{2g} orbitals is called the **crystal field splitting** and is symbolized by **Δoct**, where oct stands for octahedral.

The magnitude of Δ_{oct} depends on many factors, including the nature of the six ligands located around the central metal ion, the charge on the metal, and whether the metal is using 3*d*, 4*d*, or 5*d* orbitals. Different ligands produce different crystal field splittings. The increasing crystal field splitting produced by ligands is expressed in the **spectrochemical series**, a short version of which is given here:

$$\underset{\text{a few ligands of the spectrochemical series, in order of increasing field strength of the ligand}}{\underrightarrow{\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{H}_2\text{O} < \text{C}_2\text{O}_4{}^{2-} < \text{NH}_3 < en < \text{NO}_2{}^- < \text{CN}^-}}$$

In this series, ligands on the left cause small crystal field splittings and are **weak-field ligands**, whereas those on the right cause larger splittings and are **strong-field ligands**. Thus, the Δ_{oct} value for an octahedral complex with iodide ligands (I^-) is much smaller than the Δ_{oct} value for the same metal with cyanide ligands (CN^-).

Electrons in the *d* orbitals follow the aufbau (“filling up”) principle, which says that the orbitals will be filled to give the lowest total energy, just as in main group chemistry. When two electrons occupy the same orbital, the like charges repel each other. The energy needed to pair up two electrons in a single orbital is called the **pairing energy (P)**. Electrons will always singly occupy each orbital in a degenerate set before pairing. P is similar in magnitude to Δ_{oct}. When electrons fill the *d* orbitals, the relative magnitudes of Δ_{oct} and P determine which orbitals will be occupied.

In $[Fe(CN)_6]^{4-}$, the strong field of six cyanide ligands produces a large Δ_{oct}. Under these conditions, the electrons require less energy to pair than they require to be excited to the e_g orbitals ($\Delta_{oct} > P$). The six 3*d* electrons of the Fe^{2+} ion pair in the three t_{2g} orbitals (**Figure 19.35**). Complexes in which the electrons are paired because of the large crystal field splitting are called **low-spin complexes** because the number of unpaired electrons (spins) is minimized.

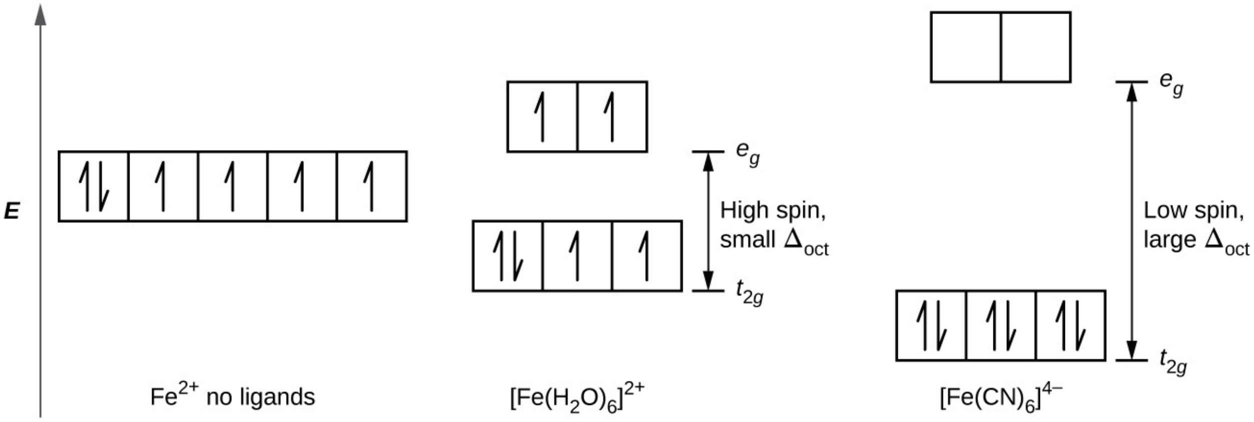


Figure 19.35 Iron(II) complexes have six electrons in the 5*d* orbitals. In the absence of a crystal field, the orbitals are degenerate. For coordination complexes with strong-field ligands such as $[Fe(CN)_6]^{4-}$, Δ_{oct} is greater than P, and the electrons pair in the lower energy t_{2g} orbitals before occupying the *eg* orbitals. With weak-field ligands such as H_2O, the ligand field splitting is less than the pairing energy, Δ_{oct} less than P, so the electrons occupy all *d* orbitals singly before any pairing occurs.

In $[Fe(H_2O)_6]^{2+}$, on the other hand, the weak field of the water molecules produces only a small crystal field splitting ($\Delta_{oct} < P$). Because it requires less energy for the electrons to occupy the e_g orbitals than to pair together, there will be an electron in each of the five 3*d* orbitals before pairing occurs. For the six *d* electrons on the iron(II) center in $[Fe(H_2O)_6]^{2+}$, there will be one pair of electrons and four unpaired electrons (**Figure 19.35**). Complexes such as the $[Fe(H_2O)_6]^{2+}$ ion, in which the electrons are unpaired because the crystal field splitting is not large enough to cause them to pair, are called **high-spin complexes** because the number of unpaired electrons (spins) is maximized.

A similar line of reasoning shows why the $[Fe(CN)_6]^{3-}$ ion is a low-spin complex with only one unpaired electron, whereas both the $[Fe(H_2O)_6]^{3+}$ and $[FeF_6]^{3-}$ ions are high-spin complexes with five unpaired electrons.

Example 19.7

High- and Low-Spin Complexes

Predict the number of unpaired electrons.

(a) $K_3[CrI_6]$

(b) $[Cu(en)_2(H_2O)_2]Cl_2$

(c) $Na_3[Co(NO_2)_6]$

Solution

The complexes are octahedral.

(a) Cr^{3+} has a d^3 configuration. These electrons will all be unpaired.

(b) Cu^{2+} is d^9, so there will be one unpaired electron.

(c) Co^{3+} has d^6 valence electrons, so the crystal field splitting will determine how many are paired. Nitrite is a strong-field ligand, so the complex will be low spin. Six electrons will go in the t_{2g} orbitals, leaving 0 unpaired.

Check Your Learning

The size of the crystal field splitting only influences the arrangement of electrons when there is a choice between pairing electrons and filling the higher-energy orbitals. For which *d*-electron configurations will there be a difference between high- and low-spin configurations in octahedral complexes?

Answer: d^4, d^5, d^6, and d^7

Example 19.8

CFT for Other Geometries

CFT is applicable to molecules in geometries other than octahedral. In octahedral complexes, remember that the lobes of the e_g set point directly at the ligands. For tetrahedral complexes, the d orbitals remain in place, but now we have only four ligands located between the axes (**Figure 19.36**). None of the orbitals points directly at the tetrahedral ligands. However, the e_g set (along the Cartesian axes) overlaps with the ligands less than does the t_{2g} set. By analogy with the octahedral case, predict the energy diagram for the d orbitals in a tetrahedral crystal field. To avoid confusion, the octahedral e_g set becomes a tetrahedral e set, and the octahedral t_{2g} set becomes a t_2 set.

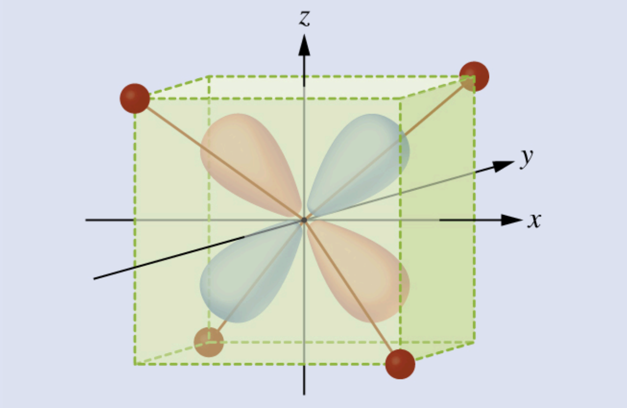
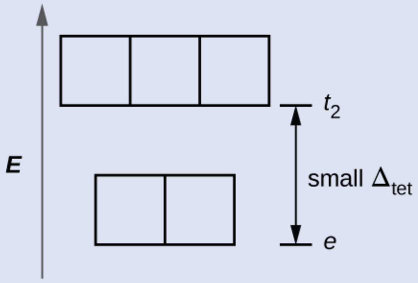


Figure 19.36 This diagram shows the orientation of the tetrahedral ligands with respect to the axis system for the orbitals.

Solution

Since CFT is based on electrostatic repulsion, the orbitals closer to the ligands will be destabilized and raised in energy relative to the other set of orbitals. The splitting is less than for octahedral complexes because the overlap is less, so Δ_{tet} is usually small $\left(\Delta_{\text{tet}} = \frac{4}{9}\Delta_{\text{oct}}\right)$:



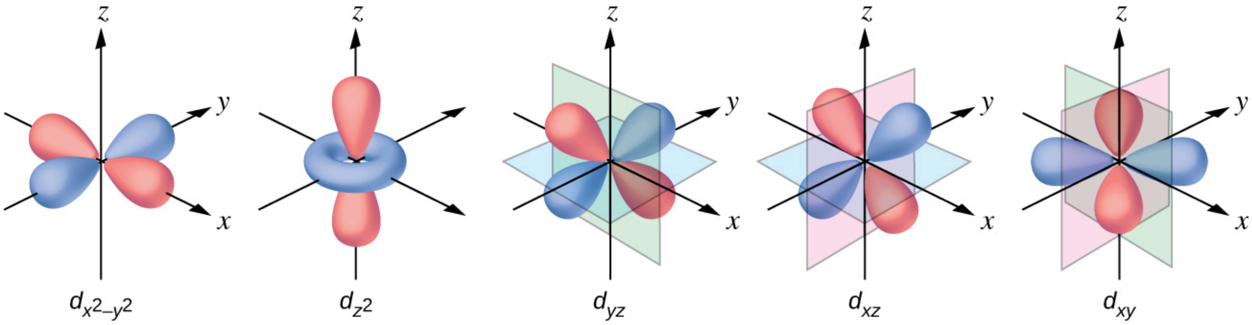
Check Your Learning

Explain how many unpaired electrons a tetrahedral d^4 ion will have.

Answer: 4; because Δ_{tet} is small, all tetrahedral complexes are high spin and the electrons go into the t_2

orbitals before pairing

The other common geometry is square planar. It is possible to consider a square planar geometry as an octahedral structure with a pair of *trans* ligands removed. The removed ligands are assumed to be on the *z*-axis. This changes the distribution of the *d* orbitals, as orbitals on or near the *z*-axis become more stable, and those on or near the *x*- or *y*-axes become less stable. This results in the octahedral t_{2g} and the e_g sets splitting and gives a more complicated pattern with no simple Δ_{oct}. The basic pattern is:



Magnetic Moments of Molecules and Ions

Experimental evidence of magnetic measurements supports the theory of high- and low-spin complexes. Remember that molecules such as O_2 that contain unpaired electrons are paramagnetic. Paramagnetic substances are attracted to magnetic fields. Many transition metal complexes have unpaired electrons and hence are paramagnetic. Molecules such as N_2 and ions such as Na^+ and $[Fe(CN)_6]^{4-}$ that contain no unpaired electrons are diamagnetic. Diamagnetic substances have a slight tendency to be repelled by magnetic fields.

When an electron in an atom or ion is unpaired, the magnetic moment due to its spin makes the entire atom or ion paramagnetic. The size of the magnetic moment of a system containing unpaired electrons is related directly to the number of such electrons: the greater the number of unpaired electrons, the larger the magnetic moment. Therefore, the observed magnetic moment is used to determine the number of unpaired electrons present. The measured magnetic moment of low-spin d^6 $[Fe(CN)_6]^{4-}$ confirms that iron is diamagnetic, whereas high-spin d^6 $[Fe(H_2O)_6]^{2+}$ has four unpaired electrons with a magnetic moment that confirms this arrangement.

Colors of Transition Metal Complexes

When atoms or molecules absorb light at the proper frequency, their electrons are excited to higher-energy orbitals. For many main group atoms and molecules, the absorbed photons are in the ultraviolet range of the electromagnetic spectrum, which cannot be detected by the human eye. For coordination compounds, the energy difference between the *d* orbitals often allows photons in the visible range to be absorbed.

The human eye perceives a mixture of all the colors, in the proportions present in sunlight, as white light. Complementary colors, those located across from each other on a color wheel, are also used in color vision. The eye perceives a mixture of two complementary colors, in the proper proportions, as white light. Likewise, when a color is missing from white light, the eye sees its complement. For example, when red photons are absorbed from white light, the eyes see the color green. When violet photons are removed from white light, the eyes see lemon yellow. The blue color of the $[Cu(NH_3)_4]^{2+}$ ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green (**Figure 19.37**).

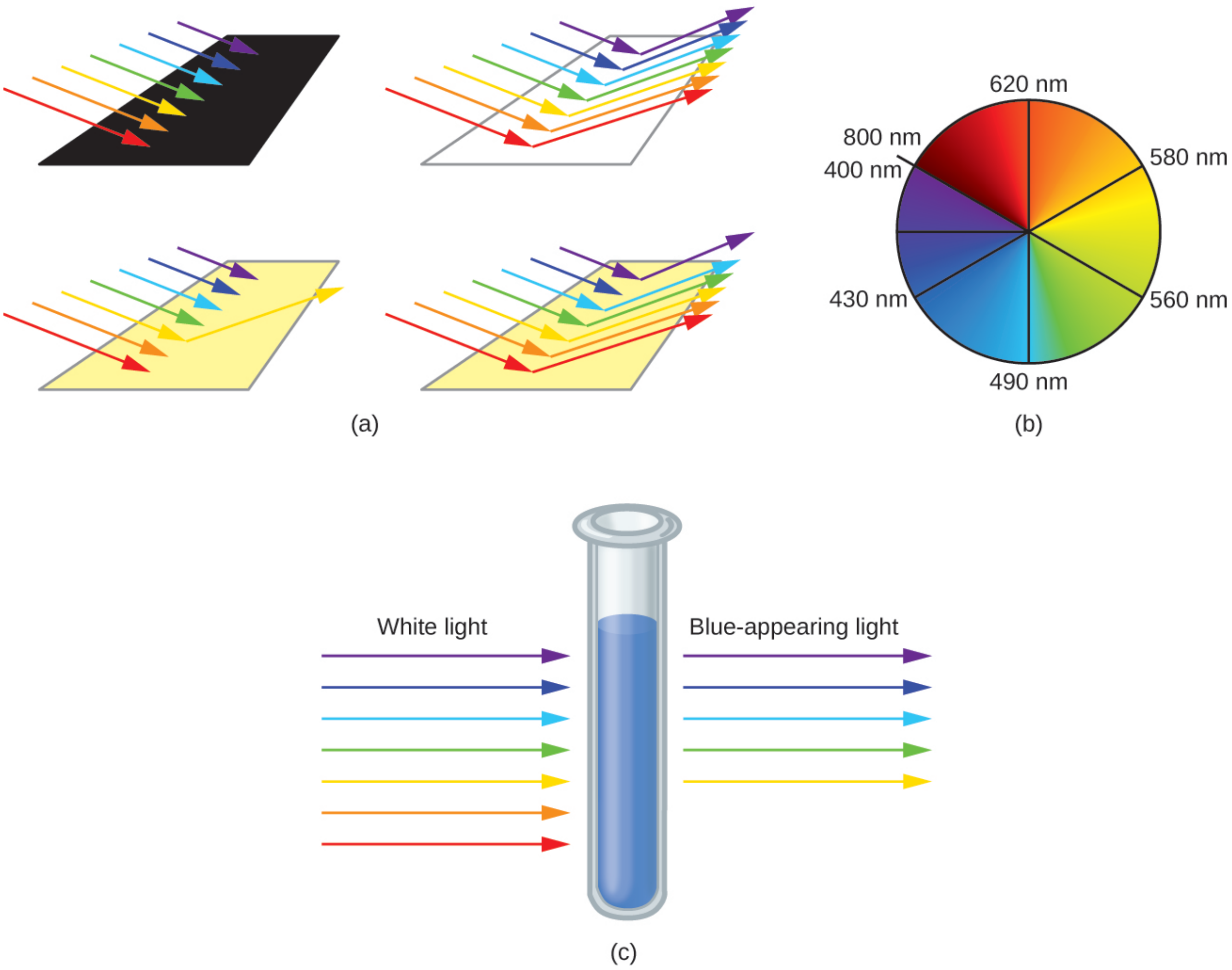


Figure 19.37 (a) An object is black if it absorbs all colors of light. If it reflects all colors of light, it is white. An object has a color if it absorbs all colors except one, such as this yellow strip. The strip also appears yellow if it absorbs the complementary color from white light (in this case, indigo). (b) Complementary colors are located directly across from one another on the color wheel. (c) A solution of $[Cu(NH_3)_4]^{2+}$ ions absorbs red and orange light, so the transmitted light appears as the complementary color, blue.

Example 19.9

Colors of Complexes

The octahedral complex $[Ti(H_2O)_6]^{3+}$ has a single *d* electron. To excite this electron from the ground state t_{2g} orbital to the e_g orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to Δ_{oct} and occurs at 499 nm. Calculate the value of Δ_{oct} in Joules and predict what color the solution will appear.

Solution

Using Planck's equation (refer to the section on electromagnetic energy), we calculate:

$$v = \frac{c}{\lambda} \text{ so } \frac{3.00 \times 10^{8} \text{ m/s}}{\frac{499 \text{ nm} \times 1 \text{ m}}{10^{9} \text{ nm}}} = 6.01 \times 10^{14} \text{ Hz}$$

$$E = hnu \text{ so } 6.63 \times 10^{-34} \text{ J·s} \times 6.01 \times 10^{14} \text{ Hz} = 3.99 \times 10^{-19} \text{ Joules/ion}$$

Because the complex absorbs 600 nm (orange) through 450 (blue), the indigo, violet, and red wavelengths will be transmitted, and the complex will appear purple.

Check Your Learning

A complex that appears green, absorbs photons of what wavelengths?

Answer: red, 620–800 nm

Small changes in the relative energies of the orbitals that electrons are transitioning between can lead to drastic shifts in the color of light absorbed. Therefore, the colors of coordination compounds depend on many factors. As shown in **Figure 19.38**, different aqueous metal ions can have different colors. In addition, different oxidation states of one metal can produce different colors, as shown for the vanadium complexes in the link below.

Figure 19.38 The partially filled *d* orbitals of the stable ions Cr^{3+}(*aq*), Fe^{3+}(*aq*), and Co^{2+}(*aq*) (left, center and right, respectively) give rise to various colors. (credit: Sahar Atwa)

The specific ligands coordinated to the metal center also influence the color of coordination complexes. For example, the iron(II) complex $[Fe(H_2O)_6]SO_4$ appears blue-green because the high-spin complex absorbs photons in the red wavelengths (**Figure 19.39**). In contrast, the low-spin iron(II) complex $K_4[Fe(CN)_6]$ appears pale yellow because it absorbs higher-energy violet photons.

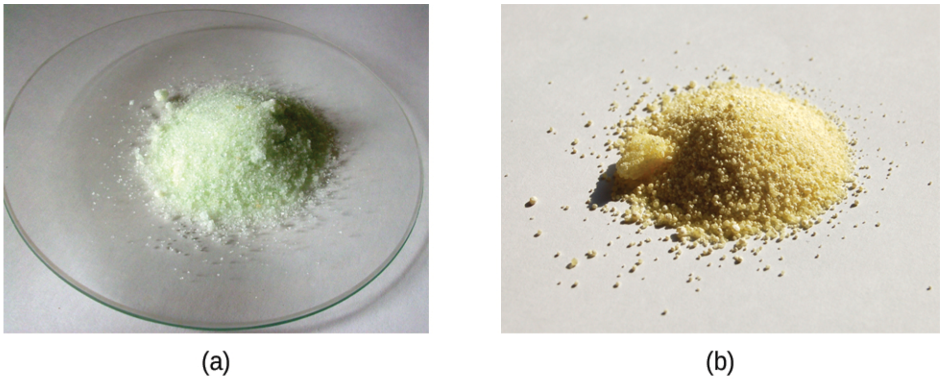


Figure 19.39 Both (a) hexaaquairon(II) sulfate and (b) potassium hexacyanoferrate(II) contain d^6 iron(II) octahedral metal centers, but they absorb photons in different ranges of the visible spectrum.

Link to Learning

Watch this **video (http://openstaxcollege.org/l/16vanadium)** of the reduction of vanadium complexes to observe the colorful effect of changing oxidation states.

In general, strong-field ligands cause a large split in the energies of *d* orbitals of the central metal atom (large Δ_{oct}). Transition metal coordination compounds with these ligands are yellow, orange, or red because they absorb higher-energy violet or blue light. On the other hand, coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

A coordination compound of the Cu^+ ion has a d^{10} configuration, and all the e_g orbitals are filled. To excite an electron to a higher level, such as the 4*p* orbital, photons of very high energy are necessary. This energy corresponds to very short wavelengths in the ultraviolet region of the spectrum. No visible light is absorbed, so the eye sees no change, and the compound appears white or colorless. A solution containing $[Cu(CN)_2]^-$, for example, is colorless. On the other hand, octahedral Cu^{2+} complexes have a vacancy in the e_g orbitals, and electrons can be excited to this level. The wavelength (energy) of the light absorbed corresponds to the visible part of the spectrum, and Cu^{2+} complexes are almost always colored—blue, blue-green violet, or yellow (**Figure 19.40**). Although CFT successfully describes many properties of coordination complexes, molecular orbital explanations (beyond the introductory scope provided here) are required to understand fully the behavior of coordination complexes.

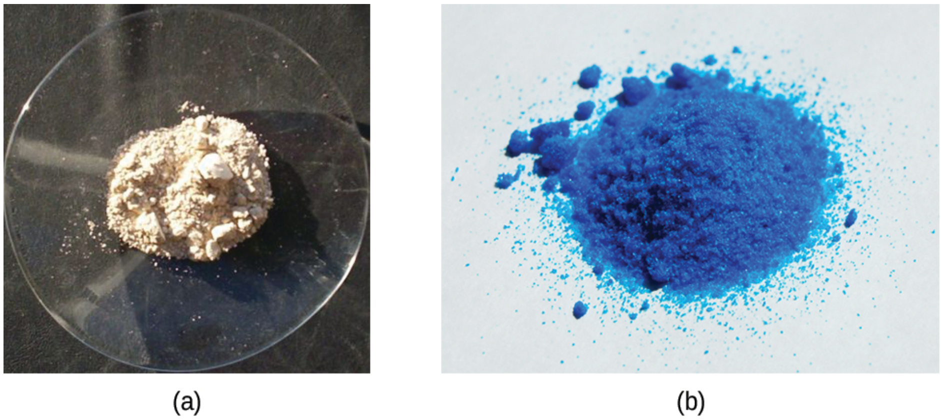


Figure 19.40 (a) Copper(I) complexes with d^{10} configurations such as CuI tend to be colorless, whereas (b) d^9 copper(II) complexes such as $Cu(NO_3)_2{\cdot}5H_2O$ are brightly colored.

Key Terms

actinide series (also, actinoid series) actinium and the elements in the second row or the *f*-block, atomic numbers 89–103

bidentate ligand ligand that coordinates to one central metal through coordinate bonds from two different atoms

central metal ion or atom to which one or more ligands is attached through coordinate covalent bonds

chelate complex formed from a polydentate ligand attached to a central metal

chelating ligand ligand that attaches to a central metal ion by bonds from two or more donor atoms

***cis* configuration** configuration of a geometrical isomer in which two similar groups are on the same side of an imaginary reference line on the molecule

coordination compound stable compound in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons

coordination compound substance consisting of atoms, molecules, or ions attached to a central atom through Lewis acid-base interactions

coordination number number of coordinate covalent bonds to the central metal atom in a complex or the number of closest contacts to an atom in a crystalline form

coordination sphere central metal atom or ion plus the attached ligands of a complex

crystal field splitting (Δ_{oct}) difference in energy between the t_{2g} and e_g sets or *t* and *e* sets of orbitals

crystal field theory model that explains the energies of the orbitals in transition metals in terms of electrostatic interactions with the ligands but does not include metal ligand bonding

***d*-block element** one of the elements in groups 3–11 with valence electrons in *d* orbitals

donor atom atom in a ligand with a lone pair of electrons that forms a coordinate covalent bond to a central metal

e_g orbitals set of two *d* orbitals that are oriented on the Cartesian axes for coordination complexes; in octahedral complexes, they are higher in energy than the t_{2g} orbitals

***f*-block element** (also, inner transition element) one of the elements with atomic numbers 58–71 or 90–103 that have valence electrons in *f* orbitals; they are frequently shown offset below the periodic table

first transition series transition elements in the fourth period of the periodic table (first row of the *d*-block), atomic numbers 21–29

fourth transition series transition elements in the seventh period of the periodic table (fourth row of the *d*-block), atomic numbers 89 and 104–111

geometric isomers isomers that differ in the way in which atoms are oriented in space relative to each other, leading to different physical and chemical properties

high-spin complex complex in which the electrons maximize the total electron spin by singly populating all of the orbitals before pairing two electrons into the lower-energy orbitals

hydrometallurgy process in which a metal is separated from a mixture by first converting it into soluble ions, extracting the ions, and then reducing the ions to precipitate the pure metal

ionization isomer (or coordination isomer) isomer in which an anionic ligand is replaced by the counter ion in the inner coordination sphere

lanthanide series (also, lanthanoid series) lanthanum and the elements in the first row or the *f*-block, atomic numbers 57–71

ligand ion or neutral molecule attached to the central metal ion in a coordination compound

linkage isomer coordination compound that possesses a ligand that can bind to the transition metal in two different ways (CN^- vs. NC^-)

low-spin complex complex in which the electrons minimize the total electron spin by pairing in the lower-energy orbitals before populating the higher-energy orbitals

monodentate ligand that attaches to a central metal through just one coordinate covalent bond

optical isomer (also, enantiomer) molecule that is a nonsuperimposable mirror image with identical chemical and physical properties, except when it reacts with other optical isomers

pairing energy (P) energy required to place two electrons with opposite spins into a single orbital

platinum metals group of six transition metals consisting of ruthenium, osmium, rhodium, iridium, palladium, and platinum that tend to occur in the same minerals and demonstrate similar chemical properties

polydentate ligand ligand that is attached to a central metal ion by bonds from two or more donor atoms, named with prefixes specifying how many donors are present (e.g., hexadentate = six coordinate bonds formed)

rare earth element collection of 17 elements including the lanthanides, scandium, and yttrium that often occur together and have similar chemical properties, making separation difficult

second transition series transition elements in the fifth period of the periodic table (second row of the *d*-block), atomic numbers 39–47

smelting process of extracting a pure metal from a molten ore

spectrochemical series ranking of ligands according to the magnitude of the crystal field splitting they induce

steel material made from iron by removing impurities in the iron and adding substances that produce alloys with properties suitable for specific uses

strong-field ligand ligand that causes larger crystal field splittings

superconductor material that conducts electricity with no resistance

t_{2g} orbitals set of three *d* orbitals aligned between the Cartesian axes for coordination complexes; in octahedral complexes, they are lowered in energy compared to the e_g orbitals according to CFT

third transition series transition elements in the sixth period of the periodic table (third row of the *d*-block), atomic numbers 57 and 72–79

***trans* configuration** configuration of a geometrical isomer in which two similar groups are on opposite sides of an imaginary reference line on the molecule

weak-field ligand ligand that causes small crystal field splittings

Summary

19.1 Occurrence, Preparation, and Properties of Transition Metals and Their Compounds

The transition metals are elements with partially filled *d* orbitals, located in the *d*-block of the periodic table. The reactivity of the transition elements varies widely from very active metals such as scandium and iron to almost inert elements, such as the platinum metals. The type of chemistry used in the isolation of the elements from their ores depends upon the concentration of the element in its ore and the difficulty of reducing ions of the elements to the metals. Metals that are more active are more difficult to reduce.

Transition metals exhibit chemical behavior typical of metals. For example, they oxidize in air upon heating and react with elemental halogens to form halides. Those elements that lie above hydrogen in the activity series react with acids, producing salts and hydrogen gas. Oxides, hydroxides, and carbonates of transition metal compounds in low oxidation states are basic. Halides and other salts are generally stable in water, although oxygen must be excluded in some cases. Most transition metals form a variety of stable oxidation states, allowing them to demonstrate a wide range of chemical reactivity.

19.2 Coordination Chemistry of Transition Metals

The transition elements and main group elements can form coordination compounds, or complexes, in which a central metal atom or ion is bonded to one or more ligands by coordinate covalent bonds. Ligands with more than one donor atom are called polydentate ligands and form chelates. The common geometries found in complexes are tetrahedral and square planar (both with a coordination number of four) and octahedral (with a coordination number of six). *Cis* and *trans* configurations are possible in some octahedral and square planar complexes. In addition to these geometrical isomers, optical isomers (molecules or ions that are mirror images but not superimposable) are possible in certain octahedral complexes. Coordination complexes have a wide variety of uses including oxygen transport in blood, water purification, and pharmaceutical use.

19.3 Spectroscopic and Magnetic Properties of Coordination Compounds

Crystal field theory treats interactions between the electrons on the metal and the ligands as a simple electrostatic effect. The presence of the ligands near the metal ion changes the energies of the metal *d* orbitals relative to their energies in the free ion. Both the color and the magnetic properties of a complex can be attributed to this crystal field splitting. The magnitude of the splitting (Δ_{oct}) depends on the nature of the ligands bonded to the metal. Strong-field ligands produce large splitting and favor low-spin complexes, in which the t_{2g} orbitals are completely filled before any electrons occupy the e_g orbitals. Weak-field ligands favor formation of high-spin complexes. The t_{2g} and the e_g orbitals are singly occupied before any are doubly occupied.

Exercises

19.1 Occurrence, Preparation, and Properties of Transition Metals and Their Compounds

1. Write the electron configurations for each of the following elements:

(a) Sc

(b) Ti

(c) Cr

(d) Fe

(e) Ru

2. Write the electron configurations for each of the following elements and its ions:

(a) Ti

(b) Ti^{2+}

(c) Ti^{3+}

(d) Ti^{4+}

3. Write the electron configurations for each of the following elements and its 3+ ions:

(a) La

(b) Sm

(c) Lu

4. Why are the lanthanoid elements not found in nature in their elemental forms?

5. Which of the following elements is most likely to be used to prepare La by the reduction of La_2O_3: Al, C, or Fe? Why?

6. Which of the following is the strongest oxidizing agent: $VO_4{}^{3}$, $CrO_4{}^{2-}$, or $MnO_4{}^{-}$?

7. Which of the following elements is most likely to form an oxide with the formula MO_3: Zr, Nb, or Mo?

8. The following reactions all occur in a blast furnace. Which of these are redox reactions?

(a) $3Fe_2O_3(s) + CO(g) \longrightarrow 2Fe_3O_4(s) + CO_2(g)$

(b) $Fe_3O_4(s) + CO(g) \longrightarrow 3FeO(s) + CO_2(g)$

(c) $FeO(s) + CO(g) \longrightarrow Fe(l) + CO_2(g)$

(d) $C(s) + O_2(g) \longrightarrow CO_2(g)$

(e) $C(s) + CO_2(g) \longrightarrow 2CO(g)$

(f) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

(g) $CaO(s) + SiO_2(s) \longrightarrow CaSiO_3(l)$

9. Why is the formation of slag useful during the smelting of iron?

10. Would you expect an aqueous manganese(VII) oxide solution to have a pH greater or less than 7.0? Justify your answer.

11. Iron(II) can be oxidized to iron(III) by dichromate ion, which is reduced to chromium(III) in acid solution. A 2.5000-g sample of iron ore is dissolved and the iron converted into iron(II). Exactly 19.17 mL of 0.0100 M $Na_2Cr_2O_7$ is required in the titration. What percentage of the ore sample was iron?

12. How many cubic feet of air at a pressure of 760 torr and 0 °C is required per ton of Fe_2O_3 to convert that Fe_2O_3 into iron in a blast furnace? For this exercise, assume air is 19% oxygen by volume.

13. Find the potentials of the following electrochemical cell:

$Cd \mid Cd^{2+}, M = 0.10 \parallel Ni^{2+}, M = 0.50 \mid Ni$

14. A 2.5624-g sample of a pure solid alkali metal chloride is dissolved in water and treated with excess silver nitrate. The resulting precipitate, filtered and dried, weighs 3.03707 g. What was the percent by mass of chloride ion in the original compound? What is the identity of the salt?

15. The standard reduction potential for the reaction $[Co(H_2O)_6]^{3+}(aq) + e^- \longrightarrow [Co(H_2O)_6]^{2+}(aq)$ is about 1.8 V. The reduction potential for the reaction $[Co(NH_3)_6]^{3+}(aq) + e^- \longrightarrow [Co(NH_3)_6]^{2+}(aq)$ is +0.1 V. Calculate the cell potentials to show whether the complex ions, $[Co(H_2O)_6]^{2+}$ and/or $[Co(NH_3)_6]^{2+}$, can be oxidized to the corresponding cobalt(III) complex by oxygen.

16. Predict the products of each of the following reactions. (Note: In addition to using the information in this chapter, also use the knowledge you have accumulated at this stage of your study, including information on the prediction of reaction products.)

(a) $\text{MnCO}_3(s) + \text{HI}(aq) \longrightarrow$

(b) $\text{CoO}(s) + \text{O}_2(g) \longrightarrow$

(c) $\text{La}(s) + \text{O}_2(g) \longrightarrow$

(d) $\text{V}(s) + \text{VCl}_4(s) \longrightarrow$

(e) $\text{Co}(s) + xs\text{F}_2(g) \longrightarrow$

(f) $\text{CrO}_3(s) + \text{CsOH}(aq) \longrightarrow$

17. Predict the products of each of the following reactions. (Note: In addition to using the information in this chapter, also use the knowledge you have accumulated at this stage of your study, including information on the prediction of reaction products.)

(a) $\text{Fe}(s) + \text{H}_2\text{SO}_4(aq) \longrightarrow$

(b) $\text{FeCl}_3(aq) + \text{NaOH}(aq) \longrightarrow$

(c) $\text{Mn(OH)}_2(s) + \text{HBr}(aq) \longrightarrow$

(d) $\text{Cr}(s) + \text{O}_2(g) \longrightarrow$

(e) $\text{Mn}_2\text{O}_3(s) + \text{HCl}(aq) \longrightarrow$

(f) $\text{Ti}(s) + xs\text{F}_2(g) \longrightarrow$

18. Describe the electrolytic process for refining copper.

19. Predict the products of the following reactions and balance the equations.

(a) Zn is added to a solution of $Cr_2(SO_4)_3$ in acid.

(b) $FeCl_2$ is added to a solution containing an excess of $\text{Cr}_2\text{O}_7{}^{2-}$ in hydrochloric acid.

(c) Cr^{2+} is added to $\text{Cr}_2\text{O}_7{}^{2-}$ in acid solution.

(d) Mn is heated with CrO_3.

(e) CrO is added to $2HNO_3$ in water.

(f) $FeCl_3$ is added to an aqueous solution of NaOH.

20. What is the gas produced when iron(II) sulfide is treated with a nonoxidizing acid?

21. Predict the products of each of the following reactions and then balance the chemical equations.

(a) Fe is heated in an atmosphere of steam.

(b) NaOH is added to a solution of $Fe(NO_3)_3$.

(c) $FeSO_4$ is added to an acidic solution of $KMnO_4$.

(d) Fe is added to a dilute solution of H_2SO_4.

(e) A solution of $Fe(NO_3)_2$ and HNO_3 is allowed to stand in air.

(f) $FeCO_3$ is added to a solution of $HClO_4$.

(g) Fe is heated in air.

22. Balance the following equations by oxidation-reduction methods; note that *three* elements change oxidation state.

$\text{Co(NO}_3)_2(s) \longrightarrow \text{Co}_2\text{O}_3(s) + \text{NO}_2(g) + \text{O}_2(g)$

23. Dilute sodium cyanide solution is slowly dripped into a slowly stirred silver nitrate solution. A white precipitate forms temporarily but dissolves as the addition of sodium cyanide continues. Use chemical equations to explain this observation. Silver cyanide is similar to silver chloride in its solubility.

24. Predict which will be more stable, $[CrO_4]^{2-}$ or $[WO_4]^{2-}$, and explain.

25. Give the oxidation state of the metal for each of the following oxides of the first transition series. (Hint: Oxides of formula M_3O_4 are examples of *mixed valence compounds* in which the metal ion is present in more than one oxidation state. It is possible to write these compound formulas in the equivalent format $MO{\cdot}M_2O_3$, to permit estimation of the metal's two oxidation states.)

(a) Sc_2O_3

(b) TiO_2

(c) V_2O_5

(d) CrO_3

(e) MnO_2

(f) Fe_3O_4

(g) Co_3O_4

(h) NiO

(i) Cu_2O

19.2 Coordination Chemistry of Transition Metals

26. Indicate the coordination number for the central metal atom in each of the following coordination compounds:

(a) $[Pt(H_2O)_2Br_2]$

(b) $[Pt(NH_3)(py)(Cl)(Br)]$ (py = pyridine, C_5H_5N)

(c) $[Zn(NH_3)_2Cl_2]$

(d) $[Zn(NH_3)(py)(Cl)(Br)]$

(e) $[Ni(H_2O)_4Cl_2]$

(f) $[Fe(en)_2(CN)_2]^+$ (en = ethylenediamine, $C_2H_8N_2$)

27. Give the coordination numbers and write the formulas for each of the following, including all isomers where appropriate:

(a) tetrahydroxozincate(II) ion (tetrahedral)

(b) hexacyanopalladate(IV) ion

(c) dichloroaurate(I) ion (note that *aurum* is Latin for "gold")

(d) diamminedichloroplatinum(II)

(e) potassium diamminetetrachlorochromate(III)

(f) hexaamminecobalt(III) hexacyanochromate(III)

(g) dibromobis(ethylenediamine) cobalt(III) nitrate

28. Give the coordination number for each metal ion in the following compounds:

(a) $[Co(CO_3)_3]^{3-}$ (note that $CO_3{}^{2-}$ is bidentate in this complex)

(b) $[Cu(NH_3)_4]^{2+}$

(c) $[Co(NH_3)_4Br_2]_2(SO_4)_3$

(d) $[Pt(NH_3)_4][PtCl_4]$

(e) $[Cr(en)_3](NO_3)_3$

(f) $[Pd(NH_3)_2Br_2]$ (square planar)

(g) $K_3[Cu(Cl)_5]$

(h) $[Zn(NH_3)_2Cl_2]$

29. Sketch the structures of the following complexes. Indicate any *cis*, *trans*, and optical isomers.

(a) $[Pt(H_2O)_2Br_2]$ (square planar)

(b) $[Pt(NH_3)(py)(Cl)(Br)]$ (square planar, py = pyridine, C_5H_5N)

(c) $[Zn(NH_3)_3Cl]^+$ (tetrahedral)

(d) $[Pt(NH_3)_3Cl]^+$ (square planar)

(e) $[Ni(H_2O)_4Cl_2]$

(f) $[Co(C_2O_4)_2Cl_2]^{3-}$ (note that $C_2O_4{}^{2-}$ is the bidentate oxalate ion, $-O_2CCO_2{}^-$)

30. Draw diagrams for any *cis*, *trans*, and optical isomers that could exist for the following (en is ethylenediamine):

(a) $[Co(en)_2(NO_2)Cl]^+$

(b) $[Co(en)_2Cl_2]^+$

(c) $[Pt(NH_3)_2Cl_4]$

(d) $[Cr(en)_3]^{3+}$

(e) $[Pt(NH_3)_2Cl_2]$

31. Name each of the compounds or ions given in **Exercise 19.28**, including the oxidation state of the metal.

32. Name each of the compounds or ions given in **Exercise 19.30**.

33. Specify whether the following complexes have isomers.

(a) tetrahedral $[Ni(CO)_2(Cl)_2]$

(b) trigonal bipyramidal $[Mn(CO)_4NO]$

(c) $[Pt(en)_2Cl_2]Cl_2$

34. Predict whether the carbonate ligand $CO_3{}^{2-}$ will coordinate to a metal center as a monodentate, bidentate, or tridentate ligand.

35. Draw the geometric, linkage, and ionization isomers for $[CoCl_5CN][CN]$.

19.3 Spectroscopic and Magnetic Properties of Coordination Compounds

36. Determine the number of unpaired electrons expected for $[Fe(NO_2)_6]^{3-}$and for $[FeF_6]^{3-}$ in terms of crystal field theory.

37. Draw the crystal field diagrams for $[Fe(NO_2)_6]^{4-}$ and $[FeF_6]^{3-}$. State whether each complex is high spin or low spin, paramagnetic or diamagnetic, and compare Δ_{oct} to P for each complex.

38. Give the oxidation state of the metal, number of *d* electrons, and the number of unpaired electrons predicted for $[Co(NH_3)_6]Cl_3$.

39. The solid anhydrous solid $CoCl_2$ is blue in color. Because it readily absorbs water from the air, it is used as a humidity indicator to monitor if equipment (such as a cell phone) has been exposed to excessive levels of moisture. Predict what product is formed by this reaction, and how many unpaired electrons this complex will have.

40. Is it possible for a complex of a metal in the transition series to have six unpaired electrons? Explain.

41. How many unpaired electrons are present in each of the following?

(a) $[CoF_6]^{3-}$ (high spin)

(b) $[Mn(CN)_6]^{3-}$ (low spin)

(c) $[Mn(CN)_6]^{4-}$ (low spin)

(d) $[MnCl_6]^{4-}$ (high spin)

(e) $[RhCl_6]^{3-}$ (low spin)

42. Explain how the diphosphate ion, $[O_3P{-}O{-}PO_3]^{4-}$, can function as a water softener that prevents the precipitation of Fe^{2+} as an insoluble iron salt.

43. For complexes of the same metal ion with no change in oxidation number, the stability increases as the number of electrons in the t_{2g} orbitals increases. Which complex in each of the following pairs of complexes is more stable?

(a) $[Fe(H_2O)_6]^{2+}$ or $[Fe(CN)_6]^{4-}$

(b) $[Co(NH_3)_6]^{3+}$ or $[CoF_6]^{3-}$

(c) $[Mn(CN)_6]^{4-}$ or $[MnCl_6]^{4-}$

44. Trimethylphosphine, $P(CH_3)_3$, can act as a ligand by donating the lone pair of electrons on the phosphorus atom. If trimethylphosphine is added to a solution of nickel(II) chloride in acetone, a blue compound that has a molecular mass of approximately 270 g and contains 21.5% Ni, 26.0% Cl, and 52.5% $P(CH_3)_3$ can be isolated. This blue compound does not have any isomeric forms. What are the geometry and molecular formula of the blue compound?

45. Would you expect the complex $[Co(en)_3]Cl_3$ to have any unpaired electrons? Any isomers?

46. Would you expect the $Mg_3[Cr(CN)_6]_2$ to be diamagnetic or paramagnetic? Explain your reasoning.

47. Would you expect salts of the gold(I) ion, Au^+, to be colored? Explain.

48. $[CuCl_4]^{2-}$ is green. $[Cu(H_2O)_6]^{2+}$is blue. Which absorbs higher-energy photons? Which is predicted to have a larger crystal field splitting?

Chapter 20

Nuclear Chemistry

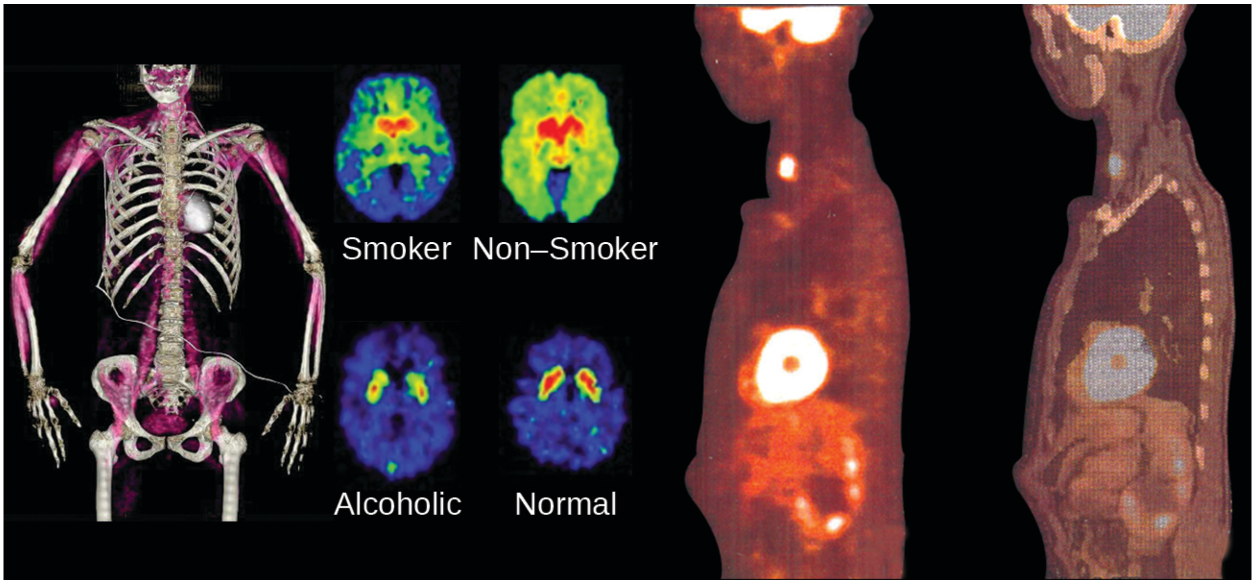


Figure 20.1 Nuclear chemistry provides the basis for many useful diagnostic and therapeutic methods in medicine, such as these positron emission tomography (PET) scans. The PET/computed tomography scan on the left shows muscle activity. The brain scans in the center show chemical differences in dopamine signaling in the brains of addicts and nonaddicts. The images on the right show an oncological application of PET scans to identify lymph node metastasis.

Chapter Outline

Introduction

The chemical reactions that we have considered in previous chapters involve changes in the *electronic* structure of the species involved, that is, the arrangement of the electrons around atoms, ions, or molecules. *Nuclear* structure, the numbers of protons and neutrons within the nuclei of the atoms involved, remains unchanged during chemical reactions.

This chapter will introduce the topic of nuclear chemistry, which began with the discovery of radioactivity in 1896 by French physicist Antoine Becquerel and has become increasingly important during the twentieth and twenty-first centuries, providing the basis for various technologies related to energy, medicine, geology, and many other areas.

20.1 Nuclear Structure and Stability

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

- Describe nuclear structure in terms of protons, neutrons, and electrons
- Calculate mass defect and binding energy for nuclei
- Explain trends in the relative stability of nuclei

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of $_{1}^{1}\text{H},$ neutrons. Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term **nuclide** and identify it by the notation $_{Z}^{A}\text{X},$ where X is the symbol for the element, A is the mass number, and Z is the atomic number (for example, $_{6}^{14}\text{C}).$ Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, $_{6}^{14}\text{C}$ is called “carbon-14.”

Protons and neutrons, collectively called **nucleons**, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm^3. If the earth’s density were equal to the average nuclear density, the earth’s radius would be only about 200 meters (earth’s actual radius is approximately 6.4×10^6 meters, 30,000 times larger). **Example 20.1** demonstrates just how great nuclear densities can be in the natural world.

Example 20.1

Density of a Neutron Star

Neutron stars form when the core of a very massive star undergoes gravitational collapse, causing the star’s outer layers to explode in a supernova. Composed almost completely of neutrons, they are the densest-known stars in the universe, with densities comparable to the average density of an atomic nucleus. A neutron star in a faraway galaxy has a mass equal to 2.4 solar masses (1 solar mass = $\text{M}_{\odot}$ = mass of the sun = 1.99×10^{30} kg) and a diameter of 26 km.

(a) What is the density of this neutron star?

(b) How does this neutron star’s density compare to the density of a uranium nucleus, which has a diameter of about 15 fm (1 fm = 10^{-15} m)?

Solution

We can treat both the neutron star and the U-235 nucleus as spheres. Then the density for both is given by:

$$d = \frac{m}{V} \qquad \text{with} \qquad V = \frac{4}{3}\pi r^3$$

(a) The radius of the neutron star is $\frac{1}{2} \times 26\text{ km} = \frac{1}{2} \times 2.6 \times 10^4\text{ m} = 1.3 \times 10^4\text{ m},$ so the density of the neutron star is:

$$d = \frac{m}{V} = \frac{m}{\frac{4}{3}\pi r^3} = \frac{2.4\left(1.99 \times 10^{30}\ \text{kg}\right)}{\frac{4}{3}\pi\left(1.3 \times 10^{4}\ \text{m}\right)^3} = 5.2 \times 10^{17}\ \text{kg/m}^3$$

(b) The radius of the U-235 nucleus is $\frac{1}{2} \times 15 \times 10^{-15}\ \text{m} = 7.5 \times 10^{-15}\ \text{m},$ so the density of the U-235 nucleus is:

$$d = \frac{m}{V} = \frac{m}{\frac{4}{3}\pi r^3} = \frac{235\ \text{amu}\left(\frac{1.66 \times 10^{-27}\ \text{kg}}{1\ \text{amu}}\right)}{\frac{4}{3}\pi\left(7.5 \times 10^{-15}\ \text{m}\right)^3} = 2.2 \times 10^{17}\ \text{kg/m}^3$$

These values are fairly similar (same order of magnitude), but the nucleus is more than twice as dense as the neutron star.

Check Your Learning

Find the density of a neutron star with a mass of 1.97 solar masses and a diameter of 13 km, and compare it to the density of a hydrogen nucleus, which has a diameter of 1.75 fm (1 fm = 1 × 10^{-15} m).

Answer: The density of the neutron star is 3.4 × 10^{18} kg/m^3. The density of a hydrogen nucleus is 6.0 × 10^{17} kg/m^3. The neutron star is 5.7 times denser than the hydrogen nucleus.

To hold positively charged protons together in the very small volume of a nucleus requires very strong attractive forces because the positively charged protons repel one another strongly at such short distances. The force of attraction that holds the nucleus together is the **strong nuclear force**. (The strong force is one of the four fundamental forces that are known to exist. The others are the electromagnetic force, the gravitational force, and the nuclear weak force.) This force acts between protons, between neutrons, and between protons and neutrons. It is very different from the electrostatic force that holds negatively charged electrons around a positively charged nucleus (the attraction between opposite charges). Over distances less than 10^{-15} meters and within the nucleus, the strong nuclear force is much stronger than electrostatic repulsions between protons; over larger distances and outside the nucleus, it is essentially nonexistent.

Link to Learning

Visit this website (http://openstaxcollege.org/l/16fourfund) for more information about the four fundamental forces.

Nuclear Binding Energy

As a simple example of the energy associated with the strong nuclear force, consider the helium atom composed of two protons, two neutrons, and two electrons. The total mass of these six subatomic particles may be calculated as:

$$\underset{\text{protons}}{(2 \times 1.0073\ \text{amu})} + \underset{\text{neutrons}}{(2 \times 1.0087\ \text{amu})} + \underset{\text{electrons}}{(2 \times 0.00055\ \text{amu})} = 4.0331\ \text{amu}$$

However, mass spectrometric measurements reveal that the mass of an ${}_{2}^{4}\text{He}$ atom is 4.0026 amu, less than the combined masses of its six constituent subatomic particles. This difference between the calculated and experimentally measured masses is known as the **mass defect** of the atom. In the case of helium, the mass defect indicates a “loss” in mass of 4.0331 amu – 4.0026 amu = 0.0305 amu. The loss in mass accompanying the formation of an atom from protons, neutrons, and electrons is due to the conversion of that mass into energy that is evolved as the atom forms. The **nuclear binding energy** is the energy produced when the atoms’ nucleons are bound together; this is also the energy needed to break a nucleus into its constituent protons and neutrons. In comparison to chemical bond energies, nuclear binding energies are *vastly* greater, as we will learn in this section. Consequently, the energy changes associated with nuclear reactions are vastly greater than are those for chemical reactions.

The conversion between mass and energy is most identifiably represented by the **mass-energy equivalence equation** as stated by Albert Einstein:

$$E = mc^2$$

where E is energy, m is mass of the matter being converted, and c is the speed of light in a vacuum. This equation can be used to find the amount of energy that results when matter is converted into energy. Using this mass-energy equivalence equation, the nuclear binding energy of a nucleus may be calculated from its mass defect, as demonstrated in **Example 20.2**. A variety of units are commonly used for nuclear binding energies, including **electron volts (eV)**, with 1 eV equaling the amount of energy necessary to the move the charge of an electron across an electric potential difference of 1 volt, making 1 eV = 1.602 × 10^{-19} J.

Example 20.2

Calculation of Nuclear Binding Energy

Determine the binding energy for the nuclide ${}^{4}_{2}\text{He}$ in:

(a) joules per mole of nuclei

(b) joules per nucleus

(c) MeV per nucleus

Solution

The mass defect for a ${}^{4}_{2}\text{He}$ nucleus is 0.0305 amu, as shown previously. Determine the binding energy in joules per nuclide using the mass-energy equivalence equation. To accommodate the requested energy units, the mass defect must be expressed in kilograms (recall that 1 J = 1 kg m^2/s^2).

(a) First, express the mass defect in g/mol. This is easily done considering the *numerical equivalence* of atomic mass (amu) and molar mass (g/mol) that results from the definitions of the amu and mole units (refer to the previous discussion in the chapter on atoms, molecules, and ions if needed). The mass defect is therefore 0.0305 g/mol. To accommodate the units of the other terms in the mass-energy equation, the mass must be expressed in kg, since 1 J = 1 kg m^2/s^2. Converting grams into kilograms yields a mass defect of 3.05 × 10^{-5} kg/mol. Substituting this quantity into the mass-energy equivalence equation yields:

$$E = mc^2 = \frac{3.05 \times 10^{-5}\ \text{kg}}{\text{mol}} \times \left(\frac{2.998 \times 10^{8}\ \text{m}}{\text{s}}\right)^2 = 2.74 \times 10^{12}\ \text{kg m}^2\,\text{s}^{-2}\,\text{mol}^{-1}$$

$$= 2.74 \times 10^{12}\ \text{J mol}^{-1} = 2.74\ \text{TJ mol}^{-1}$$

Note that this tremendous amount of energy is associated with the conversion of a very small amount of matter (about 30 mg, roughly the mass of typical drop of water).

(b) The binding energy for a single nucleus is computed from the molar binding energy using Avogadro's number:

$$E = 2.74 \times 10^{12}\ \text{J mol}^{-1} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{nuclei}} = 4.55 \times 10^{-12}\ \text{J} = 4.55\ \text{pJ}$$

(c) Recall that 1 eV = 1.602 × 10^{-19} J. Using the binding energy computed in part (b):

$$E = 4.55 \times 10^{-12}\ \text{J} \times \frac{1\ \text{eV}}{1.602 \times 10^{-19}\ \text{J}} = 2.84 \times 10^{7}\ \text{eV} = 28.4\ \text{MeV}$$

Check Your Learning

What is the binding energy for the nuclide ${}^{19}_{9}\text{F}$ (atomic mass: 18.9984 amu) in MeV per nucleus?

Answer: 148.4 MeV

Because the energy changes for breaking and forming bonds are so small compared to the energy changes for breaking or forming nuclei, the changes in mass during all ordinary chemical reactions are virtually undetectable. As described in the chapter on thermochemistry, the most energetic chemical reactions exhibit enthalpies on the order of *thousands* of kJ/mol, which is equivalent to mass differences in the nanogram range (10^{-9} g). On the other hand, nuclear binding energies are typically on the order of *billions* of kJ/mol, corresponding to mass differences in the milligram range (10^{-3} g).

Nuclear Stability

A nucleus is stable if it cannot be transformed into another configuration without adding energy from the outside. Of the thousands of nuclides that exist, about 250 are stable. A plot of the number of neutrons versus the number of protons for stable nuclei reveals that the stable isotopes fall into a narrow band. This region is known as the **band of stability** (also called the belt, zone, or valley of stability). The straight line in **Figure 20.2** represents nuclei that have a 1:1 ratio of protons to neutrons (n:p ratio). Note that the lighter stable nuclei, in general, have equal numbers of protons and neutrons. For example, nitrogen-14 has seven protons and seven neutrons. Heavier stable nuclei, however, have increasingly more neutrons than protons. For example: iron-56 has 30 neutrons and 26 protons, an n:p ratio of 1.15, whereas the stable nuclide lead-207 has 125 neutrons and 82 protons, an n:p ratio equal to 1.52. This is because larger nuclei have more proton-proton repulsions, and require larger numbers of neutrons to provide compensating strong forces to overcome these electrostatic repulsions and hold the nucleus together.

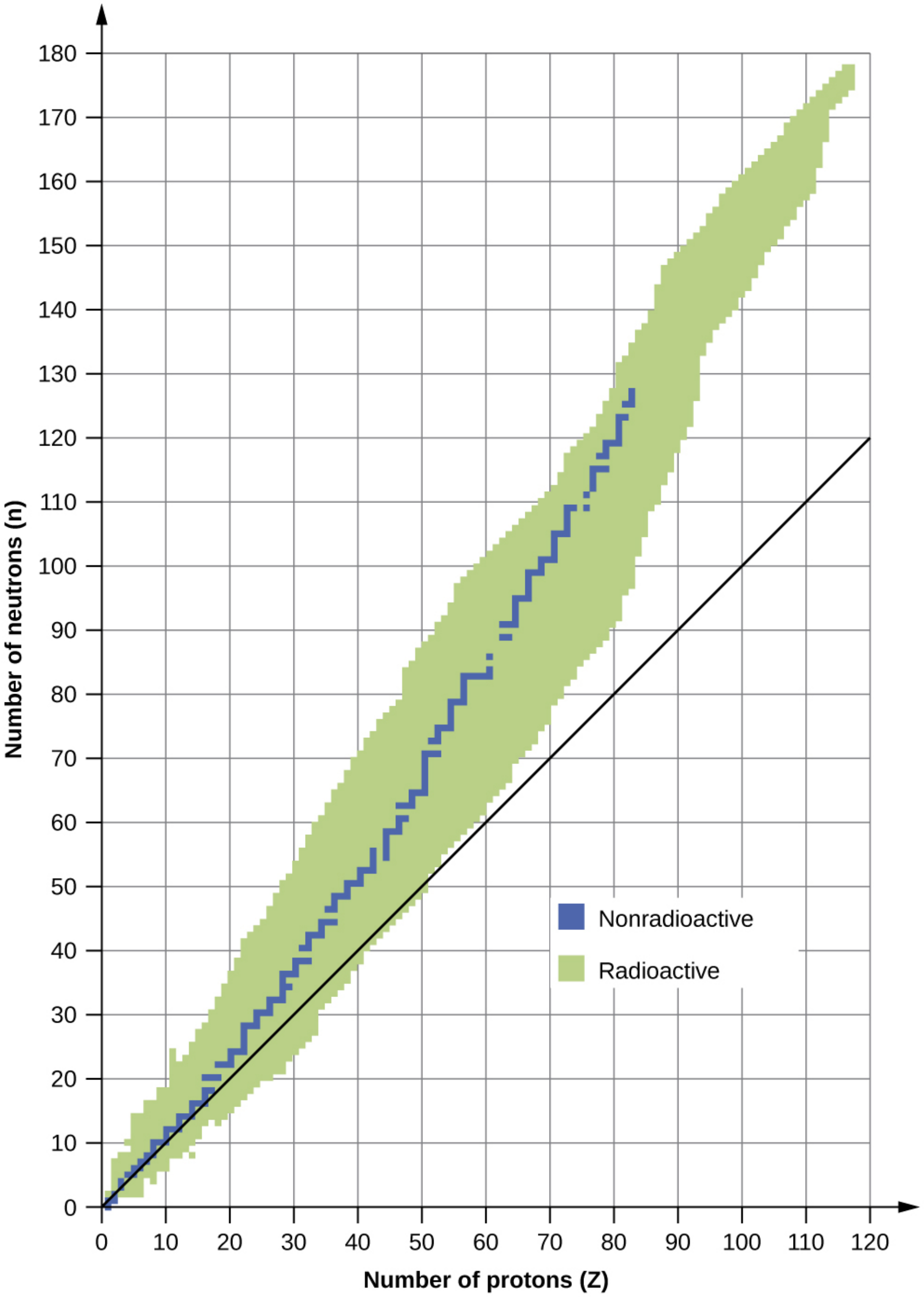


Figure 20.2 This plot shows the nuclides that are known to exist and those that are stable. The stable nuclides are indicated in blue, and the unstable nuclides are indicated in green. Note that all isotopes of elements with atomic numbers greater than 83 are unstable. The solid line is the line where n = Z.

The nuclei that are to the left or to the right of the band of stability are unstable and exhibit **radioactivity**. They change spontaneously (decay) into other nuclei that are either in, or closer to, the band of stability. These nuclear decay reactions convert one unstable isotope (or **radioisotope**) into another, more stable, isotope. We will discuss the nature and products of this radioactive decay in subsequent sections of this chapter.

Several observations may be made regarding the relationship between the stability of a nucleus and its structure. Nuclei with even numbers of protons, neutrons, or both are more likely to be stable (see Table 20.1). Nuclei with certain numbers of nucleons, known as **magic numbers**, are stable against nuclear decay. These numbers of protons or neutrons (2, 8, 20, 28, 50, 82, and 126) make complete shells in the nucleus. These are similar in concept to the stable electron shells observed for the noble gases. Nuclei that have magic numbers of both protons and neutrons, such as $^{4}_{2}\text{He}$, $^{16}_{8}\text{O}$, $^{40}_{20}\text{Ca}$, and $^{208}_{82}\text{Pb}$, are called "double magic" and are particularly stable. These trends in nuclear stability may be rationalized by considering a quantum mechanical model of nuclear energy states analogous to that used to describe electronic states earlier in this textbook. The details of this model are beyond the scope of this chapter.

Stable Nuclear Isotopes

Number of Stable Isotopes	Proton Number	Neutron Number
157	even	even
53	even	odd
50	odd	even
5	odd	odd

Table 20.1

The relative stability of a nucleus is correlated with its **binding energy per nucleon**, the total binding energy for the nucleus divided by the number or nucleons in the nucleus. For instance, we saw in **Example 20.2** that the binding energy for a $^{4}_{2}\text{He}$ nucleus is 28.4 MeV. The binding energy *per nucleon* for a $^{4}_{2}\text{He}$ nucleus is therefore:

$$\frac{28.4\ \text{MeV}}{4\ \text{nucleons}} = 7.10\ \text{MeV/nucleon}$$

In **Example 20.3**, we learn how to calculate the binding energy per nucleon of a nuclide on the curve shown in **Figure 20.3**.

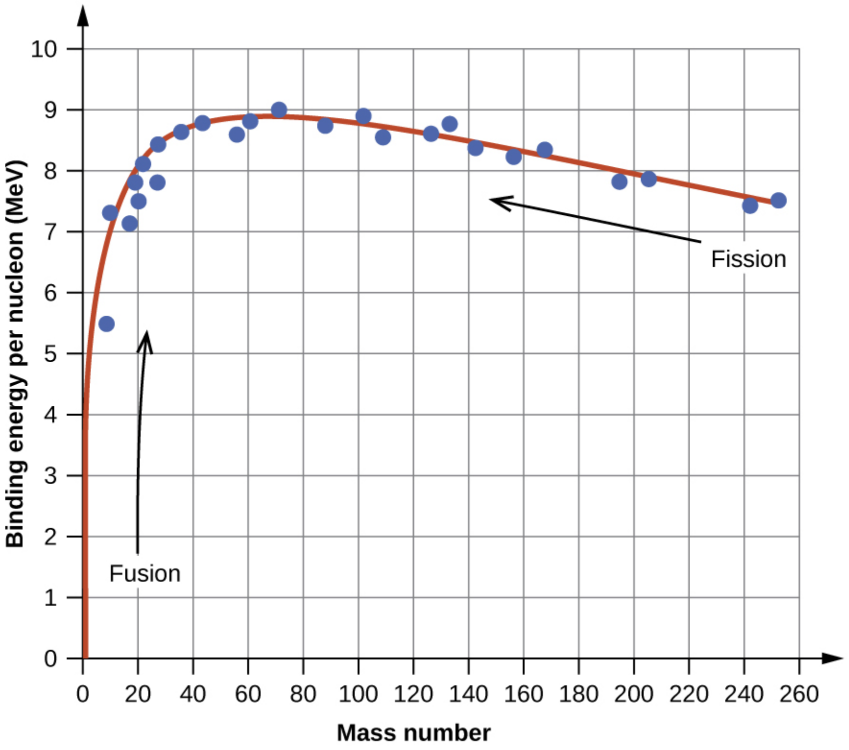


Figure 20.3 The binding energy per nucleon is largest for nuclides with mass number of approximately 56.

Example 20.3

Calculation of Binding Energy per Nucleon

The iron nuclide ${}^{56}_{26}\text{Fe}$ lies near the top of the binding energy curve (**Figure 20.3**) and is one of the most stable nuclides. What is the binding energy per nucleon (in MeV) for the nuclide ${}^{56}_{26}\text{Fe}$ (atomic mass of 55.9349 amu)?

Solution

As in **Example 20.2**, we first determine the mass defect of the nuclide, which is the difference between the mass of 26 protons, 30 neutrons, and 26 electrons, and the observed mass of an ${}^{56}_{26}\text{Fe}$ atom:

$$\begin{aligned}\text{Mass defect} &= [(26 \times 1.0073\text{ amu}) + (30 \times 1.0087\text{ amu}) + (26 \times 0.00055\text{ amu})] - 55.9349\text{ amu}\\ &= 56.4651\text{ amu} - 55.9349\text{ amu}\\ &= 0.5302\text{ amu}\end{aligned}$$

We next calculate the binding energy for one nucleus from the mass defect using the mass-energy equivalence equation:

$$\begin{aligned}E = mc^2 &= 0.5302\text{ amu} \times \frac{1.6605 \times 10^{-27}\text{ kg}}{1\text{ amu}} \times \left(2.998 \times 10^8\text{ m/s}\right)^2\\ &= 7.913 \times 10^{-11}\text{ kg·m/s}^2\\ &= 7.913 \times 10^{-11}\text{ J}\end{aligned}$$

We then convert the binding energy in joules per nucleus into units of MeV per nuclide:

$$7.913 \times 10^{-11}\ \text{J} \times \frac{1\ \text{MeV}}{1.602 \times 10^{-13}\ \text{J}} = 493.9\ \text{MeV}$$

Finally, we determine the binding energy per nucleon by dividing the total nuclear binding energy by the number of nucleons in the atom:

$$\text{Binding energy per nucleon} = \frac{493.9\ \text{MeV}}{56} = 8.820\ \text{MeV/nucleon}$$

Note that this is almost 25% larger than the binding energy per nucleon for ${}_{2}^{4}\text{He}$.

(Note also that this is the same process as in **Example 20.1**, but with the additional step of dividing the total nuclear binding energy by the number of nucleons.)

Check Your Learning

What is the binding energy per nucleon in ${}_{9}^{19}\text{F}$ (atomic mass, 18.9984 amu)?

Answer: 7.810 MeV/nucleon

20.2 Nuclear Equations

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

- Identify common particles and energies involved in nuclear reactions
- Write and balance nuclear equations

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are **nuclear reactions**. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in **Figure 20.4**. Protons $\left({}_{1}^{1}\text{p},\right.$ also represented by the symbol $\left.{}_{1}^{1}\text{H}\right)$ and neutrons $\left({}_{0}^{1}\text{n}\right)$ are the constituents of atomic nuclei, and have been described previously. **Alpha particles** $\left({}_{2}^{4}\text{He},\right.$ also represented by the symbol $\left.{}_{2}^{4}\alpha\right)$ are high-energy helium nuclei. **Beta particles** $\left({}_{-1}^{0}\beta,\right.$ also represented by the symbol $\left.{}_{-1}^{0}\text{e}\right)$ are high-energy electrons, and gamma rays are photons of very high-energy electromagnetic radiation. **Positrons** $\left({}_{+1}^{0}\text{e},\right.$ also represented by the symbol $\left.{}_{+1}^{0}\beta\right)$ are positively charged electrons ("anti-electrons"). The subscripts and superscripts are necessary for balancing nuclear equations, but are usually optional in other circumstances. For example, an alpha particle is a helium nucleus (He) with a charge of +2 and a mass number of 4, so it is symbolized ${}_{2}^{4}\text{He}$. This works because, in general, the ion charge is not important in the balancing of nuclear equations.

Name	Symbol(s)	Representation	Description
Alpha particle	${}^{4}_{2}\text{He}$ or ${}^{4}_{2}\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	${}^{\ 0}_{-1}\text{e}$ or ${}^{\ 0}_{-1}\beta$		(High-energy) electrons
Positron	${}^{\ 0}_{+1}\text{e}$ or ${}^{\ 0}_{+1}\beta$		Particles with the same mass as an electron but with 1 unit of positive charge
Proton	${}^{1}_{1}\text{H}$ or ${}^{1}_{1}\text{p}$		Nuclei of hydrogen atoms
Neutron	${}^{1}_{0}\text{n}$		Particles with a mass approximately equal to that of a proton but with no charge
Gamma ray	γ		Very high-energy electromagnetic radiation

Figure 20.4 Although many species are encountered in nuclear reactions, this table summarizes the names, symbols, representations, and descriptions of the most common of these.

Note that positrons are exactly like electrons, except they have the opposite charge. They are the most common example of **antimatter**, particles with the same mass but the opposite state of another property (for example, charge) than ordinary matter. When antimatter encounters ordinary matter, both are annihilated and their mass is converted into energy in the form of **gamma rays (γ)**—and other much smaller subnuclear particles, which are beyond the scope of this chapter—according to the mass-energy equivalence equation $E = mc^2$, seen in the preceding section. For example, when a positron and an electron collide, both are annihilated and two gamma ray photons are created:

$${}^{\ 0}_{-1}\text{e} + {}^{\ 0}_{+1}\text{e} \longrightarrow \gamma + \gamma$$

As seen in the chapter discussing light and electromagnetic radiation, gamma rays compose short wavelength, high-energy electromagnetic radiation and are (much) more energetic than better-known X-rays that can behave as particles in the wave-particle duality sense. Gamma rays are a type of high energy electromagnetic radiation produced when a nucleus undergoes a transition from a higher to a lower energy state, similar to how a photon is produced by an electronic transition from a higher to a lower energy level. Due to the much larger energy differences between nuclear energy shells, gamma rays emanating from a nucleus have energies that are typically millions of times larger than electromagnetic radiation emanating from electronic transitions.

Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of nucleons (subatomic particles within the atoms' nuclei) rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that $^{17}_{8}\text{O}$ is a product of the nuclear reaction of $^{14}_{7}\text{N}$ and $^{4}_{2}\text{He}$ if we knew that a proton, $^{1}_{1}\text{H},$ was one of the two products. **Example 20.4** shows how we can identify a nuclide by balancing the nuclear reaction.

Example 20.4

Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 $\left(^{25}_{12}\text{Mg}\right)$ produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$$^{25}_{12}\text{Mg} + {}^{4}_{2}\text{He} \longrightarrow {}^{1}_{1}\text{H} + {}^{A}_{Z}\text{X}$$

where A is the mass number and Z is the atomic number of the new nuclide, X. Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$25 + 4 = \text{A} + 1, \;\; \text{or A} = 28$$

Similarly, the charges must balance, so:

$$12 + 2 = \text{Z} + 1, \;\; \text{and Z} = 13$$

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is $^{28}_{13}\text{Al}.$

Check Your Learning

The nuclide $^{125}_{53}\text{I}$ combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Answer: $^{125}_{53}\text{I} + {}^{0}_{-1}\text{e} \longrightarrow {}^{125}_{52}\text{Te}$

Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie Curie and her husband Pierre in 1898. It decays, emitting α particles:

$$^{212}_{84}\text{Po} \longrightarrow {}^{208}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

- The first nuclide to be prepared by artificial means was an isotope of oxygen, ^{17}O. It was made by Ernest Rutherford in 1919 by bombarding nitrogen atoms with α particles:

$$^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

- James Chadwick discovered the neutron in 1932, as a previously unknown neutral particle produced along with ^{12}C by the nuclear reaction between ^{9}Be and ^{4}He:

$$^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}$$

- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of molybdenum by deuterons (heavy hydrogen, $^{2}_{1}\text{H}$), by Emilio Segre and Carlo Perrier in 1937:

$$^{2}_{1}\text{H} + {}^{97}_{42}\text{Mo} \longrightarrow 2{}^{1}_{0}\text{n} + {}^{97}_{43}\text{Tc}$$

- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{87}_{35}\text{Br} + {}^{146}_{57}\text{La} + 3{}^{1}_{0}\text{n}$$

20.3 Radioactive Decay

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

- Recognize common modes of radioactive decay
- Identify common particles and energies involved in nuclear decay reactions
- Write and balance nuclear decay equations
- Calculate kinetic parameters for decay processes, including half-life
- Describe common radiometric dating techniques

Following the somewhat serendipitous discovery of radioactivity by Becquerel, many prominent scientists began to investigate this new, intriguing phenomenon. Among them were Marie Curie (the first woman to win a Nobel Prize, and the only person to win two Nobel Prizes in different sciences—chemistry and physics), who was the first to coin the term “radioactivity,” and Ernest Rutherford (of gold foil experiment fame), who investigated and named three of the most common types of radiation. During the beginning of the twentieth century, many radioactive substances were discovered, the properties of radiation were investigated and quantified, and a solid understanding of radiation and nuclear decay was developed.

The spontaneous change of an unstable nuclide into another is **radioactive decay**. The unstable nuclide is called the **parent nuclide**; the nuclide that results from the decay is known as the **daughter nuclide**. The daughter nuclide may be stable, or it may decay itself. The radiation produced during radioactive decay is such that the daughter nuclide lies closer to the band of stability than the parent nuclide, so the location of a nuclide relative to the band of stability can serve as a guide to the kind of decay it will undergo (**Figure 20.5**).

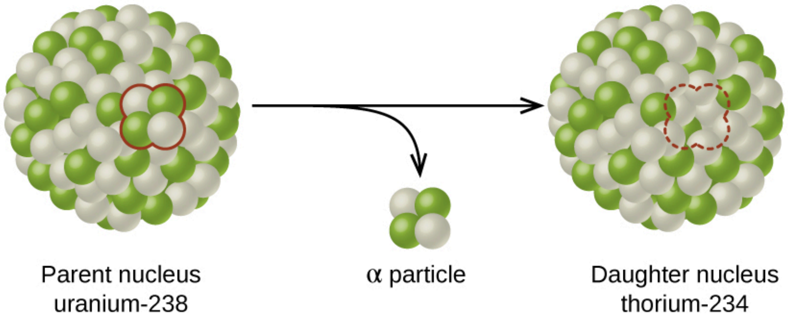


Figure 20.5 A nucleus of uranium-238 (the parent nuclide) undergoes α decay to form thorium-234 (the daughter nuclide). The alpha particle removes two protons (green) and two neutrons (gray) from the uranium-238 nucleus.

Link to Learning

Although the radioactive decay of a nucleus is too small to see with the naked eye, we can indirectly view radioactive decay in an environment called a cloud chamber. Click **here (http://openstaxcollege.org/l/16cloudchamb)** to learn about cloud chambers and to view an interesting Cloud Chamber Demonstration from the Jefferson Lab.

Types of Radioactive Decay

Ernest Rutherford’s experiments involving the interaction of radiation with a magnetic or electric field (**Figure 20.6**) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β particles; and a third was uncharged electromagnetic waves, γ rays. We now know that α particles are high-energy helium nuclei, β particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.

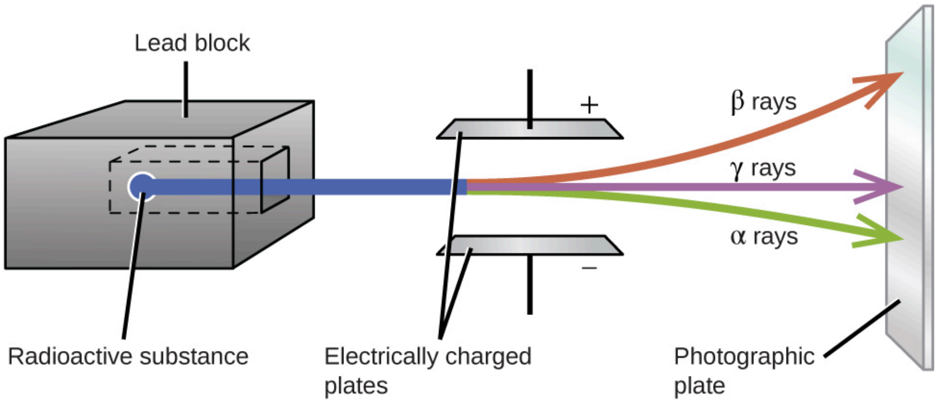


Figure 20.6 Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged.

Alpha (α) decay is the emission of an α particle from the nucleus. For example, polonium-210 undergoes α decay:

$$ {}^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\text{He} + {}^{206}_{82}\text{Pb} \qquad \text{or} \qquad {}^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\alpha + {}^{206}_{82}\text{Pb} $$

Alpha decay occurs primarily in heavy nuclei ($A > 200$, $Z > 83$). Because the loss of an α particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide, the daughter nuclide has a larger n:p ratio than the parent nuclide. If the parent nuclide undergoing α decay lies below the band of stability (refer to **Figure 20.2**), the daughter nuclide will lie closer to the band.

Beta (β) decay is the emission of an electron from a nucleus. Iodine-131 is an example of a nuclide that undergoes β decay:

$$ {}^{131}_{53}\text{I} \longrightarrow {}^{\ 0}_{-1}\text{e} + {}^{131}_{54}\text{Xe} \qquad \text{or} \qquad {}^{131}_{53}\text{I} \longrightarrow {}^{\ 0}_{-1}\beta + {}^{131}_{54}\text{Xe} $$

Beta decay, which can be thought of as the conversion of a neutron into a proton and a β particle, is observed in nuclides with a large n:p ratio. The beta particle (electron) emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Such nuclei lie above the band of stability. Emission of an electron does not change the mass number of the nuclide but does increase the number of its protons and decrease the number of its neutrons. Consequently, the n:p ratio is decreased, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Gamma emission (γ emission) is observed when a nuclide is formed in an excited state and then decays to its ground state with the emission of a γ ray, a quantum of high-energy electromagnetic radiation. The presence of a nucleus in an excited state is often indicated by an asterisk (*). Cobalt-60 emits γ radiation and is used in many applications including cancer treatment:

$$ {}^{60}_{27}\text{Co}^{*} \longrightarrow {}^{0}_{0}\gamma + {}^{60}_{27}\text{Co} $$

There is no change in mass number or atomic number during the emission of a γ ray unless the γ emission accompanies one of the other modes of decay.

Positron emission (β^+ decay) is the emission of a positron from the nucleus. Oxygen-15 is an example of a nuclide that undergoes positron emission:

$$ {}^{15}_{8}\mathrm{O} \longrightarrow {}^{0}_{+1}\mathrm{e} + {}^{15}_{7}\mathrm{N} \qquad \text{or} \qquad {}^{15}_{8}\mathrm{O} \longrightarrow {}^{0}_{+1}\beta + {}^{15}_{7}\mathrm{N} $$

Positron emission is observed for nuclides in which the n:p ratio is low. These nuclides lie below the band of stability. Positron decay is the conversion of a proton into a neutron with the emission of a positron. The n:p ratio increases, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Electron capture occurs when one of the inner electrons in an atom is captured by the atom's nucleus. For example, potassium-40 undergoes electron capture:

$$ {}^{40}_{19}\mathrm{K} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{40}_{18}\mathrm{Ar} $$

Electron capture occurs when an inner shell electron combines with a proton and is converted into a neutron. The loss of an inner shell electron leaves a vacancy that will be filled by one of the outer electrons. As the outer electron drops into the vacancy, it will emit energy. In most cases, the energy emitted will be in the form of an X-ray. Like positron emission, electron capture occurs for "proton-rich" nuclei that lie below the band of stability. Electron capture has the same effect on the nucleus as does positron emission: The atomic number is decreased by one and the mass number does not change. This increases the n:p ratio, and the daughter nuclide lies closer to the band of stability than did the parent nuclide. Whether electron capture or positron emission occurs is difficult to predict. The choice is primarily due to kinetic factors, with the one requiring the smaller activation energy being the one more likely to occur.

Figure 20.7 summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

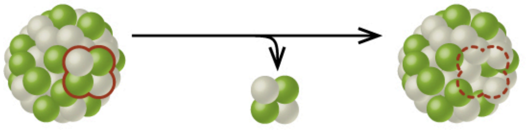
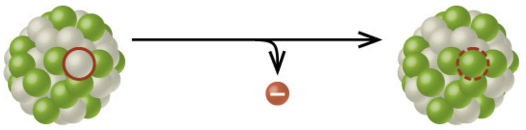
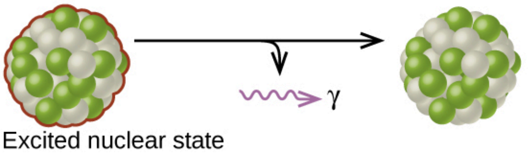
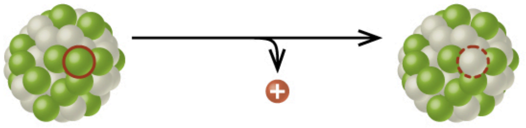
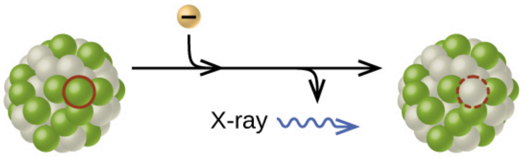
Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^{A}_{Z}\mathrm{X} \quad {}^{4}_{2}\mathrm{He} + {}^{A-4}_{Z-2}\mathrm{Y}$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^{A}_{Z}\mathrm{X} \quad {}^{0}_{-1}\mathrm{e} + {}_{Z+1}^{A}\mathrm{Y}$		A: unchanged Z: increase by 1
Gamma decay	${}^{A}_{Z}\mathrm{X} \quad {}^{0}_{0}\gamma + {}^{A}_{Z}\mathrm{Y}$		A: unchanged Z: unchanged
Positron emission	${}^{A}_{Z}\mathrm{X} \quad {}^{0}_{+1}\mathrm{e} + {}_{Y-1}^{A}\mathrm{Y}$		A: unchanged Z: decrease by 1
Electron capture	${}^{A}_{Z}\mathrm{X} \quad {}^{0}_{-1}\mathrm{e} + {}_{Y-1}^{A}\mathrm{Y}$		A: unchanged Z: decrease by 1

Figure 20.7 This table summarizes the type, nuclear equation, representation, and any changes in the mass or atomic numbers for various types of decay.

Chemistry in Everyday Life

PET Scan

Positron emission tomography (PET) scans use radiation to diagnose and track health conditions and monitor medical treatments by revealing how parts of a patient's body function (**Figure 20.8**). To perform a PET scan, a positron-emitting radioisotope is produced in a cyclotron and then attached to a substance that is used by the part of the body being investigated. This "tagged" compound, or radiotracer, is then put into the patient (injected via IV or breathed in as a gas), and how it is used by the tissue reveals how that organ or other area of the body functions.

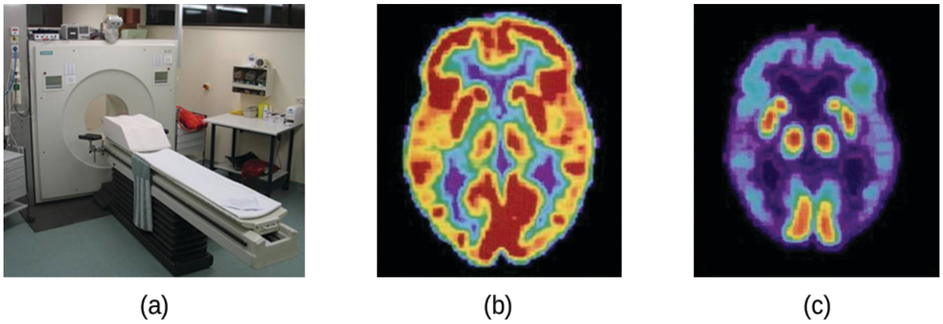

(a) (b) (c)

Figure 20.8 A PET scanner (a) uses radiation to provide an image of how part of a patient's body functions. The scans it produces can be used to image a healthy brain (b) or can be used for diagnosing medical conditions such as Alzheimer's disease (c). (credit a: modification of work by Jens Maus)

For example, F-18 is produced by proton bombardment of ^{18}O $\left({}^{18}_{8}\text{O} + {}^{1}_{1}\text{p} \longrightarrow {}^{18}_{9}\text{F} + {}^{1}_{0}\text{n}\right)$ and incorporated into a glucose analog called fludeoxyglucose (FDG). How FDG is used by the body provides critical diagnostic information; for example, since cancers use glucose differently than normal tissues, FDG can reveal cancers. The ^{18}F emits positrons that interact with nearby electrons, producing a burst of gamma radiation. This energy is detected by the scanner and converted into a detailed, three-dimensional, color image that shows how that part of the patient's body functions. Different levels of gamma radiation produce different amounts of brightness and colors in the image, which can then be interpreted by a radiologist to reveal what is going on. PET scans can detect heart damage and heart disease, help diagnose Alzheimer's disease, indicate the part of a brain that is affected by epilepsy, reveal cancer, show what stage it is, and how much it has spread, and whether treatments are effective. Unlike magnetic resonance imaging and X-rays, which only show how something looks, the big advantage of PET scans is that they show how something functions. PET scans are now usually performed in conjunction with a computed tomography scan.

Radioactive Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or **radioactive decay series**. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. The neptunium series is a fourth series, which is no longer significant on the earth because of the short half-lives of the species involved. Each series is characterized by a parent (first member) that has a long half-life and a series of daughter nuclides that ultimately lead to a stable end-product—that is, a nuclide on the band of stability (**Figure 20.9**). In all three series, the end-product is a stable isotope of lead. The neptunium series, previously thought to terminate with bismuth-209, terminates with thallium-205.

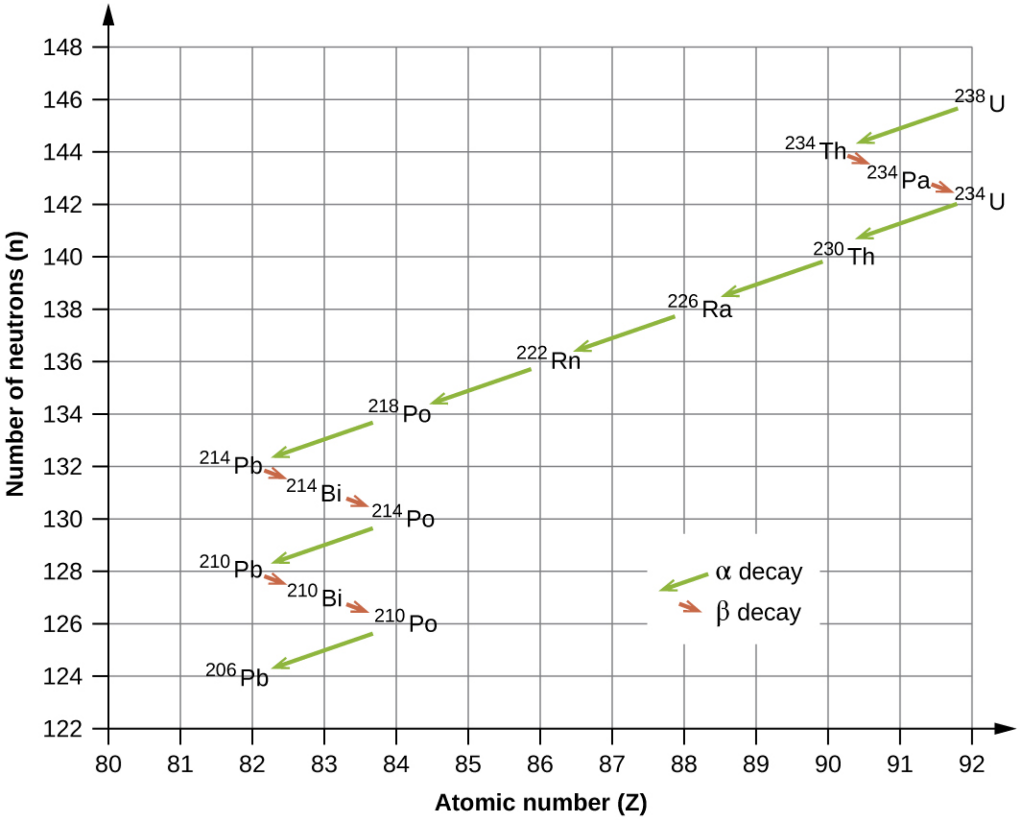


Figure 20.9 Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant **half-life** ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, cobalt-60, an isotope that emits gamma rays used to treat cancer, has a half-life of 5.27 years (**Figure 20.10**). In a given cobalt-60 source, since half of the $^{60}_{27}\text{Co}$ nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

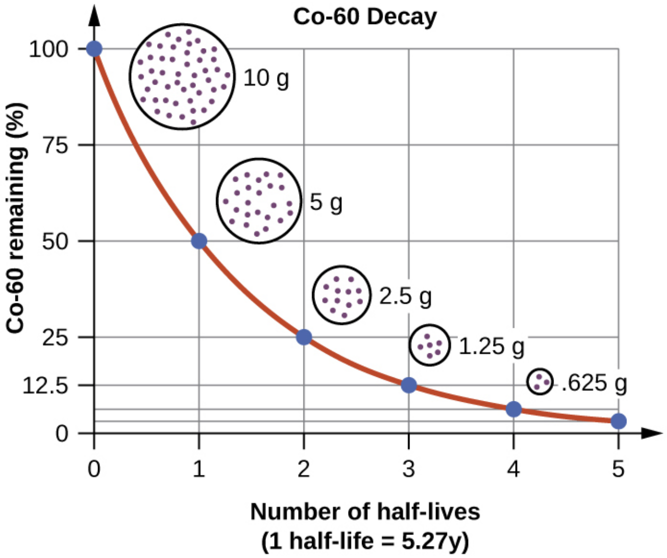


Figure 20.10 For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

Since nuclear decay follows first-order kinetics, we can adapt the mathematical relationships used for first-order chemical reactions. We generally substitute the number of nuclei, N, for the concentration. If the rate is stated in nuclear decays per second, we refer to it as the activity of the radioactive sample. The rate for radioactive decay is:

decay rate = λN with λ = the decay constant for the particular radioisotope

The decay constant, λ, which is the same as a rate constant discussed in the kinetics chapter. It is possible to express the decay constant in terms of the half-life, $t_{1/2}$:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} \qquad \text{or} \qquad t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

The first-order equations relating amount, N, and time are:

$$N_t = N_0 e^{-kt} \qquad \text{or} \qquad t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right)$$

where N_0 is the initial number of nuclei or moles of the isotope, and N_t is the number of nuclei/moles remaining at time t. **Example 20.5** applies these calculations to find the rates of radioactive decay for specific nuclides.

Example 20.5

Rates of Radioactive Decay

${}^{60}_{27}\text{Co}$ decays with a half-life of 5.27 years to produce ${}^{60}_{28}\text{Ni}$.

(a) What is the decay constant for the radioactive disintegration of cobalt-60?

(b) Calculate the fraction of a sample of the ${}^{60}_{27}\text{Co}$ isotope that will remain after 15 years.

(c) How long does it take for a sample of ${}^{60}_{27}\text{Co}$ to disintegrate to the extent that only 2.0% of the original amount remains?

Solution

(a) The value of the rate constant is given by:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5.27\ \text{y}} = 0.132\ \text{y}^{-1}$$

(b) The fraction of ${}^{60}_{27}\text{Co}$ that is left after time t is given by $\frac{N_t}{N_0}$. Rearranging the first-order relationship $N_t = N_0e^{-\lambda t}$ to solve for this ratio yields:

$$\frac{N_t}{N_0} = e^{-\lambda t} = e^{-(0.132/\text{y})(15.0/\text{y})} = 0.138$$

The fraction of ${}^{60}_{27}\text{Co}$ that will remain after 15.0 years is 0.138. Or put another way, 13.8% of the ${}^{60}_{27}\text{Co}$ originally present will remain after 15 years.

(c) 2.00% of the original amount of ${}^{60}_{27}\text{Co}$ is equal to $0.0200 \times N_0$. Substituting this into the equation for time for first-order kinetics, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) = -\frac{1}{0.132\ \text{y}^{-1}}\ln\left(\frac{0.0200 \times N_0}{N_0}\right) = 29.6\ \text{y}$$

Check Your Learning

Radon-222, ${}^{222}_{86}\text{Rn}$, has a half-life of 3.823 days. How long will it take a sample of radon-222 with a mass of 0.750 g to decay into other elements, leaving only 0.100 g of radon-222?

Answer: 11.1 days

Because each nuclide has a specific number of nucleons, a particular balance of repulsion and attraction, and its own degree of stability, the half-lives of radioactive nuclides vary widely. For example: the half-life of ${}^{209}_{83}\text{Bi}$ is 1.9×10^{19} years; ${}^{239}_{94}\text{Ra}$ is 24,000 years; ${}^{222}_{86}\text{Rn}$ is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The half-lives of a number of radioactive isotopes important to medicine are shown in **Table 20.2**, and others are listed in **Appendix M**.

Half-lives of Radioactive Isotopes Important to Medicine

Type[1]	Decay Mode	Half-Life	Uses
F-18	β^+ decay	110. minutes	PET scans
Co-60	β decay, γ decay	5.27 years	cancer treatment
Tc-99m	γ decay	8.01 hours	scans of brain, lung, heart, bone
I-131	β decay	8.02 days	thyroid scans and treatment
Tl-201	electron capture	73 hours	heart and arteries scans; cardiac stress tests

Table 20.2

Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of "dating" the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. This process is **radiometric dating** and has been responsible for many breakthrough scientific discoveries about the geological

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[1] The "m" in Tc-99m stands for "metastable," indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.

history of the earth, the evolution of life, and the history of human civilization. We will explore some of the most common types of radioactive dating and how the particular isotopes work for each type.

Radioactive Dating Using Carbon-14

The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called **radiocarbon dating** or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: $^{12}_{6}\text{C},$ which constitutes about 99% of the carbon on earth; $^{13}_{6}\text{C},$ about 1% of the total; and trace amounts of $^{14}_{6}\text{C}.$ Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$^{14}_{7}\text{N} + ^{1}_{0}\text{n} \longrightarrow ^{14}_{6}\text{C} + ^{1}_{1}\text{H}$$

All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of $^{14}_{6}\text{CO}_2$ to $^{12}_{6}\text{CO}_2$ depends on the ratio of $^{14}_{6}\text{CO}$ to $^{12}_{6}\text{CO}$ in the atmosphere. The natural abundance of $^{14}_{6}\text{CO}$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of $^{14}_{6}\text{C}\,^{14}_{6}\text{CO}_2$ and $^{12}_{6}\text{CO}_2$ into plants is a regular part of the photosynthesis process, which means that the $^{14}_{6}\text{C}:\,^{12}_{6}\text{C}$ ratio found in a living plant is the same as the $^{14}_{6}\text{C}:\,^{12}_{6}\text{C}$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because $^{12}_{6}\text{C}$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$^{14}_{6}\text{C} \longrightarrow ^{12}_{7}\text{N} + ^{0}_{-1}\text{e}$$

Thus, the $^{14}_{6}\text{C}:\,^{12}_{6}\text{C}$ ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). **Figure 20.11** visually depicts this process.

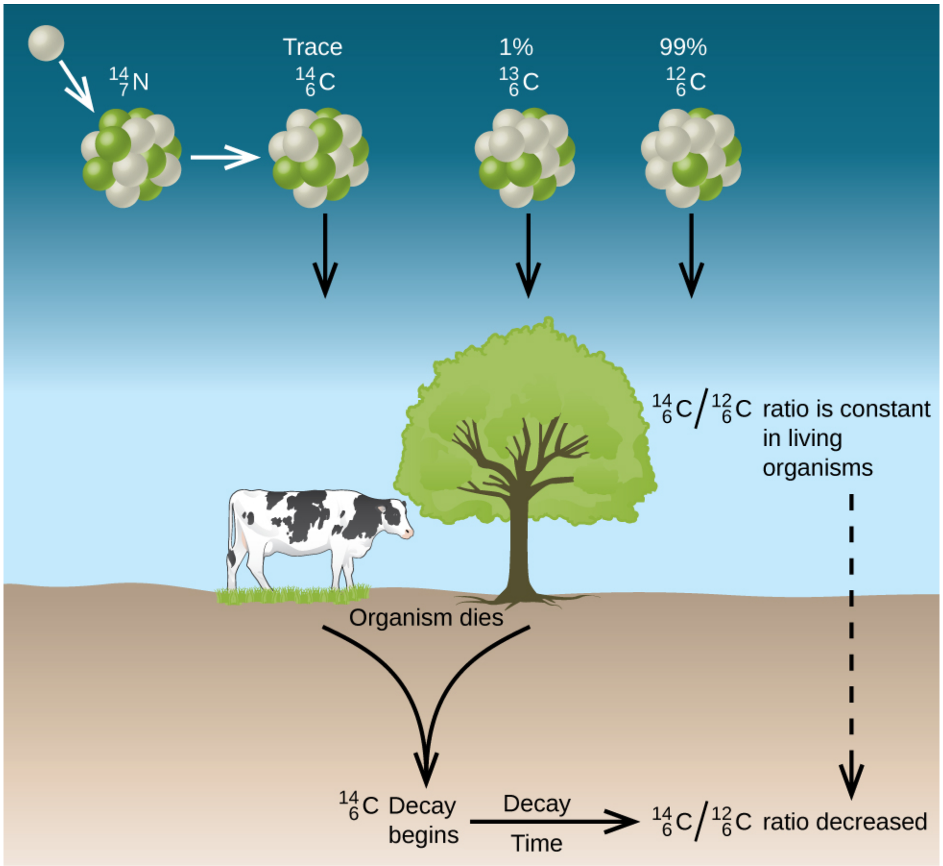


Figure 20.11 Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died).

For example, with the half-life of $^{14}_{6}C$ being 5730 years, if the $^{14}_{6}C:^{12}_{6}C$ ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of $^{14}_{6}C:^{12}_{6}C$ ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

Link to Learning

Visit this **website (http://openstaxcollege.org/l/16phetradiom)** to perform simulations of radiometric dating.

Example 20.6

Radiocarbon Dating

A tiny piece of paper (produced from formerly living plant matter) taken from the Dead Sea Scrolls has an activity of 10.8 disintegrations per minute per gram of carbon. If the initial C-14 activity was 13.6 disintegrations/min/g of C, estimate the age of the Dead Sea Scrolls.

Solution

The rate of decay (number of disintegrations/minute/gram of carbon) is proportional to the amount of radioactive C-14 left in the paper, so we can substitute the rates for the amounts, N, in the relationship:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) \longrightarrow t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right)$$

where the subscript 0 represents the time when the plants were cut to make the paper, and the subscript t represents the current time.

The decay constant can be determined from the half-life of C-14, 5730 years:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730\text{ y}} = 1.21 \times 10^{-4}\text{ y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right) = -\frac{1}{1.21 \times 10^{-4}\text{ y}^{-1}}\ln\left(\frac{10.8\text{ dis/min/g C}}{13.6\text{ dis/min/g C}}\right) = 1910\text{ y}$$

Therefore, the Dead Sea Scrolls are approximately 1900 years old (**Figure 20.12**).

Figure 20.12 Carbon-14 dating has shown that these pages from the Dead Sea Scrolls were written or copied on paper made from plants that died between 100 BC and AD 50.

Check Your Learning

More accurate dates of the reigns of ancient Egyptian pharaohs have been determined recently using plants that were preserved in their tombs. Samples of seeds and plant matter from King Tutankhamun's tomb have a C-14 decay rate of 9.07 disintegrations/min/g of C. How long ago did King Tut's reign come to an end?

Answer: about 3350 years ago, or approximately 1340 BC

There have been some significant, well-documented changes to the ${}^{14}_{6}\text{C}:{}^{12}_{6}\text{C}$ ratio. The accuracy of a straightforward application of this technique depends on the ${}^{14}_{6}\text{C}:{}^{12}_{6}\text{C}$ ratio in a living plant being the same now as it was in an earlier era, but this is not always valid. Due to the increasing accumulation of CO_2 molecules (largely ${}^{12}_{6}\text{CO}_2$) in the atmosphere caused by combustion of fossil fuels (in which essentially all of the ${}^{14}_{6}\text{C}$ has decayed), the ratio of ${}^{14}_{6}\text{C}:{}^{12}_{6}\text{C}$ in the atmosphere may be changing. This manmade increase in ${}^{12}_{6}\text{CO}_2$ in the atmosphere causes the ${}^{14}_{6}\text{C}:{}^{12}_{6}\text{C}$ ratio to decrease, and this in turn affects the ratio in currently living organisms on the earth. Fortunately, however, we can use other data, such as tree dating via examination of annual growth rings, to calculate correction factors. With these correction factors, accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. For example, uranium-238 (which decays in a series of steps into lead-206) can be used for establishing the age of rocks (and the approximate age of the oldest rocks on earth). Since U-238 has a half-life of 4.5 billion years, it takes that amount of time for half of the original U-238 to decay into Pb-206. In a sample of rock that does not contain appreciable amounts of Pb-208, the most abundant isotope of lead, we can assume that lead was not present when the rock was formed. Therefore, by measuring and analyzing the ratio of U-238:Pb-206, we can determine the age of the rock. This assumes that all of the lead-206 present came from the decay of uranium-238. If there is additional lead-206 present, which is indicated by the presence of other lead isotopes in the sample, it is necessary to make an adjustment. Potassium-argon dating uses a similar method. K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

Example 20.7

Radioactive Dating of Rocks

An igneous rock contains 9.58×10^{-5} g of U-238 and 2.51×10^{-5} g of Pb-206, and much, much smaller amounts of Pb-208. Determine the approximate time at which the rock formed.

Solution

The sample of rock contains very little Pb-208, the most common isotope of lead, so we can safely assume that all the Pb-206 in the rock was produced by the radioactive decay of U-238. When the rock formed, it contained all of the U-238 currently in it, plus some U-238 that has since undergone radioactive decay.

The amount of U-238 currently in the rock is:

$$9.58 \times 10^{-5}\ \cancel{\text{g U}} \times \left(\frac{1\ \text{mol U}}{238\ \cancel{\text{g U}}}\right) = 4.03 \times 10^{-7}\ \text{mol U}$$

Because when one mole of U-238 decays, it produces one mole of Pb-206, the amount of U-238 that has undergone radioactive decay since the rock was formed is:

$$2.51 \times 10^{-5}\ \cancel{\text{g Pb}} \times \left(\frac{1\ \cancel{\text{mol Pb}}}{206\ \cancel{\text{g Pb}}}\right) \times \left(\frac{1\ \text{mol U}}{1\ \cancel{\text{mol Pb}}}\right) = 1.22 \times 10^{-7}\ \text{mol U}$$

The total amount of U-238 originally present in the rock is therefore:

$$4.03 \times 10^{-7}\ \text{mol} + 1.22 \times 10^{-7}\ \text{mol} = 5.25 \times 10^{-7}\ \text{mol U}$$

The amount of time that has passed since the formation of the rock is given by:

$$t = -\frac{1}{\lambda} \ln\left(\frac{N_t}{N_0}\right)$$

with N_0 representing the original amount of U-238 and N_t representing the present amount of U-238.

U-238 decays into Pb-206 with a half-life of 4.5×10^9 y, so the decay constant λ is:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9\ \text{y}} = 1.54 \times 10^{-10}\ \text{y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{1.54 \times 10^{-10}\ \text{y}^{-1}} \ln\left(\frac{4.03 \times 10^{-7}\ \cancel{\text{mol U}}}{5.25 \times 10^{-7}\ \cancel{\text{mol U}}}\right) = 1.7 \times 10^{9}\ \text{y}$$

Therefore, the rock is approximately 1.7 billion years old.

Check Your Learning

A sample of rock contains 6.14×10^{-4} g of Rb-87 and 3.51×10^{-5} g of Sr-87. Calculate the age of the rock. (The half-life of the β decay of Rb-87 is 4.7×10^{10} y.)

Answer: 3.7×10^{9} y

20.4 Transmutation and Nuclear Energy

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

- Describe the synthesis of transuranium nuclides
- Explain nuclear fission and fusion processes
- Relate the concepts of critical mass and nuclear chain reactions
- Summarize basic requirements for nuclear fission and fusion reactors

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Scientists learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a **transmutation** reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

$$^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

The $^{17}_{8}\text{O}$ and $^{1}_{1}\text{H}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called **particle accelerators** are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules. When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors. The Chemistry in Everyday Life feature that follows discusses a famous particle accelerator that made worldwide news.

Chemistry in Everyday Life

CERN Particle Accelerator

Located near Geneva, the CERN (“Conseil Européen pour la Recherche Nucléaire,” or European Council for Nuclear Research) Laboratory is the world’s premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (**Figure 20.13**). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.

Figure 20.13 A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and resulted in the awarding of the 2013 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Link to Learning

Famous physicist Brian Cox talks about his work on the Large Hadron Collider at CERN, providing an entertaining and engaging **tour (http://openstaxcollege.org/l/16tedCERN)** of this massive project and the physics behind it.

View a short **video (http://openstaxcollege.org/l/16CERNvideo)** from CERN, describing the basics of how its particle accelerators work.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$
\begin{aligned}
&{}^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{239}_{92}\text{U} \\
&{}^{239}_{92}\text{U} \longrightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\text{e} \qquad \text{half-life} = 23.5\ \text{min} \\
&{}^{239}_{93}\text{Np} \longrightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\text{e} \qquad \text{half-life} = 2.36\ \text{days}
\end{aligned}
$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the decay of uranium. Some of the neutrons that are released during U-235 decay combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. It is possible to summarize these equations as:

$$ {}^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{239}_{92}\text{U} \xrightarrow{\beta^-} {}^{239}_{93}\text{Np} \xrightarrow{\beta^-} {}^{239}_{94}\text{Pu} $$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called **transuranium elements**. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in **Table 20.3**.

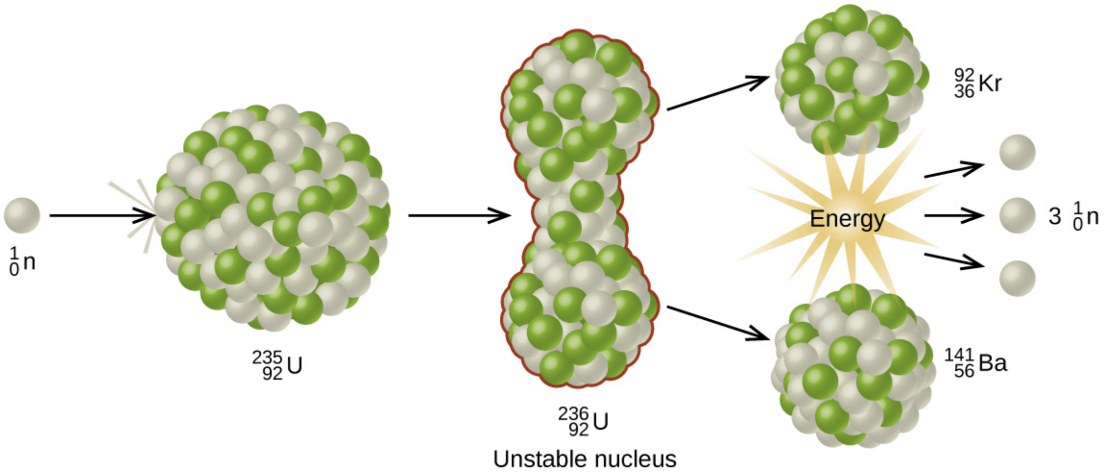
Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	${}^{239}_{94}\text{Pu} + {}^{1}_{0}\text{n} \longrightarrow {}^{240}_{95}\text{Am} + {}^{0}_{-1}\text{e}$
curium	Cm	96	${}^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$
californium	Cf	98	${}^{242}_{96}\text{Cm} + {}^{4}_{2}\text{He} \longrightarrow {}^{245}_{98}\text{Cf} + {}^{1}_{0}\text{n}$
einsteinium	Es	99	${}^{238}_{92}\text{U} + 15{}^{1}_{0}\text{n} \longrightarrow {}^{253}_{99}\text{Es} + 7{}^{0}_{-1}\text{e}$
mendelevium	Md	101	${}^{253}_{99}\text{Es} + {}^{4}_{2}\text{He} \longrightarrow {}^{256}_{101}\text{Md} + {}^{1}_{0}\text{n}$
nobelium	No	102	${}^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \longrightarrow {}^{254}_{102}\text{No} + 4{}^{1}_{0}\text{n}$
rutherfordium	Rf	104	${}^{249}_{98}\text{Cf} + {}^{12}_{6}\text{C} \longrightarrow {}^{257}_{104}\text{Rf} + 4{}^{1}_{0}\text{n}$
seaborgium	Sg	106	${}^{206}_{82}\text{Pb} + {}^{54}_{24}\text{Cr} \longrightarrow {}^{257}_{106}\text{Sg} + 3{}^{1}_{0}\text{n}$ ${}^{249}_{98}\text{Cf} + {}^{18}_{8}\text{O} \longrightarrow {}^{263}_{106}\text{Sg} + 4{}^{1}_{0}\text{n}$
meitnerium	Mt	107	${}^{209}_{83}\text{Bi} + {}^{58}_{26}\text{Fe} \longrightarrow {}^{266}_{109}\text{Mt} + {}^{1}_{0}\text{n}$

Table 20.3

Nuclear Fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the “peak” of the binding energy graph near 56 (see **Figure 20.3**). Sometimes neutrons are also produced. This decomposition is called **fission**, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in **Figure 20.14**.



$${}^{235}_{92}U + {}^{0}_{1}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{141}_{36}Ba + {}^{92}_{36}Kr + 3\ {}^{1}_{0}n$$

Figure 20.14 When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman’s fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in **Figure 20.15**. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

$$
{}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{236}_{92}\text{U} \longrightarrow {}^{90}_{38}\text{Sr} + {}^{144}_{54}\text{Xe} + 2\,{}^{1}_{0}\text{n}
$$

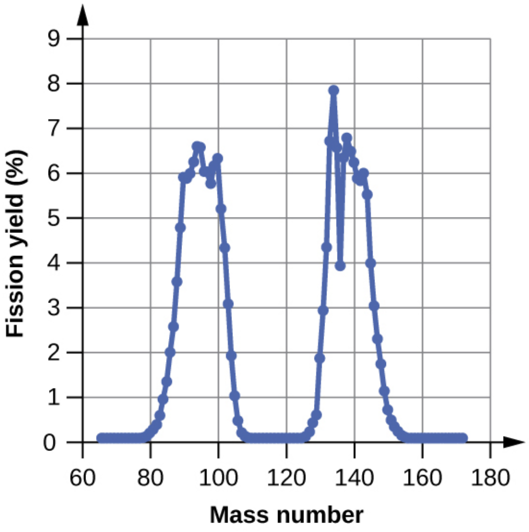
$$
{}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{236}_{92}\text{U} \longrightarrow {}^{87}_{35}\text{Br} + {}^{146}_{57}\text{La} + 3\,{}^{1}_{0}\text{n}
$$

$$
{}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{236}_{92}\text{U} \longrightarrow {}^{96}_{37}\text{Rb} + {}^{137}_{55}\text{Cs} + 3\,{}^{1}_{0}\text{n}
$$

$$
{}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{236}_{92}\text{U} \longrightarrow {}^{137}_{52}\text{Te} + {}^{97}_{40}\text{Zr} + 2\,{}^{1}_{0}\text{n}
$$

$$
{}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{236}_{92}\text{U} \longrightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3\,{}^{1}_{0}\text{n}
$$

(a)



(b)

Figure 20.15 (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

Link to Learning

View this **link (http://openstaxcollege.org/l/16fission)** to see a simulation of nuclear fission.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this “lost” mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two “medium-sized” nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear **chain reaction** (see **Figure 20.16**). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

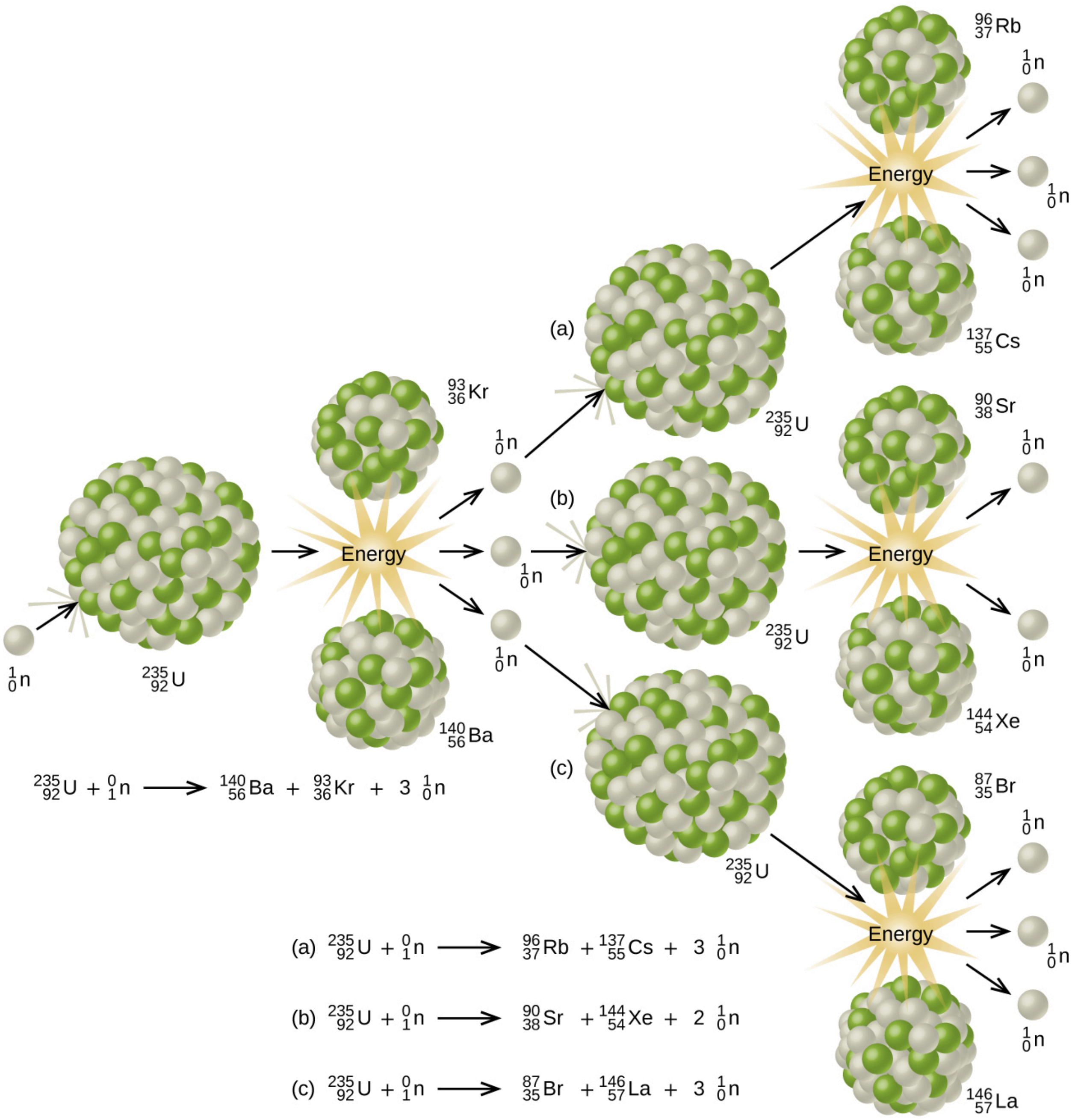


Figure 20.16 The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be **fissile** or **fissionable**. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a **critical mass**. An amount of fissionable material that cannot sustain a chain reaction is a **subcritical mass**. An amount of material in which there is an increasing rate of fission is known as a **supercritical mass**. The critical mass depends on the type of material:

its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (**Figure 20.17**).

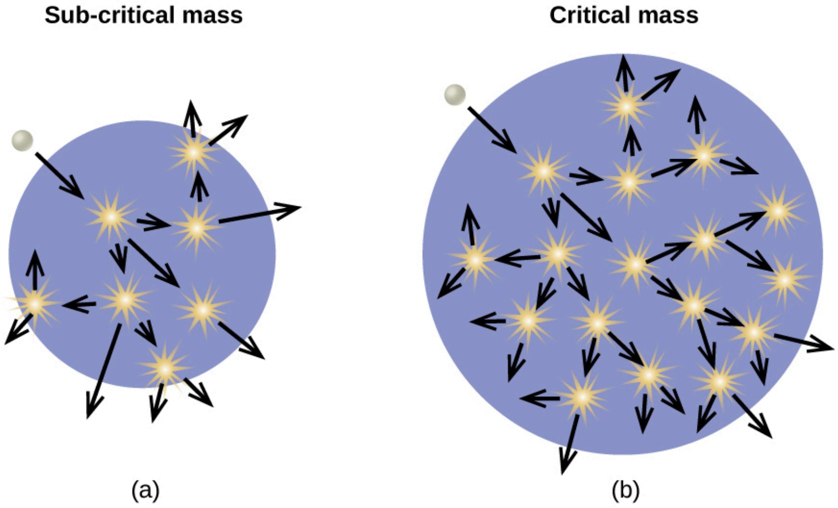


Figure 20.17 (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

An atomic bomb (**Figure 20.18**) contains several pounds of fissionable material, ${}_{92}^{235}\text{U}$ or ${}_{94}^{239}\text{Pu},$ a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.

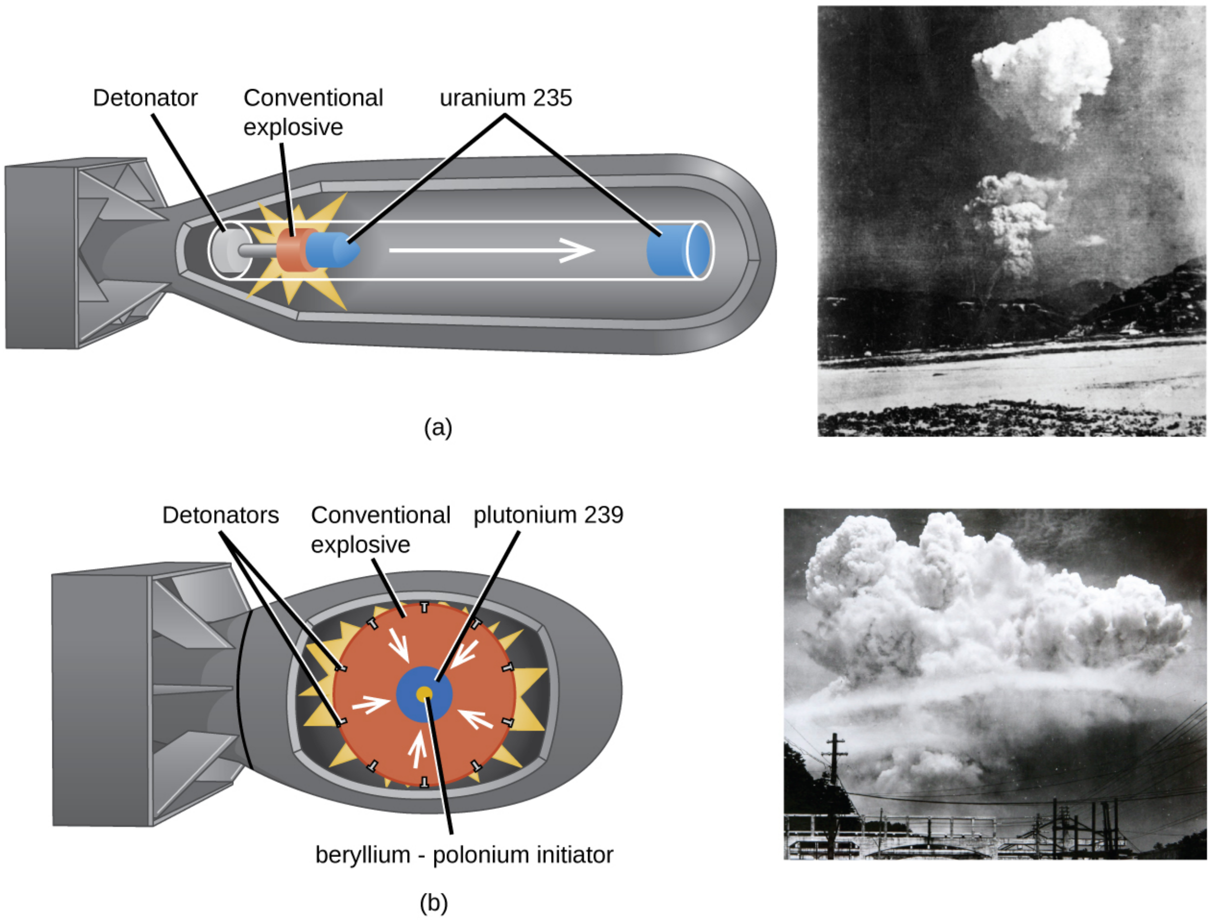


Figure 20.18 (a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 9, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.

Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a **nuclear reactor** (**Figure 20.19**). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.

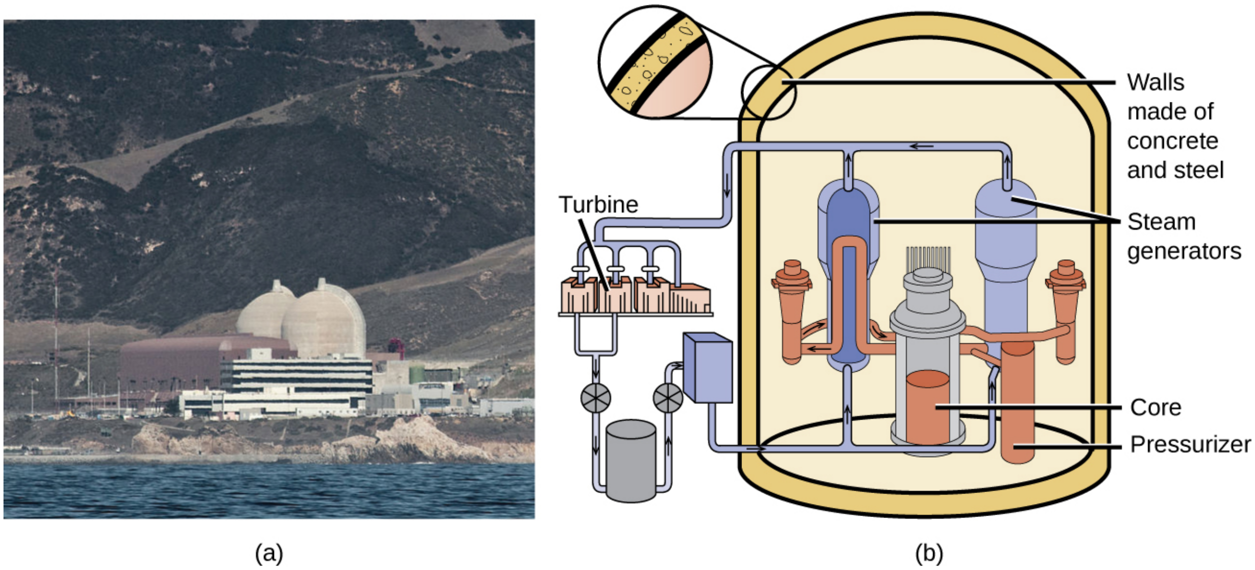


Figure 20.19 (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by “Mike” Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)

Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3% nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham’s law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (refer back to Figure 20.17). They must first be slowed to be absorbed by the fuel and produce additional nuclear reactions. A **nuclear moderator** is a substance that slows the neutrons to a speed that is low enough to cause fission. Early reactors used high-purity graphite as a moderator. Modern reactors in the US exclusively use heavy water $\left(^2_1H_2O\right)$ or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

Reactor Coolants

A nuclear **reactor coolant** is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

Control Rods

Nuclear reactors use **control rods** (Figure 20.20) to control the fission rate of the nuclear fuel by adjusting the number of slow neutrons present to keep the rate of the chain reaction at a safe level. Control rods are made of boron, cadmium, hafnium, or other elements that are able to absorb neutrons. Boron-10, for example, absorbs neutrons by a reaction that produces lithium-7 and alpha particles:

$$^{10}_{5}\text{B} + {}^{1}_{0}\text{n} \longrightarrow {}^{7}_{3}\text{Li} + {}^{4}_{2}\text{He}$$

When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.

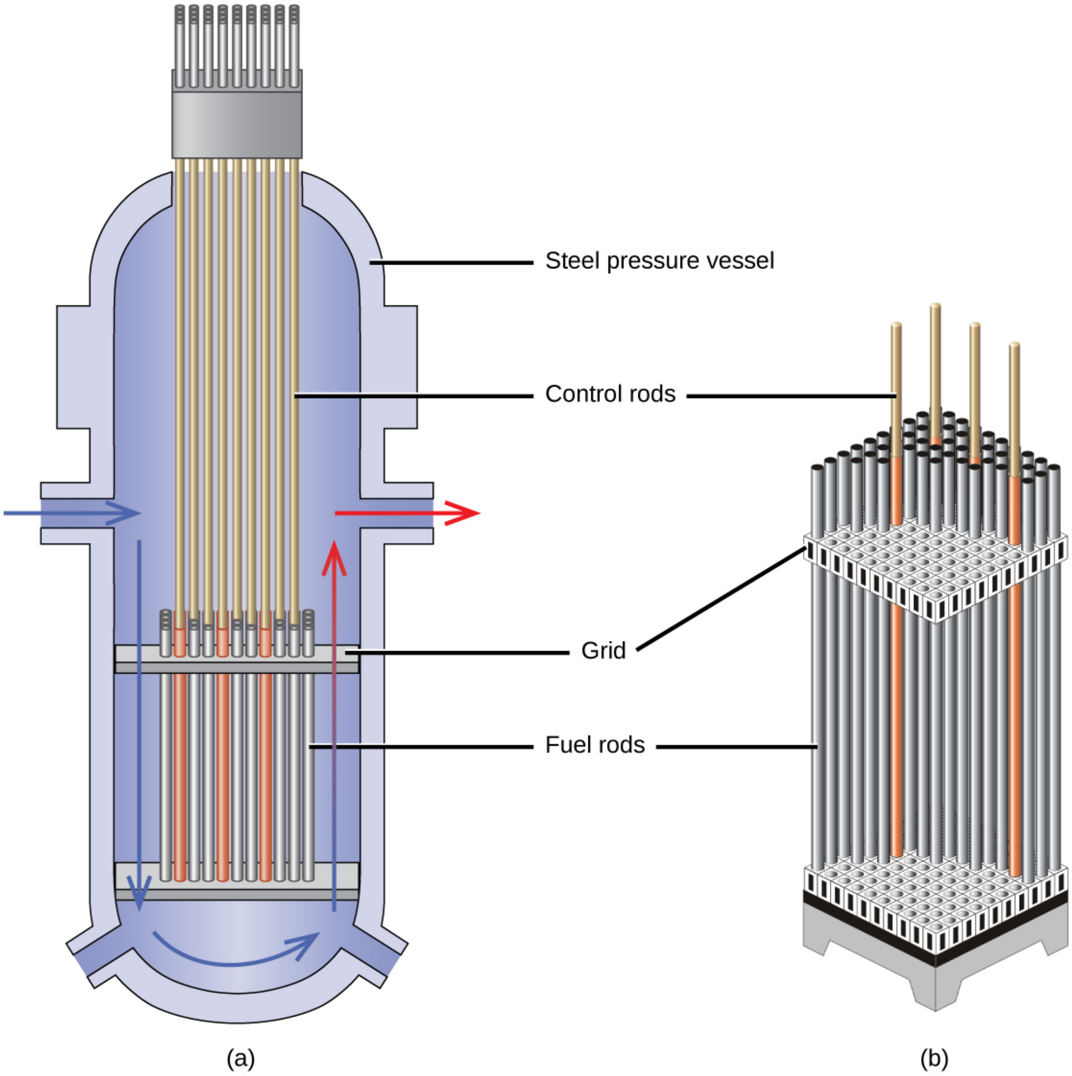


Figure 20.20 The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, http://glossary.periodni.com/glossary.php?en=control+rod)

Shield and Containment System

During its operation, a nuclear reactor produces neutrons and other radiation. Even when shut down, the decay products are radioactive. In addition, an operating reactor is thermally very hot, and high pressures result from the circulation of water or another coolant through it. Thus, a reactor must withstand high temperatures and pressures, and must protect operating personnel from the radiation. Reactors are equipped with a **containment system** (or shield) that consists of three parts:

1. The reactor vessel, a steel shell that is 3–20-centimeters thick and, with the moderator, absorbs much of the radiation produced by the reactor
2. A main shield of 1–3 meters of high-density concrete
3. A personnel shield of lighter materials that protects operators from γ rays and X-rays

In addition, reactors are often covered with a steel or concrete dome that is designed to contain any radioactive materials might be released by a reactor accident.

Link to Learning

Click here to watch a **3-minute video (http://openstaxcollege.org/l/16nucreactors)** from the Nuclear Energy Institute on how nuclear reactors work.

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

Chemistry in Everyday Life

Nuclear Accidents

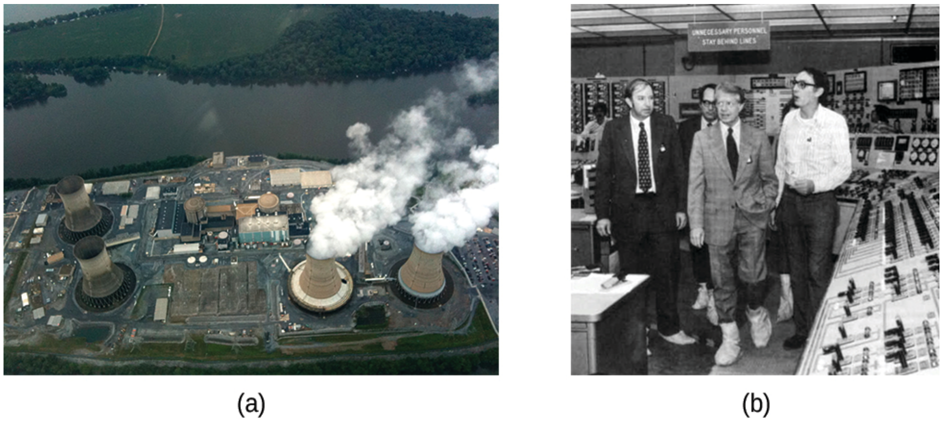
The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\text{Zr}(s) + 2\text{H}_2\text{O}(g) \longrightarrow \text{ZrO}_2(s) + 2\text{H}_2(g)$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (**Figure 20.21**).



(a) (b)

Figure 20.21 (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (**Figure 20.22**).

(a) (b)

Figure 20.22 (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by “Live Action Hero”/Flickr)

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

Link to Learning

Explore the information in this **link (http://openstaxcollege.org/l/16wastemgmt)** to learn about the approaches to nuclear waste management.

Nuclear Fusion and Fusion Reactors

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called **fusion**. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + 2\,{}^{0}_{+1}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6 × 10^{11} kJ of energy per mole of $^{4}_{2}\text{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8 × 10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, $^{2}_{1}$ and a triton, $^{3}_{1}$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$$^{2}_{1}\text{H} + ^{3}_{1}\text{H} \longrightarrow ^{4}_{2}\text{He} + 2^{1}_{0}\text{n}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69 × 10^{9} kilojoules per mole of $^{4}_{2}\text{He}$ formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

Another much more beneficial way to create fusion reactions is in a **fusion reactor**, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (**Figure 20.23**). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.

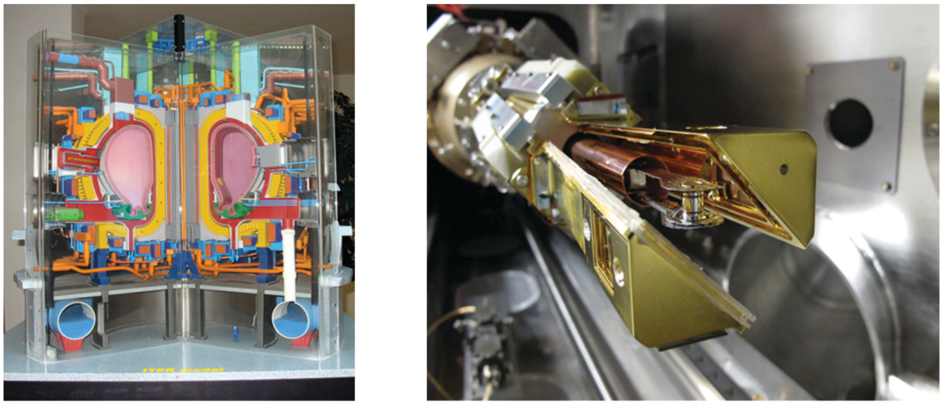

(a) (b)

Figure 20.23 (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving large-scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

20.5 Uses of Radioisotopes

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

- List common applications of radioactive isotopes

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a **radioactive tracer** (or **radioactive label**). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism. Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

Radioisotopes have revolutionized medical practice (see **Appendix M**), where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 $({}_{43}^{99}\text{Tc})$, thallium-201 $({}_{81}^{201}\text{Tl})$, iodine-131 $({}_{53}^{131}\text{I})$, and sodium-24 $({}_{11}^{24}\text{Na})$. Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 (**Figure 20.24**) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.

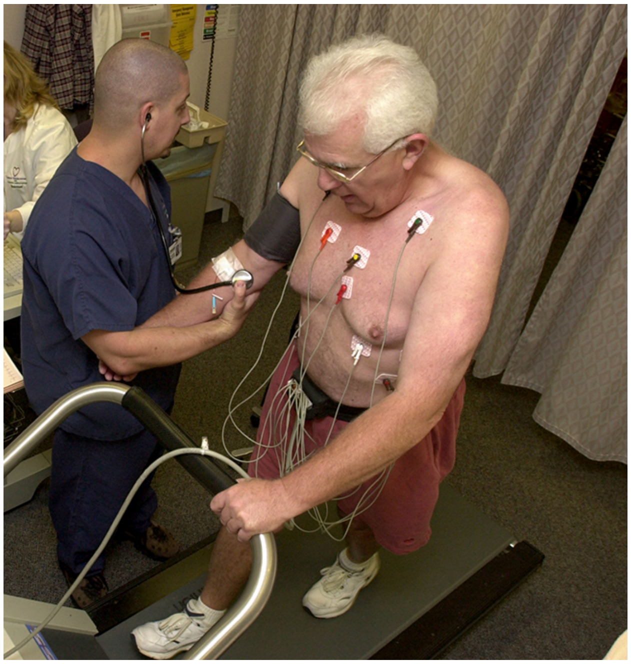


Figure 20.24 Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "Blue0ctane"/Wikimedia Commons)

Radioisotopes used in medicine typically have short half-lives—for example, the ubiquitous Tc-99m has a half-life of

6.01 hours. This makes Tc-99m essentially impossible to store and prohibitively expensive to transport, so it is made on-site instead. Hospitals and other medical facilities use Mo-99 (which is primarily extracted from U-235 fission products) to generate Tc-99. Mo-99 undergoes β decay with a half-life of 66 hours, and the Tc-99 is then chemically extracted (**Figure 20.25**). The parent nuclide Mo-99 is part of a molybdate ion, $\mathrm{MoO_4}^{2-}$; when it decays, it forms the pertechnetate ion, $\mathrm{TcO_4}^{-}$. These two water-soluble ions are separated by column chromatography, with the higher charge molybdate ion adsorbing onto the alumina in the column, and the lower charge pertechnetate ion passing through the column in the solution. A few micrograms of Mo-99 can produce enough Tc-99 to perform as many as 10,000 tests.

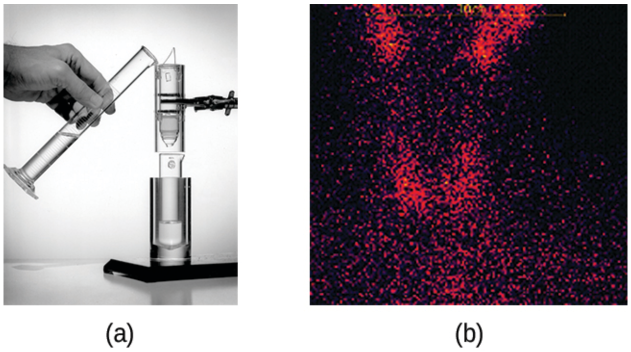


Figure 20.25 (a) The first Tc-99m generator (circa 1958) is used to separate Tc-99 from Mo-99. The $\mathrm{MoO_4}^{2-}$ is retained by the matrix in the column, whereas the $\mathrm{TcO_4}^{-}$ passes through and is collected. (b) Tc-99 was used in this scan of the neck of a patient with Grave’s disease. The scan shows the location of high concentrations of Tc-99. (credit a: modification of work by the Department of Energy; credit b: modification of work by “MBq”/Wikimedia Commons)

Radioisotopes can also be used, typically in higher doses than as a tracer, as treatment. **Radiation therapy** is the use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing (**Figure 20.26**). A cancer patient may receive **external beam radiation therapy** delivered by a machine outside the body, or **internal radiation therapy (brachytherapy)** from a radioactive substance that has been introduced into the body. Note that **chemotherapy** is similar to internal radiation therapy in that the cancer treatment is injected into the body, but differs in that chemotherapy uses chemical rather than radioactive substances to kill the cancer cells.

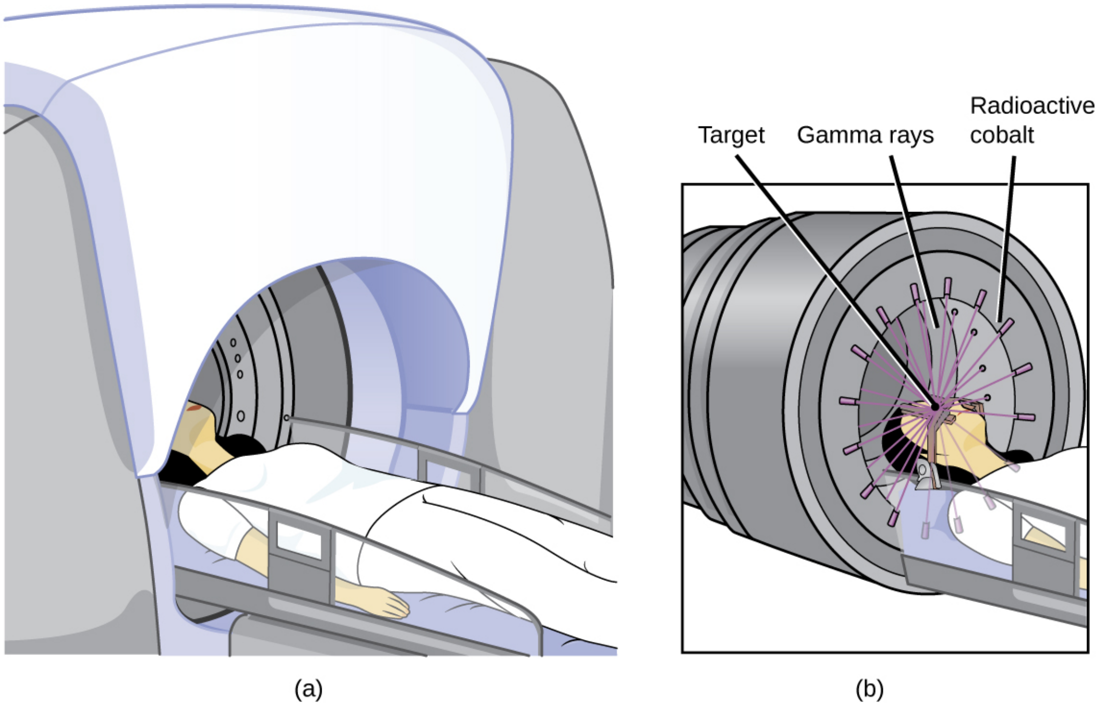


Figure 20.26 The cartoon in (a) shows a cobalt-60 machine used in the treatment of cancer. The diagram in (b) shows how the gantry of the Co-60 machine swings through an arc, focusing radiation on the targeted region (tumor) and minimizing the amount of radiation that passes through nearby regions.

Cobalt-60 is a synthetic radioisotope produced by the neutron activation of Co-59, which then undergoes β decay to form Ni-60, along with the emission of γ radiation. The overall process is:

$$ {}^{59}_{27}\text{Co} + {}^{1}_{0}\text{n} \longrightarrow {}^{60}_{27}\text{Co} \longrightarrow {}^{60}_{28}\text{Ni} + {}^{0}_{-1}\beta + 2{}^{0}_{0}\gamma $$

The overall decay scheme for this is shown graphically in **Figure 20.27**.

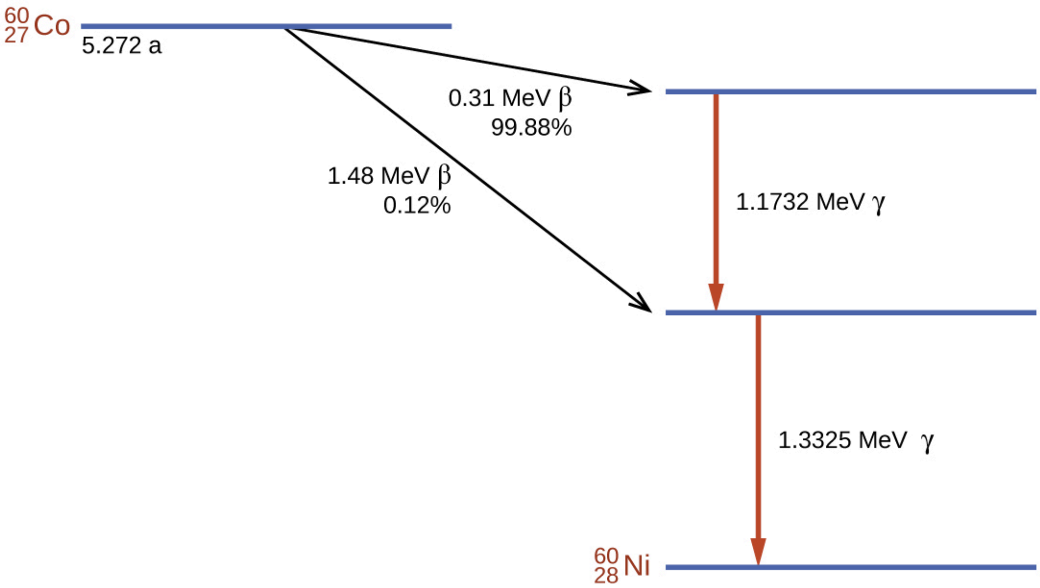


Figure 20.27 Co-60 undergoes a series of radioactive decays. The γ emissions are used for radiation therapy.

Radioisotopes are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope C-14 was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

$$6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g),$$

but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of $^{14}_{6}\text{C}$. At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Commercial applications of radioactive materials are equally diverse (**Figure 20.28**). They include determining the thickness of films and thin metal sheets by exploiting the penetration power of various types of radiation. Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring. Many foods are preserved by radiation that kills microorganisms that cause the foods to spoil.

Figure 20.28 Common commercial uses of radiation include (a) X-ray examination of luggage at an airport and (b) preservation of food. (credit a: modification of work by the Department of the Navy; credit b: modification of work by the US Department of Agriculture)

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (**Figure 20.29**). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.

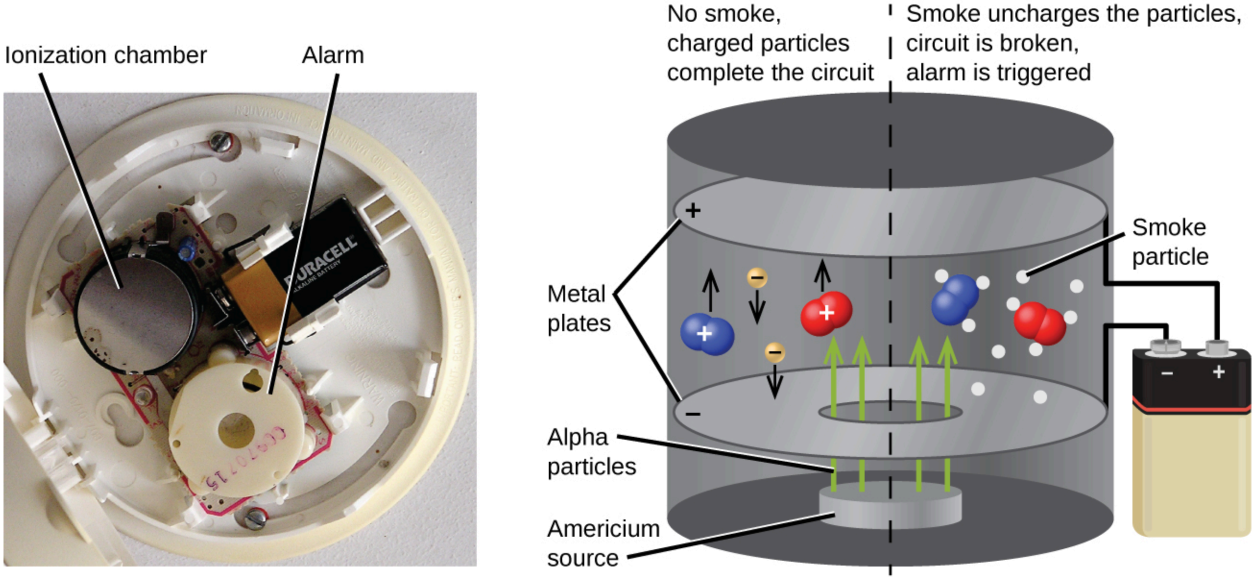


Figure 20.29 Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

20.6 Biological Effects of Radiation

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

- Describe the biological impact of ionizing radiation
- Define units for measuring radiation exposure
- Explain the operation of common tools for detecting radioactivity
- List common sources of radiation exposure in the US

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (**Figure 20.30**).

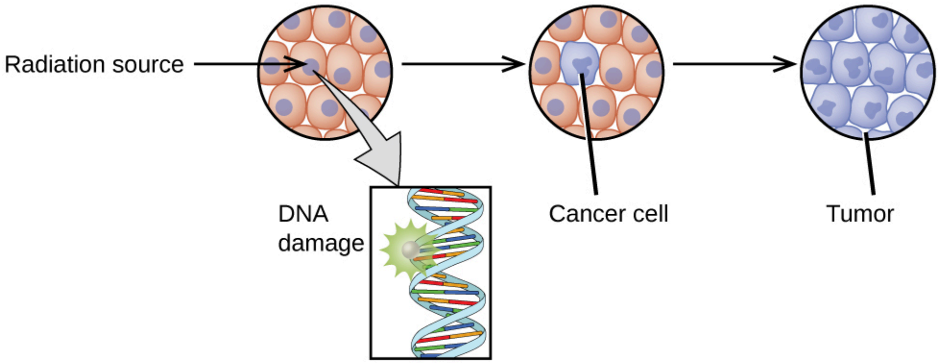


Figure 20.30 Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

Ionizing and Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of **nonionizing radiation** (for example, light and microwaves) and **ionizing radiation**, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (**Figure 20.31**).

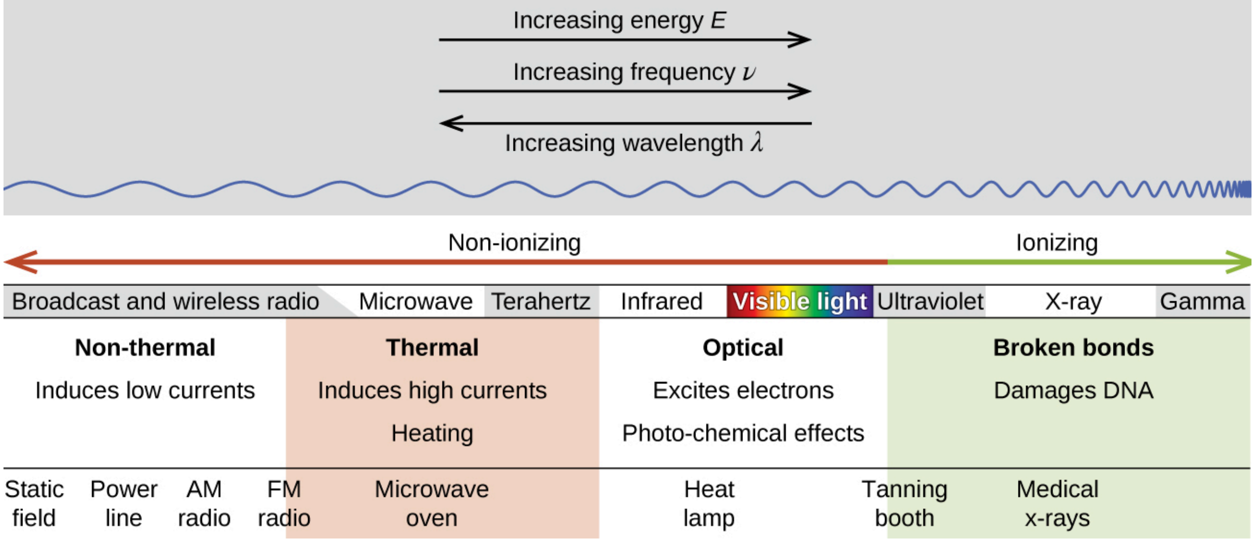
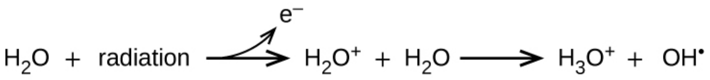


Figure 20.31 Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:



$$H_2O + \text{radiation} \xrightarrow{e^-} H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^{\bullet}$$

Because the hydroxyl radical has an unpaired electron, it is highly reactive. (This is true of any substance with unpaired electrons, known as a free radical.) This hydroxyl radical can react with all kinds of biological molecules (DNA, proteins, enzymes, and so on), causing damage to the molecules and disrupting physiological processes. Examples of direct and indirect damage are shown in **Figure 20.32**.

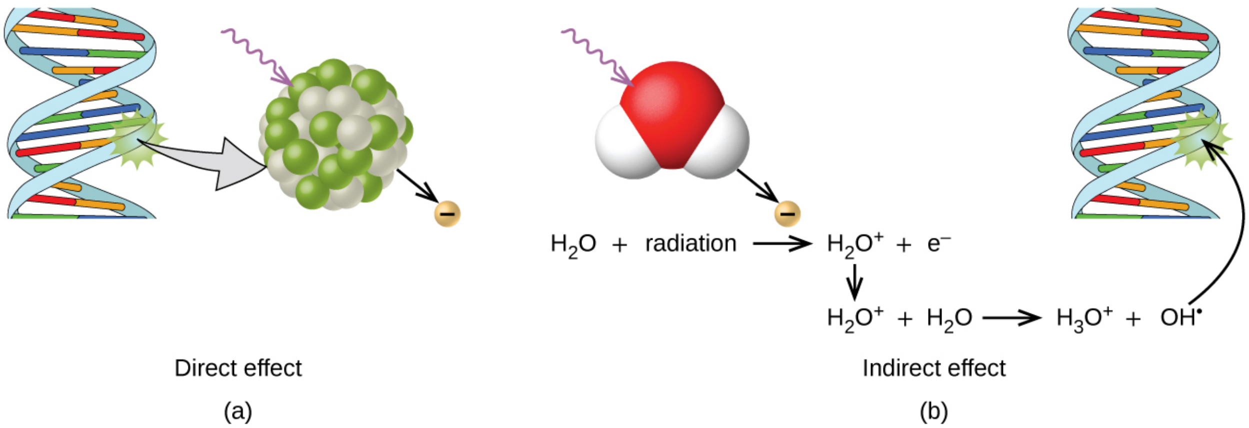


Figure 20.32 Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (**Figure 20.33**). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

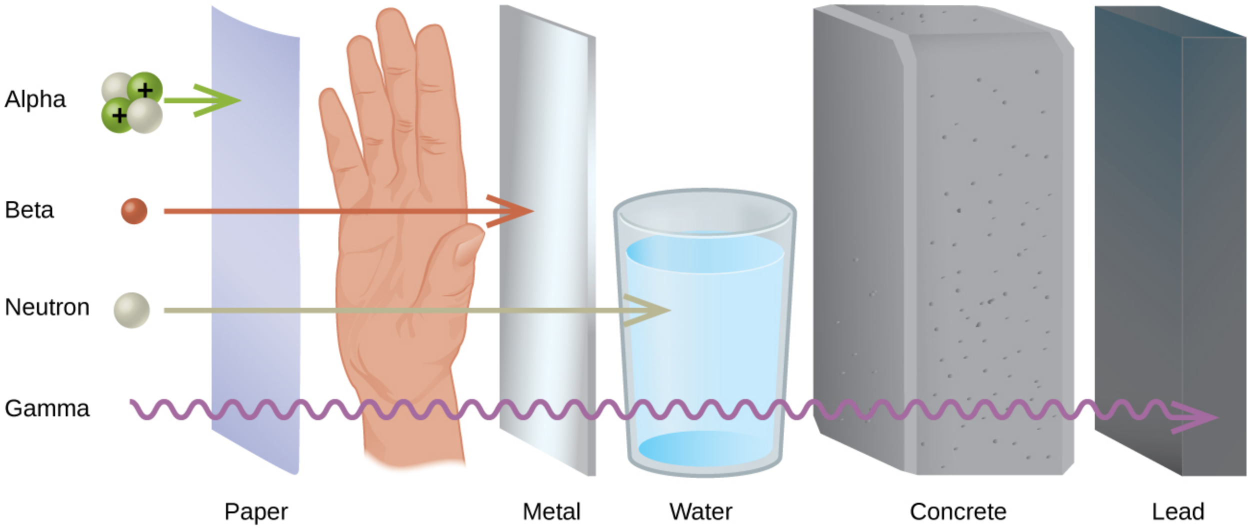


Figure 20.33 The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

Chemistry in Everyday Life

Radon Exposure

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238 (**Figure 20.9**), which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (**Figure 20.34**).

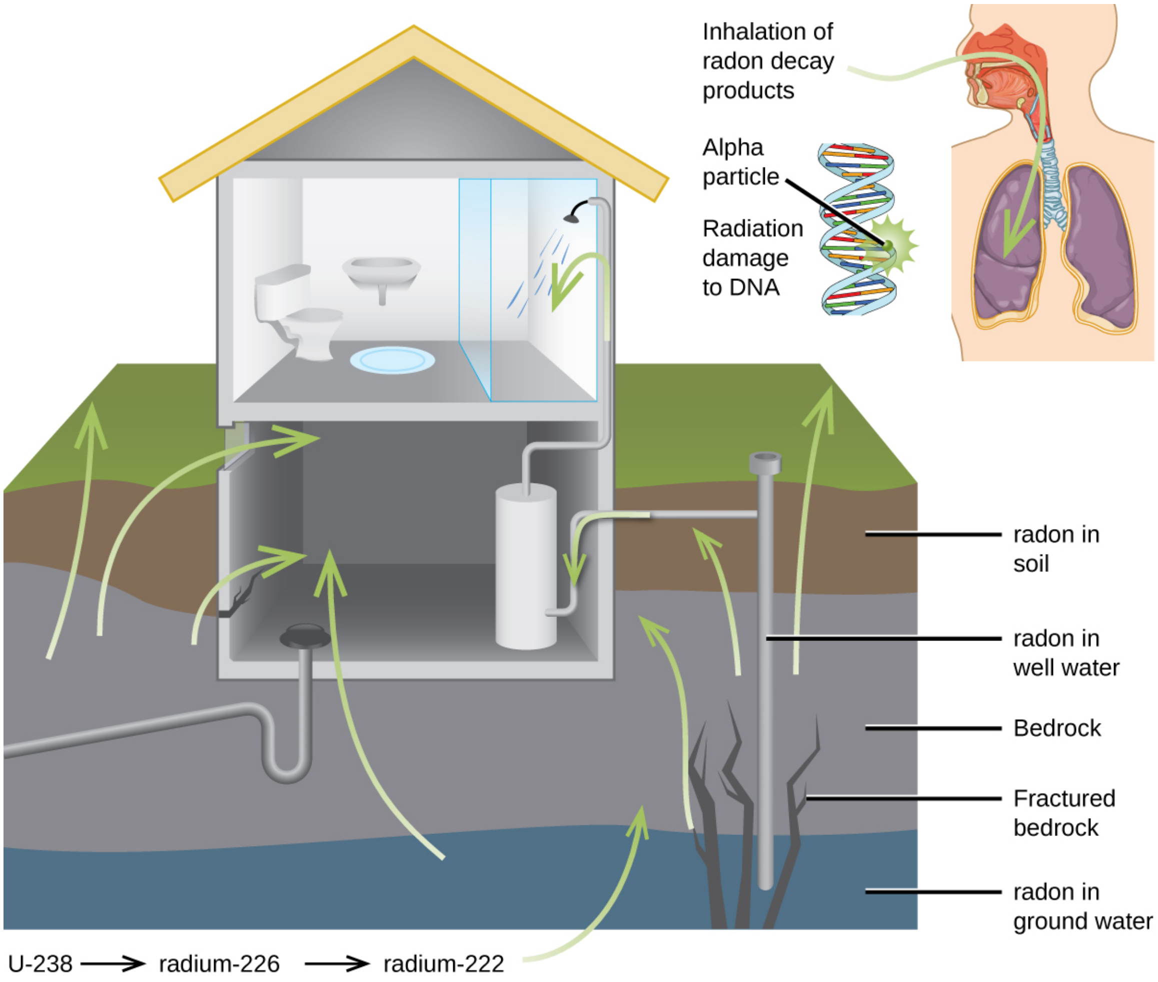


Figure 20.34 Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

Radon is found in buildings across the country, with amounts depending on where you live. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the levels found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure 20.35). Probably the best-known radiation instrument, the **Geiger counter** (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A **scintillation counter** contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. **Radiation dosimeters** also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

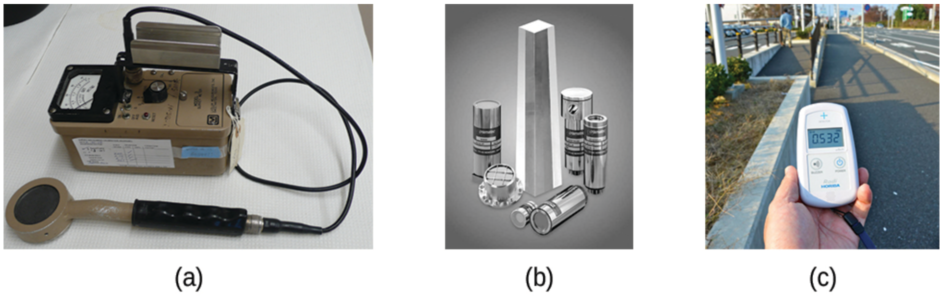


Figure 20.35 Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (credit c: modification of work by “osaMu”/Wikimedia commons)

A variety of units are used to measure various aspects of radiation (**Figure 20.36**). The SI unit for rate of radioactive decay is the **becquerel (Bq)**, with 1 Bq = 1 disintegration per second. The **curie (Ci)** and **millicurie (mCi)** are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7×10^{10} disintegrations per second). The SI unit for measuring radiation dose is the **gray (Gy)**, with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the **radiation absorbed dose (rad)** is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the **sievert (Sv)**. This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose. The **roentgen equivalent for man (rem)** is the unit for radiation damage that is used most frequently in medicine (100 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy) along with a biological factor referred to as the **RBE** (for **relative biological effectiveness**) that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

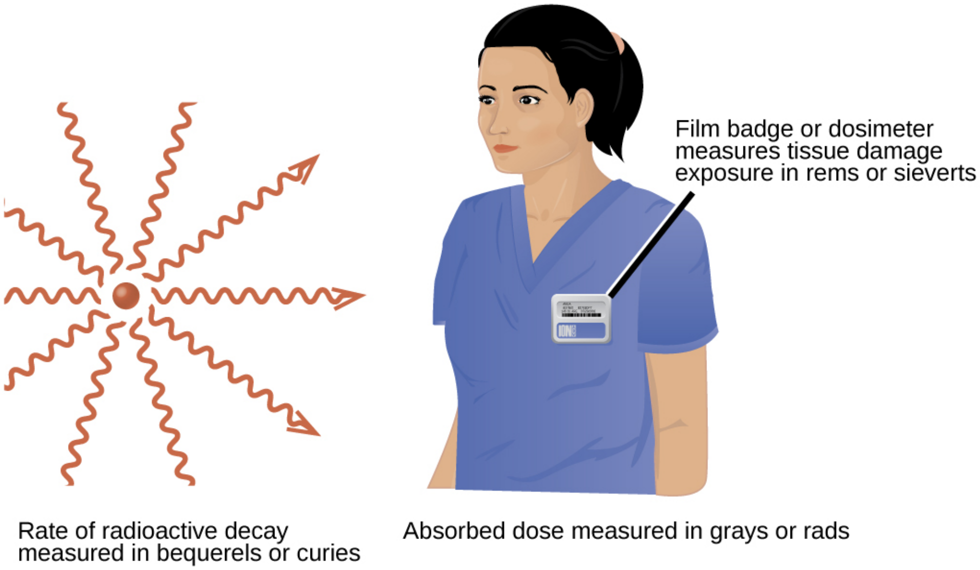


Figure 20.36 Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does.

Units of Radiation Measurement

Table 20.4 summarizes the units used for measuring radiation.

Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7 × 10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE × Gy
	roentgen equivalent for man (rem)		Rem = RBE × rad

Table 20.4

Example 20.8

Amount of Radiation

Cobalt-60 ($t_{1/2}$ = 5.26 y) is used in cancer therapy since the γ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.

(a) What is its activity in Bq?

(b) What is its activity in Ci?

Solution

The activity is given by:

$$\text{Activity} = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right)N = \left(\frac{\ln 2}{5.26\text{ y}}\right) \times 5.00\text{ g} = 0.659\,\frac{\text{g}}{\text{y}}\text{ of Co}-60\text{ that decay}$$

And to convert this to decays per second:

$$0.659\,\frac{\text{g}}{\text{y}} \times \frac{1\text{ y}}{365\text{ d}} \times \frac{1\text{ d}}{24\text{ h}} \times \frac{1\text{ h}}{3600\text{ s}} \times \frac{1\text{ mol}}{59.9\text{ g}} \times \frac{6.02 \times 10^{23}\text{ atoms}}{1\text{ mol}} \times \frac{1\text{ decay}}{1\text{ atom}}$$
$$= 2.10 \times 10^{14}\,\frac{\text{decay}}{\text{s}}$$

(a) Since 1 Bq = $\frac{1\text{ decay}}{\text{s}}$, the activity in Becquerel (Bq) is:

$$2.10 \times 10^{14}\,\frac{\text{decay}}{\text{s}} \times \left(\frac{1\text{ Bq}}{1\,\frac{\text{decay}}{\text{s}}}\right) = 2.10 \times 10^{14}\text{ Bq}$$

(b) Since 1 Ci = $\frac{3.7 \times 10^{11}\text{ decay}}{\text{s}}$, the activity in curie (Ci) is:

$$2.10 \times 10^{14}\ \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Ci}}{3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}} \right) = 5.7 \times 10^{2}\ \text{Ci}$$

Check Your Learning

Tritium is a radioactive isotope of hydrogen ($t_{1/2}$ = 12.32 y) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

Answer: (a) 3.56×10^{11} Bq; (b) 0.962 Ci

Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in **Figure 20.37**, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

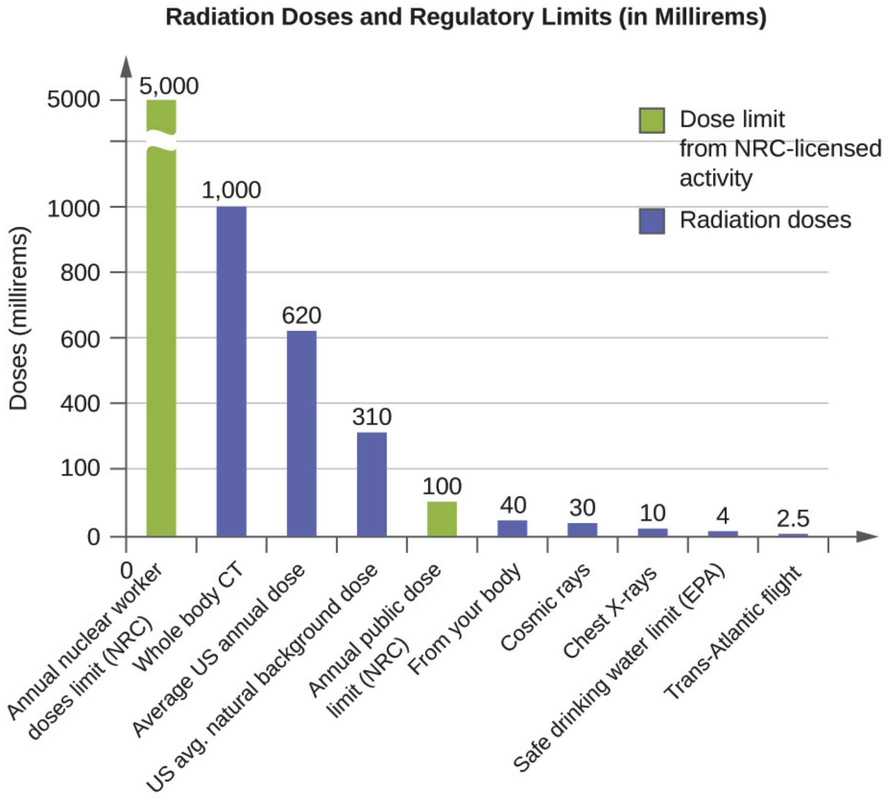


Figure 20.37 The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission)

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in **Table 20.5**.

Health Effects of Radiation[2]

Exposure (rem)	Health Effect	Time to Onset (without treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness;	minutes
	death	hours to days

Table 20.5

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

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[2] Source: US Environmental Protection Agency

Key Terms

alpha (α) decay loss of an alpha particle during radioactive decay

alpha particle $\left(\boldsymbol{\alpha} \text{ or } {}^{4}_{2}\mathbf{He} \text{ or } {}^{4}_{2}\boldsymbol{\alpha}\right)$ high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

antimatter particles with the same mass but opposite properties (such as charge) of ordinary particles

band of stability (also, belt of stability, zone of stability, or valley of stability) region of graph of number of protons versus number of neutrons containing stable (nonradioactive) nuclides

becquerel (Bq) SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s

beta (β) decay breakdown of a neutron into a proton, which remains in the nucleus, and an electron, which is emitted as a beta particle

beta particle $\left(\boldsymbol{\beta} \text{ or } {}^{0}_{-1}\mathbf{e} \text{ or } {}^{0}_{-1}\boldsymbol{\beta}\right)$ high-energy electron

binding energy per nucleon total binding energy for the nucleus divided by the number of nucleons in the nucleus

chain reaction repeated fission caused when the neutrons released in fission bombard other atoms

chemotherapy similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

containment system (also, shield) a three-part structure of materials that protects the exterior of a nuclear fission reactor and operating personnel from the high temperatures, pressures, and radiation levels inside the reactor

control rod material inserted into the fuel assembly that absorbs neutrons and can be raised or lowered to adjust the rate of a fission reaction

critical mass amount of fissionable material that will support a self-sustaining (nuclear fission) chain reaction

curie (Ci) larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

daughter nuclide nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

electron capture combination of a core electron with a proton to yield a neutron within the nucleus

electron volt (eV) measurement unit of nuclear binding energies, with 1 eV equaling the amount energy due to the moving an electron across an electric potential difference of 1 volt

external beam radiation therapy radiation delivered by a machine outside the body

fissile (or fissionable) when a material is capable of sustaining a nuclear fission reaction

fission splitting of a heavier nucleus into two or more lighter nuclei, usually accompanied by the conversion of mass into large amounts of energy

fusion combination of very light nuclei into heavier nuclei, accompanied by the conversion of mass into large amounts of energy

fusion reactor nuclear reactor in which fusion reactions of light nuclei are controlled

gamma (γ) emission decay of an excited-state nuclide accompanied by emission of a gamma ray

gamma ray **(γ or $^{0}_{0}\gamma$)** short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

Geiger counter instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube

gray (Gy) SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue

half-life ($t_{1/2}$) time required for half of the atoms in a radioactive sample to decay

internal radiation therapy (also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

ionizing radiation radiation that can cause a molecule to lose an electron and form an ion

magic number nuclei with specific numbers of nucleons that are within the band of stability

mass defect difference between the mass of an atom and the summed mass of its constituent subatomic particles (or the mass “lost” when nucleons are brought together to form a nucleus)

mass-energy equivalence equation Albert Einstein’s relationship showing that mass and energy are equivalent

millicurie (mCi) larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

nonionizing radiation radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules

nuclear binding energy energy lost when an atom’s nucleons are bound together (or the energy needed to break a nucleus into its constituent protons and neutrons)

nuclear chemistry study of the structure of atomic nuclei and processes that change nuclear structure

nuclear fuel fissionable isotope present in sufficient quantities to provide a self-sustaining chain reaction in a nuclear reactor

nuclear moderator substance that slows neutrons to a speed low enough to cause fission

nuclear reaction change to a nucleus resulting in changes in the atomic number, mass number, or energy state

nuclear reactor environment that produces energy via nuclear fission in which the chain reaction is controlled and sustained without explosion

nuclear transmutation conversion of one nuclide into another nuclide

nucleon collective term for protons and neutrons in a nucleus

nuclide nucleus of a particular isotope

parent nuclide unstable nuclide that changes spontaneously into another (daughter) nuclide

particle accelerator device that uses electric and magnetic fields to increase the kinetic energy of nuclei used in transmutation reactions

positron **($^{0}_{+1}\beta$ or $^{0}_{+1}e$)** antiparticle to the electron; it has identical properties to an electron, except for having the opposite (positive) charge

positron emission (also, β^+ decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

radiation absorbed dose (rad) SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy

radiation dosimeter device that measures ionizing radiation and is used to determine personal radiation exposure

radiation therapy use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

radioactive decay spontaneous decay of an unstable nuclide into another nuclide

radioactive decay series chains of successive disintegrations (radioactive decays) that ultimately lead to a stable end-product

radioactive tracer (also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

radioactivity phenomenon exhibited by an unstable nucleon that spontaneously undergoes change into a nucleon that is more stable; an unstable nucleon is said to be radioactive

radiocarbon dating highly accurate means of dating objects 30,000–50,000 years old that were derived from once-living matter; achieved by calculating the ratio of ${}_{6}^{14}\text{C}:{}_{6}^{12}\text{C}$ in the object vs. the ratio of ${}_{6}^{14}\text{C}:{}_{6}^{12}\text{C}$ in the present-day atmosphere

radioisotope isotope that is unstable and undergoes conversion into a different, more stable isotope

radiometric dating use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

reactor coolant assembly used to carry the heat produced by fission in a reactor to an external boiler and turbine where it is transformed into electricity

relative biological effectiveness (RBE) measure of the relative damage done by radiation

roentgen equivalent man (rem) unit for radiation damage, frequently used in medicine; 100 rem = 1 Sv

scintillation counter instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation

sievert (Sv) SI unit measuring tissue damage caused by radiation; takes into account energy and biological effects of radiation

strong nuclear force force of attraction between nucleons that holds a nucleus together

subcritical mass amount of fissionable material that cannot sustain a chain reaction; less than a critical mass

supercritical mass amount of material in which there is an increasing rate of fission

transmutation reaction bombardment of one type of nuclei with other nuclei or neutrons

transuranium element element with an atomic number greater than 92; these elements do not occur in nature

Key Equations

- $E = mc^2$
- decay rate = λN

- $t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$
- rem = RBE × rad
- Sv = RBE × Gy

Summary

20.1 Nuclear Structure and Stability

An atomic nucleus consists of protons and neutrons, collectively called nucleons. Although protons repel each other, the nucleus is held tightly together by a short-range, but very strong, force called the strong nuclear force. A nucleus has less mass than the total mass of its constituent nucleons. This “missing” mass is the mass defect, which has been converted into the binding energy that holds the nucleus together according to Einstein’s mass-energy equivalence equation, $E = mc^2$. Of the many nuclides that exist, only a small number are stable. Nuclides with even numbers of protons or neutrons, or those with magic numbers of nucleons, are especially likely to be stable. These stable nuclides occupy a narrow band of stability on a graph of number of protons versus number of neutrons. The binding energy per nucleon is largest for the elements with mass numbers near 56; these are the most stable nuclei.

20.2 Nuclear Equations

Nuclei can undergo reactions that change their number of protons, number of neutrons, or energy state. Many different particles can be involved in nuclear reactions. The most common are protons, neutrons, positrons (which are positively charged electrons), alpha (α) particles (which are high-energy helium nuclei), beta (β) particles (which are high-energy electrons), and gamma (γ) rays (which compose high-energy electromagnetic radiation). As with chemical reactions, nuclear reactions are always balanced. When a nuclear reaction occurs, the total mass (number) and the total charge remain unchanged.

20.3 Radioactive Decay

Nuclei that have unstable n:p ratios undergo spontaneous radioactive decay. The most common types of radioactivity are α decay, β decay, γ emission, positron emission, and electron capture. Nuclear reactions also often involve γ rays, and some nuclei decay by electron capture. Each of these modes of decay leads to the formation of a new nucleus with a more stable n:p ratio. Some substances undergo radioactive decay series, proceeding through multiple decays before ending in a stable isotope. All nuclear decay processes follow first-order kinetics, and each radioisotope has its own characteristic half-life, the time that is required for half of its atoms to decay. Because of the large differences in stability among nuclides, there is a very wide range of half-lives of radioactive substances. Many of these substances have found useful applications in medical diagnosis and treatment, determining the age of archaeological and geological objects, and more.

20.4 Transmutation and Nuclear Energy

It is possible to produce new atoms by bombarding other atoms with nuclei or high-speed particles. The products of these transmutation reactions can be stable or radioactive. A number of artificial elements, including technetium, astatine, and the transuranium elements, have been produced in this way.

Nuclear power as well as nuclear weapon detonations can be generated through fission (reactions in which a heavy nucleus is split into two or more lighter nuclei and several neutrons). Because the neutrons may induce additional fission reactions when they combine with other heavy nuclei, a chain reaction can result. Useful power is obtained if the fission process is carried out in a nuclear reactor. The conversion of light nuclei into heavier nuclei (fusion) also produces energy. At present, this energy has not been contained adequately and is too expensive to be feasible for commercial energy production.

20.5 Uses of Radioisotopes

Compounds known as radioactive tracers can be used to follow reactions, track the distribution of a substance, diagnose and treat medical conditions, and much more. Other radioactive substances are helpful for controlling pests, visualizing structures, providing fire warnings, and for many other applications. Hundreds of millions of nuclear medicine tests and procedures, using a wide variety of radioisotopes with relatively short half-lives, are performed every year in the US. Most of these radioisotopes have relatively short half-lives; some are short enough that the radioisotope must be made on-site at medical facilities. Radiation therapy uses high-energy radiation to kill cancer cells by damaging their DNA. The radiation used for this treatment may be delivered externally or internally.

20.6 Biological Effects of Radiation

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating but potentially most damaging and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, and including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source, and limiting time of exposure.

Exercises

20.1 Nuclear Structure and Stability

1. Write the following isotopes in hyphenated form (e.g., “carbon-14”)

(a) ${}_{11}^{24}\text{Na}$

(b) ${}_{13}^{29}\text{Al}$

(c) ${}_{36}^{73}\text{Kr}$

(d) ${}_{77}^{194}\text{Ir}$

2. Write the following isotopes in nuclide notation (e.g., $\text{"}{}_{6}^{14}\text{C"}\big)$

(a) oxygen-14

(b) copper-70

(c) tantalum-175

(d) francium-217

3. For the following isotopes that have missing information, fill in the missing information to complete the notation

(a) ${}_{14}^{34}\text{X}$

(b) ${}_{\text{X}}^{36}\text{P}$

(c) ${}_{\text{X}}^{57}\text{Mn}$

(d) ${}_{56}^{121}\text{X}$

4. For each of the isotopes in **Exercise 20.1**, determine the numbers of protons, neutrons, and electrons in a neutral atom of the isotope.

5. Write the nuclide notation, including charge if applicable, for atoms with the following characteristics:

(a) 25 protons, 20 neutrons, 24 electrons

(b) 45 protons, 24 neutrons, 43 electrons

(c) 53 protons, 89 neutrons, 54 electrons

(d) 97 protons, 146 neutrons, 97 electrons

6. Calculate the density of the $^{24}_{12}\text{Mg}$ nucleus in g/mL, assuming that it has the typical nuclear diameter of 1×10^{-13} cm and is spherical in shape.

7. What are the two principal differences between nuclear reactions and ordinary chemical changes?

8. The mass of the atom $^{23}_{11}\text{Na}$ is 22.9898 amu.

(a) Calculate its binding energy per atom in millions of electron volts.

(b) Calculate its binding energy per nucleon.

9. Which of the following nuclei lie within the band of stability shown in **Figure 20.2**?

(a) chlorine-37

(b) calcium-40

(c) ^{204}Bi

(d) ^{56}Fe

(e) ^{206}Pb

(f) ^{211}Pb

(g) ^{222}Rn

(h) carbon-14

10. Which of the following nuclei lie within the band of stability shown in **Figure 20.2**?

(a) argon-40

(b) oxygen-16

(c) ^{122}Ba

(d) ^{58}Ni

(e) ^{205}Tl

(f) ^{210}Tl

(g) ^{226}Ra

(h) magnesium-24

20.2 Nuclear Equations

11. Write a brief description or definition of each of the following:

(a) nucleon

(b) α particle

(c) β particle

(d) positron

(e) γ ray

(f) nuclide

(g) mass number

(h) atomic number

12. Which of the various particles (α particles, β particles, and so on) that may be produced in a nuclear reaction are actually nuclei?

13. Complete each of the following equations by adding the missing species:

(a) $^{27}_{13}\text{Al} + ^{4}_{2}\text{He} \longrightarrow \,?\, + ^{1}_{0}\text{n}$

(b) $^{239}_{94}\text{Pu} + \,?\, \longrightarrow ^{242}_{96}\text{Cm} + ^{1}_{0}\text{n}$

(c) $^{14}_{7}\text{N} + ^{4}_{2}\text{He} \longrightarrow \,?\, + ^{1}_{1}\text{H}$

(d) $^{235}_{92}\text{U} \longrightarrow \,?\, + ^{135}_{55}\text{Cs} + 4^{1}_{0}\text{n}$

14. Complete each of the following equations:

(a) $^{7}_{3}\text{Li} + \,?\, \longrightarrow 2^{4}_{2}\text{He}$

(b) $^{14}_{6}\text{C} \longrightarrow ^{14}_{7}\text{N} + \,?$

(c) $^{27}_{13}\text{Al} + ^{4}_{2}\text{He} \longrightarrow \,?\, + ^{1}_{0}\text{n}$

(d) $^{250}_{96}\text{Cm} \longrightarrow \,?\, + ^{98}_{38}\text{Sr} + 4^{1}_{0}\text{n}$

15. Write a balanced equation for each of the following nuclear reactions:

(a) the production of ^{17}O from ^{14}N by α particle bombardment

(b) the production of ^{14}C from ^{14}N by neutron bombardment

(c) the production of ^{233}Th from ^{232}Th by neutron bombardment

(d) the production of ^{239}U from ^{238}U by $^{2}_{1}\text{H}$ bombardment

16. Technetium-99 is prepared from ^{98}Mo. Molybdenum-98 combines with a neutron to give molybdenum-99, an unstable isotope that emits a β particle to yield an excited form of technetium-99, represented as $^{99}\text{Tc}^{*}$. This excited nucleus relaxes to the ground state, represented as ^{99}Tc, by emitting a γ ray. The ground state of ^{99}Tc then emits a β particle. Write the equations for each of these nuclear reactions.

17. The mass of the atom $^{19}_{9}\text{F}$ is 18.99840 amu.

(a) Calculate its binding energy per atom in millions of electron volts.

(b) Calculate its binding energy per nucleon.

18. For the reaction $^{14}_{6}\text{C} \longrightarrow ^{14}_{7}\text{N} + \,?,$ if 100.0 g of carbon reacts, what volume of nitrogen gas (N_2) is produced at 273K and 1 atm?

20.3 Radioactive Decay

19. What are the types of radiation emitted by the nuclei of radioactive elements?

20. What changes occur to the atomic number and mass of a nucleus during each of the following decay scenarios?

(a) an α particle is emitted

(b) a β particle is emitted

(c) γ radiation is emitted

(d) a positron is emitted

(e) an electron is captured

21. What is the change in the nucleus that results from the following decay scenarios?

(a) emission of a β particle

(b) emission of a β^+ particle

(c) capture of an electron

22. Many nuclides with atomic numbers greater than 83 decay by processes such as electron emission. Explain the observation that the emissions from these unstable nuclides also normally include α particles.

23. Why is electron capture accompanied by the emission of an X-ray?

24. Explain, in terms of **Figure 20.2**, how unstable heavy nuclides (atomic number > 83) may decompose to form nuclides of greater stability (a) if they are below the band of stability and (b) if they are above the band of stability.

25. Which of the following nuclei is most likely to decay by positron emission? Explain your choice.

(a) chromium-53

(b) manganese-51

(c) iron-59

26. The following nuclei do not lie in the band of stability. How would they be expected to decay? Explain your answer.

(a) ${}^{34}_{15}\text{P}$

(b) ${}^{239}_{92}\text{U}$

(c) ${}^{38}_{20}\text{Ca}$

(d) ${}^{3}_{1}\text{H}$

(e) ${}^{245}_{94}\text{Pu}$

27. The following nuclei do not lie in the band of stability. How would they be expected to decay?

(a) ${}^{28}_{15}\text{P}$

(b) ${}^{235}_{92}\text{U}$

(c) ${}^{37}_{20}\text{Ca}$

(d) ${}^{9}_{3}\text{Li}$

(e) ${}^{245}_{96}\text{Cm}$

28. Predict by what mode(s) of spontaneous radioactive decay each of the following unstable isotopes might proceed:

(a) ${}_{2}^{6}\text{He}$

(b) ${}_{30}^{60}\text{Zn}$

(c) ${}_{91}^{235}\text{Pa}$

(d) ${}_{94}^{241}\text{Np}$

(e) ${}^{18}\text{F}$

(f) ${}^{129}\text{Ba}$

(g) ${}^{237}\text{Pu}$

29. Write a nuclear reaction for each step in the formation of ${}_{84}^{218}\text{Po}$ from ${}_{98}^{238}\text{U},$ which proceeds by a series of decay reactions involving the step-wise emission of α, β, β, α, α, α particles, in that order.

30. Write a nuclear reaction for each step in the formation of ${}_{82}^{208}\text{Pb}$ from ${}_{90}^{228}\text{Th},$ which proceeds by a series of decay reactions involving the step-wise emission of α, α, α, α, β, β, α particles, in that order.

31. Define the term half-life and illustrate it with an example.

32. A 1.00×10^{-6}-g sample of nobelium, ${}_{102}^{254}\text{No},$ has a half-life of 55 seconds after it is formed. What is the percentage of ${}_{102}^{254}\text{No}$ remaining at the following times?

(a) 5.0 min after it forms

(b) 1.0 h after it forms

33. ${}^{239}\text{Pu}$ is a nuclear waste byproduct with a half-life of 24,000 y. What fraction of the ${}^{239}\text{Pu}$ present today will be present in 1000 y?

34. The isotope ${}^{208}\text{Tl}$ undergoes β decay with a half-life of 3.1 min.

(a) What isotope is produced by the decay?

(b) How long will it take for 99.0% of a sample of pure ${}^{208}\text{Tl}$ to decay?

(c) What percentage of a sample of pure ${}^{208}\text{Tl}$ remains un-decayed after 1.0 h?

35. If 1.000 g of ${}_{88}^{226}\text{Ra}$ produces 0.0001 mL of the gas ${}_{86}^{222}\text{Rn}$ at STP (standard temperature and pressure) in 24 h, what is the half-life of ${}^{226}\text{Ra}$ in years?

36. The isotope ${}_{38}^{90}\text{Sr}$ is one of the extremely hazardous species in the residues from nuclear power generation. The strontium in a 0.500-g sample diminishes to 0.393 g in 10.0 y. Calculate the half-life.

37. Technetium-99 is often used for assessing heart, liver, and lung damage because certain technetium compounds are absorbed by damaged tissues. It has a half-life of 6.0 h. Calculate the rate constant for the decay of ${}_{43}^{99}\text{Tc}.$

38. What is the age of mummified primate skin that contains 8.25% of the original quantity of ${}^{14}\text{C}$?

39. A sample of rock was found to contain 8.23 mg of rubidium-87 and 0.47 mg of strontium-87.

(a) Calculate the age of the rock if the half-life of the decay of rubidium by β emission is 4.7×10^{10} y.

(b) If some ${}_{38}^{87}\text{Sr}$ was initially present in the rock, would the rock be younger, older, or the same age as the age calculated in (a)? Explain your answer.

40. A laboratory investigation shows that a sample of uranium ore contains 5.37 mg of ${}_{92}^{238}\text{U}$ and 2.52 mg of ${}_{82}^{206}\text{Pb}.$ Calculate the age of the ore. The half-life of ${}_{92}^{238}\text{U}$ is 4.5×10^{9} yr.

41. Plutonium was detected in trace amounts in natural uranium deposits by Glenn Seaborg and his associates in 1941. They proposed that the source of this ^{239}Pu was the capture of neutrons by ^{238}U nuclei. Why is this plutonium not likely to have been trapped at the time the solar system formed 4.7 × 10^9 years ago?

42. A $^{7}_{4}\text{Be}$ atom (mass = 7.0169 amu) decays into a $^{7}_{3}\text{Li}$ atom (mass = 7.0160 amu) by electron capture. How much energy (in millions of electron volts, MeV) is produced by this reaction?

43. A $^{8}_{5}\text{B}$ atom (mass = 8.0246 amu) decays into a $^{8}_{4}\text{B}$ atom (mass = 8.0053 amu) by loss of a β^+ particle (mass = 0.00055 amu) or by electron capture. How much energy (in millions of electron volts) is produced by this reaction?

44. Isotopes such as ^{26}Al (half-life: 7.2 × 10^5 years) are believed to have been present in our solar system as it formed, but have since decayed and are now called extinct nuclides.

(a) ^{26}Al decays by β^+ emission or electron capture. Write the equations for these two nuclear transformations.

(b) The earth was formed about 4.7 × 10^9 (4.7 billion) years ago. How old was the earth when 99.999999% of the ^{26}Al originally present had decayed?

45. Write a balanced equation for each of the following nuclear reactions:

(a) bismuth-212 decays into polonium-212

(b) beryllium-8 and a positron are produced by the decay of an unstable nucleus

(c) neptunium-239 forms from the reaction of uranium-238 with a neutron and then spontaneously converts into plutonium-239

(d) strontium-90 decays into yttrium-90

46. Write a balanced equation for each of the following nuclear reactions:

(a) mercury-180 decays into platinum-176

(b) zirconium-90 and an electron are produced by the decay of an unstable nucleus

(c) thorium-232 decays and produces an alpha particle and a radium-228 nucleus, which decays into actinium-228 by beta decay

(d) neon-19 decays into fluorine-19

20.4 Transmutation and Nuclear Energy

47. Write the balanced nuclear equation for the production of the following transuranium elements:

(a) berkelium-244, made by the reaction of Am-241 and He-4

(b) fermium-254, made by the reaction of Pu-239 with a large number of neutrons

(c) lawrencium-257, made by the reaction of Cf-250 and B-11

(d) dubnium-260, made by the reaction of Cf-249 and N-15

48. How does nuclear fission differ from nuclear fusion? Why are both of these processes exothermic?

49. Both fusion and fission are nuclear reactions. Why is a very high temperature required for fusion, but not for fission?

50. Cite the conditions necessary for a nuclear chain reaction to take place. Explain how it can be controlled to produce energy, but not produce an explosion.

51. Describe the components of a nuclear reactor.

52. In usual practice, both a moderator and control rods are necessary to operate a nuclear chain reaction safely for the purpose of energy production. Cite the function of each and explain why both are necessary.

53. Describe how the potential energy of uranium is converted into electrical energy in a nuclear power plant.

54. The mass of a hydrogen atom $(^{1}_{1}\text{H})$ is 1.007825 amu; that of a tritium atom $(^{3}_{1}\text{H})$ is 3.01605 amu; and that of an α particle is 4.00150 amu. How much energy in kilojoules per mole of $^{4}_{2}\text{He}$ produced is released by the following fusion reaction: $^{1}_{1}\text{H} + ^{3}_{1}\text{H} \longrightarrow ^{4}_{2}\text{He}.$

20.5 Uses of Radioisotopes

55. How can a radioactive nuclide be used to show that the equilibrium:

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$$

is a dynamic equilibrium?

56. Technetium-99m has a half-life of 6.01 hours. If a patient injected with technetium-99m is safe to leave the hospital once 75% of the dose has decayed, when is the patient allowed to leave?

57. Iodine that enters the body is stored in the thyroid gland from which it is released to control growth and metabolism. The thyroid can be imaged if iodine-131 is injected into the body. In larger doses, I-133 is also used as a means of treating cancer of the thyroid. I-131 has a half-life of 8.70 days and decays by β^- emission.

(a) Write an equation for the decay.

(b) How long will it take for 95.0% of a dose of I-131 to decay?

20.6 Biological Effects of Radiation

58. If a hospital were storing radioisotopes, what is the minimum containment needed to protect against:

(a) cobalt-60 (a strong γ emitter used for irradiation)

(b) molybdenum-99 (a beta emitter used to produce technetium-99 for imaging)

59. Based on what is known about Radon-222's primary decay method, why is inhalation so dangerous?

60. Given specimens uranium-232 ($t_{1/2}$ = 68.9 y) and uranium-233 ($t_{1/2}$ = 159,200 y) of equal mass, which one would have greater activity and why?

61. A scientist is studying a 2.234 g sample of thorium-229 ($t_{1/2}$ = 7340 y) in a laboratory.

(a) What is its activity in Bq?

(b) What is its activity in Ci?

62. Given specimens neon-24 ($t_{1/2}$ = 3.38 min) and bismuth-211 ($t_{1/2}$ = 2.14 min) of equal mass, which one would have greater activity and why?

Chapter 21

Organic Chemistry

Figure 21.1 All organic compounds contain carbon and most are formed by living things, although they are also formed by geological and artificial processes. (credit left: modification of work by Jon Sullivan; credit left middle: modification of work by Deb Tremper; credit right middle: modification of work by “annszyp”/Wikimedia Commons; credit right: modification of work by George Shuklin)

Chapter Outline

Introduction

All living things on earth are formed mostly of carbon compounds. The prevalence of carbon compounds in living things has led to the epithet “carbon-based” life. The truth is we know of no other kind of life. Early chemists regarded substances isolated from *organisms* (plants and animals) as a different type of matter that could not be synthesized artificially, and these substances were thus known as *organic compounds*. The widespread belief called vitalism held that organic compounds were formed by a vital force present only in living organisms. The German chemist Friedrich Wohler was one of the early chemists to refute this aspect of vitalism, when, in 1828, he reported the synthesis of urea, a component of many body fluids, from nonliving materials. Since then, it has been recognized that organic molecules obey the same natural laws as inorganic substances, and the category of organic compounds has evolved to include both natural and synthetic compounds that contain carbon. Some carbon-containing compounds are *not* classified as organic, for example, carbonates and cyanides, and simple oxides, such as CO and CO_2. Although a single, precise definition has yet to be identified by the chemistry community, most agree that a defining trait of organic molecules is the presence of carbon as the principal element, bonded to hydrogen and other carbon atoms.

Today, organic compounds are key components of plastics, soaps, perfumes, sweeteners, fabrics, pharmaceuticals, and many other substances that we use every day. The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry. In this chapter, we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings.

21.1 Hydrocarbons

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

- Explain the importance of hydrocarbons and the reason for their diversity
- Name saturated and unsaturated hydrocarbons, and molecules derived from them
- Describe the reactions characteristic of saturated and unsaturated hydrocarbons
- Identify structural and geometric isomers of hydrocarbons

The largest database[1] of organic compounds lists about 10 million substances, which include compounds originating from living organisms and those synthesized by chemists. The number of potential organic compounds has been estimated[2] at 10^{60}—an astronomically high number. The existence of so many organic molecules is a consequence of the ability of carbon atoms to form up to four strong bonds to other carbon atoms, resulting in chains and rings of many different sizes, shapes, and complexities.

The simplest **organic compounds** contain only the elements carbon and hydrogen, and are called hydrocarbons. Even though they are composed of only two types of atoms, there is a wide variety of hydrocarbons because they may consist of varying lengths of chains, branched chains, and rings of carbon atoms, or combinations of these structures. In addition, hydrocarbons may differ in the types of carbon-carbon bonds present in their molecules. Many hydrocarbons are found in plants, animals, and their fossils; other hydrocarbons have been prepared in the laboratory. We use hydrocarbons every day, mainly as fuels, such as natural gas, acetylene, propane, butane, and the principal components of gasoline, diesel fuel, and heating oil. The familiar plastics polyethylene, polypropylene, and polystyrene are also hydrocarbons. We can distinguish several types of hydrocarbons by differences in the bonding between carbon atoms. This leads to differences in geometries and in the hybridization of the carbon orbitals.

Alkanes

Alkanes, or **saturated hydrocarbons**, contain only single covalent bonds between carbon atoms. Each of the carbon atoms in an alkane has sp^3 hybrid orbitals and is bonded to four other atoms, each of which is either carbon or hydrogen. The Lewis structures and models of methane, ethane, and pentane are illustrated in **Figure 21.2**. Carbon chains are usually drawn as straight lines in Lewis structures, but one has to remember that Lewis structures are not intended to indicate the geometry of molecules. Notice that the carbon atoms in the structural models (the ball-and-stick and space-filling models) of the pentane molecule do not lie in a straight line. Because of the sp^3 hybridization, the bond angles in carbon chains are close to 109.5°, giving such chains in an alkane a zigzag shape.

The structures of alkanes and other organic molecules may also be represented in a less detailed manner by condensed structural formulas (or simply, *condensed formulas*). Instead of the usual format for chemical formulas in which each element symbol appears just once, a condensed formula is written to suggest the bonding in the molecule. These formulas have the appearance of a Lewis structure from which most or all of the bond symbols have been removed. Condensed structural formulas for ethane and pentane are shown at the bottom of **Figure 21.2**, and several additional examples are provided in the exercises at the end of this chapter.

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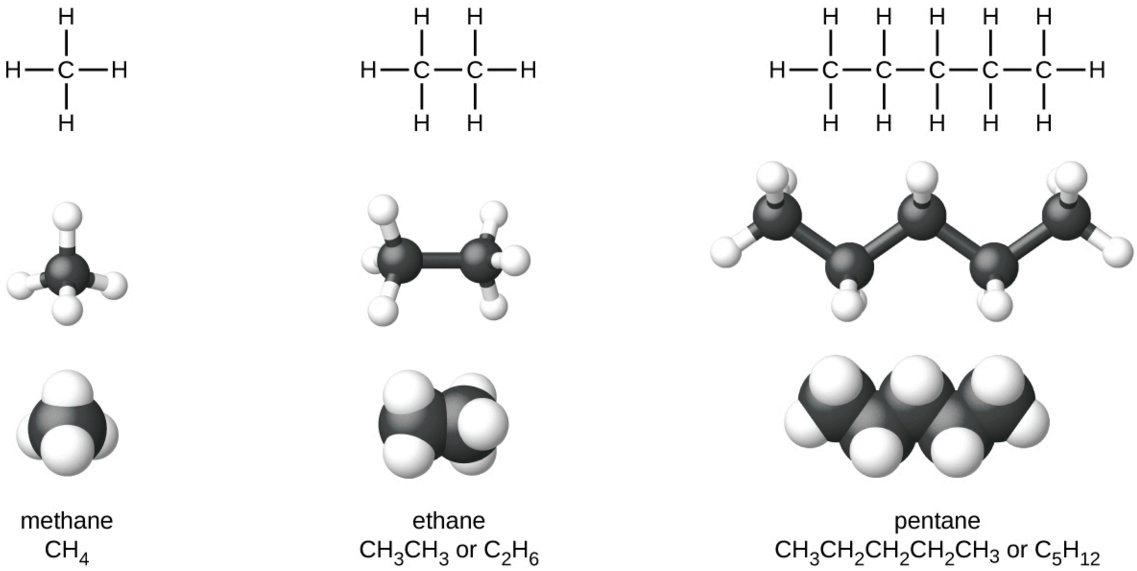
1. This is the Beilstein database, now available through the Reaxys site (www.elsevier.com/online-tools/reaxys).
2. Peplow, Mark. “Organic Synthesis: The Robo-Chemist,” *Nature* 512 (2014): 20–2.



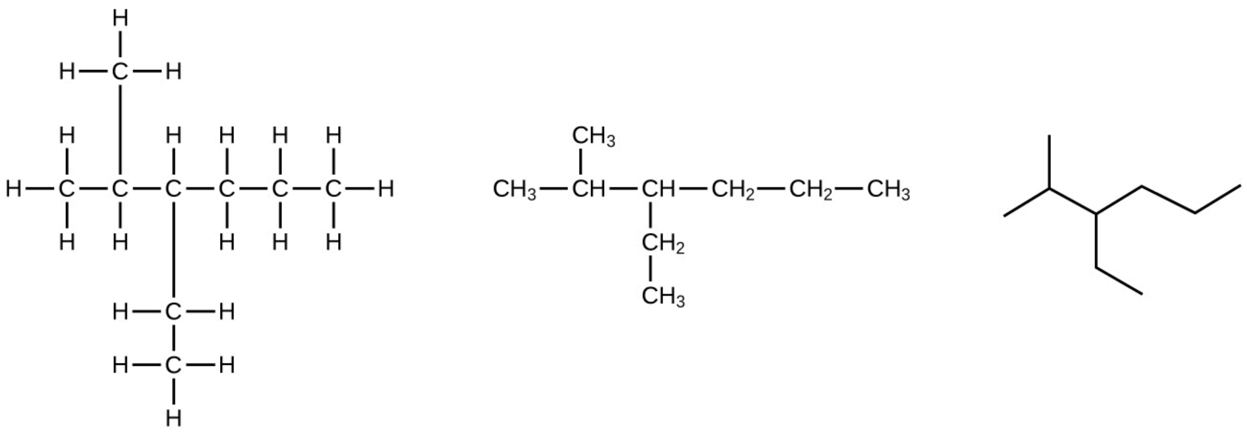
methane
CH_4

ethane
CH_3CH_3 or C_2H_6

pentane
$CH_3CH_2CH_2CH_2CH_3$ or C_5H_{12}

Figure 21.2 Pictured are the Lewis structures, ball-and-stick models, and space-filling models for molecules of methane, ethane, and pentane.

A common method used by organic chemists to simplify the drawings of larger molecules is to use a **skeletal structure** (also called a line-angle structure). In this type of structure, carbon atoms are not symbolized with a C, but represented by each end of a line or bend in a line. Hydrogen atoms are not drawn if they are attached to a carbon. Other atoms besides carbon and hydrogen are represented by their elemental symbols. **Figure 21.3** shows three different ways to draw the same structure.



Expanded formula

Condensed formula

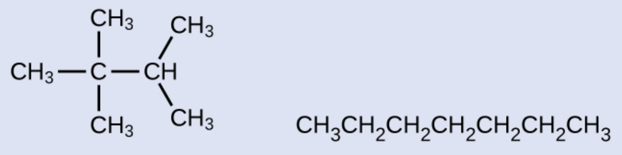
Skeletal structure

Figure 21.3 The same structure can be represented three different ways: an expanded formula, a condensed formula, and a skeletal structure.

Example 21.1

Drawing Skeletal Structures

Draw the skeletal structures for these two molecules:



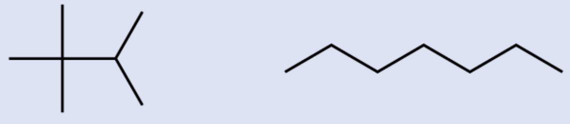
$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$

(a)

(b)

Solution

Each carbon atom is converted into the end of a line or the place where lines intersect. All hydrogen atoms attached to the carbon atoms are left out of the structure (although we still need to recognize they are there):

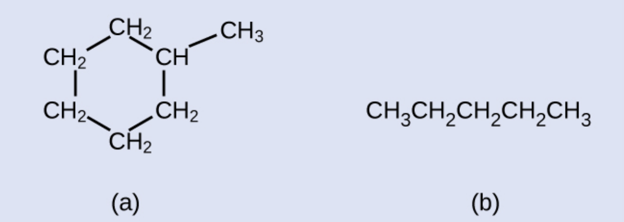


(a)

(b)

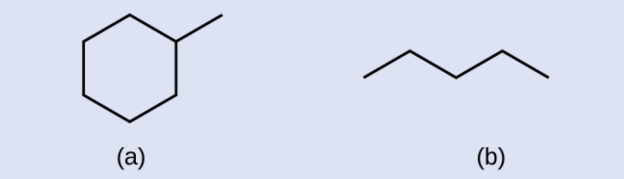
Check Your Learning

Draw the skeletal structures for these two molecules:



(a) (b)

Answer:

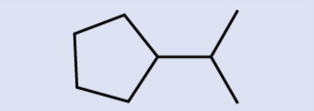


(a) (b)

Example 21.2

Interpreting Skeletal Structures

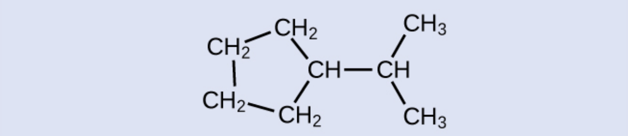
Identify the chemical formula of the molecule represented here:



Solution

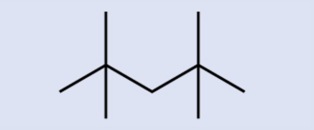
There are eight places where lines intersect or end, meaning that there are eight carbon atoms in the molecule. Since we know that carbon atoms tend to make four bonds, each carbon atom will have the number of hydrogen atoms that are required for four bonds. This compound contains 16 hydrogen atoms for a molecular formula of C_8H_{16}.

Location of the hydrogen atoms:



Check Your Learning

Identify the chemical formula of the molecule represented here:



Answer: C_9H_{20}

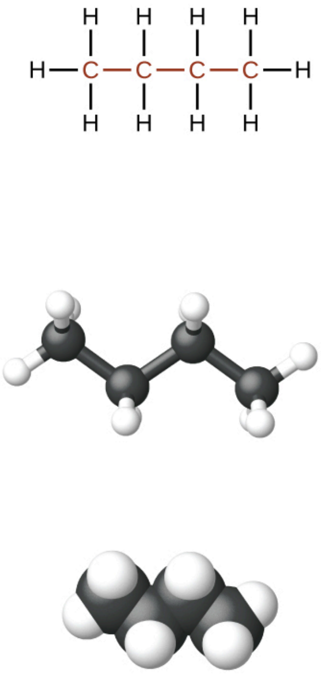
All alkanes are composed of carbon and hydrogen atoms, and have similar bonds, structures, and formulas; noncyclic alkanes all have a formula of C_nH_{2n+2}. The number of carbon atoms present in an alkane has no limit. Greater numbers of atoms in the molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of the molecules. Properties such as melting point and boiling point (**Table 21.1**) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

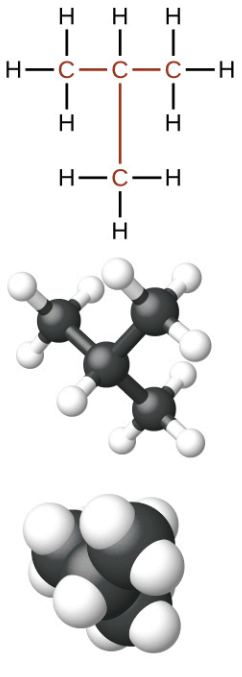
Properties of Some Alkanes[3]

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP[4]	Number of Structural Isomers
methane	CH_4	–182.5	–161.5	gas	1
ethane	C_2H_6	–183.3	–88.6	gas	1
propane	C_3H_8	–187.7	–42.1	gas	1
butane	C_4H_{10}	–138.3	–0.5	gas	2
pentane	C_5H_{12}	–129.7	36.1	liquid	3
hexane	C_6H_{14}	–95.3	68.7	liquid	5
heptane	C_7H_{16}	–90.6	98.4	liquid	9
octane	C_8H_{18}	–56.8	125.7	liquid	18
nonane	C_9H_{20}	–53.6	150.8	liquid	35
decane	$C_{10}H_{22}$	–29.7	174.0	liquid	75
tetradecane	$C_{14}H_{30}$	5.9	253.5	solid	1858
octadecane	$C_{18}H_{38}$	28.2	316.1	solid	60,523

Table 21.1

Hydrocarbons with the same formula, including alkanes, can have different structures. For example, two alkanes have the formula C_4H_{10}: They are called *n*-butane and 2-methylpropane (or isobutane), and have the following Lewis structures:


n-butane


2-methylpropane

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3. Physical properties for C_4H_{10} and heavier molecules are those of the *normal isomer*, *n*-butane, *n*-pentane, etc.
4. STP indicates a temperature of 0 °C and a pressure of 1 atm.

The compounds *n*-butane and 2-methylpropane are structural isomers (the term constitutional isomers is also commonly used). Constitutional isomers have the same molecular formula but different spatial arrangements of the atoms in their molecules. The *n*-butane molecule contains an *unbranched chain*, meaning that no carbon atom is bonded to more than two other carbon atoms. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching. The compound 2–methylpropane has a branched chain (the carbon atom in the center of the Lewis structure is bonded to three other carbon atoms)

Identifying isomers from Lewis structures is not as easy as it looks. Lewis structures that look different may actually represent the same isomers. For example, the three structures in **Figure 21.4** all represent the same molecule, *n*-butane, and hence are not different isomers. They are identical because each contains an unbranched chain of four carbon atoms.

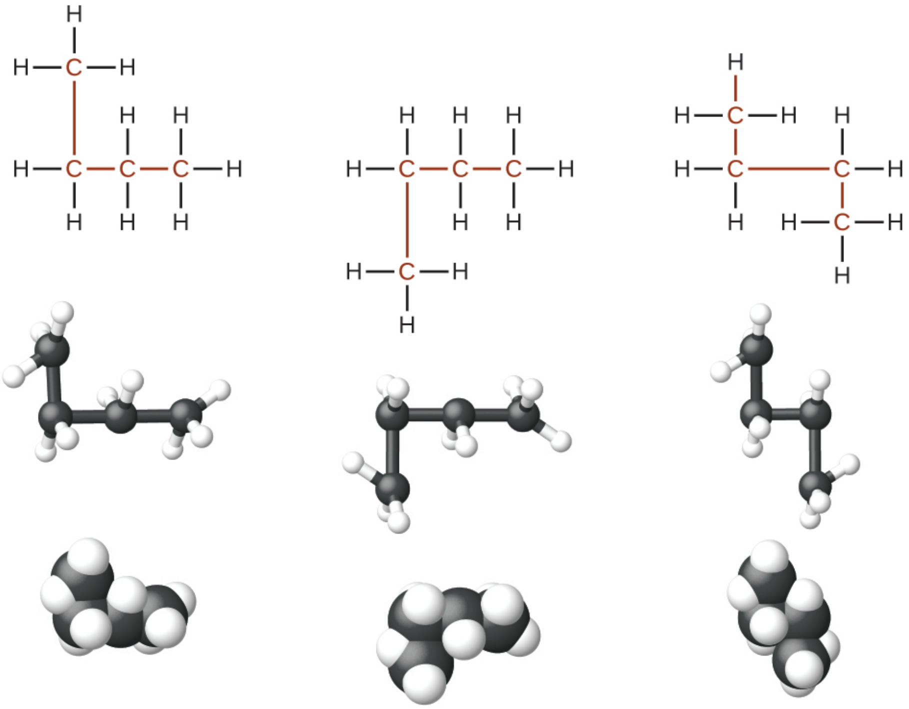
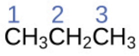


Figure 21.4 These three representations of the structure of n-butane are not isomers because they all contain the same arrangement of atoms and bonds.

The Basics of Organic Nomenclature: Naming Alkanes

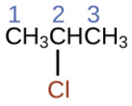
The International Union of Pure and Applied Chemistry (IUPAC) has devised a system of nomenclature that begins with the names of the alkanes and can be adjusted from there to account for more complicated structures. The nomenclature for alkanes is based on two rules:

1. To name an alkane, first identify the longest chain of carbon atoms in its structure. A two-carbon chain is called ethane; a three-carbon chain, propane; and a four-carbon chain, butane. Longer chains are named as follows: pentane (five-carbon chain), hexane (6), heptane (7), octane (8), nonane (9), and decane (10). These prefixes can be seen in the names of the alkanes described in **Table 21.1**.
2. Add prefixes to the name of the longest chain to indicate the positions and names of **substituents**. Substituents are branches or functional groups that replace hydrogen atoms on a chain. The position of a substituent or branch is identified by the number of the carbon atom it is bonded to in the chain. We number the carbon atoms in the chain by counting from the end of the chain nearest the substituents. Multiple substituents are named individually and placed in alphabetical order at the front of the name.



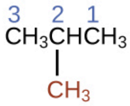
$\overset{1}{CH_3}\overset{2}{CH_2}\overset{3}{CH_3}$

propane



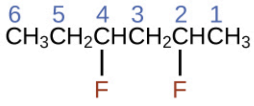
$\overset{1}{CH_3}\underset{\underset{Cl}{|}}{\overset{2}{CH}}\overset{3}{CH_3}$

2-chloropropane



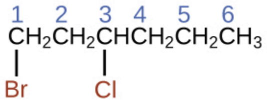
$\overset{3}{CH_3}\underset{\underset{CH_3}{|}}{\overset{2}{CH}}\overset{1}{CH_3}$

2-methylpropane



$\overset{6}{CH_3}\overset{5}{CH_2}\underset{\underset{F}{|}}{\overset{4}{CH}}\overset{3}{CH_2}\underset{\underset{F}{|}}{\overset{2}{CH}}\overset{1}{CH_3}$

2,4-difluorohexane



$\underset{\underset{Br}{|}}{\overset{1}{CH_2}}\overset{2}{CH_2}\underset{\underset{Cl}{|}}{\overset{3}{CH}}\overset{4}{CH_2}\overset{5}{CH_2}\overset{6}{CH_3}$

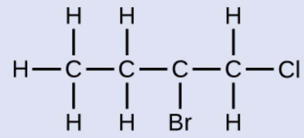
1-bromo-3-chlorohexane

When more than one substituent is present, either on the same carbon atom or on different carbon atoms, the substituents are listed alphabetically. Because the carbon atom numbering begins at the end closest to a substituent, the longest chain of carbon atoms is numbered in such a way as to produce the lowest number for the substituents. The ending *-o* replaces *-ide* at the end of the name of an electronegative substituent (in ionic compounds, the negatively charged ion ends with *-ide* like chloride; in organic compounds, such atoms are treated as substituents and the *-o* ending is used). The number of substituents of the same type is indicated by the prefixes *di-* (two), *tri-* (three), *tetra-* (four), and so on (for example, *difluoro-* indicates two fluoride substituents).

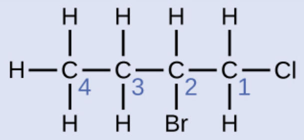
Example 21.3

Naming Halogen-substituted Alkanes

Name the molecule whose structure is shown here:



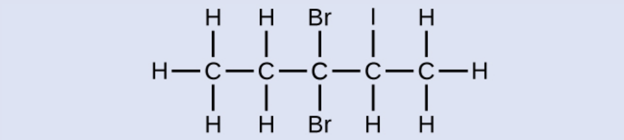
Solution



The four-carbon chain is numbered from the end with the chlorine atom. This puts the substituents on positions 1 and 2 (numbering from the other end would put the substituents on positions 3 and 4). Four carbon atoms means that the base name of this compound will be butane. The bromine at position 2 will be described by adding 2-bromo-; this will come at the beginning of the name, since bromo- comes before chloro- alphabetically. The chlorine at position 1 will be described by adding 1-chloro-, resulting in the name of the molecule being 2-bromo-1-chlorobutane.

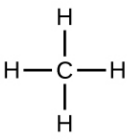
Check Your Learning

Name the following molecule:

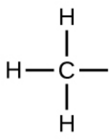


Answer: 3,3-dibromo-2-iodopentane

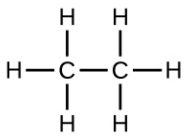
We call a substituent that contains one less hydrogen than the corresponding alkane an alkyl group. The name of an **alkyl group** is obtained by dropping the suffix *-ane* of the alkane name and adding *-yl*:



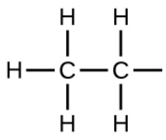
methane



methyl group



ethane



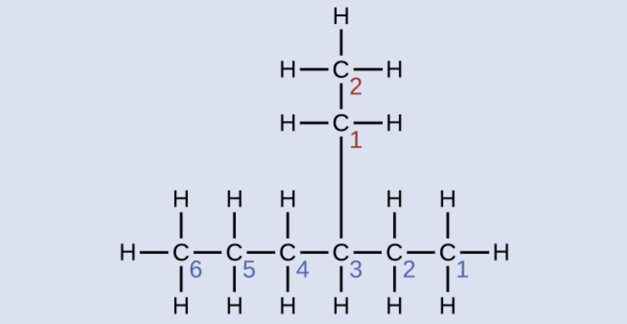
ethyl group

The open bonds in the methyl and ethyl groups indicate that these alkyl groups are bonded to another atom.

Example 21.4

Naming Substituted Alkanes

Name the molecule whose structure is shown here:

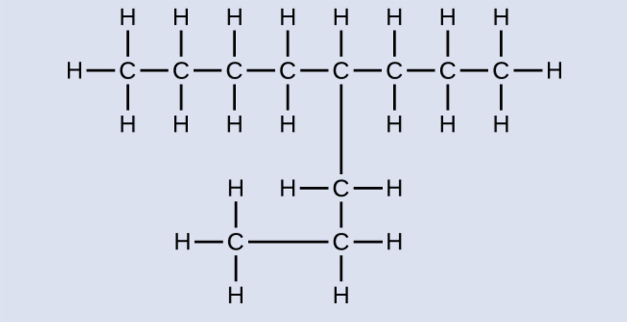


Solution

The longest carbon chain runs horizontally across the page and contains six carbon atoms (this makes the base of the name hexane, but we will also need to incorporate the name of the branch). In this case, we want to number from right to left (as shown by the blue numbers) so the branch is connected to carbon 3 (imagine the numbers from left to right—this would put the branch on carbon 4, violating our rules). The branch attached to position 3 of our chain contains two carbon atoms (numbered in red)—so we take our name for two carbons *eth-* and attach *-yl* at the end to signify we are describing a branch. Putting all the pieces together, this molecule is 3-ethylhexane.

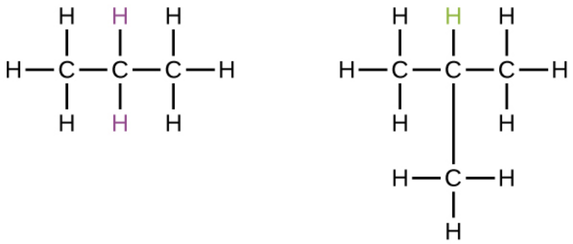
Check Your Learning

Name the following molecule:



Answer: 4-propyloctane

Some hydrocarbons can form more than one type of alkyl group when the hydrogen atoms that would be removed have different "environments" in the molecule. This diversity of possible alkyl groups can be identified in the following way: The four hydrogen atoms in a methane molecule are equivalent; they all have the same environment. They are equivalent because each is bonded to a carbon atom (the same carbon atom) that is bonded to three hydrogen atoms. (It may be easier to see the equivalency in the ball and stick models in **Figure 21.2**. Removal of any one of the four hydrogen atoms from methane forms a methyl group. Likewise, the six hydrogen atoms in ethane are equivalent (**Figure 21.2**) and removing any one of these hydrogen atoms produces an ethyl group. Each of the six hydrogen atoms is bonded to a carbon atom that is bonded to two other hydrogen atoms and a carbon atom. However, in both propane and 2–methylpropane, there are hydrogen atoms in two different environments, distinguished by the adjacent atoms or groups of atoms:



propane 2-methylpropane

Each of the six equivalent hydrogen atoms of the first type in propane and each of the nine equivalent hydrogen atoms of that type in 2-methylpropane (all shown in black) are bonded to a carbon atom that is bonded to only one other carbon atom. The two purple hydrogen atoms in propane are of a second type. They differ from the six hydrogen atoms of the first type in that they are bonded to a carbon atom bonded to two other carbon atoms. The green hydrogen atom in 2-methylpropane differs from the other nine hydrogen atoms in that molecule and from the purple hydrogen atoms in propane. The green hydrogen atom in 2-methylpropane is bonded to a carbon atom bonded to three other carbon atoms. Two different alkyl groups can be formed from each of these molecules, depending on which hydrogen atom is removed. The names and structures of these and several other alkyl groups are listed in **Figure 21.5**.

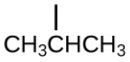
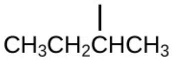
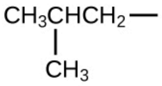
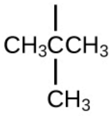
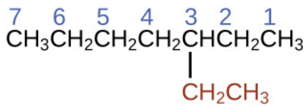
Alkyl Group	**Structure**
methyl	CH_3-
ethyl	CH_3CH_2-
n-propyl	$CH_3CH_2CH_2-$
isopropyl	 $CH_3\overset{\vert}{C}HCH_3$
n-butyl	$CH_3CH_2CH_2CH_2-$
sec-butyl	 $CH_3CH_2\overset{\vert}{C}HCH_3$
isobutyl	 $CH_3\underset{\substack{\vert\\CH_3}}{C}HCH_2-$
tert-butyl	 $CH_3\overset{\vert}{\underset{\substack{\vert\\CH_3}}{C}}CH_3$

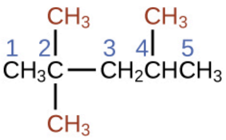
Figure 21.5 This listing gives the names and formulas for various alkyl groups formed by the removal of hydrogen atoms from different locations.

Note that alkyl groups do not exist as stable independent entities. They are always a part of some larger molecule. The location of an alkyl group on a hydrocarbon chain is indicated in the same way as any other substituent:



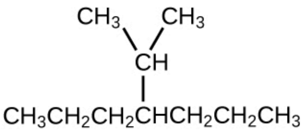
$$CH_3CH_2CH_2CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}CH_2CH_3$$

3-ethylheptane



$$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2\overset{\displaystyle CH_3}{C}HCH_3$$

2,2,4-trimethylpentane



4-isopropylheptane

Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C–H or C–C single bonds. Combustion is one such reaction:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. As a consequence, alkanes are excellent fuels. For example, methane, CH_4, is the principal component of natural gas. Butane, C_4H_{10}, used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (see **Figure 21.6**). You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.

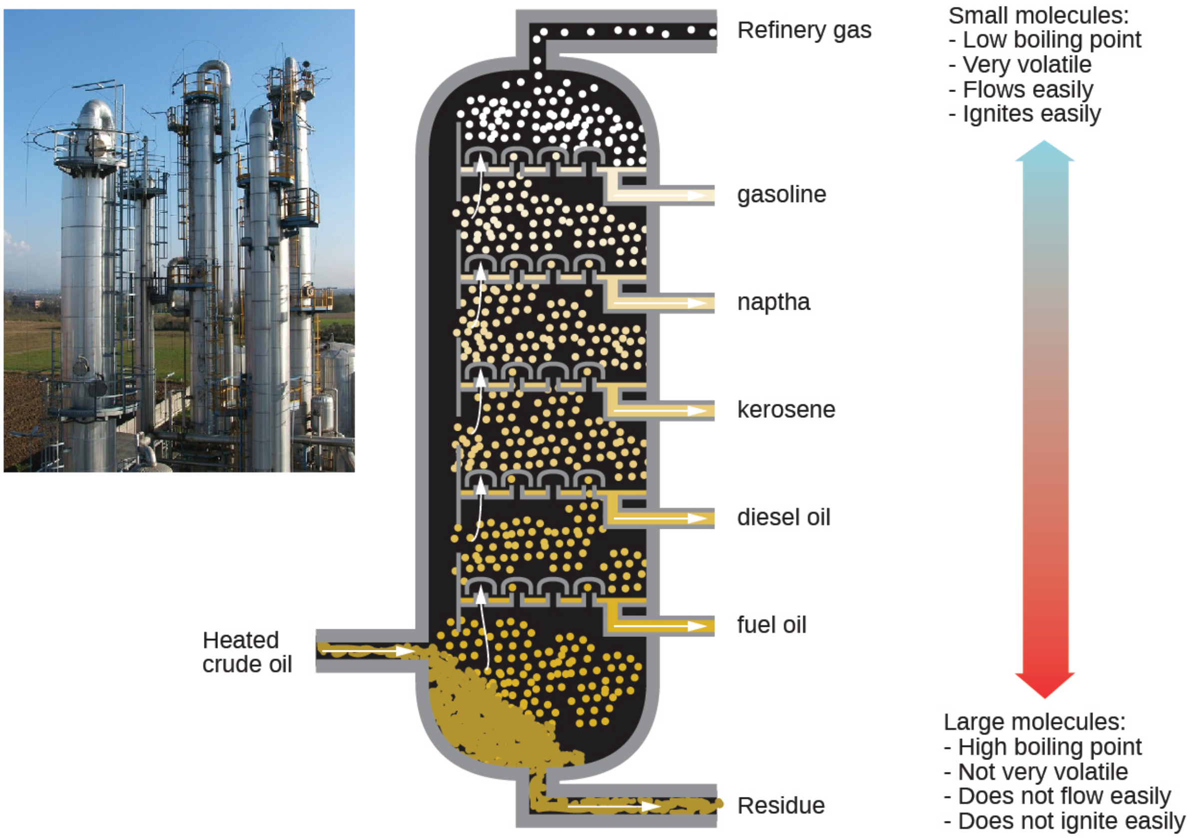
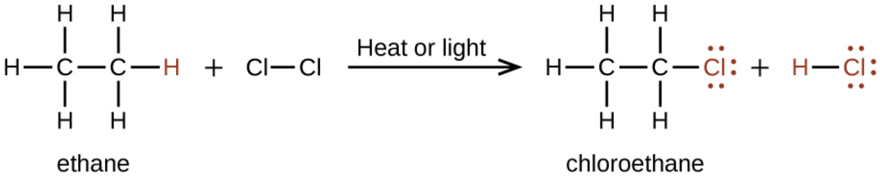


Figure 21.6 In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

In a **substitution reaction**, another typical reaction of alkanes, one or more of the alkane's hydrogen atoms is replaced with a different atom or group of atoms. No carbon-carbon bonds are broken in these reactions, and the hybridization of the carbon atoms does not change. For example, the reaction between ethane and molecular chlorine depicted here is a substitution reaction:



The C–Cl portion of the chloroethane molecule is an example of a **functional group**, the part or moiety of a molecule that imparts a specific chemical reactivity. The types of functional groups present in an organic molecule are major determinants of its chemical properties and are used as a means of classifying organic compounds as detailed in the remaining sections of this chapter.

Link to Learning

Want more practice naming alkanes? Watch this brief video tutorial (http://openstaxcollege.org/l/16alkanes) to review the nomenclature process.

Alkenes

Organic compounds that contain one or more double or triple bonds between carbon atoms are described as unsaturated. You have likely heard of unsaturated fats. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms. Unsaturated hydrocarbon molecules that contain one or more double bonds are called **alkenes**. Carbon atoms linked by a double bond are bound together by two bonds, one σ bond and one π bond. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Ethene, C_2H_4, is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure 21.7); the butene isomers follow in the series. Four carbon atoms in the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.

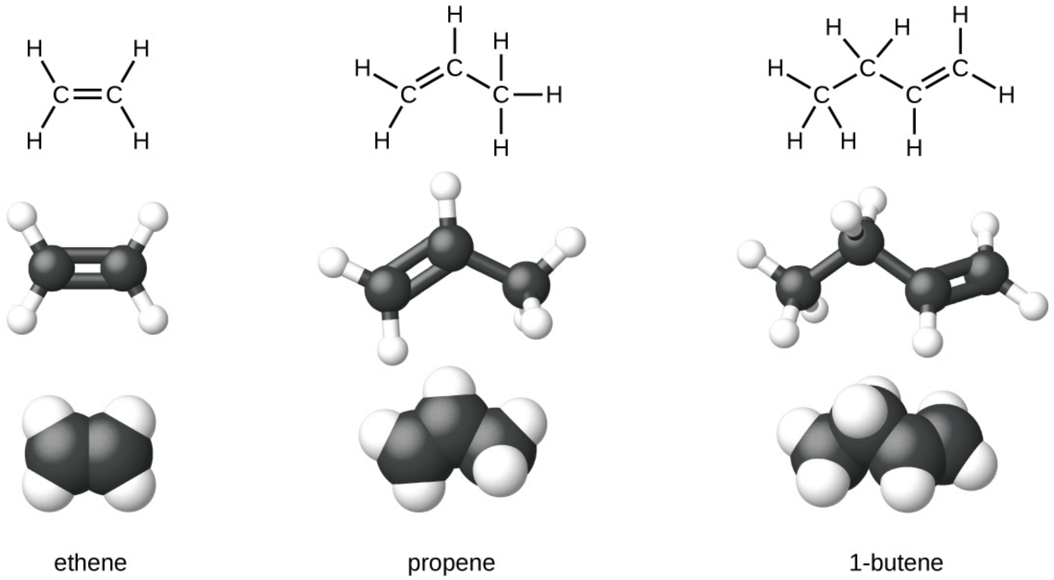


Figure 21.7 Expanded structures, ball-and-stick structures, and space-filling models for the alkenes ethene, propene, and 1-butene are shown.

Ethylene (the common industrial name for ethene) is a basic raw material in the production of polyethylene and other important compounds. Over 135 million tons of ethylene were produced worldwide in 2010 for use in the polymer, petrochemical, and plastic industries. Ethylene is produced industrially in a process called cracking, in which the long hydrocarbon chains in a petroleum mixture are broken into smaller molecules.

Chemistry in Everyday Life

Recycling Plastics

Polymers (from Greek words *poly* meaning “many” and *mer* meaning “parts”) are large molecules made up of repeating units, referred to as monomers. Polymers can be natural (starch is a polymer of sugar residues and proteins are polymers of amino acids) or synthetic [like polyethylene, polyvinyl chloride (PVC), and polystyrene]. The variety of structures of polymers translates into a broad range of properties and uses that make them integral parts of our everyday lives. Adding functional groups to the structure of a polymer can result in significantly different properties (see the discussion about Kevlar later in this chapter).

An example of a polymerization reaction is shown in **Figure 21.8**. The monomer ethylene (C_2H_4) is a gas at room temperature, but when polymerized, using a transition metal catalyst, it is transformed into a solid material made up of long chains of $–CH_2–$ units called polyethylene. Polyethylene is a commodity plastic used primarily for packaging (bags and films).

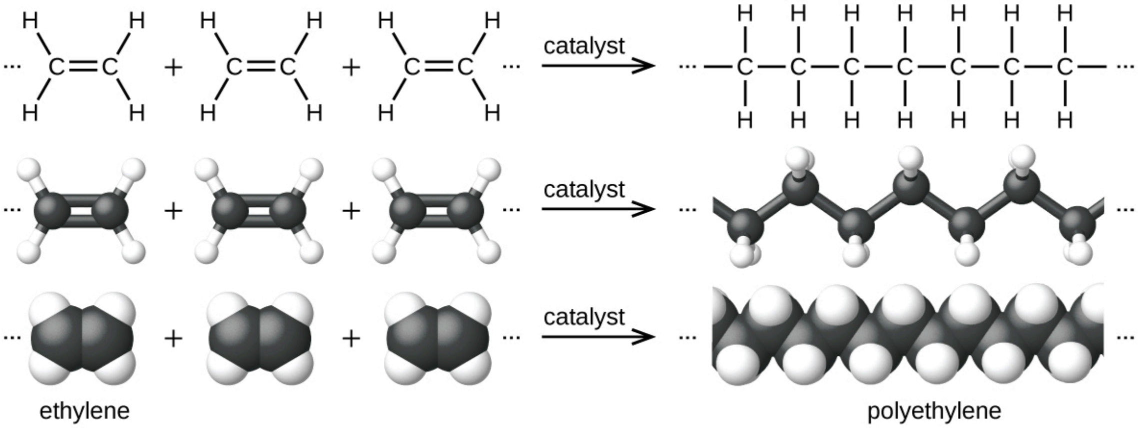


Figure 21.8 The reaction for the polymerization of ethylene to polyethylene is shown.

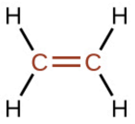
Polyethylene is a member of one subset of synthetic polymers classified as plastics. Plastics are synthetic organic solids that can be molded; they are typically organic polymers with high molecular masses. Most of the monomers that go into common plastics (ethylene, propylene, vinyl chloride, styrene, and ethylene terephthalate) are derived from petrochemicals and are not very biodegradable, making them candidate materials for recycling. Recycling plastics helps minimize the need for using more of the petrochemical supplies and also minimizes the environmental damage caused by throwing away these nonbiodegradable materials.

Plastic recycling is the process of recovering waste, scrap, or used plastics, and reprocessing the material into useful products. For example, polyethylene terephthalate (soft drink bottles) can be melted down and used for plastic furniture, in carpets, or for other applications. Other plastics, like polyethylene (bags) and polypropylene (cups, plastic food containers), can be recycled or reprocessed to be used again. Many areas of the country have recycling programs that focus on one or more of the commodity plastics that have been assigned a recycling code (see **Figure 21.9**). These operations have been in effect since the 1970s and have made the production of some plastics among the most efficient industrial operations today.

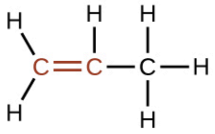
♳ PETE **polyethylene terephthalate (PETE)**	Soda bottles and oven-ready food trays
♴ HDPE **high-density polyethylene (HDPE)**	Bottles for milk and dishwashing liquids
♵ V **polyvinyl chloride (PVC)**	Food trays, plastic wrap, bottles for mineral water and shampoo
♶ LDPE **low density polyethylene (LDPE)**	Shopping bags and garbage bags
♷ PP **polypropylene (PP)**	Margarine tubs, microwaveable food trays
♸ PS **polystyrene (PS)**	Yogurt tubs, foam meat trays, egg cartons, vending cups, plastic cutlery, packaging for electronics and toys
♹ OTHER **any other plastics (OTHER)**	Plastics that do not fall into any of the above categories One example is melamine resin (plastic plates, plastic cups)

Figure 21.9 Each type of recyclable plastic is imprinted with a code for easy identification.

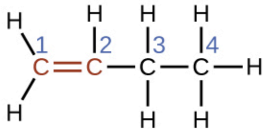
The name of an alkene is derived from the name of the alkane with the same number of carbon atoms. The presence of the double bond is signified by replacing the suffix *-ane* with the suffix *-ene*. The location of the double bond is identified by naming the smaller of the numbers of the carbon atoms participating in the double bond:



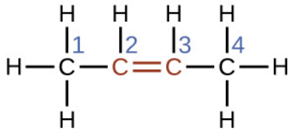
ethene
(ethylene)



propene
(propylene)



1-butene



2-butene

Isomers of Alkenes

Molecules of 1-butene and 2-butene are structural isomers; the arrangement of the atoms in these two molecules differs. As an example of arrangement differences, the first carbon atom in 1-butene is bonded to two hydrogen atoms; the first carbon atom in 2-butene is bonded to three hydrogen atoms.

The compound 2-butene and some other alkenes also form a second type of isomer called a geometric isomer. In a set of geometric isomers, the same types of atoms are attached to each other in the same order, but the geometries of the two molecules differ. Geometric isomers of alkenes differ in the orientation of the groups on either side of a $\text{C}=\text{C}$

bond.

Carbon atoms are free to rotate around a single bond but not around a double bond; a double bond is rigid. This makes it possible to have two isomers of 2-butene, one with both methyl groups on the same side of the double bond and one with the methyl groups on opposite sides. When structures of butene are drawn with 120° bond angles around the sp^2-hybridized carbon atoms participating in the double bond, the isomers are apparent. The 2-butene isomer in which the two methyl groups are on the same side is called a *cis*-isomer; the one in which the two methyl groups are on opposite sides is called a *trans*-isomer (**Figure 21.10**). The different geometries produce different physical properties, such as boiling point, that may make separation of the isomers possible:

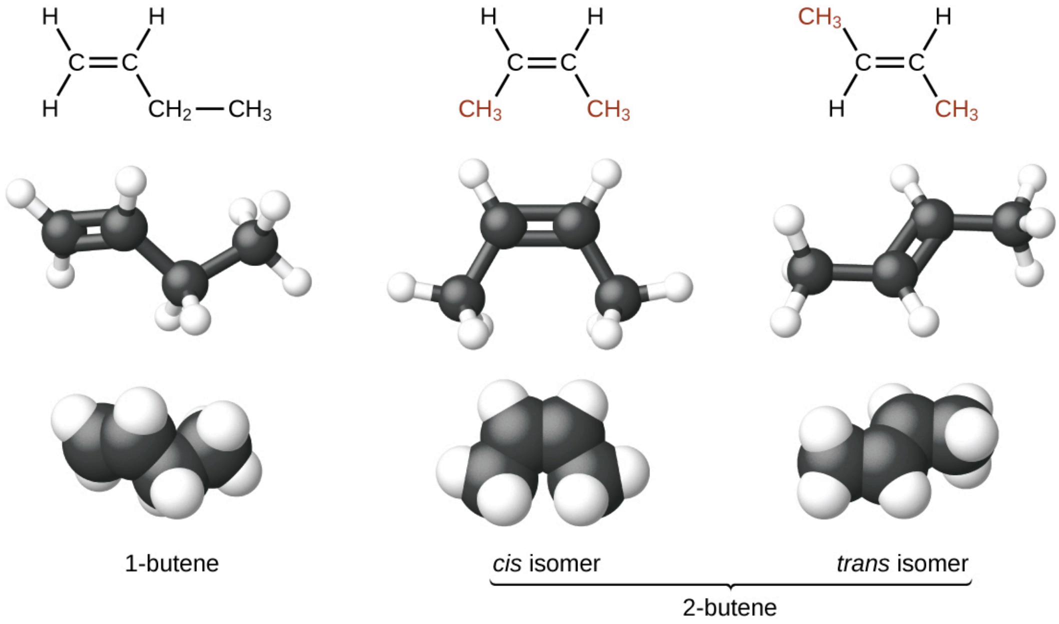
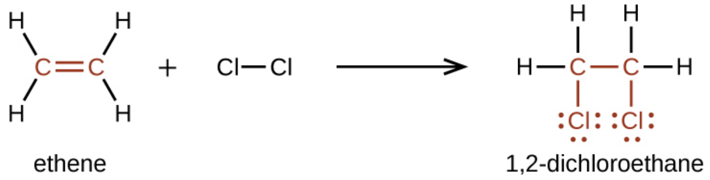


Figure 21.10 These molecular models show the structural and geometric isomers of butene.

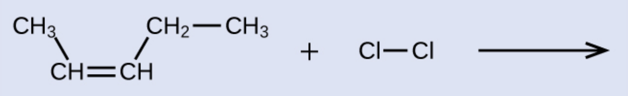
Alkenes are much more reactive than alkanes because the $C=C$ moiety is a reactive functional group. A π bond, being a weaker bond, is disrupted much more easily than a σ bond. Thus, alkenes undergo a characteristic reaction in which the π bond is broken and replaced by two σ bonds. This reaction is called an **addition reaction**. The hybridization of the carbon atoms in the double bond in an alkene changes from sp^2 to sp^3 during an addition reaction. For example, halogens add to the double bond in an alkene instead of replacing hydrogen, as occurs in an alkane:



Example 21.5

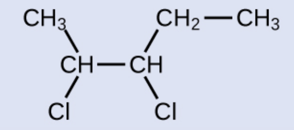
Alkene Reactivity and Naming

Provide the IUPAC names for the reactant and product of the halogenation reaction shown here:



Solution

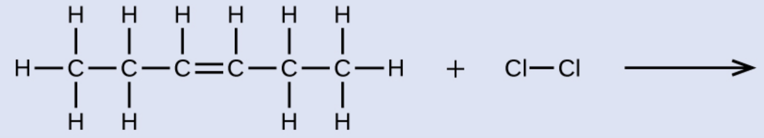
The reactant is a five-carbon chain that contains a carbon-carbon double bond, so the base name will be pentene. We begin counting at the end of the chain closest to the double bond—in this case, from the left—the double bond spans carbons 2 and 3, so the name becomes 2-pentene. Since there are two carbon-containing groups attached to the two carbon atoms in the double bond—and they are on the same side of the double bond—this molecule is the *cis*-isomer, making the name of the starting alkene *cis*-2-pentene. The product of the halogenation reaction will have two chlorine atoms attached to the carbon atoms that were a part of the carbon-carbon double bond:



This molecule is now a substituted alkane and will be named as such. The base of the name will be pentane. We will count from the end that numbers the carbon atoms where the chlorine atoms are attached as 2 and 3, making the name of the product 2,3-dichloropentane.

Check Your Learning

Provide names for the reactant and product of the reaction shown:



Answer: reactant: cis-3-hexene product: 3,4-dichlorohexane

Alkynes

Hydrocarbon molecules with one or more triple bonds are called **alkynes**; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond are bound together by one σ bond and two π bonds. The *sp*-hybridized carbons involved in the triple bond have bond angles of 180°, giving these types of bonds a linear, rod-like shape.

The simplest member of the alkyne series is ethyne, C_2H_2, commonly called acetylene. The Lewis structure for ethyne, a linear molecule, is:

$$\mathrm{H{-}C{\equiv}C{-}H}$$

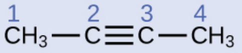
ethyne (acetylene)

The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix *-yne* is used to indicate a triple bond in the chain. For example, $CH_3CH_2C\equiv CH$ is called 1-butyne.

Example 21.6

Structure of Alkynes

Describe the geometry and hybridization of the carbon atoms in the following molecule:



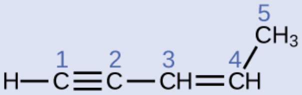
$$\overset{1}{\mathrm{CH_3}}-\overset{2}{\mathrm{C}}\equiv\overset{3}{\mathrm{C}}-\overset{4}{\mathrm{CH_3}}$$

Solution

Carbon atoms 1 and 4 have four single bonds and are thus tetrahedral with sp^3 hybridization. Carbon atoms 2 and 3 are involved in the triple bond, so they have linear geometries and would be classified as *sp* hybrids.

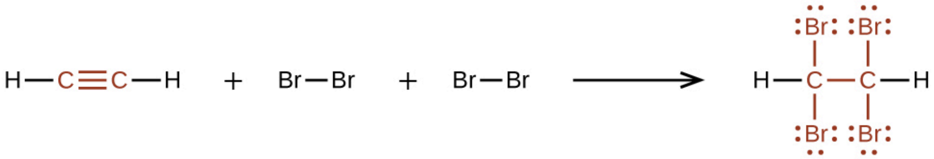
Check Your Learning

Identify the hybridization and bond angles at the carbon atoms in the molecule shown:



Answer: carbon 1: *sp*, 180°; carbon 2: *sp*, 180°; carbon 3: sp^2, 120°; carbon 4: sp^2, 120°; carbon 5: sp^3, 109.5°

Chemically, the alkynes are similar to the alkenes. Since the $\text{C} \equiv \text{C}$ functional group has two π bonds, alkynes typically react even more readily, and react with twice as much reagent in addition reactions. The reaction of acetylene with bromine is a typical example:

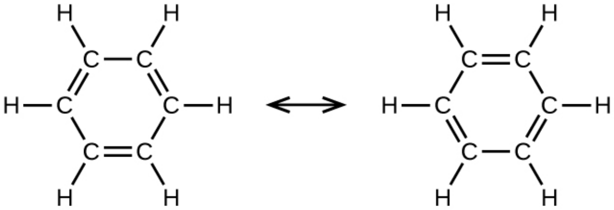


1,1,2,2-tetrabromoethane

Acetylene and the other alkynes also burn readily. An acetylene torch takes advantage of the high heat of combustion for acetylene.

Aromatic Hydrocarbons

Benzene, C_6H_6, is the simplest member of a large family of hydrocarbons, called **aromatic hydrocarbons**. These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory. (To review these concepts, refer to the earlier chapters on chemical bonding). The resonance structures for benzene, C_6H_6, are:



Valence bond theory describes the benzene molecule and other planar aromatic hydrocarbon molecules as hexagonal rings of sp^2-hybridized carbon atoms with the unhybridized *p* orbital of each carbon atom perpendicular to the plane of the ring. Three valence electrons in the sp^2 hybrid orbitals of each carbon atom and the valence electron of each hydrogen atom form the framework of σ bonds in the benzene molecule. The fourth valence electron of each carbon atom is shared with an adjacent carbon atom in their unhybridized *p* orbitals to yield the π bonds. Benzene does not, however, exhibit the characteristics typical of an alkene. Each of the six bonds between its carbon atoms is equivalent and exhibits properties that are intermediate between those of a C–C single bond and a $\text{C} = \text{C}$ double bond. To represent this unique bonding, structural formulas for benzene and its derivatives are typically drawn with single bonds between the carbon atoms and a circle within the ring as shown in **Figure 21.11**.

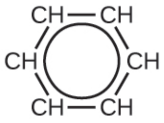
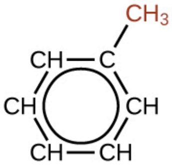
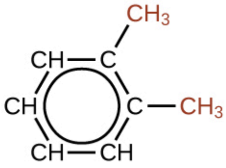


Figure 21.11 This condensed formula shows the unique bonding structure of benzene.

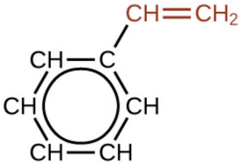
There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:



toluene



xylene



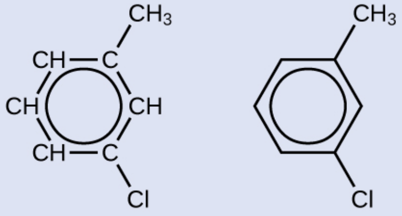
styrene

Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene.

Example 21.7

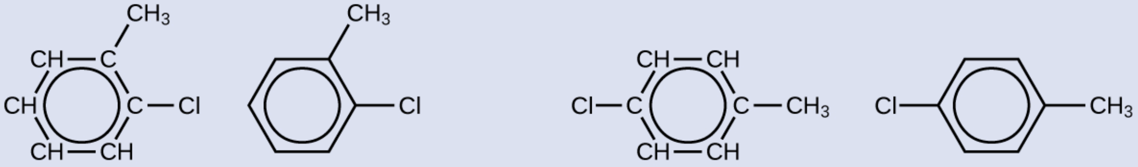
Structure of Aromatic Hydrocarbons

One possible isomer created by a substitution reaction that replaces a hydrogen atom attached to the aromatic ring of toluene with a chlorine atom is shown here. Draw two other possible isomers in which the chlorine atom replaces a different hydrogen atom attached to the aromatic ring:



Solution

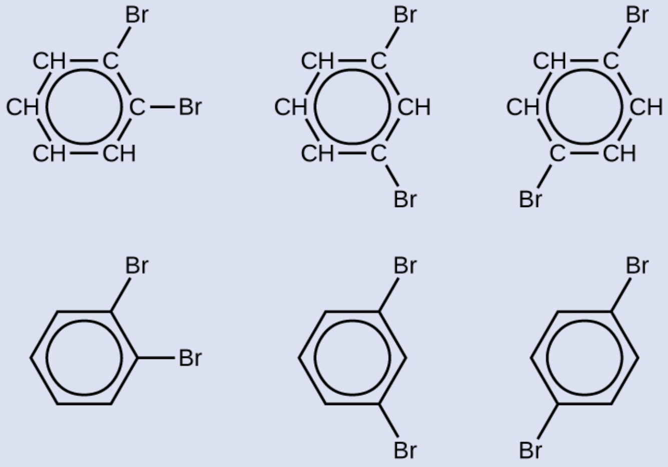
Since the six-carbon ring with alternating double bonds is necessary for the molecule to be classified as aromatic, appropriate isomers can be produced only by changing the positions of the chloro-substituent relative to the methyl-substituent:



Check Your Learning

Draw three isomers of a six-membered aromatic ring compound substituted with two bromines.

Answer:



21.2 Alcohols and Ethers

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

- Describe the structure and properties of alcohols
- Describe the structure and properties of ethers
- Name and draw structures for alcohols and ethers

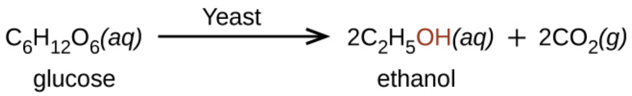
In this section, we will learn about alcohols and ethers.

Alcohols

Incorporation of an oxygen atom into carbon- and hydrogen-containing molecules leads to new functional groups and new families of compounds. When the oxygen atom is attached by single bonds, the molecule is either an alcohol or ether.

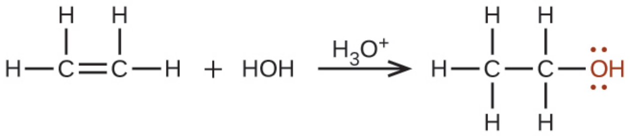
Alcohols are derivatives of hydrocarbons in which an –OH group has replaced a hydrogen atom. Although all alcohols have one or more hydroxyl (–OH) functional groups, they do not behave like bases such as NaOH and KOH. NaOH and KOH are ionic compounds that contain OH^- ions. Alcohols are covalent molecules; the –OH group in an alcohol molecule is attached to a carbon atom by a covalent bond.

Ethanol, CH_3CH_2OH, also called ethyl alcohol, is a particularly important alcohol for human use. Ethanol is the alcohol produced by some species of yeast that is found in wine, beer, and distilled drinks. It has long been prepared by humans harnessing the metabolic efforts of yeasts in fermenting various sugars:

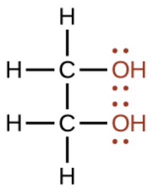


$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{Yeast}} \underset{\text{ethanol}}{2C_2H_5OH(aq)} + 2CO_2(g)$$

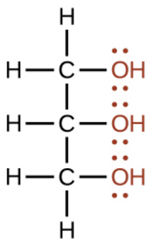
Large quantities of ethanol are synthesized from the addition reaction of water with ethylene using an acid as a catalyst:



Alcohols containing two or more hydroxyl groups can be made. Examples include 1,2-ethanediol (ethylene glycol, used in antifreeze) and 1,2,3-propanetriol (glycerine, used as a solvent for cosmetics and medicines):



1,2-ethanediol



1,2,3-propanetriol

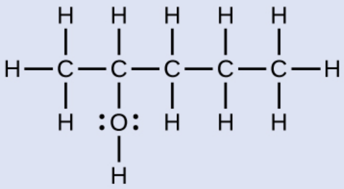
Naming Alcohols

The name of an alcohol comes from the hydrocarbon from which it was derived. The final *-e* in the name of the hydrocarbon is replaced by *-ol*, and the carbon atom to which the –OH group is bonded is indicated by a number placed before the name.[5]

Example 21.8

Naming Alcohols

Consider the following example. How should it be named?

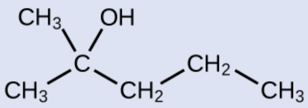


Solution

The carbon chain contains five carbon atoms. If the hydroxyl group was not present, we would have named this molecule pentane. To address the fact that the hydroxyl group is present, we change the ending of the name to *-ol*. In this case, since the –OH is attached to carbon 2 in the chain, we would name this molecule 2-pentanol.

Check Your Learning

Name the following molecule:



Answer: 2-methyl-2-pentanol

Ethers

Ethers are compounds that contain the functional group –O–. Ethers do not have a designated suffix like the other

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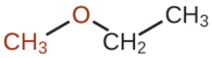
5. The IUPAC adopted new nomenclature guidelines in 2013 that require this number to be placed as an “infix” rather than a prefix. For example, the new name for 2-propanol would be propan-2-ol. Widespread adoption of this new nomenclature will take some time, and students are encouraged to be familiar with both the old and new naming protocols.

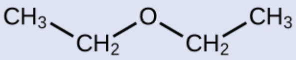
types of molecules we have named so far. In the IUPAC system, the oxygen atom and the smaller carbon branch are named as an alkoxy substituent and the remainder of the molecule as the base chain, as in alkanes. As shown in the following compound, the red symbols represent the smaller alkyl group and the oxygen atom, which would be named "methoxy." The larger carbon branch would be ethane, making the molecule methoxyethane. Many ethers are referred to with common names instead of the IUPAC system names. For common names, the two branches connected to the oxygen atom are named separately and followed by "ether." The common name for the compound shown in **Example 21.9** is ethylmethyl ether:



Example 21.9

Naming Ethers

Provide the IUPAC and common name for the ether shown here:



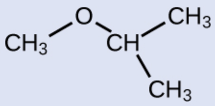
Solution

IUPAC: The molecule is made up of an ethoxy group attached to an ethane chain, so the IUPAC name would be ethoxyethane.

Common: The groups attached to the oxygen atom are both ethyl groups, so the common name would be diethyl ether.

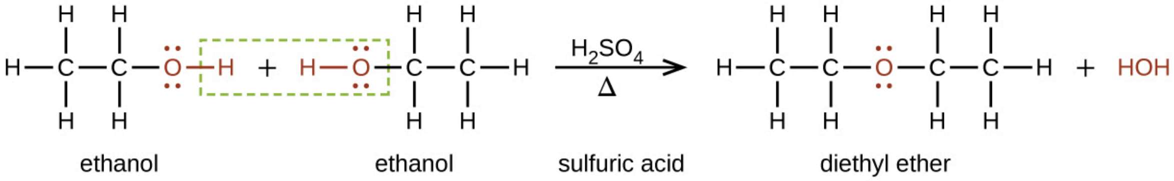
Check Your Learning

Provide the IUPAC and common name for the ether shown:



Answer: IUPAC: 2-methoxypropane; common: isopropylmethyl ether

Ethers can be obtained from alcohols by the elimination of a molecule of water from two molecules of the alcohol. For example, when ethanol is treated with a limited amount of sulfuric acid and heated to 140 °C, diethyl ether and water are formed:



In the general formula for ethers, R—O—R, the hydrocarbon groups (R) may be the same or different. Diethyl ether, the most widely used compound of this class, is a colorless, volatile liquid that is highly flammable. It was first used in 1846 as an anesthetic, but better anesthetics have now largely taken its place. Diethyl ether and other ethers are presently used primarily as solvents for gums, fats, waxes, and resins. *Tertiary*-butyl methyl ether, $C_4H_9OCH_3$ (abbreviated MTBE—italicized portions of names are not counted when ranking the groups alphabetically—so butyl comes before methyl in the common name), is used as an additive for gasoline. MTBE belongs to a group of chemicals known as oxygenates due to their capacity to increase the oxygen content of gasoline.

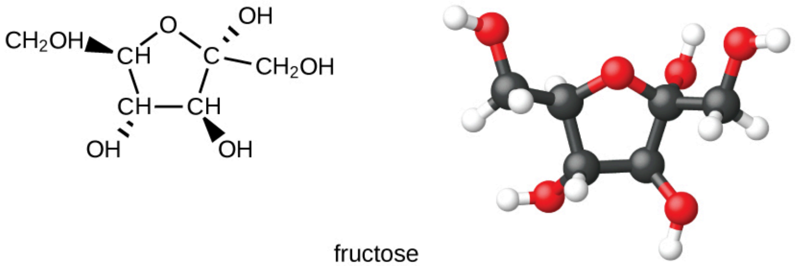
Link to Learning

Want more practice naming ethers? This brief **video review (http://openstaxcollege.org/l/16ethers)** summarizes the nomenclature for ethers.

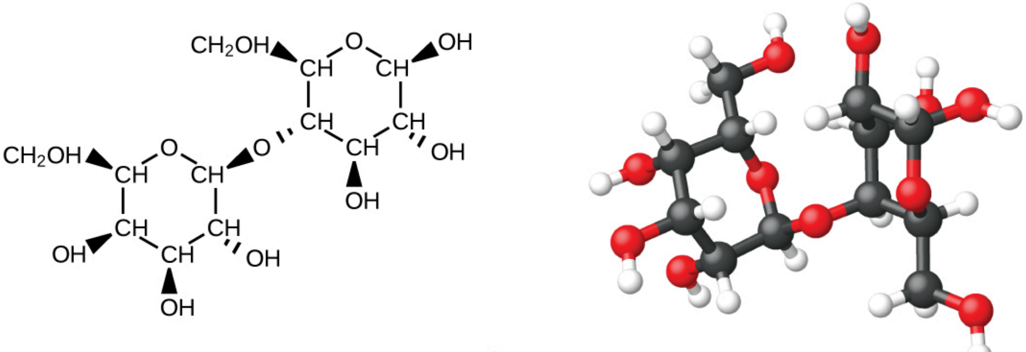
Chemistry in Everyday Life

Carbohydrates and Diabetes

Carbohydrates are large biomolecules made up of carbon, hydrogen, and oxygen. The dietary forms of carbohydrates are foods rich in these types of molecules, like pastas, bread, and candy. The name “carbohydrate” comes from the formula of the molecules, which can be described by the general formula $C_m(H_2O)_n$, which shows that they are in a sense “carbon and water” or “hydrates of carbon.” In many cases, *m* and *n* have the same value, but they can be different. The smaller carbohydrates are generally referred to as “sugars,” the biochemical term for this group of molecules is “saccharide” from the Greek word for sugar (**Figure 21.12**). Depending on the number of sugar units joined together, they may be classified as monosaccharides (one sugar unit), disaccharides (two sugar units), oligosaccharides (a few sugars), or polysaccharides (the polymeric version of sugars—polymers were described in the feature box earlier in this chapter on recycling plastics). The scientific names of sugars can be recognized by the suffix *-ose* at the end of the name (for instance, fruit sugar is a monosaccharide called “fructose” and milk sugar is a disaccharide called lactose composed of two monosaccharides, glucose and galactose, connected together). Sugars contain some of the functional groups we have discussed: Note the alcohol groups present in the structures and how monosaccharide units are linked to form a disaccharide by formation of an ether.



fructose



lactose

Figure 21.12 The illustrations show the molecular structures of fructose, a five-carbon monosaccharide, and of lactose, a disaccharide composed of two isomeric, six-carbon sugars.

Organisms use carbohydrates for a variety of functions. Carbohydrates can store energy, such as the polysaccharides glycogen in animals or starch in plants. They also provide structural support, such as the polysaccharide cellulose in plants and the modified polysaccharide chitin in fungi and animals. The sugars ribose and deoxyribose are components of the backbones of RNA and DNA, respectively. Other sugars play key roles in the function of the immune system, in cell-cell recognition, and in many other biological roles.

Diabetes is a group of metabolic diseases in which a person has a high sugar concentration in their blood (**Figure 21.13**). Diabetes may be caused by insufficient insulin production by the pancreas or by the body's cells not responding properly to the insulin that is produced. In a healthy person, insulin is produced when it is needed and functions to transport glucose from the blood into the cells where it can be used for energy. The long-term complications of diabetes can include loss of eyesight, heart disease, and kidney failure.

In 2013, it was estimated that approximately 3.3% of the world's population (~380 million people) suffered from diabetes, resulting in over a million deaths annually. Prevention involves eating a healthy diet, getting plenty of exercise, and maintaining a normal body weight. Treatment involves all of these lifestyle practices and may require injections of insulin.

Figure 21.13 Diabetes is a disease characterized by high concentrations of glucose in the blood. Treating diabetes involves making lifestyle changes, monitoring blood-sugar levels, and sometimes insulin injections. (credit: "Blausen Medical Communications"/Wikimedia Commons)

21.3 Aldehydes, Ketones, Carboxylic Acids, and Esters

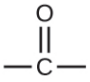
By the end of this section, you will be able to:

- Describe the structure and properties of aldehydes, ketones, carboxylic acids and esters

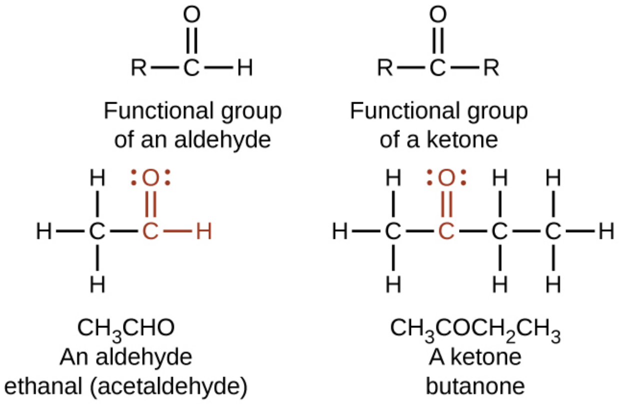
Another class of organic molecules contains a carbon atom connected to an oxygen atom by a double bond, commonly called a carbonyl group. The trigonal planar carbon in the carbonyl group can attach to two other substituents leading to several subfamilies (aldehydes, ketones, carboxylic acids and esters) described in this section.

Aldehydes and Ketones

Both **aldehydes** and **ketones** contain a **carbonyl group**, a functional group with a carbon-oxygen double bond. The names for aldehyde and ketone compounds are derived using similar nomenclature rules as for alkanes and alcohols, and include the class-identifying suffixes *-al* and *-one*, respectively:



In an aldehyde, the carbonyl group is bonded to at least one hydrogen atom. In a ketone, the carbonyl group is bonded to two carbon atoms:



Functional group of an aldehyde

Functional group of a ketone

CH_3CHO
An aldehyde
ethanal (acetaldehyde)

$CH_3COCH_2CH_3$
A ketone
butanone

As text, an aldehyde group is represented as –CHO; a ketone is represented as –C(O)– or –CO–.

In both aldehydes and ketones, the geometry around the carbon atom in the carbonyl group is trigonal planar; the carbon atom exhibits sp^2 hybridization. Two of the sp^2 orbitals on the carbon atom in the carbonyl group are used to form σ bonds to the other carbon or hydrogen atoms in a molecule. The remaining sp^2 hybrid orbital forms a σ bond to the oxygen atom. The unhybridized *p* orbital on the carbon atom in the carbonyl group overlaps a *p* orbital on the oxygen atom to form the π bond in the double bond.

Like the $\text{C}=\text{O}$ bond in carbon dioxide, the $\text{C}=\text{O}$ bond of a carbonyl group is polar (recall that oxygen is significantly more electronegative than carbon, and the shared electrons are pulled toward the oxygen atom and away from the carbon atom). Many of the reactions of aldehydes and ketones start with the reaction between a Lewis base and the carbon atom at the positive end of the polar $\text{C}=\text{O}$ bond to yield an unstable intermediate that subsequently undergoes one or more structural rearrangements to form the final product (**Figure 21.14**).

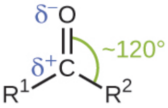
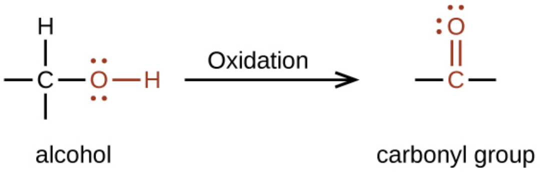


Figure 21.14 The carbonyl group is polar, and the geometry of the bonds around the central carbon is trigonal planar.

The importance of molecular structure in the reactivity of organic compounds is illustrated by the reactions that produce aldehydes and ketones. We can prepare a carbonyl group by oxidation of an alcohol—for organic molecules, oxidation of a carbon atom is said to occur when a carbon-hydrogen bond is replaced by a carbon-oxygen bond. The reverse reaction—replacing a carbon-oxygen bond by a carbon-hydrogen bond—is a reduction of that carbon atom. Recall that oxygen is generally assigned a –2 oxidation number unless it is elemental or attached to a fluorine. Hydrogen is generally assigned an oxidation number of +1 unless it is attached to a metal. Since carbon does not have a specific rule, its oxidation number is determined algebraically by factoring the atoms it is attached to and the overall charge of the molecule or ion. In general, a carbon atom attached to an oxygen atom will have a more positive oxidation number and a carbon atom attached to a hydrogen atom will have a more negative oxidation number. This should fit nicely with your understanding of the polarity of C–O and C–H bonds. The other reagents and possible products of these reactions are beyond the scope of this chapter, so we will focus only on the changes to the carbon atoms:



Example 21.10

Oxidation and Reduction in Organic Chemistry

Methane represents the completely reduced form of an organic molecule that contains one carbon atom. Sequentially replacing each of the carbon-hydrogen bonds with a carbon-oxygen bond would lead to an alcohol, then an aldehyde, then a carboxylic acid (discussed later), and, finally, carbon dioxide:

$$\mathrm{CH_4 \longrightarrow CH_3OH \longrightarrow CH_2O \longrightarrow HCO_2H \longrightarrow CO_2}$$

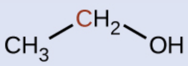
What are the oxidation numbers for the carbon atoms in the molecules shown here?

Solution

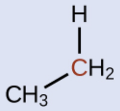
In this example, we can calculate the oxidation number (review the chapter on oxidation-reduction reactions if necessary) for the carbon atom in each case (note how this would become difficult for larger molecules with additional carbon atoms and hydrogen atoms, which is why organic chemists use the definition dealing with replacing C–H bonds with C–O bonds described). For CH_4, the carbon atom carries a –4 oxidation number (the hydrogen atoms are assigned oxidation numbers of +1 and the carbon atom balances that by having an oxidation number of –4). For the alcohol (in this case, methanol), the carbon atom has an oxidation number of –2 (the oxygen atom is assigned –2, the four hydrogen atoms each are assigned +1, and the carbon atom balances the sum by having an oxidation number of –2; note that compared to the carbon atom in CH_4, this carbon atom has lost two electrons so it was oxidized); for the aldehyde, the carbon atom's oxidation number is 0 (–2 for the oxygen atom and +1 for each hydrogen atom already balances to 0, so the oxidation number for the carbon atom is 0); for the carboxylic acid, the carbon atom's oxidation number is +2 (two oxygen atoms each at –2 and two hydrogen atoms at +1); and for carbon dioxide, the carbon atom's oxidation number is +4 (here, the carbon atom needs to balance the –4 sum from the two oxygen atoms).

Check Your Learning

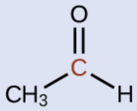
Indicate whether the marked carbon atoms in the three molecules here are oxidized or reduced relative to the marked carbon atom in ethanol:



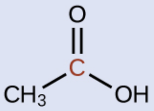
There is no need to calculate oxidation states in this case; instead, just compare the types of atoms bonded to the marked carbon atoms:



(a)



(b)



(c)

Answer: (a) reduced (bond to oxygen atom replaced by bond to hydrogen atom); (b) oxidized (one bond to hydrogen atom replaced by one bond to oxygen atom); (c) oxidized (2 bonds to hydrogen atoms have been replaced by bonds to an oxygen atom)

Aldehydes are commonly prepared by the oxidation of alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:

$$\underset{\text{alcohol}}{CH_3CH_2CH_2OH} \longrightarrow \underset{\text{aldehyde}}{CH_3CH_2CHO}$$

Alcohols that have their –OH groups in the middle of the chain are necessary to synthesize a ketone, which requires the carbonyl group to be bonded to two other carbon atoms:

$$\underset{\text{alcohol}}{CH_3CH(OH)CH_3} \longrightarrow \underset{\text{ketone}}{CH_3COCH_3}$$

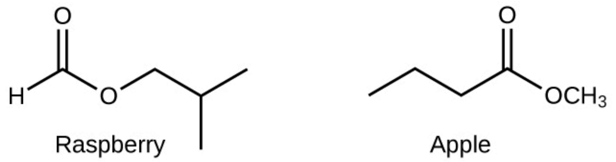
An alcohol with its –OH group bonded to a carbon atom that is bonded to no or one other carbon atom will form an aldehyde. An alcohol with its –OH group attached to two other carbon atoms will form a ketone. If three carbons are attached to the carbon bonded to the –OH, the molecule will not have a C–H bond to be replaced, so it will not be susceptible to oxidation.

Formaldehyde, an aldehyde with the formula HCHO, is a colorless gas with a pungent and irritating odor. It is sold in an aqueous solution called formalin, which contains about 37% formaldehyde by weight. Formaldehyde causes coagulation of proteins, so it kills bacteria (and any other living organism) and stops many of the biological processes that cause tissue to decay. Thus, formaldehyde is used for preserving tissue specimens and embalming bodies. It is also used to sterilize soil or other materials. Formaldehyde is used in the manufacture of Bakelite, a hard plastic having high chemical and electrical resistance.

Dimethyl ketone, CH_3COCH_3, commonly called acetone, is the simplest ketone. It is made commercially by fermenting corn or molasses, or by oxidation of 2-propanol. Acetone is a colorless liquid. Among its many uses are as a solvent for lacquer (including fingernail polish), cellulose acetate, cellulose nitrate, acetylene, plastics, and varnishes; as a paint and varnish remover; and as a solvent in the manufacture of pharmaceuticals and chemicals.

Carboxylic Acids and Esters

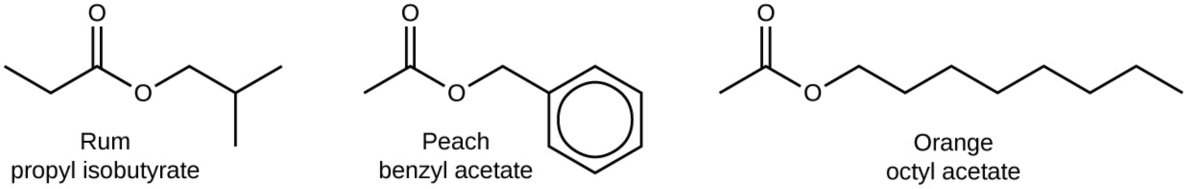
The odor of vinegar is caused by the presence of acetic acid, a carboxylic acid, in the vinegar. The odor of ripe bananas and many other fruits is due to the presence of esters, compounds that can be prepared by the reaction of a carboxylic acid with an alcohol. Because esters do not have hydrogen bonds between molecules, they have lower vapor pressures than the alcohols and carboxylic acids from which they are derived (see **Figure 21.15**).



Raspberry
iso-butyl formate

Apple
butyl acetate

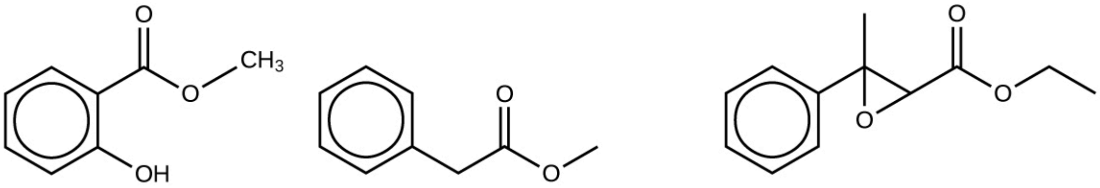
Pineapple
ethyl butyrate



Rum
propyl isobutyrate

Peach
benzyl acetate

Orange
octyl acetate



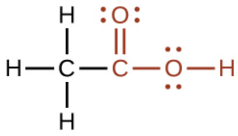
Wintergreen
methyl salicylate

Honey
methyl phenylacetate

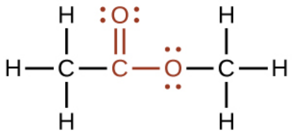
Strawberry
ethyl methylphenylglycidate

Figure 21.15 Esters are responsible for the odors associated with various plants and their fruits.

Both **carboxylic acids** and **esters** contain a carbonyl group with a second oxygen atom bonded to the carbon atom in the carbonyl group by a single bond. In a carboxylic acid, the second oxygen atom also bonds to a hydrogen atom. In an ester, the second oxygen atom bonds to another carbon atom. The names for carboxylic acids and esters include prefixes that denote the lengths of the carbon chains in the molecules and are derived following nomenclature rules similar to those for inorganic acids and salts (see these examples):



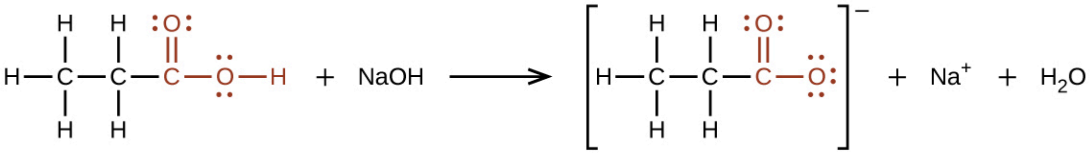
ethanoic acid
(acetic acid)



methyl ethanoate
(methyl acetate)

The functional groups for an acid and for an ester are shown in red in these formulas.

The hydrogen atom in the functional group of a carboxylic acid will react with a base to form an ionic salt:

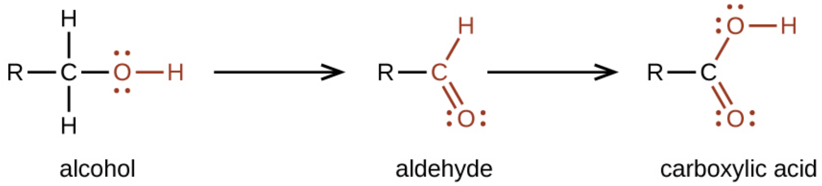


propionic acid

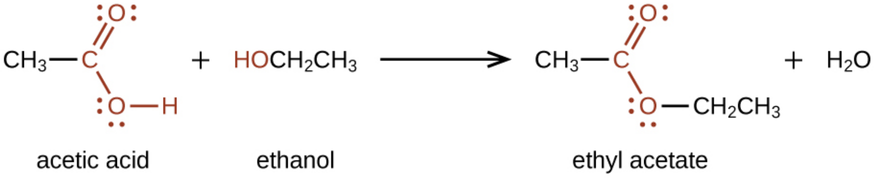
proprionate ion

Carboxylic acids are weak acids (see the chapter on acids and bases), meaning they are not 100% ionized in water. Generally only about 1% of the molecules of a carboxylic acid dissolved in water are ionized at any given time. The remaining molecules are undissociated in solution.

We prepare carboxylic acids by the oxidation of aldehydes or alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:



Esters are produced by the reaction of acids with alcohols. For example, the ester ethyl acetate, $CH_3CO_2CH_2CH_3$, is formed when acetic acid reacts with ethanol:



The simplest carboxylic acid is formic acid, HCO_2H, known since 1670. Its name comes from the Latin word *formicus*, which means “ant”; it was first isolated by the distillation of red ants. It is partially responsible for the pain and irritation of ant and wasp stings, and is responsible for a characteristic odor of ants that can be sometimes detected in their nests.

Acetic acid, CH_3CO_2H, constitutes 3–6% vinegar. Cider vinegar is produced by allowing apple juice to ferment without oxygen present. Yeast cells present in the juice carry out the fermentation reactions. The fermentation reactions change the sugar present in the juice to ethanol, then to acetic acid. Pure acetic acid has a penetrating odor and produces painful burns. It is an excellent solvent for many organic and some inorganic compounds, and it is essential in the production of cellulose acetate, a component of many synthetic fibers such as rayon.

The distinctive and attractive odors and flavors of many flowers, perfumes, and ripe fruits are due to the presence of one or more esters (**Figure 21.16**). Among the most important of the natural esters are fats (such as lard, tallow, and butter) and oils (such as linseed, cottonseed, and olive oils), which are esters of the trihydroxyl alcohol glycerine, $C_3H_5(OH)_3$, with large carboxylic acids, such as palmitic acid, $CH_3(CH_2)_{14}CO_2H$, stearic acid, $CH_3(CH_2)_{16}CO_2H$, and oleic acid, $CH_3(CH_2)_7CH = CH(CH_2)_7CO_2H.$ Oleic acid is an unsaturated acid; it contains a $C = C$ double bond. Palmitic and stearic acids are saturated acids that contain no double or triple bonds.

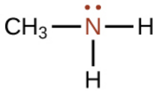
Figure 21.16 Over 350 different volatile molecules (many members of the ester family) have been identified in strawberries. (credit: Rebecca Siegel)

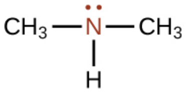
21.4 Amines and Amides

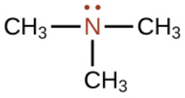
By the end of this section, you will be able to:

- Describe the structure and properties of an amine
- Describe the structure and properties of an amide

Amines are molecules that contain carbon-nitrogen bonds. The nitrogen atom in an amine has a lone pair of electrons and three bonds to other atoms, either carbon or hydrogen. Various nomenclatures are used to derive names for amines, but all involve the class-identifying suffix *–ine* as illustrated here for a few simple examples:


methyl amine


dimethyl amine


trimethyl amine

In some amines, the nitrogen atom replaces a carbon atom in an aromatic hydrocarbon. Pyridine (**Figure 21.17**) is one such heterocyclic amine. A heterocyclic compound contains atoms of two or more different elements in its ring structure.

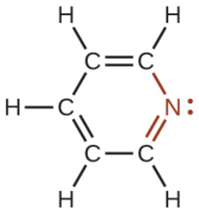


Figure 21.17 The illustration shows one of the resonance structures of pyridine.

How Sciences Interconnect

DNA in Forensics and Paternity

The genetic material for all living things is a polymer of four different molecules, which are themselves a combination of three subunits. The genetic information, the code for developing an organism, is contained in the specific sequence of the four molecules, similar to the way the letters of the alphabet can be sequenced to form words that convey information. The information in a DNA sequence is used to form two other types of polymers, one of which are proteins. The proteins interact to form a specific type of organism with individual characteristics.

A genetic molecule is called DNA, which stands for deoxyribonucleic acid. The four molecules that make up DNA are called nucleotides. Each nucleotide consists of a single- or double-ringed molecule containing nitrogen, carbon, oxygen, and hydrogen called a nitrogenous base. Each base is bonded to a five-carbon sugar called deoxyribose. The sugar is in turn bonded to a phosphate group $(-PO_4{}^{3-})$ When new DNA is made, a polymerization reaction occurs that binds the phosphate group of one nucleotide to the sugar group of a second nucleotide. The nitrogenous bases of each nucleotide stick out from this sugar-phosphate backbone. DNA is actually formed from two such polymers coiled around each other and held together by hydrogen bonds between the nitrogenous bases. Thus, the two backbones are on the outside of the coiled pair of strands, and the bases are on the inside. The shape of the two strands wound around each other is called a double helix (see **Figure 21.18**).

It probably makes sense that the sequence of nucleotides in the DNA of a cat differs from those of a dog. But it is also true that the sequences of the DNA in the cells of two individual pugs differ. Likewise, the sequences of DNA in you and a sibling differ (unless your sibling is an identical twin), as do those between you and an unrelated individual. However, the DNA sequences of two related individuals are more similar than the sequences of two unrelated individuals, and these similarities in sequence can be observed in various ways. This is the principle behind DNA fingerprinting, which is a method used to determine whether two DNA samples came from related (or the same) individuals or unrelated individuals.

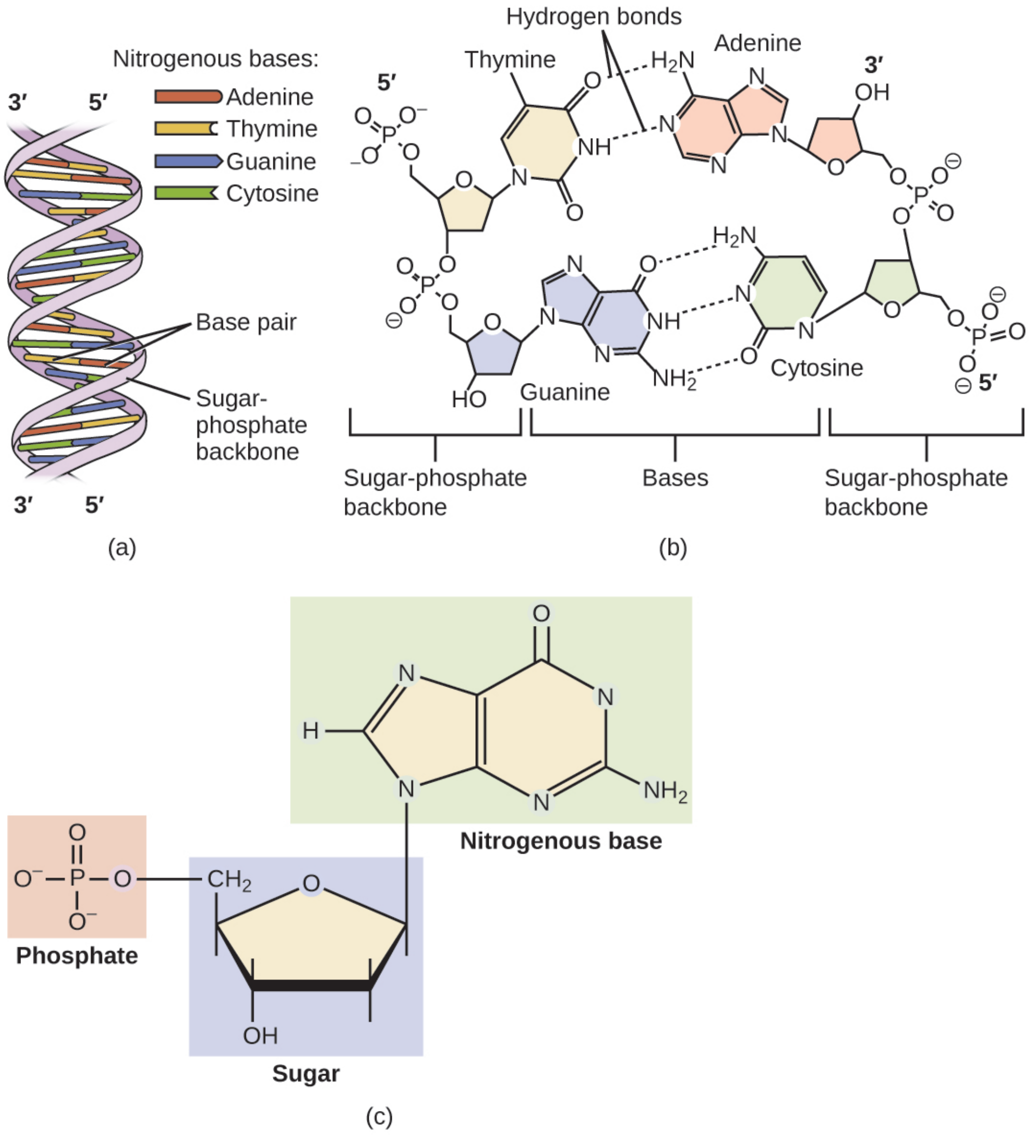


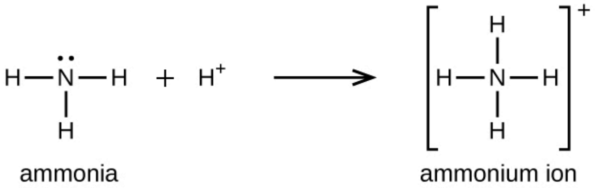
Figure 21.18 DNA is an organic molecule and the genetic material for all living organisms. (a) DNA is a double helix consisting of two single DNA strands hydrogen bonded together at each nitrogenous base. (b) This detail shows the hydrogen bonding (dotted lines) between nitrogenous bases on each DNA strand and the way in which each nucleotide is joined to the next, forming a backbone of sugars and phosphate groups along each strand. (c) This detail shows the structure of one of the four nucleotides that makes up the DNA polymer. Each nucleotide consists of a nitrogenous base (a double-ring molecule, in this case), a five-carbon sugar (deoxyribose), and a phosphate group.

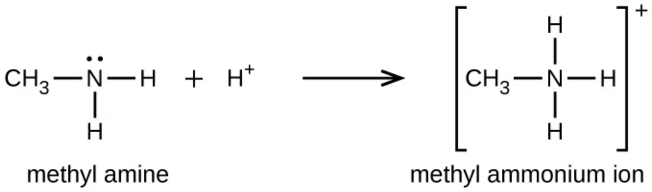
Using similarities in sequences, technicians can determine whether a man is the father of a child (the identity of the mother is rarely in doubt, except in the case of an adopted child and a potential birth mother). Likewise, forensic geneticists can determine whether a crime scene sample of human tissue, such as blood or skin cells, contains DNA that matches exactly the DNA of a suspect.

Link to Learning

Watch this **video animation (http://openstaxcollege.org/l/16dnapackaging)** of how DNA is packaged for a visual lesson in its structure.

Like ammonia, amines are weak bases due to the lone pair of electrons on their nitrogen atoms:





The basicity of an amine’s nitrogen atom plays an important role in much of the compound’s chemistry. Amine functional groups are found in a wide variety of compounds, including natural and synthetic dyes, polymers, vitamins, and medications such as penicillin and codeine. They are also found in many molecules essential to life, such as amino acids, hormones, neurotransmitters, and DNA.

How Sciences Interconnect

Addictive Alkaloids

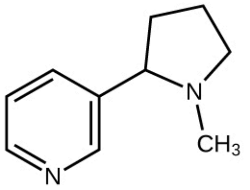
Since ancient times, plants have been used for medicinal purposes. One class of substances, called *alkaloids*, found in many of these plants has been isolated and found to contain cyclic molecules with an amine functional group. These amines are bases. They can react with H_3O^+ in a dilute acid to form an ammonium salt, and this property is used to extract them from the plant:

$$R_3N + H_3O^+ + Cl^- \longrightarrow \left[R_3NH^+\right]Cl^- + H_2O$$

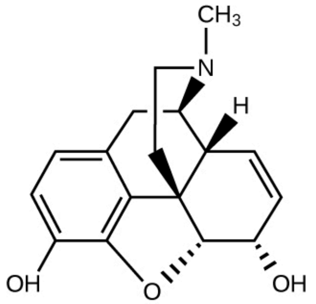
The name alkaloid means “like an alkali.” Thus, an alkaloid reacts with acid. The free compound can be recovered after extraction by reaction with a base:

$$\left[R_3NH^+\right]Cl^- + OH^- \longrightarrow R_3N + H_2O + Cl^-$$

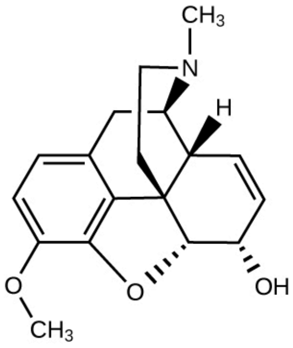
The structures of many naturally occurring alkaloids have profound physiological and psychotropic effects in humans. Examples of these drugs include nicotine, morphine, codeine, and heroin. The plant produces these substances, collectively called secondary plant compounds, as chemical defenses against the numerous pests that attempt to feed on the plant:



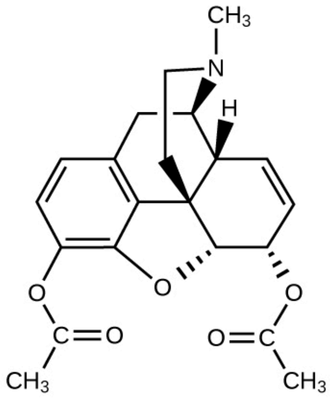
nicotine



morphine



codeine

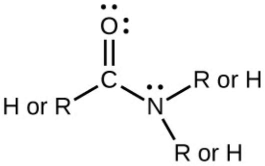


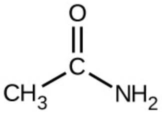
heroin

In these diagrams, as is common in representing structures of large organic compounds, carbon atoms in the rings and the hydrogen atoms bonded to them have been omitted for clarity. The solid wedges indicate bonds that extend out of the page. The dashed wedges indicate bonds that extend into the page. Notice that small changes to a part of the molecule change the properties of morphine, codeine, and heroin. Morphine, a strong narcotic used to relieve pain, contains two hydroxyl functional groups, located at the bottom of the molecule in this structural formula. Changing one of these hydroxyl groups to a methyl ether group forms codeine, a less potent drug used as a local anesthetic. If both hydroxyl groups are converted to esters of acetic acid, the powerfully addictive drug heroin results (**Figure 21.19**).

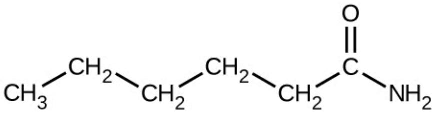
Figure 21.19 Poppies can be used in the production of opium, a plant latex that contains morphine from which other opiates, such as heroin, can be synthesized. (credit: Karen Roe)

Amides are molecules that contain nitrogen atoms connected to the carbon atom of a carbonyl group. Like amines, various nomenclature rules may be used to name amides, but all include use of the class-specific suffix *-amide*:



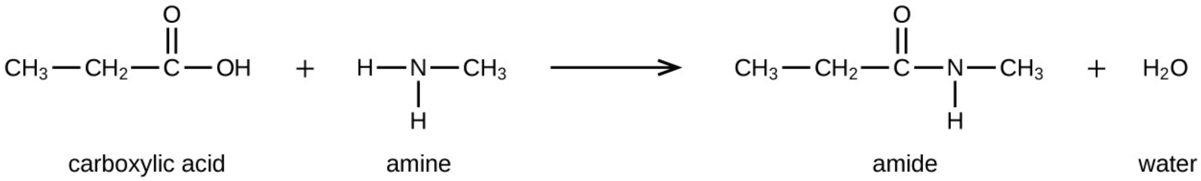


acetamide



hexanamide

Amides can be produced when carboxylic acids react with amines or ammonia in a process called amidation. A water molecule is eliminated from the reaction, and the amide is formed from the remaining pieces of the carboxylic acid and the amine (note the similarity to formation of an ester from a carboxylic acid and an alcohol discussed in the previous section):



$$CH_3-CH_2-\overset{\overset{\large O}{\|}}{C}-OH + H-\underset{\underset{\large H}{|}}{N}-CH_3 \longrightarrow CH_3-CH_2-\overset{\overset{\large O}{\|}}{C}-\underset{\underset{\large H}{|}}{N}-CH_3 + H_2O$$

The reaction between amines and carboxylic acids to form amides is biologically important. It is through this reaction that amino acids (molecules containing both amine and carboxylic acid substituents) link together in a polymer to form proteins.

How Sciences Interconnect

Proteins and Enzymes

Proteins are large biological molecules made up of long chains of smaller molecules called amino acids. Organisms rely on proteins for a variety of functions—proteins transport molecules across cell membranes, replicate DNA, and catalyze metabolic reactions, to name only a few of their functions. The properties of proteins are functions of the combination of amino acids that compose them and can vary greatly. Interactions between amino acid sequences in the chains of proteins result in the folding of the chain into specific, three-dimensional structures that determine the protein’s activity.

Amino acids are organic molecules that contain an amine functional group (–NH_2), a carboxylic acid functional group (–COOH), and a side chain (that is specific to each individual amino acid). Most living things build proteins from the same 20 different amino acids. Amino acids connect by the formation of a peptide bond, which is a covalent bond formed between two amino acids when the carboxylic acid group of one amino acid reacts with the amine group of the other amino acid. The formation of the bond results in the production of a molecule of water (in general, reactions that result in the production of water when two other molecules combine are referred to as condensation reactions). The resulting bond—between the carbonyl group carbon atom and the amine nitrogen atom is called a peptide link or peptide bond. Since each of the original amino acids has an unreacted group (one has an unreacted amine and the other an unreacted carboxylic acid), more peptide bonds can form to other amino acids, extending the structure. (**Figure 21.20**) A chain of connected amino acids is called a polypeptide. Proteins contain at least one long polypeptide chain.

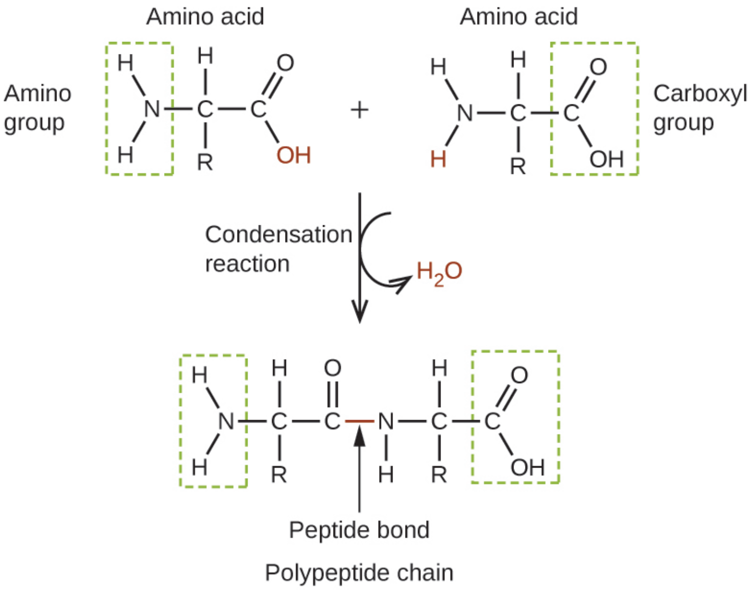


Figure 21.20 This condensation reaction forms a dipeptide from two amino acids and leads to the formation of water.

Enzymes are large biological molecules, mostly composed of proteins, which are responsible for the thousands of metabolic processes that occur in living organisms. Enzymes are highly specific catalysts; they speed up the rates of certain reactions. Enzymes function by lowering the activation energy of the reaction they are catalyzing, which can dramatically increase the rate of the reaction. Most reactions catalyzed by enzymes have rates that are millions of times faster than the noncatalyzed version. Like all catalysts, enzymes are not consumed during the reactions that they catalyze. Enzymes do differ from other catalysts in how specific they are for their substrates (the molecules that an enzyme will convert into a different product). Each enzyme is only capable of speeding up one or a few very specific reactions or types of reactions. Since the function of enzymes is so specific, the lack or malfunctioning of an enzyme can lead to serious health consequences. One disease that is the result of an enzyme malfunction is phenylketonuria. In this disease, the enzyme that catalyzes the first step in the degradation of the amino acid phenylalanine is not functional (**Figure 21.21**). Untreated, this can lead to an accumulation of phenylalanine, which can lead to intellectual disabilities.

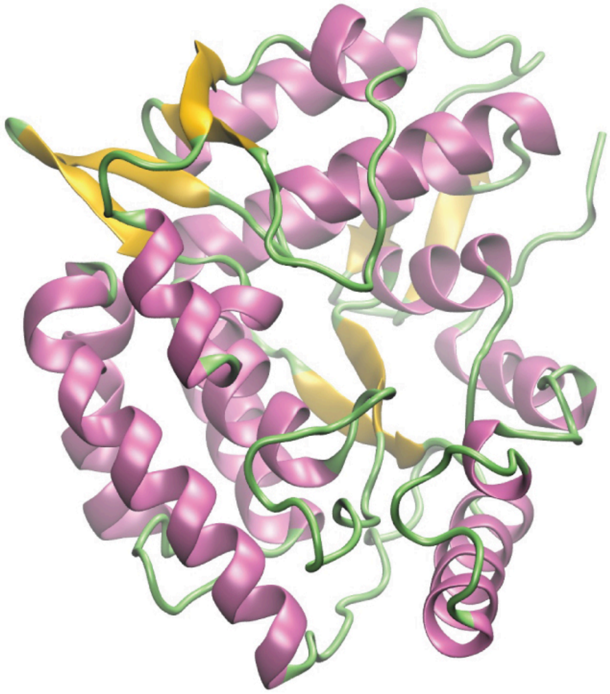


Figure 21.21 A computer rendering shows the three-dimensional structure of the enzyme phenylalanine hydroxylase. In the disease phenylketonuria, a defect in the shape of phenylalanine hydroxylase causes it to lose its function in breaking down phenylalanine.

Chemistry in Everyday Life

Kevlar

Kevlar (**Figure 21.22**) is a synthetic polymer made from two monomers 1,4-phenylene-diamine and terephthaloyl chloride (Kevlar is a registered trademark of DuPont). Kevlar’s first commercial use was as a replacement for steel in racing tires. Kevlar is typically spun into ropes or fibers. The material has a high tensile strength-to-weight ratio (it is about 5 times stronger than an equal weight of steel), making it useful for many applications from bicycle tires to sails to body armor.

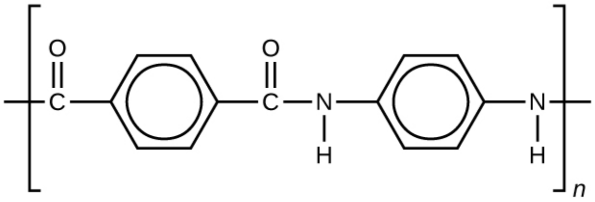


Figure 21.22 This illustration shows the formula for polymeric Kevlar.

The material owes much of its strength to hydrogen bonds between polymer chains (refer back to the chapter on intermolecular interactions). These bonds form between the carbonyl group oxygen atom (which has a partial negative charge due to oxygen's electronegativity) on one monomer and the partially positively charged hydrogen atom in the N–H bond of an adjacent monomer in the polymer structure (see dashed line in **Figure 21.23**). There is additional strength derived from the interaction between the unhybridized *p* orbitals in the six-membered rings, called aromatic stacking.

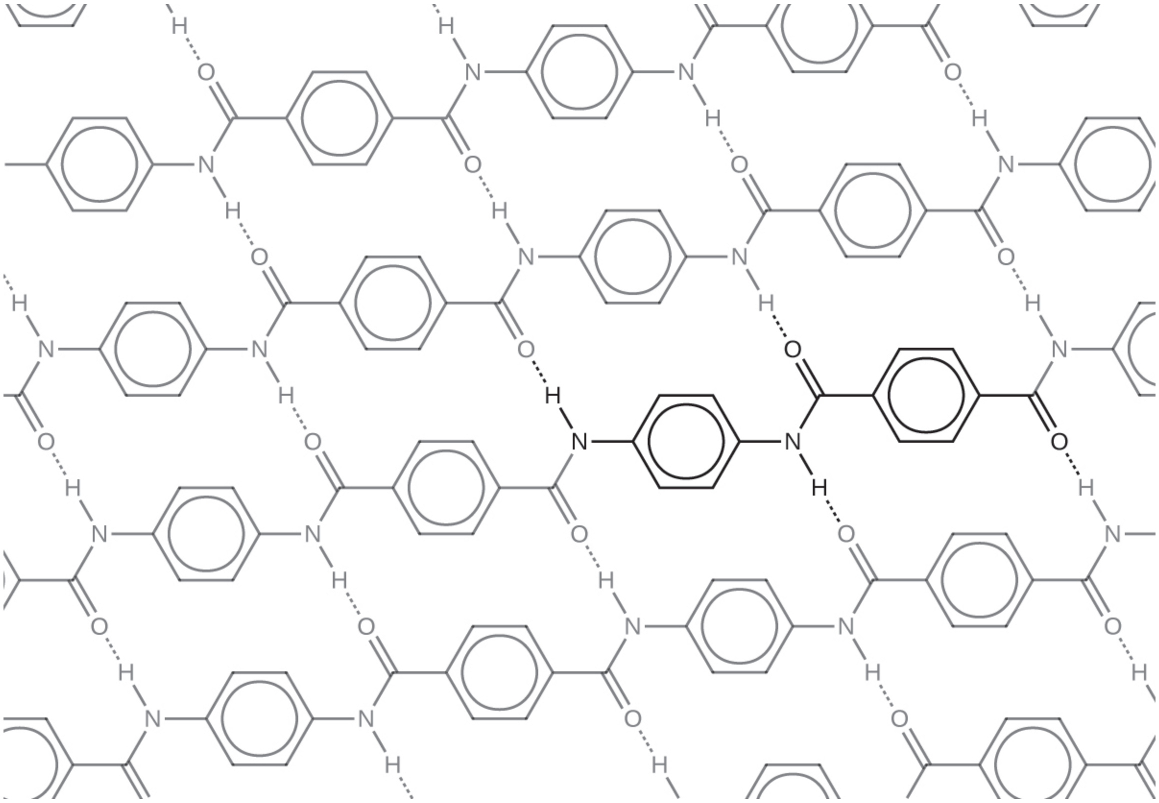


Figure 21.23 The diagram shows the polymer structure of Kevlar, with hydrogen bonds between polymer chains represented by dotted lines.

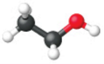
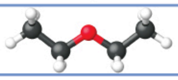
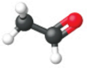
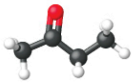
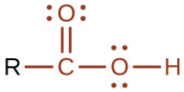
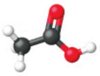
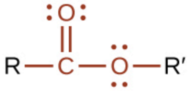
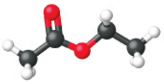
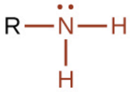
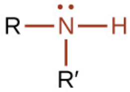
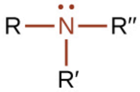
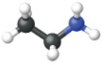
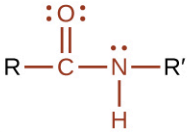
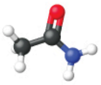
Kevlar may be best known as a component of body armor, combat helmets, and face masks. Since the 1980s, the US military has used Kevlar as a component of the PASGT (personal armor system for ground troops) helmet and vest. Kevlar is also used to protect armored fighting vehicles and aircraft carriers. Civilian applications include protective gear for emergency service personnel such as body armor for police officers and heat-resistant clothing for fire fighters. Kevlar based clothing is considerably lighter and thinner than equivalent gear made from other materials (**Figure 21.24**).


(a) (b) (c)

Figure 21.24 (a) These soldiers are sorting through pieces of a Kevlar helmet that helped absorb a grenade blast. Kevlar is also used to make (b) canoes and (c) marine mooring lines. (credit a: modification of work by “Cla68”/Wikimedia Commons; credit b: modification of work by “OakleyOriginals”/Flickr; credit c: modification of work by Casey H. Kyhl)

In addition to its better-known uses, Kevlar is also often used in cryogenics for its very low thermal conductivity (along with its high strength). Kevlar maintains its high strength when cooled to the temperature of liquid nitrogen (–196 °C).

The table here summarizes the structures discussed in this chapter:

Compound Name	Structure of Compound and Functional Group (red)	Example	
		Formula	Name
alkene	$C{=}C$	C_2H_4 	ethene
alkyne	$C{\equiv}C$	C_2H_2 	ethyne
alcohol	$R-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H$	CH_3CH_2OH 	ethanol
ether	$R-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-R'$	$(C_2H_5)_2O$ 	diethyl ether
aldehyde	 $R-\overset{\overset{:\ddot{O}:}{\Vert}}{C}-H$	CH_3CHO 	ethanal
ketone	 $R-\overset{\overset{:\ddot{O}:}{\Vert}}{C}-R'$	$CH_3COCH_2CH_3$ 	methyl ethyl ketone
carboxylic acid	 $R-\overset{\overset{:\ddot{O}:}{\Vert}}{C}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H$	CH_3COOH 	acetic acid
ester	 $R-\overset{\overset{:\ddot{O}:}{\Vert}}{C}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-R'$	$CH_3CO_2CH_2CH_3$ 	ethyl acetate
amine	 $R-\underset{\underset{H}{\vert}}{\ddot{N}}-H$  $R-\underset{\underset{R'}{\vert}}{\ddot{N}}-H$  $R-\underset{\underset{R'}{\vert}}{\ddot{N}}-R''$	$C_2H_5NH_2$ 	ethylamine
amide	 $R-\overset{\overset{:\ddot{O}:}{\Vert}}{C}-\underset{\underset{H}{\vert}}{\ddot{N}}-R'$	CH_3CONH_2 	acetamide

Key Terms

addition reaction reaction in which a double carbon-carbon bond forms a single carbon-carbon bond by the addition of a reactant. Typical reaction for an alkene.

alcohol organic compound with a hydroxyl group (–OH) bonded to a carbon atom

aldehyde organic compound containing a carbonyl group bonded to two hydrogen atoms or a hydrogen atom and a carbon substituent

alkane molecule consisting of only carbon and hydrogen atoms connected by single (σ) bonds

alkene molecule consisting of carbon and hydrogen containing at least one carbon-carbon double bond

alkyl group substituent, consisting of an alkane missing one hydrogen atom, attached to a larger structure

alkyne molecule consisting of carbon and hydrogen containing at least one carbon-carbon triple bond

amide organic molecule that features a nitrogen atom connected to the carbon atom in a carbonyl group

amine organic molecule in which a nitrogen atom is bonded to one or more alkyl group

aromatic hydrocarbon cyclic molecule consisting of carbon and hydrogen with delocalized alternating carbon-carbon single and double bonds, resulting in enhanced stability

carbonyl group carbon atom double bonded to an oxygen atom

carboxylic acid organic compound containing a carbonyl group with an attached hydroxyl group

ester organic compound containing a carbonyl group with an attached oxygen atom that is bonded to a carbon substituent

ether organic compound with an oxygen atom that is bonded to two carbon atoms

functional group part of an organic molecule that imparts a specific chemical reactivity to the molecule

ketone organic compound containing a carbonyl group with two carbon substituents attached to it

organic compound natural or synthetic compound that contains carbon

saturated hydrocarbon molecule containing carbon and hydrogen that has only single bonds between carbon atoms

skeletal structure shorthand method of drawing organic molecules in which carbon atoms are represented by the ends of lines and bends in between lines, and hydrogen atoms attached to the carbon atoms are not shown (but are understood to be present by the context of the structure)

substituent branch or functional group that replaces hydrogen atoms in a larger hydrocarbon chain

substitution reaction reaction in which one atom replaces another in a molecule

Summary

21.1 Hydrocarbons

Strong, stable bonds between carbon atoms produce complex molecules containing chains, branches, and rings. The chemistry of these compounds is called organic chemistry. Hydrocarbons are organic compounds composed of only carbon and hydrogen. The alkanes are saturated hydrocarbons—that is, hydrocarbons that contain only single bonds. Alkenes contain one or more carbon-carbon double bonds. Alkynes contain one or more carbon-carbon triple bonds. Aromatic hydrocarbons contain ring structures with delocalized π electron systems.

21.2 Alcohols and Ethers

Many organic compounds that are not hydrocarbons can be thought of as derivatives of hydrocarbons. A hydrocarbon derivative can be formed by replacing one or more hydrogen atoms of a hydrocarbon by a functional group, which contains at least one atom of an element other than carbon or hydrogen. The properties of hydrocarbon derivatives are determined largely by the functional group. The –OH group is the functional group of an alcohol. The –R–O–R– group is the functional group of an ether.

21.3 Aldehydes, Ketones, Carboxylic Acids, and Esters

Functional groups related to the carbonyl group include the –CHO group of an aldehyde, the –CO– group of a ketone, the $–CO_2H$ group of a carboxylic acid, and the $–CO_2R$ group of an ester. The carbonyl group, a carbon-oxygen double bond, is the key structure in these classes of organic molecules: Aldehydes contain at least one hydrogen atom attached to the carbonyl carbon atom, ketones contain two carbon groups attached to the carbonyl carbon atom, carboxylic acids contain a hydroxyl group attached to the carbonyl carbon atom, and esters contain an oxygen atom attached to another carbon group connected to the carbonyl carbon atom. All of these compounds contain oxidized carbon atoms relative to the carbon atom of an alcohol group.

21.4 Amines and Amides

The addition of nitrogen into an organic framework leads to two families of molecules. Compounds containing a nitrogen atom bonded in a hydrocarbon framework are classified as amines. Compounds that have a nitrogen atom bonded to one side of a carbonyl group are classified as amides. Amines are a basic functional group. Amines and carboxylic acids can combine in a condensation reaction to form amides.

Exercises

21.1 Hydrocarbons

1. Write the chemical formula and Lewis structure of the following, each of which contains five carbon atoms:

(a) an alkane

(b) an alkene

(c) an alkyne

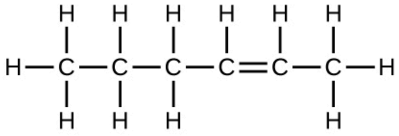
2. What is the difference between the hybridization of carbon atoms’ valence orbitals in saturated and unsaturated hydrocarbons?

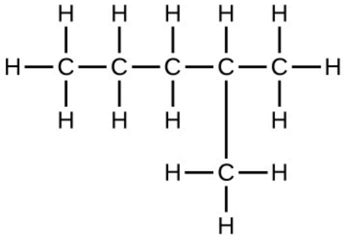
3. On a microscopic level, how does the reaction of bromine with a saturated hydrocarbon differ from its reaction with an unsaturated hydrocarbon? How are they similar?

4. On a microscopic level, how does the reaction of bromine with an alkene differ from its reaction with an alkyne? How are they similar?

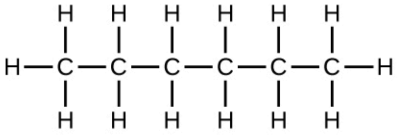
5. Explain why unbranched alkenes can form geometric isomers while unbranched alkanes cannot. Does this explanation involve the macroscopic domain or the microscopic domain?

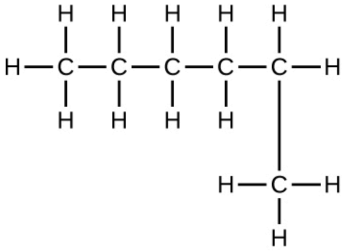
6. Explain why these two molecules are not isomers:





7. Explain why these two molecules are not isomers:





8. How does the carbon-atom hybridization change when polyethylene is prepared from ethylene?

9. Write the Lewis structure and molecular formula for each of the following hydrocarbons:

(a) hexane

(b) 3-methylpentane

(c) *cis*-3-hexene

(d) 4-methyl-1-pentene

(e) 3-hexyne

(f) 4-methyl-2-pentyne

10. Write the chemical formula, condensed formula, and Lewis structure for each of the following hydrocarbons:

(a) heptane

(b) 3-methylhexane

(c) *trans*-3-heptene

(d) 4-methyl-1-hexene

(e) 2-heptyne

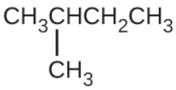
(f) 3,4-dimethyl-1-pentyne

11. Give the complete IUPAC name for each of the following compounds:

(a) $CH_3CH_2CBr_2CH_3$

(b) $(CH_3)_3CCl$

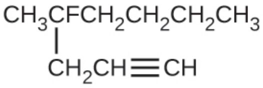
(c)



$CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$

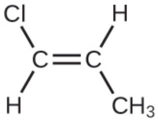
(d) $CH_3CH_2C\equiv CH\ CH_3CH_2C\equiv CH$

(e)



$CH_3\underset{\underset{\displaystyle CH_2CH\equiv CH}{|}}{C}FCH_2CH_2CH_2CH_3$

(f)



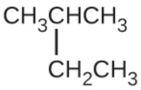
(g) $(CH_3)_2CHCH_2CH=CH_2$

12. Give the complete IUPAC name for each of the following compounds:

(a) $(CH_3)_2CHF$

(b) $CH_3CHClCHClCH_3$

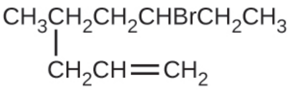
(c)



$CH_3\underset{\underset{\displaystyle CH_2CH_3}{|}}{C}HCH_3$

(d) $CH_3CH_2CH=CHCH_3$

(e)



$CH_3\underset{\underset{\displaystyle CH_2CH=CH_2}{|}}{C}H_2CH_2CHBrCH_2CH_3$

(f) $(CH_3)_3CCH_2C\equiv CH$

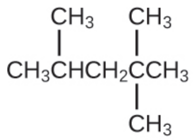
13. Butane is used as a fuel in disposable lighters. Write the Lewis structure for each isomer of butane.

14. Write Lewis structures and name the five structural isomers of hexane.

15. Write Lewis structures for the *cis–trans* isomers of $CH_3CH=CHCl$.

16. Write structures for the three isomers of the aromatic hydrocarbon xylene, $C_6H_4(CH_3)_2$.

17. Isooctane is the common name of the isomer of C_8H_{18} used as the standard of 100 for the gasoline octane rating:



(a) What is the IUPAC name for the compound?

(b) Name the other isomers that contain a five-carbon chain with three methyl substituents.

18. Write Lewis structures and IUPAC names for the alkyne isomers of C_4H_6.

19. Write Lewis structures and IUPAC names for all isomers of C_4H_9Cl.

20. Name and write the structures of all isomers of the propyl and butyl alkyl groups.

21. Write the structures for all the isomers of the $–C_5H_{11}$ alkyl group.

22. Write Lewis structures and describe the molecular geometry at each carbon atom in the following compounds:

(a) *cis*-3-hexene

(b) *cis*-1-chloro-2-bromoethene

(c) 2-pentyne

(d) *trans*-6-ethyl-7-methyl-2-octene

23. Benzene is one of the compounds used as an octane enhancer in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene:

$$3C_2H_2 \longrightarrow C_6H_6$$

Draw Lewis structures for these compounds, with resonance structures as appropriate, and determine the hybridization of the carbon atoms in each.

24. Teflon is prepared by the polymerization of tetrafluoroethylene. Write the equation that describes the polymerization using Lewis symbols.

25. Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

(a) 1 mol of 1-butyne reacts with 2 mol of iodine.

(b) Pentane is burned in air.

26. Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

(a) 2-butene reacts with chlorine.

(b) benzene burns in air.

27. What mass of 2-bromopropane could be prepared from 25.5 g of propene? Assume a 100% yield of product.

28. Acetylene is a very weak acid; however, it will react with moist silver(I) oxide and form water and a compound composed of silver and carbon. Addition of a solution of HCl to a 0.2352-g sample of the compound of silver and carbon produced acetylene and 0.2822 g of AgCl.

(a) What is the empirical formula of the compound of silver and carbon?

(b) The production of acetylene on addition of HCl to the compound of silver and carbon suggests that the carbon is present as the acetylide ion, $C_2{}^{2-}$. Write the formula of the compound showing the acetylide ion.

29. Ethylene can be produced by the pyrolysis of ethane:

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

How many kilograms of ethylene is produced by the pyrolysis of 1.000×10^3 kg of ethane, assuming a 100.0% yield?

21.2 Alcohols and Ethers

30. Why do the compounds hexane, hexanol, and hexene have such similar names?

31. Write condensed formulas and provide IUPAC names for the following compounds:

(a) ethyl alcohol (in beverages)

(b) methyl alcohol (used as a solvent, for example, in shellac)

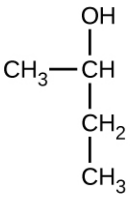
(c) ethylene glycol (antifreeze)

(d) isopropyl alcohol (used in rubbing alcohol)

(e) glycerine

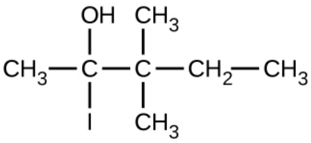
32. Give the complete IUPAC name for each of the following compounds:

(a)



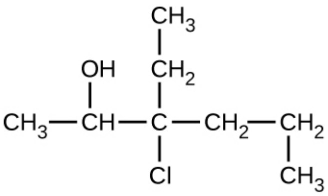
$CH_3-\underset{\underset{CH_3}{CH_2}}{\overset{OH}{CH}}$

(b)



$CH_3-\overset{OH}{\underset{I}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$

(c)



$CH_3-\overset{OH}{CH}-\underset{Cl}{\overset{\overset{CH_3}{CH_2}}{C}}-CH_2-\underset{CH_3}{CH_2}$

33. Give the complete IUPAC name and the common name for each of the following compounds:

(a)

$$CH_3-CH_2-O-CH_2-CH_2-CH_2-CH_3$$

(b)

$$CH_3-CH_2-O-CH_2-CH_2-CH_3$$

(c)

$$CH_3-O-CH_2-CH_2-CH_3$$

34. Write the condensed structures of both isomers with the formula C_2H_6O. Label the functional group of each isomer.

35. Write the condensed structures of all isomers with the formula $C_2H_6O_2$. Label the functional group (or groups) of each isomer.

36. Draw the condensed formulas for each of the following compounds:

(a) dipropyl ether

(b) 2,2-dimethyl-3-hexanol

(c) 2-ethoxybutane

37. MTBE, Methyl *tert*-butyl ether, $CH_3OC(CH_3)_3$, is used as an oxygen source in oxygenated gasolines. MTBE is manufactured by reacting 2-methylpropene with methanol.

(a) Using Lewis structures, write the chemical equation representing the reaction.

(b) What volume of methanol, density 0.7915 g/mL, is required to produce exactly 1000 kg of MTBE, assuming a 100% yield?

38. Write two complete balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

(a) propanol is converted to dipropyl ether

(b) propene is treated with water in dilute acid.

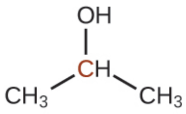
39. Write two complete balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

(a) 2-butene is treated with water in dilute acid

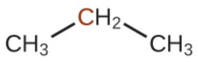
(b) ethanol is dehydrated to yield ethene

21.3 Aldehydes, Ketones, Carboxylic Acids, and Esters

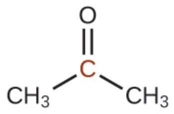
40. Order the following molecules from least to most oxidized, based on the marked carbon atom:



(a)



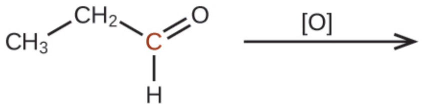
(b)



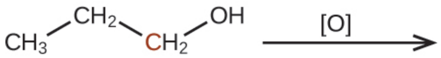
(c)

41. Predict the products of oxidizing the molecules shown in this problem. In each case, identify the product that will result from the minimal increase in oxidation state for the highlighted carbon atom:

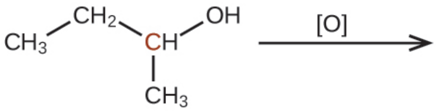
(a)



(b)

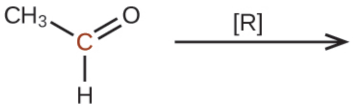


(c)

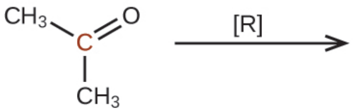


42. Predict the products of reducing the following molecules. In each case, identify the product that will result from the minimal decrease in oxidation state for the highlighted carbon atom:

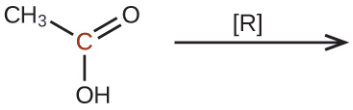
(a)



(b)



(c)



43. Explain why it is not possible to prepare a ketone that contains only two carbon atoms.

44. How does hybridization of the substituted carbon atom change when an alcohol is converted into an aldehyde? An aldehyde to a carboxylic acid?

45. Fatty acids are carboxylic acids that have long hydrocarbon chains attached to a carboxylate group. How does a saturated fatty acid differ from an unsaturated fatty acid? How are they similar?

46. Write a condensed structural formula, such as CH_3CH_3, and describe the molecular geometry at each carbon atom.

(a) propene

(b) 1-butanol

(c) ethyl propyl ether

(d) *cis*-4-bromo-2-heptene

(e) 2,2,3-trimethylhexane

(f) formaldehyde

47. Write a condensed structural formula, such as CH_3CH_3, and describe the molecular geometry at each carbon atom.

(a) 2-propanol

(b) acetone

(c) dimethyl ether

(d) acetic acid

(e) 3-methyl-1-hexene

48. The foul odor of rancid butter is caused by butyric acid, $CH_3CH_2CH_2CO_2H$.

(a) Draw the Lewis structure and determine the oxidation number and hybridization for each carbon atom in the molecule.

(b) The esters formed from butyric acid are pleasant-smelling compounds found in fruits and used in perfumes. Draw the Lewis structure for the ester formed from the reaction of butyric acid with 2-propanol.

49. Write the two-resonance structures for the acetate ion.

50. Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures:

(a) ethanol reacts with propionic acid

(b) benzoic acid, $C_6H_5CO_2H$, is added to a solution of sodium hydroxide

51. Write two complete balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

(a) 1-butanol reacts with acetic acid

(b) propionic acid is poured onto solid calcium carbonate

52. Yields in organic reactions are sometimes low. What is the percent yield of a process that produces 13.0 g of ethyl acetate from 10.0 g of CH_3CO_2H?

53. Alcohols A, B, and C all have the composition $C_4H_{10}O$. Molecules of alcohol A contain a branched carbon chain and can be oxidized to an aldehyde; molecules of alcohol B contain a linear carbon chain and can be oxidized to a ketone; and molecules of alcohol C can be oxidized to neither an aldehyde nor a ketone. Write the Lewis structures of these molecules.

21.4 Amines and Amides

54. Write the Lewis structures of both isomers with the formula C_2H_7N.

55. What is the molecular structure about the nitrogen atom in trimethyl amine and in the trimethyl ammonium ion, $(CH_3)_3NH^+$? What is the hybridization of the nitrogen atom in trimethyl amine and in the trimethyl ammonium ion?

56. Write the two resonance structures for the pyridinium ion, $C_5H_5NH^+$.

57. Draw Lewis structures for pyridine and its conjugate acid, the pyridinium ion, $C_5H_5NH^+$. What are the geometries and hybridizations about the nitrogen atoms in pyridine and in the pyridinium ion?

58. Write the Lewis structures of all isomers with the formula C_3H_7ON that contain an amide linkage.

59. Write two complete balanced equations for the following reaction, one using condensed formulas and one using Lewis structures.

Methyl amine is added to a solution of HCl.

60. Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

Ethylammonium chloride is added to a solution of sodium hydroxide.

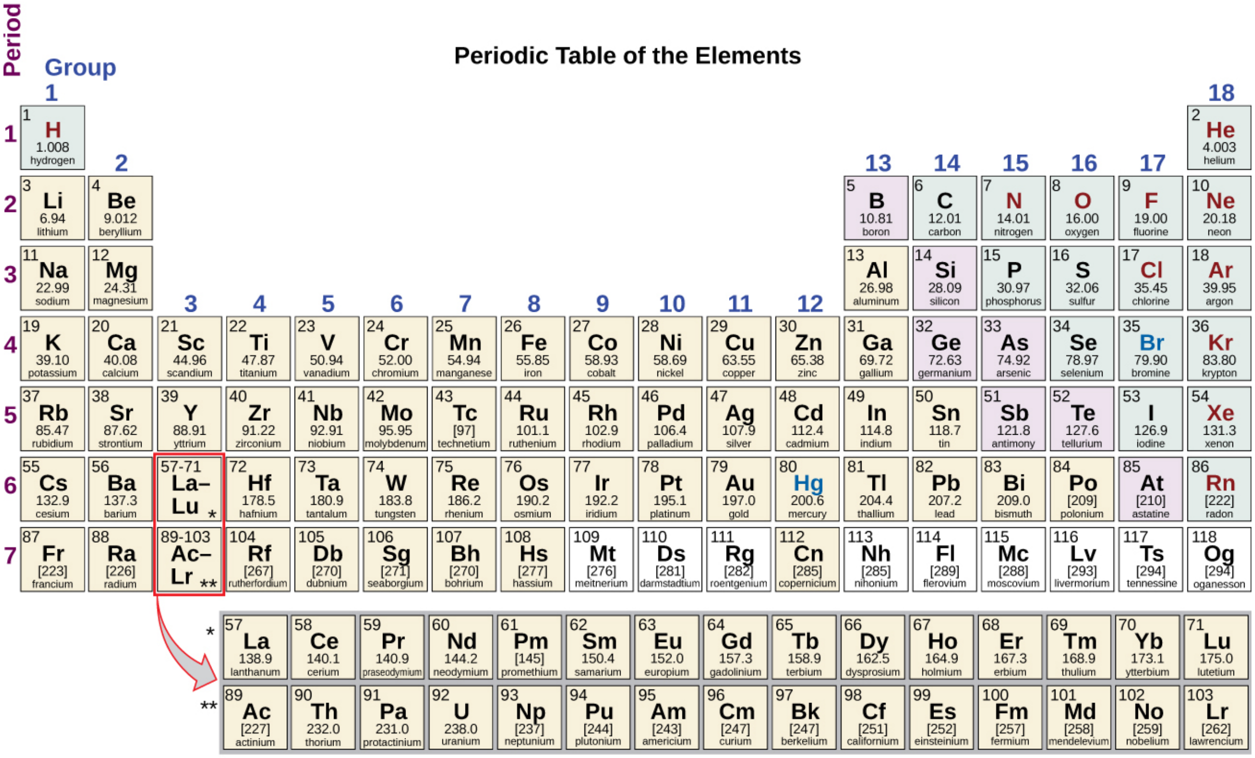
61. Identify any carbon atoms that change hybridization and the change in hybridization during the reactions in **Exercise 21.26**.

62. Identify any carbon atoms that change hybridization and the change in hybridization during the reactions in **Exercise 21.39**.

63. Identify any carbon atoms that change hybridization and the change in hybridization during the reactions in **Exercise 21.51**.

Appendix A

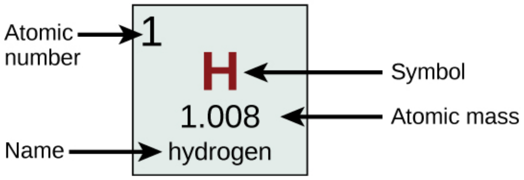
The Periodic Table



Periodic Table of the Elements

Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008 hydrogen																	2 He 4.003 helium
2	3 Li 6.94 lithium	4 Be 9.012 beryllium											5 B 10.81 boron	6 C 12.01 carbon	7 N 14.01 nitrogen	8 O 16.00 oxygen	9 F 19.00 fluorine	10 Ne 20.18 neon
3	11 Na 22.99 sodium	12 Mg 24.31 magnesium											13 Al 26.98 aluminum	14 Si 28.09 silicon	15 P 30.97 phosphorus	16 S 32.06 sulfur	17 Cl 35.45 chlorine	18 Ar 39.95 argon
4	19 K 39.10 potassium	20 Ca 40.08 calcium	21 Sc 44.96 scandium	22 Ti 47.87 titanium	23 V 50.94 vanadium	24 Cr 52.00 chromium	25 Mn 54.94 manganese	26 Fe 55.85 iron	27 Co 58.93 cobalt	28 Ni 58.69 nickel	29 Cu 63.55 copper	30 Zn 65.38 zinc	31 Ga 69.72 gallium	32 Ge 72.63 germanium	33 As 74.92 arsenic	34 Se 78.97 selenium	35 Br 79.90 bromine	36 Kr 83.80 krypton
5	37 Rb 85.47 rubidium	38 Sr 87.62 strontium	39 Y 88.91 yttrium	40 Zr 91.22 zirconium	41 Nb 92.91 niobium	42 Mo 95.95 molybdenum	43 Tc [97] technetium	44 Ru 101.1 ruthenium	45 Rh 102.9 rhodium	46 Pd 106.4 palladium	47 Ag 107.9 silver	48 Cd 112.4 cadmium	49 In 114.8 indium	50 Sn 118.7 tin	51 Sb 121.8 antimony	52 Te 127.6 tellurium	53 I 126.9 iodine	54 Xe 131.3 xenon
6	55 Cs 132.9 cesium	56 Ba 137.3 barium	57-71 La–Lu *	72 Hf 178.5 hafnium	73 Ta 180.9 tantalum	74 W 183.8 tungsten	75 Re 186.2 rhenium	76 Os 190.2 osmium	77 Ir 192.2 iridium	78 Pt 195.1 platinum	79 Au 197.0 gold	80 Hg 200.6 mercury	81 Tl 204.4 thallium	82 Pb 207.2 lead	83 Bi 209.0 bismuth	84 Po [209] polonium	85 At [210] astatine	86 Rn [222] radon
7	87 Fr [223] francium	88 Ra [226] radium	89-103 Ac–Lr **	104 Rf [267] rutherfordium	105 Db [270] dubnium	106 Sg [271] seaborgium	107 Bh [270] bohrium	108 Hs [277] hassium	109 Mt [276] meitnerium	110 Ds [281] darmstadtium	111 Rg [282] roentgenium	112 Cn [285] copernicium	113 Nh [285] nihonium	114 Fl [289] flerovium	115 Mc [288] moscovium	116 Lv [293] livermorium	117 Ts [294] tennessine	118 Og [294] oganesson

*	57 La 138.9 lanthanum	58 Ce 140.1 cerium	59 Pr 140.9 praseodymium	60 Nd 144.2 neodymium	61 Pm [145] promethium	62 Sm 150.4 samarium	63 Eu 152.0 europium	64 Gd 157.3 gadolinium	65 Tb 158.9 terbium	66 Dy 162.5 dysprosium	67 Ho 164.9 holmium	68 Er 167.3 erbium	69 Tm 168.9 thulium	70 Yb 173.1 ytterbium	71 Lu 175.0 lutetium
**	89 Ac [227] actinium	90 Th 232.0 thorium	91 Pa 231.0 protactinium	92 U 238.0 uranium	93 Np [237] neptunium	94 Pu [244] plutonium	95 Am [243] americium	96 Cm [247] curium	97 Bk [247] berkelium	98 Cf [251] californium	99 Es [252] einsteinium	100 Fm [257] fermium	101 Md [258] mendelevium	102 No [259] nobelium	103 Lr [262] lawrencium



Color Code	
▢ Metal	**Solid**
▢ Metalloid	**Liquid**
▢ Nonmetal	**Gas**

Figure A1

Appendix B

Essential Mathematics

Exponential Arithmetic

Exponential notation is used to express very large and very small numbers as a product of two numbers. The first number of the product, the *digit term*, is usually a number not less than 1 and not equal to or greater than 10. The second number of the product, the *exponential term*, is written as 10 with an exponent. Some examples of exponential notation are:

$$\begin{aligned}
1000 &= 1 \times 10^{3} \\
100 &= 1 \times 10^{2} \\
10 &= 1 \times 10^{1} \\
1 &= 1 \times 10^{0} \\
0.1 &= 1 \times 10^{-1} \\
0.001 &= 1 \times 10^{-3} \\
2386 &= 2.386 \times 1000 = 2.386 \times 10^{3} \\
0.123 &= 1.23 \times 0.1 = 1.23 \times 10^{-1}
\end{aligned}$$

The power (exponent) of 10 is equal to the number of places the decimal is shifted to give the digit number. The exponential method is particularly useful notation for every large and very small numbers. For example, $1,230,000,000 = 1.23 \times 10^{9}$, and $0.00000000036 = 3.6 \times 10^{-10}$.

Addition of Exponentials

Convert all numbers to the same power of 10, add the digit terms of the numbers, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Example B1

Adding Exponentials

Add 5.00×10^{-5} and 3.00×10^{-3}.

Solution

$$\begin{aligned} 3.00 \times 10^{-3} &= 300 \times 10^{-5} \\ (5.00 \times 10^{-5}) + (300 \times 10^{-5}) &= 305 \times 10^{-5} = 3.05 \times 10^{-3} \end{aligned}$$

Subtraction of Exponentials

Convert all numbers to the same power of 10, take the difference of the digit terms, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Example B2

Subtracting Exponentials

Subtract 4.0×10^{-7} from 5.0×10^{-6}.

Solution

$$4.0 \times 10^{-7} = 0.40 \times 10^{-6}$$
$$(5.0 \times 10^{-6}) - (0.40 \times 10^{-6}) = 4.6 \times 10^{-6}$$

Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

Example B3

Multiplying Exponentials

Multiply 4.2×10^{-8} by 2.0×10^{3}.

Solution

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^{3}) = (4.2 \times 2.0) \times 10^{(-8)+(+3)} = 8.4 \times 10^{-5}$$

Division of Exponentials

Divide the digit term of the numerator by the digit term of the denominator and subtract the exponents of the exponential terms.

Example B4

Dividing Exponentials

Divide 3.6×10^{5} by 6.0×10^{-4}.

Solution

$$\frac{3.6 \times 10^{-5}}{6.0 \times 10^{-4}} = \left(\frac{3.6}{6.0}\right) \times 10^{(-5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2}$$

Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

Example B5

Squaring Exponentials

Square the number 4.0×10^{-6}.

Solution

$$(4.0 \times 10^{-6})^2 = 4 \times 4 \times 10^{2 \times (-6)} = 16 \times 10^{-12} = 1.6 \times 10^{-11}$$

Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

Example B6

Cubing Exponentials

Cube the number 2×10^{4}.

Solution

$$(2 \times 10^4)^3 = 2 \times 2 \times 2 \times 10^{3 \times 4} = 8 \times 10^{12}$$

Taking Square Roots of Exponentials

If necessary, decrease or increase the exponential term so that the power of 10 is evenly divisible by 2. Extract the square root of the digit term and divide the exponential term by 2.

Example B7

Finding the Square Root of Exponentials

Find the square root of 1.6×10^{-7}.

Solution

$$1.6 \times 10^{-7} = 16 \times 10^{-8}$$

$$\sqrt{16 \times 10^{-8}} = \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times 10^{-\frac{8}{2}} = 4.0 \times 10^{-4}$$

Significant Figures

A beekeeper reports that he has 525,341 bees. The last three figures of the number are obviously inaccurate, for during the time the keeper was counting the bees, some of them died and others hatched; this makes it quite difficult to determine the exact number of bees. It would have been more reasonable if the beekeeper had reported the number 525,000. In other words, the last three figures are not significant, except to set the position of the decimal point. Their exact values have no useful meaning in this situation. When reporting quantities, use only as many significant figures as the accuracy of the measurement warrants.

The importance of significant figures lies in their application to fundamental computation. In addition and subtraction, the sum or difference should contain as many digits to the right of the decimal as that in the least certain of the numbers used in the computation (indicated by underscoring in the following example).

Example B8

Addition and Subtraction with Significant Figures

Add 4.383 g and 0.0023 g.

Solution

$$\begin{array}{l} 4.38\underline{3}\text{ g} \\ \underline{0.002\underline{3}\text{ g}} \\ 4.38\underline{5}\text{ g} \end{array}$$

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

Example B9

Multiplication and Division with Significant Figures

Multiply 0.6238 by 6.6.

Solution

$$0.623\underline{8} \times 6.\underline{6} = 4.\underline{1}$$

When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 (“round up”). Do not change the retained digit if the digits that follow are less than 5 (“round down”). If the retained digit is followed by 5, round up if the retained digit is odd, or round down if it is even (after rounding, the retained digit will thus always be even).

The Use of Logarithms and Exponential Numbers

The common logarithm of a number (log) is the power to which 10 must be raised to equal that number. For example, the common logarithm of 100 is 2, because 10 must be raised to the second power to equal 100. Additional examples follow.

Logarithms and Exponential Numbers

Number	Number Expressed Exponentially	Common Logarithm
1000	10^3	3
10	10^1	1
1	10^0	0
0.1	10^{-1}	−1
0.001	10^{-3}	−3

Table B1

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,

$$60 = 10^{1.7782}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is −1.4069, or

$$0.03918 \;=\; 10^{-1.4069} \;=\; \frac{1}{10^{1.4069}}$$

To obtain the common logarithm of a number, use the *log* button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate 10^x (where x is the logarithm of the number).

The natural logarithm of a number (ln) is the power to which e must be raised to equal the number; e is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,

$$10 = e^{2.303} = 2.7182818^{2.303}$$

To obtain the natural logarithm of a number, use the *ln* button on your calculator. To calculate a number from its natural logarithm, enter the natural logarithm and take the inverse ln of the natural logarithm, or calculate e^x (where x is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

1. The logarithm of a product of two numbers is the sum of the logarithms of the two numbers.

$$\log xy = \log x + \log y, \text{ and } \ln xy = \ln x + \ln y$$

2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers.

$$\log \frac{x}{y} = \log x - \log y, \text{ and } \ln \frac{x}{y} = \ln x - \ln y$$

3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.

$$\log x^n = n\log x \text{ and } \ln x^n = n\ln x$$

The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.

$$ax^2 + bx + c = 0$$

The solution or roots for any quadratic equation can be calculated using the following formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Example B10

Solving Quadratic Equations

Solve the quadratic equation $3x^2 + 13x - 10 = 0$.

Solution

Substituting the values $a = 3$, $b = 13$, $c = -10$ in the formula, we obtain

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3}$$

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6}$$

The two roots are therefore

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \text{ and } x = \frac{-13 - 17}{6} = -5$$

Quadratic equations constructed on physical data always have real roots, and of these real roots, often only those having positive values are of any significance.

Two-Dimensional (*x*-*y*) Graphing

The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled (x), and a vertical axis corresponding to the dependent variable, or the variable whose value is being observed or measured (y).

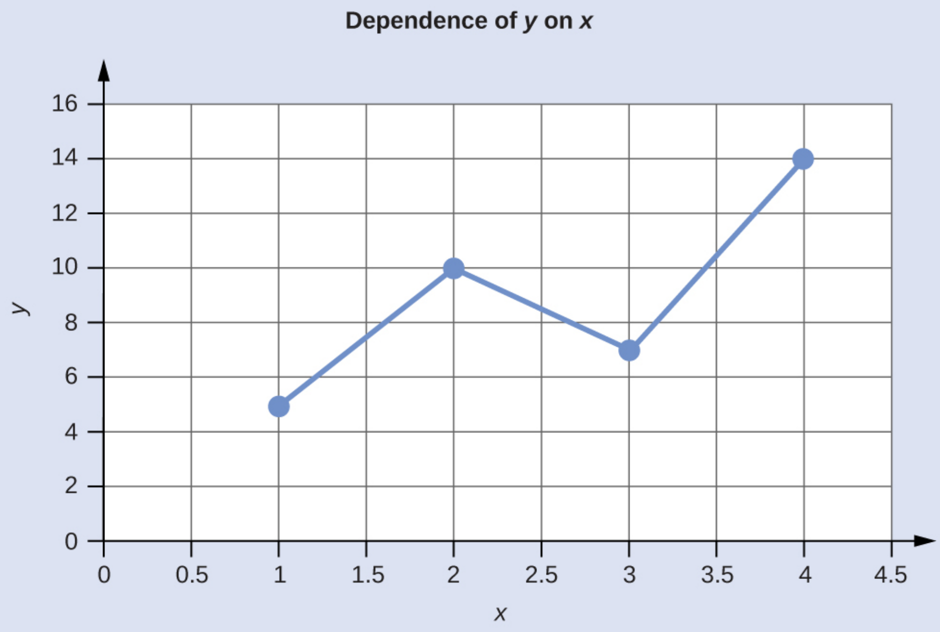
When the value of y is changing as a function of x (that is, different values of x correspond to different values of y), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for (x,y) data pairs.

Example B11

Graphing the Dependence of *y* on *x*

x	*y*
1	5
2	10
3	7
4	14

This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of y on x.



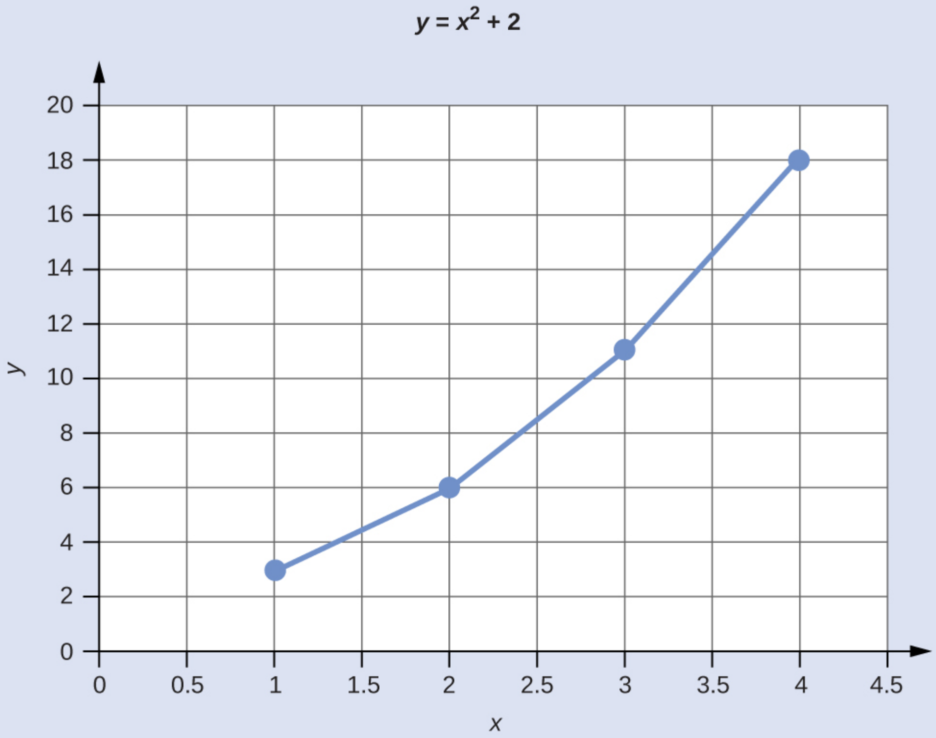
If the function that describes the dependence of *y* on *x* is known, it may be used to compute x,y data pairs that may subsequently be plotted.

Example B12

Plotting Data Pairs

If we know that $y = x^2 + 2$, we can produce a table of a few (x,y) values and then plot the line based on the data shown here.

x	$y = x^2 + 2$
1	3
2	6
3	11
4	18


$y = x^2 + 2$
y
x
20
18
16
14
12
10
8
6
4
2
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5

Appendix C

Units And Conversion Factors

Units of Length

meter (m)	= 39.37 inches (in.) = 1.094 yards (yd)
centimeter (cm)	= 0.01 m (exact, definition)
millimeter (mm)	= 0.001 m (exact, definition)
kilometer (km)	= 1000 m (exact, definition)
angstrom (Å)	= 10^{-8} cm (exact, definition) = 10^{-10} m (exact, definition)
yard (yd)	= 0.9144 m
inch (in.)	= 2.54 cm (exact, definition)
mile (US)	= 1.60934 km

Table C1

Units of Volume

liter (L)	= 0.001 m^3 (exact, definition) = 1000 cm^3 (exact, definition) = 1.057 (US) quarts
milliliter (mL)	= 0.001 L (exact, definition) = 1 cm^3 (exact, definition)
microliter (μL)	= 10^{-6} L (exact, definition) = 10^{-3} cm^3 (exact, definition)
liquid quart (US)	= 32 (US) liquid ounces (exact, definition) = 0.25 (US) gallon (exact, definition) = 0.9463 L
dry quart	= 1.1012 L
cubic foot (US)	= 28.316 L

Table C2

Units of Mass

gram (g)	= 0.001 kg (exact, definition)
milligram (mg)	= 0.001 g (exact, definition)
kilogram (kg)	= 1000 g (exact, definition) = 2.205 lb

Table C3

Units of Mass

ton (metric)	=1000 kg (exact, definition) = 2204.62 lb
ounce (oz)	= 28.35 g
pound (lb)	= 0.4535924 kg
ton (short)	=2000 lb (exact, definition) = 907.185 kg
ton (long)	= 2240 lb (exact, definition) = 1.016 metric ton

Table C3

Units of Energy

4.184 joule (J)	= 1 thermochemical calorie (cal)
1 thermochemical calorie (cal)	= 4.184×10^{7} erg
erg	= 10^{-7} J (exact, definition)
electron-volt (eV)	= 1.60218×10^{-19} J = 23.061 kcal mol^{-1}
liter·atmosphere	= 24.217 cal = 101.325 J (exact, definition)
nutritional calorie (Cal)	= 1000 cal (exact, definition) = 4184 J
British thermal unit (BTU)	= 1054.804 J[1]

Table C4

Units of Pressure

torr	= 1 mm Hg (exact, definition)
pascal (Pa)	= N m^{-2} (exact, definition) = kg m^{-1} s^{-2} (exact, definition)
atmosphere (atm)	= 760 mm Hg (exact, definition) = 760 torr (exact, definition) = 101,325 N m^{-2} (exact, definition) = 101,325 Pa (exact, definition)
bar	= 10^{5} Pa (exact, definition) = 10^{5} kg m^{-1} s^{-2} (exact, definition)

Table C5

---

[1] BTU is the amount of energy needed to heat one pound of water by one degree Fahrenheit. Therefore, the exact relationship of BTU to joules and other energy units depends on the temperature at which BTU is measured. 59 °F (15 °C) is the most widely used reference temperature for BTU definition in the United States. At this temperature, the conversion factor is the one provided in this table.

Appendix D

Fundamental Physical Constants

Fundamental Physical Constants

Name and Symbol	Value
atomic mass unit (amu)	$1.6605402 \times 10^{-27}$ kg
Avogadro's number	6.0221367×10^{23} mol^{-1}
Boltzmann's constant (k)	1.380658×10^{-23} J K^{-1}
charge-to-mass ratio for electron (e/m_e)	$1.75881962 \times 10^{11}$ C kg^{-1}
electron charge (e)	$1.60217733 \times 10^{-19}$ C
electron rest mass (m_e)	$9.1093897 \times 10^{-31}$ kg
Faraday's constant (F)	9.6485309×10^{4} C mol^{-1}
gas constant (R)	8.205784×10^{-2} L atm mol^{-1} K^{-1} = 8.314510 J mol^{-1} K^{-1}
molar volume of an ideal gas, 1 atm, 0 °C	22.41409 L mol^{-1}
molar volume of an ideal gas, 1 bar, 0 °C	22.71108 L mol^{-1}
neutron rest mass (m_n)	$1.6749274 \times 10^{-27}$ kg
Planck's constant (h)	$6.6260755 \times 10^{-34}$ J s
proton rest mass (m_p)	$1.6726231 \times 10^{-27}$ kg
Rydberg constant (R)	$1.0973731534 \times 10^{7}$ m^{-1} = $2.1798736 \times 10^{-18}$ J
speed of light (in vacuum) (c)	2.99792458×10^{8} m s^{-1}

Table D1

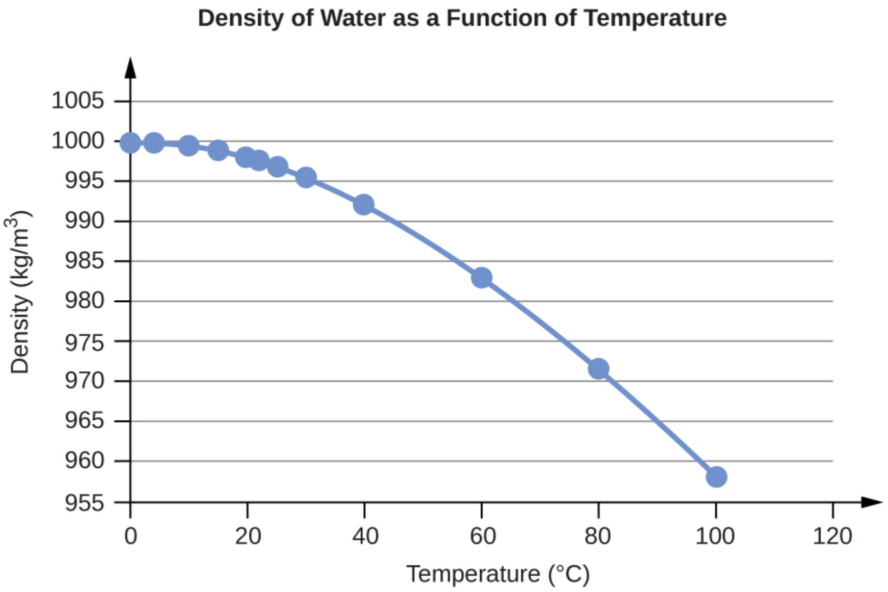
Appendix E

Water Properties

Water Density (g/mL) at Different Temperatures (°C)

Temperature	Density (g/mL)
0	0.9998395
4	0.9999720 (density maximum)
10	0.9997026
15	0.9991026
20	0.9982071
22	0.9977735
25	0.9970479
30	0.9956502
40	0.9922
60	0.9832
80	0.9718
100	0.9584

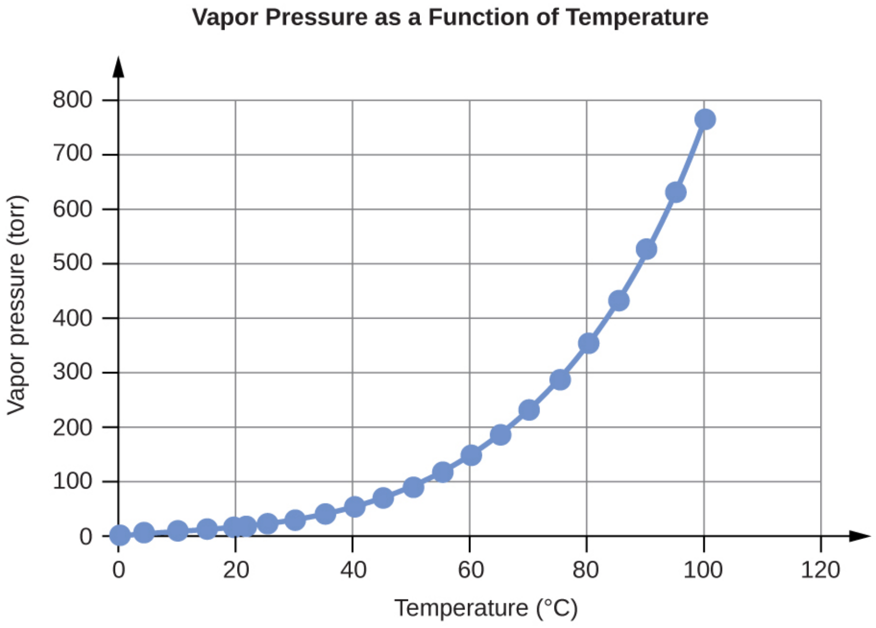
Table E1



Water Vapor Pressure at Different Temperatures (°C)

Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
0	4.6	613.2812
4	6.1	813.2642
10	9.2	1226.562
15	12.8	1706.522
20	17.5	2333.135
22	19.8	2639.776
25	23.8	3173.064
30	31.8	4239.64
35	42.2	5626.188
40	55.3	7372.707
45	71.9	9585.852
50	92.5	12332.29
55	118.0	15732
60	149.4	19918.31
65	187.5	24997.88
70	233.7	31157.35
75	289.1	38543.39
80	355.1	47342.64
85	433.6	57808.42
90	525.8	70100.71
95	633.9	84512.82
100	760.0	101324.7

Table E2



Water K_w and pK_w at Different Temperatures (°C)

Temperature	K_w 10^{-14}	pK_w[1]
0	0.112	14.95
5	0.182	14.74
10	0.288	14.54
15	0.465	14.33
20	0.671	14.17
25	0.991	14.00
30	1.432	13.84
35	2.042	13.69
40	2.851	13.55
45	3.917	13.41
50	5.297	13.28
55	7.080	13.15
60	9.311	13.03
75	19.95	12.70
100	56.23	12.25

Table E3

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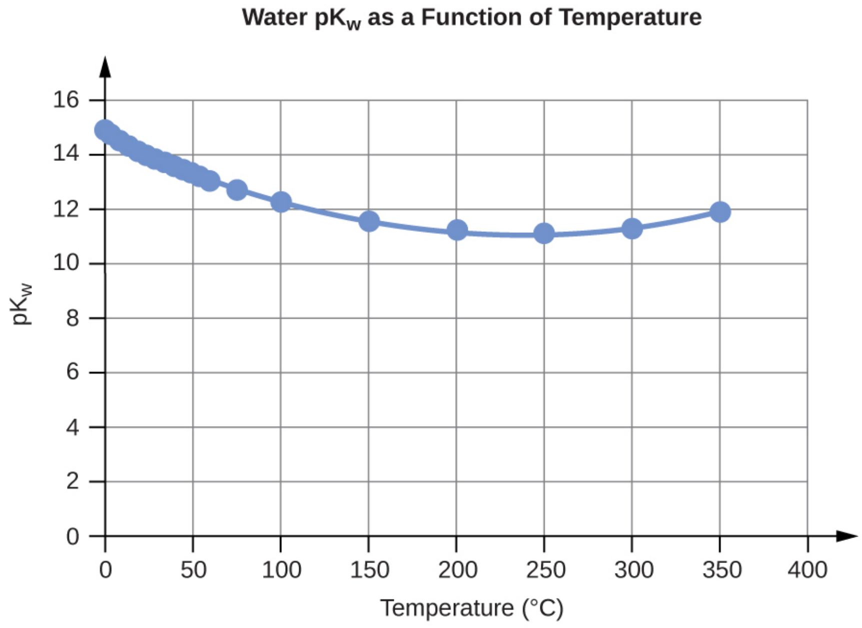
[1] $pK_w = -\log_{10}(K_w)$



Specific Heat Capacity for Water

C°($H_2O(l)$) = 4.184 $J{\cdot}g^{-1}{\cdot}°C^{-1}$
C°($H_2O(s)$) = 1.864 $J{\cdot}K^{-1}{\cdot}g^{-1}$
C°($H_2O(g)$) = 2.093 $J{\cdot}K^{-1}{\cdot}g^{-1}$

Table E4

Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions

	Temperature (K)	Δ*H* (kJ/mol)
melting	273.15	6.088
boiling	373.15	40.656 (44.016 at 298 K)

Table E5

Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants

K_f = 1.86°C·kg·mol^{-1} (cryoscopic constant)
K_b = 0.51°C·kg·mol^{-1} (ebullioscopic constant)

Table E6

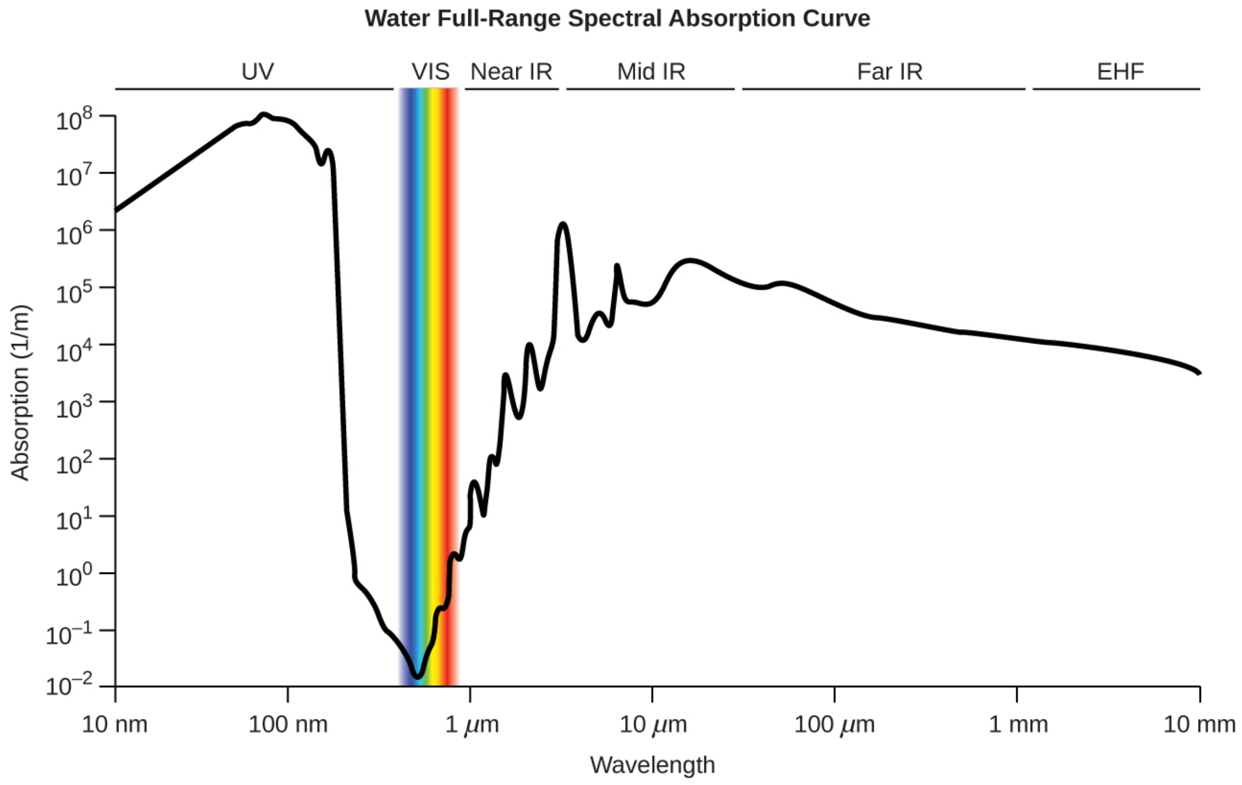


Figure E1 The plot shows the extent of light absorption versus wavelength for water. Absorption is reported in reciprocal meters and corresponds to the inverse of the distance light may travel through water before its intensity is diminished by 1/*e* (~37%).

Appendix F

Composition Of Commercial Acids And Bases

Composition of Commercial Acids and Bases

Acid or Base[1]	Density (g/mL)[2]	Percentage by Mass	Molarity
acetic acid, glacial	1.05	99.5%	17.4
aqueous ammonia[3]	0.90	28%	14.8
hydrochloric acid	1.18	36%	11.6
nitric acid	1.42	71%	16.0
perchloric acid	1.67	70%	11.65
phosphoric acid	1.70	85%	14.7
sodium hydroxide	1.53	50%	19.1
sulfuric acid	1.84	96%	18.0

Table F1

---

[1] Acids and bases are commercially available as aqueous solutions. This table lists properties (densities and concentrations) of common acid and base solutions. Nominal values are provided in cases where the manufacturer cites a range of concentrations and densities.

[2] This column contains specific gravity data. In the case of this table, specific gravity is the ratio of density of a substance to the density of pure water at the same conditions. Specific gravity is often cited on commercial labels.

[3] This solution is sometimes called “ammonium hydroxide,” although this term is not chemically accurate.

Appendix G

Standard Thermodynamic Properties For Selected Substances

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH°_f (kJ mol^{-})	ΔG°_f (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
aluminum			
$Al(s)$	0	0	28.3
$Al(g)$	324.4	285.7	164.54
$Al^{3+}(aq)$	–531	–485	–321.7
$Al_2O_3(s)$	–1676	–1582	50.92
$AlF_3(s)$	–1510.4	–1425	66.5
$AlCl_3(s)$	–704.2	–628.8	110.67
$AlCl_3{\cdot}6H_2O(s)$	–2691.57	–2269.40	376.56
$Al_2S_3(s)$	–724.0	–492.4	116.9
$Al_2(SO_4)_3(s)$	–3445.06	–3506.61	239.32
antimony			
$Sb(s)$	0	0	45.69
$Sb(g)$	262.34	222.17	180.16
$Sb_4O_6(s)$	–1440.55	–1268.17	220.92
$SbCl_3(g)$	–313.8	–301.2	337.80
$SbCl_5(g)$	–394.34	–334.29	401.94
$Sb_2S_3(s)$	–174.89	–173.64	182.00
$SbCl_3(s)$	–382.17	–323.72	184.10
$SbOCl(s)$	–374.0	—	—
arsenic			
$As(s)$	0	0	35.1
$As(g)$	302.5	261.0	174.21
$As_4(g)$	143.9	92.4	314
$As_4O_6(s)$	–1313.94	–1152.52	214.22
$As_2O_5(s)$	–924.87	–782.41	105.44

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$AsCl_3(g)$	–261.50	–248.95	327.06
$As_2S_3(s)$	–169.03	–168.62	163.59
$AsH_3(g)$	66.44	68.93	222.78
$H_3AsO_4(s)$	–906.3	—	—
barium			
$Ba(s)$	0	0	62.5
$Ba(g)$	180	146	170.24
$Ba^{2+}(aq)$	–537.6	–560.8	9.6
$BaO(s)$	–548.0	–520.3	72.1
$BaCl_2(s)$	–855.0	–806.7	123.7
$BaSO_4(s)$	–1473.2	–1362.3	132.2
beryllium			
$Be(s)$	0	0	9.50
$Be(g)$	324.3	286.6	136.27
$BeO(s)$	–609.4	–580.1	13.8
bismuth			
$Bi(s)$	0	0	56.74
$Bi(g)$	207.1	168.2	187.00
$Bi_2O_3(s)$	–573.88	–493.7	151.5
$BiCl_3(s)$	–379.07	–315.06	176.98
$Bi_2S_3(s)$	–143.1	–140.6	200.4
boron			
$B(s)$	0	0	5.86
$B(g)$	565.0	521.0	153.4
$B_2O_3(s)$	–1273.5	–1194.3	53.97
$B_2H_6(g)$	36.4	87.6	232.1
$H_3BO_3(s)$	–1094.33	–968.92	88.83
$BF_3(g)$	–1136.0	–1119.4	254.4
$BCl_3(g)$	–403.8	–388.7	290.1
$B_3N_3H_6(l)$	–540.99	–392.79	199.58
$HBO_2(s)$	–794.25	–723.41	37.66

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
bromine			
$Br_2(l)$	0	0	152.23
$Br_2(g)$	30.91	3.142	245.5
$Br(g)$	111.88	82.429	175.0
$Br^{-}(aq)$	–120.9	–102.82	80.71
$BrF_3(g)$	–255.60	–229.45	292.42
$HBr(g)$	–36.3	–53.43	198.7
cadmium			
$Cd(s)$	0	0	51.76
$Cd(g)$	112.01	77.41	167.75
$Cd^{2+}(aq)$	–75.90	–77.61	–73.2
$CdO(s)$	–258.2	–228.4	54.8
$CdCl_2(s)$	–391.5	–343.9	115.3
$CdSO_4(s)$	–933.3	–822.7	123.0
$CdS(s)$	–161.9	–156.5	64.9
calcium			
$Ca(s)$	0	0	41.6
$Ca(g)$	178.2	144.3	154.88
$Ca^{2+}(aq)$	–542.96	–553.04	–55.2
$CaO(s)$	–634.9	–603.3	38.1
$Ca(OH)_2(s)$	–985.2	–897.5	83.4
$CaSO_4(s)$	–1434.5	–1322.0	106.5
$CaSO_4{\cdot}2H_2O(s)$	–2022.63	–1797.45	194.14
$CaCO_3(s)$ (calcite)	–1220.0	–1081.4	110.0
$CaSO_3{\cdot}H_2O(s)$	–1752.68	–1555.19	184.10
carbon			
$C(s)$ (graphite)	0	0	5.740
$C(s)$ (diamond)	1.89	2.90	2.38
$C(g)$	716.681	671.2	158.1
$CO(g)$	–110.52	–137.15	197.7
$CO_2(g)$	–393.51	–394.36	213.8

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$CO_3{}^{2-}(aq)$	–677.1	–527.8	–56.9
$CH_4(g)$	–74.6	–50.5	186.3
$CH_3OH(l)$	–239.2	–166.6	126.8
$CH_3OH(g)$	–201.0	–162.3	239.9
$CCl_4(l)$	–128.2	–62.5	214.4
$CCl_4(g)$	–95.7	–58.2	309.7
$CHCl_3(l)$	–134.1	–73.7	201.7
$CHCl_3(g)$	–103.14	–70.34	295.71
$CS_2(l)$	89.70	65.27	151.34
$CS_2(g)$	116.9	66.8	238.0
$C_2H_2(g)$	227.4	209.2	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	–84.0	–32.0	229.2
$CH_3CO_2H(l)$	–484.3	–389.9	159.8
$CH_3CO_2H(g)$	–434.84	–376.69	282.50
$C_2H_5OH(l)$	–277.6	–174.8	160.7
$C_2H_5OH(g)$	–234.8	–167.9	281.6
$HCO_3{}^{-}(aq)$	–691.11	–587.06	95
$C_3H_8(g)$	–103.8	–23.4	270.3
$C_6H_6(g)$	82.927	129.66	269.2
$C_6H_6(l)$	49.1	124.50	173.4
$CH_2Cl_2(l)$	–124.2	–63.2	177.8
$CH_2Cl_2(g)$	–95.4	–65.90	270.2
$CH_3Cl(g)$	–81.9	–60.2	234.6
$C_2H_5Cl(l)$	–136.52	–59.31	190.79
$C_2H_5Cl(g)$	–112.17	–60.39	276.00
$C_2N_2(g)$	308.98	297.36	241.90
$HCN(l)$	108.9	125.0	112.8
$HCN(g)$	135.5	124.7	201.8
cesium			
$Cs^+(aq)$	–248	–282.0	133

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
chlorine			
$Cl_2(g)$	0	0	223.1
$Cl(g)$	121.3	105.70	165.2
$Cl^-(aq)$	–167.2	–131.2	56.5
$ClF(g)$	–54.48	–55.94	217.78
$ClF_3(g)$	–158.99	–118.83	281.50
$Cl_2O(g)$	80.3	97.9	266.2
$Cl_2O_7(l)$	238.1	—	—
$Cl_2O_7(g)$	272.0	—	—
$HCl(g)$	–92.307	–95.299	186.9
$HClO_4(l)$	–40.58	—	—
chromium			
$Cr(s)$	0	0	23.77
$Cr(g)$	396.6	351.8	174.50
$CrO_4{}^{2-}(aq)$	–881.2	–727.8	50.21
$Cr_2O_7{}^{2-}(aq)$	–1490.3	–1301.1	261.9
$Cr_2O_3(s)$	–1139.7	–1058.1	81.2
$CrO_3(s)$	–589.5	—	—
$(NH_4)_2Cr_2O_7(s)$	–1806.7	—	—
cobalt			
$Co(s)$	0	0	30.0
$Co^{2+}(aq)$	–67.4	–51.5	–155
$Co^{3+}(aq)$	92	134	–305.0
$CoO(s)$	–237.9	–214.2	52.97
$Co_3O_4(s)$	–910.02	–794.98	114.22
$Co(NO_3)_2(s)$	–420.5	—	—
copper			
$Cu(s)$	0	0	33.15
$Cu(g)$	338.32	298.58	166.38
$Cu^+(aq)$	51.9	50.2	–26
$Cu^{2+}(aq)$	64.77	65.49	–99.6

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH°_f (kJ mol^{-})	ΔG°_f (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$\text{CuO}(s)$	–157.3	–129.7	42.63
$\text{Cu}_2\text{O}(s)$	–168.6	–146.0	93.14
$\text{CuS}(s)$	–53.1	–53.6	66.5
$\text{Cu}_2\text{S}(s)$	–79.5	–86.2	120.9
$\text{CuSO}_4(s)$	–771.36	–662.2	109.2
$\text{Cu(NO}_3)_2(s)$	–302.9	—	—
fluorine			
$\text{F}_2(g)$	0	0	202.8
$\text{F}(g)$	79.4	62.3	158.8
$\text{F}^-(aq)$	–332.6	–278.8	–13.8
$\text{F}_2\text{O}(g)$	24.7	41.9	247.43
$\text{HF}(g)$	–273.3	–275.4	173.8
hydrogen			
$\text{H}_2(g)$	0	0	130.7
$\text{H}(g)$	217.97	203.26	114.7
$\text{H}^+(aq)$	0	0	0
$\text{OH}^-(aq)$	–230.0	–157.2	–10.75
$\text{H}_3\text{O}^+(aq)$	–285.8		69.91
$\text{H}_2\text{O}(l)$	–285.83	–237.1	70.0
$\text{H}_2\text{O}(g)$	–241.82	–228.59	188.8
$\text{H}_2\text{O}_2(l)$	–187.78	–120.35	109.6
$\text{H}_2\text{O}_2(g)$	–136.3	–105.6	232.7
$\text{HF}(g)$	–273.3	–275.4	173.8
$\text{HCl}(g)$	–92.307	–95.299	186.9
$\text{HBr}(g)$	–36.3	–53.43	198.7
$\text{HI}(g)$	26.48	1.70	206.59
$\text{H}_2\text{S}(g)$	–20.6	–33.4	205.8
$\text{H}_2\text{Se}(g)$	29.7	15.9	219.0
iodine			
$\text{I}_2(s)$	0	0	116.14
$\text{I}_2(g)$	62.438	19.3	260.7

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
I(*g*)	106.84	70.2	180.8
I^-(*aq*)	–55.19	–51.57	11.13
IF(*g*)	95.65	–118.49	236.06
ICl(*g*)	17.78	–5.44	247.44
IBr(*g*)	40.84	3.72	258.66
IF_7(*g*)	–943.91	–818.39	346.44
HI(*g*)	26.48	1.70	206.59
iron			
Fe(*s*)	0	0	27.3
Fe(*g*)	416.3	370.7	180.5
Fe^{2+}(*aq*)	–89.1	–78.90	–137.7
Fe^{3+}(*aq*)	–48.5	–4.7	–315.9
Fe_2O_3(*s*)	–824.2	–742.2	87.40
Fe_3O_4(*s*)	–1118.4	–1015.4	146.4
$Fe(CO)_5$(*l*)	–774.04	–705.42	338.07
$Fe(CO)_5$(*g*)	–733.87	–697.26	445.18
$FeCl_2$(*s*)	–341.79	–302.30	117.95
$FeCl_3$(*s*)	–399.49	–334.00	142.3
FeO(*s*)	–272.0	–255.2	60.75
$Fe(OH)_2$(*s*)	–569.0	–486.5	88.
$Fe(OH)_3$(*s*)	–823.0	–696.5	106.7
FeS(*s*)	–100.0	–100.4	60.29
Fe_3C(*s*)	25.10	20.08	104.60
lead			
Pb(*s*)	0	0	64.81
Pb(*g*)	195.2	162.	175.4
Pb^{2+}(*aq*)	–1.7	–24.43	10.5
PbO(*s*) (yellow)	–217.32	–187.89	68.70
PbO(*s*) (red)	–218.99	–188.93	66.5
$Pb(OH)_2$(*s*)	–515.9	—	—
PbS(*s*)	–100.4	–98.7	91.2

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	$\Delta H^\circ_\mathrm{f}$ (kJ mol^{-})	$\Delta G^\circ_\mathrm{f}$ (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$Pb(NO_3)_2(s)$	–451.9	—	—
$PbO_2(s)$	–277.4	–217.3	68.6
$PbCl_2(s)$	–359.4	–314.1	136.0
lithium			
$Li(s)$	0	0	29.1
$Li(g)$	159.3	126.6	138.8
$Li^+(aq)$	–278.5	–293.3	13.4
$LiH(s)$	–90.5	–68.3	20.0
$Li(OH)(s)$	–487.5	–441.5	42.8
$LiF(s)$	–616.0	–587.5	35.7
$Li_2CO_3(s)$	–1216.04	–1132.19	90.17
magnesium			
$Mg^{2+}(aq)$	–466.9	–454.8	–138.1
manganese			
$Mn(s)$	0	0	32.0
$Mn(g)$	280.7	238.5	173.7
$Mn^{2+}(aq)$	–220.8	–228.1	–73.6
$MnO(s)$	–385.2	–362.9	59.71
$MnO_2(s)$	–520.03	–465.1	53.05
$Mn_2O_3(s)$	–958.97	–881.15	110.46
$Mn_3O_4(s)$	–1378.83	–1283.23	155.64
$MnO_4{}^-(aq)$	–541.4	–447.2	191.2
$MnO_4{}^{2-}(aq)$	–653.0	–500.7	59
mercury			
$Hg(l)$	0	0	75.9
$Hg(g)$	61.4	31.8	175.0
$Hg^{2+}(aq)$		164.8	
$Hg^{2+}(aq)$	172.4	153.9	84.5
$HgO(s)$ (red)	–90.83	–58.5	70.29
$HgO(s)$ (yellow)	–90.46	–58.43	71.13
$HgCl_2(s)$	–224.3	–178.6	146.0

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$Hg_2Cl_2(s)$	–265.4	–210.7	191.6
$HgS(s)$ (red)	–58.16	–50.6	82.4
$HgS(s)$ (black)	–53.56	–47.70	88.28
$HgSO_4(s)$	–707.51	–594.13	0.00
nickel			
$Ni^{2+}(aq)$	–64.0	–46.4	–159
nitrogen			
$N_2(g)$	0	0	191.6
$N(g)$	472.704	455.5	153.3
$NO(g)$	90.25	87.6	210.8
$NO_2(g)$	33.2	51.30	240.1
$N_2O(g)$	81.6	103.7	220.0
$N_2O_3(g)$	83.72	139.41	312.17
$NO_3{}^-(aq)$	–205.0	–108.7	146.4
$N_2O_4(g)$	11.1	99.8	304.4
$N_2O_5(g)$	11.3	115.1	355.7
$NH_3(g)$	–45.9	–16.5	192.8
$NH_4{}^+(aq)$	–132.5	–79.31	113.4
$N_2H_4(l)$	50.63	149.43	121.21
$N_2H_4(g)$	95.4	159.4	238.5
$NH_4NO_3(s)$	–365.56	–183.87	151.08
$NH_4Cl(s)$	–314.43	–202.87	94.6
$NH_4Br(s)$	–270.8	–175.2	113.0
$NH_4I(s)$	–201.4	–112.5	117.0
$NH_4NO_2(s)$	–256.5	—	—
$HNO_3(l)$	–174.1	–80.7	155.6
$HNO_3(g)$	–133.9	–73.5	266.9
oxygen			
$O_2(g)$	0	0	205.2
$O(g)$	249.17	231.7	161.1
$O_3(g)$	142.7	163.2	238.9

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
phosphorus			
$P_4(s)$	0	0	164.4
$P_4(g)$	58.91	24.4	280.0
$P(g)$	314.64	278.25	163.19
$PH_3(g)$	5.4	13.5	210.2
$PCl_3(g)$	–287.0	–267.8	311.78
$PCl_5(g)$	–374.9	–305.0	364.4
$P_4O_6(s)$	–1640.1	—	—
$P_4O_{10}(s)$	–2984.0	–2697.0	228.86
$PO_4{}^{3-}(aq)$	–1277	–1019	–222
$HPO_3(s)$	–948.5	—	—
$HPO_4{}^{2-}(aq)$	–1292.1	–1089.3	–33
$H_2PO_4{}^{2-}(aq)$	–1296.3	–1130.4	90.4
$H_3PO_2(s)$	–604.6	—	—
$H_3PO_3(s)$	–964.4	—	—
$H_3PO_4(s)$	–1279.0	–1119.1	110.50
$H_3PO_4(l)$	–1266.9	–1124.3	110.5
$H_4P_2O_7(s)$	–2241.0	—	—
$POCl_3(l)$	–597.1	–520.8	222.5
$POCl_3(g)$	–558.5	–512.9	325.5
potassium			
$K(s)$	0	0	64.7
$K(g)$	89.0	60.5	160.3
$K^+(aq)$	–252.4	–283.3	102.5
$KF(s)$	–576.27	–537.75	66.57
$KCl(s)$	–436.5	–408.5	82.6
rubidium			
$Rb^+(aq)$	–246	–282.2	124
silicon			
$Si(s)$	0	0	18.8
$Si(g)$	450.0	405.5	168.0

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$SiO_2(s)$	–910.7	–856.3	41.5
$SiH_4(g)$	34.3	56.9	204.6
$H_2SiO_3(s)$	–1188.67	–1092.44	133.89
$H_4SiO_4(s)$	–1481.14	–1333.02	192.46
$SiF_4(g)$	–1615.0	–1572.8	282.8
$SiCl_4(l)$	–687.0	–619.8	239.7
$SiCl_4(g)$	–662.75	–622.58	330.62
SiC(*s, beta cubic*)	–73.22	–70.71	16.61
SiC(*s, alpha hexagonal*)	–71.55	–69.04	16.48
silver			
$Ag(s)$	0	0	42.55
$Ag(g)$	284.9	246.0	172.89
$Ag^+(aq)$	105.6	77.11	72.68
$Ag_2O(s)$	–31.05	–11.20	121.3
$AgCl(s)$	–127.0	–109.8	96.3
$Ag_2S(s)$	–32.6	–40.7	144.0
sodium			
$Na(s)$	0	0	51.3
$Na(g)$	107.5	77.0	153.7
$Na^+(aq)$	–240.1	–261.9	59
$Na_2O(s)$	–414.2	–375.5	75.1
$NaCl(s)$	–411.2	–384.1	72.1
strontium			
$Sr^{2+}(aq)$	–545.8	–557.3	–32.6
sulfur			
$S_8(s)$ (rhombic)	0	0	256.8
$S(g)$	278.81	238.25	167.82
$S^{2-}(aq)$	41.8	83.7	22
$SO_2(g)$	–296.83	–300.1	248.2
$SO_3(g)$	–395.72	–371.06	256.76
$SO_4{}^{2-}(aq)$	–909.3	–744.5	20.1

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol⁻)	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$S_2O_3{}^{2-}(aq)$	–648.5	–522.5	67
$H_2S(g)$	–20.6	–33.4	205.8
$HS^-(aq)$	–17.7	12.6	61.1
$H_2SO_4(l)$	–813.989	690.00	156.90
$HSO_4{}^{2-}(aq)$	–885.75	–752.87	126.9
$H_2S_2O_7(s)$	–1273.6	—	—
$SF_4(g)$	–728.43	–684.84	291.12
$SF_6(g)$	–1220.5	–1116.5	291.5
$SCl_2(l)$	–50	—	—
$SCl_2(g)$	–19.7	—	—
$S_2Cl_2(l)$	–59.4	—	—
$S_2Cl_2(g)$	–19.50	–29.25	319.45
$SOCl_2(g)$	–212.55	–198.32	309.66
$SOCl_2(l)$	–245.6	—	—
$SO_2Cl_2(l)$	–394.1	—	—
$SO_2Cl_2(g)$	–354.80	–310.45	311.83
tin			
$Sn(s)$	0	0	51.2
$Sn(g)$	301.2	266.2	168.5
$SnO(s)$	–285.8	–256.9	56.5
$SnO_2(s)$	–577.6	–515.8	49.0
$SnCl_4(l)$	–511.3	–440.1	258.6
$SnCl_4(g)$	–471.5	–432.2	365.8
titanium			
$Ti(s)$	0	0	30.7
$Ti(g)$	473.0	428.4	180.3
$TiO_2(s)$	–944.0	–888.8	50.6
$TiCl_4(l)$	–804.2	–737.2	252.4
$TiCl_4(g)$	–763.2	–726.3	353.2
tungsten			
$W(s)$	0	0	32.6

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	$\Delta H^\circ_\mathrm{f}$ (kJ mol^{-})	$\Delta G^\circ_\mathrm{f}$ (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$W(g)$	849.4	807.1	174.0
$WO_3(s)$	–842.9	–764.0	75.9
zinc			
$Zn(s)$	0	0	41.6
$Zn(g)$	130.73	95.14	160.98
$Zn^{2+}(aq)$	–153.9	–147.1	–112.1
$ZnO(s)$	–350.5	–320.5	43.7
$ZnCl_2(s)$	–415.1	–369.43	111.5
$ZnS(s)$	–206.0	–201.3	57.7
$ZnSO_4(s)$	–982.8	–871.5	110.5
$ZnCO_3(s)$	–812.78	–731.57	82.42
complexes			
$[Co(NH_3)_4(NO_2)_2]NO_3$, *cis*	–898.7	—	—
$[Co(NH_3)_4(NO_2)_2]NO_3$, *trans*	–896.2	—	—
$NH_4[Co(NH_3)_2(NO_2)_4]$	–837.6	—	—
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$	–2733.0	—	—
$[Co(NH_3)_4Cl_2]Cl$, *cis*	–874.9	—	—
$[Co(NH_3)_4Cl_2]Cl$, *trans*	–877.4	—	—
$[Co(en)_2(NO_2)_2]NO_3$, *cis*	–689.5	—	—
$[Co(en)_2Cl_2]Cl$, *cis*	–681.2	—	—
$[Co(en)_2Cl_2]Cl$, *trans*	–677.4	—	—
$[Co(en)_3](ClO_4)_3$	–762.7	—	—
$[Co(en)_3]Br_2$	–595.8	—	—
$[Co(en)_3]I_2$	–475.3	—	—
$[Co(en)_3]I_3$	–519.2	—	—
$[Co(NH_3)_6](ClO_4)_3$	–1034.7	–221.1	615
$[Co(NH_3)_5NO_2](NO_3)_2$	–1088.7	–412.9	331
$[Co(NH_3)_6](NO_3)_3$	–1282.0	–524.5	448
$[Co(NH_3)_5Cl]Cl_2$	–1017.1	–582.5	366.1
$[Pt(NH_3)_4]Cl_2$	–725.5	—	—
$[Ni(NH_3)_6]Cl_2$	–994.1	—	—

Table G1

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$[Ni(NH_3)_6]Br_2$	–923.8	—	—
$[Ni(NH_3)_6]I_2$	–808.3	—	—

Table G1

Appendix H

Ionization Constants Of Weak Acids

Ionization Constants of Weak Acids

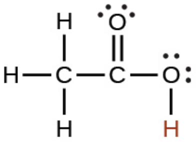
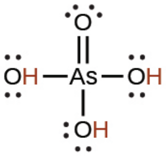
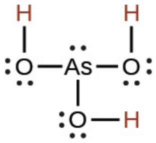
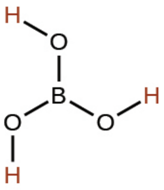
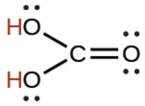
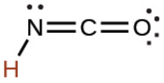
Acid	Formula	K_a at 25 °C	Lewis Structure
acetic	CH_3CO_2H	1.8×10^{-5}	
arsenic	H_3AsO_4	5.5×10^{-3}	
	$H_2AsO_4^-$	1.7×10^{-7}	
	$HAsO_4^{2-}$	3.0×10^{-12}	
arsenous	H_3AsO_3	5.1×10^{-10}	
boric	H_3BO_3	5.4×10^{-10}	
carbonic	H_2CO_3	4.3×10^{-7}	
	HCO_3^-	4.7×10^{-11}	
cyanic	$HCNO$	2×10^{-4}	

Table H1

Ionization Constants of Weak Acids

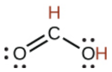
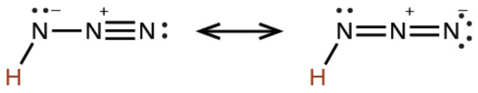
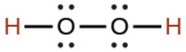
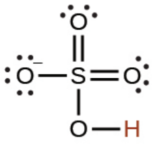
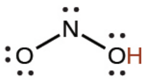
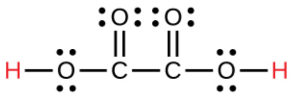
Acid	Formula	K_a at 25 °C	Lewis Structure
formic	HCO_2H	1.8×10^{-4}	
hydrazoic	HN_3	2.5×10^{-5}	
hydrocyanic	HCN	4.9×10^{-10}	
hydrofluoric	HF	6.4×10^{-4}	
hydrogen peroxide	H_2O_2	2.4×10^{-12}	
hydrogen selenide	H_2Se	1.29×10^{-4}	
	HSe^-	1×10^{-12}	
hydrogen sulfate ion	$HSO_4^{\ -}$	1.2×10^{-2}	
hydrogen sulfide	H_2S	8.9×10^{-8}	
	HS^-	1.0×10^{-19}	
hydrogen telluride	H_2Te	2.3×10^{-3}	
	HTe^-	1.6×10^{-11}	
hypobromous	$HBrO$	2.8×10^{-9}	
hypochlorous	$HClO$	2.9×10^{-8}	
nitrous	HNO_2	4.6×10^{-4}	
oxalic	$H_2C_2O_4$	6.0×10^{-2}	
	$HC_2O_4^{\ -}$	6.1×10^{-5}	

Table H1

Ionization Constants of Weak Acids

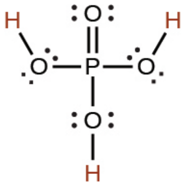
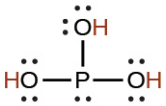
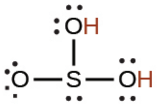
Acid	Formula	K_a at 25 °C	Lewis Structure
phosphoric	H_3PO_4	7.5×10^{-3}	
	$H_2PO_4^-$	6.2×10^{-8}	
	HPO_4^{2-}	4.2×10^{-13}	
phosphorous	H_3PO_3	5×10^{-2}	
	$H_2PO_3^-$	2.0×10^{-7}	
sulfurous	H_2SO_3	1.6×10^{-2}	
	HSO_3^-	6.4×10^{-8}	

Table H1

Appendix I

Ionization Constants Of Weak Bases

Ionization Constants of Weak Bases

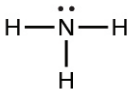
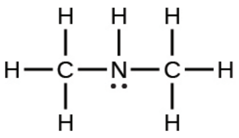
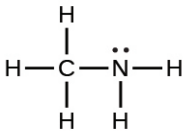
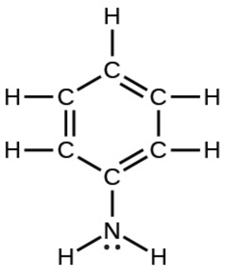
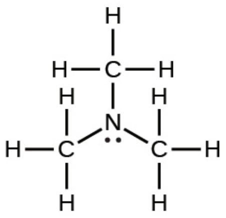
Base	Lewis Structure	K_b at 25 °C
ammonia		1.8×10^{-5}
dimethylamine		5.9×10^{-4}
methylamine		4.4×10^{-4}
phenylamine (aniline)		4.3×10^{-10}
trimethylamine		6.3×10^{-5}

Table I1

Appendix J

Solubility Products

Solubility Products

Substance	K_{sp} at 25 °C
aluminum	
$Al(OH)_3$	2×10^{-32}
barium	
$BaCO_3$	1.6×10^{-9}
$BaC_2O_4\cdot 2H_2O$	1.1×10^{-7}
$BaSO_4$	2.3×10^{-8}
$BaCrO_4$	8.5×10^{-11}
BaF_2	2.4×10^{-5}
$Ba(OH)_2\cdot 8H_2O$	5.0×10^{-3}
$Ba_3(PO_4)_2$	6×10^{-39}
$Ba_3(AsO_4)_2$	1.1×10^{-13}
bismuth	
$BiO(OH)$	4×10^{-10}
$BiOCl$	1.8×10^{-31}
Bi_2S_3	1×10^{-97}
cadmium	
$Cd(OH)_2$	5.9×10^{-15}
CdS	1.0×10^{-28}
$CdCO_3$	5.2×10^{-12}
calcium	
$Ca(OH)_2$	1.3×10^{-6}
$CaCO_3$	8.7×10^{-9}
$CaSO4\cdot 2H_2O$	6.1×10^{-5}
$CaC_2O_4\cdot H_2O$	1.96×10^{-8}
$Ca_3(PO_4)_2$	1.3×10^{-32}
$CaHPO_4$	7×10^{-7}
CaF_2	4.0×10^{-11}
chromium	

Table J1

Solubility Products

Substance	K_{sp} at 25 °C
$Cr(OH)_3$	6.7×10^{-31}
cobalt	
$Co(OH)_2$	2.5×10^{-16}
$CoS(\alpha)$	5×10^{-22}
$CoS(\beta)$	3×10^{-26}
$CoCO_3$	1.4×10^{-13}
$Co(OH)_3$	2.5×10^{-43}
copper	
$CuCl$	1.2×10^{-6}
$CuBr$	6.27×10^{-9}
CuI	1.27×10^{-12}
$CuSCN$	1.6×10^{-11}
Cu_2S	2.5×10^{-48}
$Cu(OH)_2$	2.2×10^{-20}
CuS	8.5×10^{-45}
$CuCO_3$	2.5×10^{-10}
iron	
$Fe(OH)_2$	1.8×10^{-15}
$FeCO_3$	2.1×10^{-11}
FeS	3.7×10^{-19}
$Fe(OH)_3$	4×10^{-38}
lead	
$Pb(OH)_2$	1.2×10^{-15}
PbF_2	4×10^{-8}
$PbCl_2$	1.6×10^{-5}
$PbBr_2$	4.6×10^{-6}
PbI_2	1.4×10^{-8}
$PbCO_3$	1.5×10^{-15}
PbS	7×10^{-29}
$PbCrO_4$	2×10^{-16}
$PbSO_4$	1.3×10^{-8}

Table J1

Solubility Products

Substance	K_{sp} at 25 °C
$Pb_3(PO_4)_2$	1×10^{-54}
magnesium	
$Mg(OH)_2$	8.9×10^{-12}
$MgCO_3 \cdot 3H_2O$	*ca* 1×10^{-5}
$MgNH_4PO_4$	3×10^{-13}
MgF_2	6.4×10^{-9}
MgC_2O_4	7×10^{-7}
manganese	
$Mn(OH)_2$	2×10^{-13}
$MnCO_3$	8.8×10^{-11}
MnS	2.3×10^{-13}
mercury	
$Hg_2O \cdot H_2O$	3.6×10^{-26}
Hg_2Cl_2	1.1×10^{-18}
Hg_2Br_2	1.3×10^{-22}
Hg_2I_2	4.5×10^{-29}
Hg_2CO_3	9×10^{-15}
Hg_2SO_4	7.4×10^{-7}
Hg_2S	1.0×10^{-47}
Hg_2CrO_4	2×10^{-9}
HgS	1.6×10^{-54}
nickel	
$Ni(OH)_2$	1.6×10^{-16}
$NiCO_3$	1.4×10^{-7}
$NiS(\alpha)$	4×10^{-20}
$NiS(\beta)$	1.3×10^{-25}
potassium	
$KClO_4$	1.05×10^{-2}
K_2PtCl_6	7.48×10^{-6}
$KHC_4H_4O_6$	3×10^{-4}
silver	

Table J1

Solubility Products

Substance	K_{sp} at 25 °C
$\frac{1}{2}\text{Ag}_2\text{O}(\text{Ag}^+ + \text{OH}^-)$	2×10^{-8}
AgCl	1.6×10^{-10}
AgBr	5.0×10^{-13}
AgI	1.5×10^{-16}
AgCN	1.2×10^{-16}
AgSCN	1.0×10^{-12}
Ag_2S	1.6×10^{-49}
Ag_2CO_3	8.1×10^{-12}
Ag_2CrO_4	9.0×10^{-12}
$Ag_4Fe(CN)_6$	1.55×10^{-41}
Ag_2SO_4	1.2×10^{-5}
Ag_3PO_4	1.8×10^{-18}
strontium	
$Sr(OH)_2{\cdot}8H_2O$	3.2×10^{-4}
$SrCO_3$	7×10^{-10}
$SrCrO_4$	3.6×10^{-5}
$SrSO_4$	3.2×10^{-7}
$SrC_2O_4{\cdot}H_2O$	4×10^{-7}
thallium	
TlCl	1.7×10^{-4}
TlSCN	1.6×10^{-4}
Tl_2S	6×10^{-22}
$Tl(OH)_3$	6.3×10^{-46}
tin	
$Sn(OH)_2$	3×10^{-27}
SnS	1×10^{-26}
$Sn(OH)_4$	1.0×10^{-57}
zinc	
$ZnCO_3$	2×10^{-10}

Table J1

Appendix K

Formation Constants For Complex Ions

Formation Constants for Complex Ions

Equilibrium	K_f
$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	7×10^{19}
$Cd^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$	1.3×10^{7}
$Cd^{2+} + 4CN^- \rightleftharpoons [Cd(CN)_4]^{2-}$	3×10^{18}
$Co^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}$	1.3×10^{5}
$Co^{3+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	2.3×10^{33}
$Cu^{+} + 2CN \rightleftharpoons [Cu(CN)_2]^-$	1.0×10^{16}
$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	1.7×10^{13}
$Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$	1.5×10^{35}
$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	2×10^{43}
$Fe^{3+} + 6SCN^- \rightleftharpoons [Fe(SCN)_6]^{3-}$	3.2×10^{3}
$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.1×10^{16}
$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	2.0×10^{8}
$Ag^{+} + 2Cl^- \rightleftharpoons [AgCl_2]^-$	1.8×10^{5}
$Ag^{+} + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	1×10^{21}
$Ag^{+} + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.7×10^{7}
$Zn^{2+} + 4CN^- \rightleftharpoons [Zn(CN)_4]^{2-}$	2.1×10^{19}
$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	2×10^{15}
$Fe^{3+} + SCN^- \rightleftharpoons [Fe(SCN)]^{2+}$	8.9×10^{2}
$Ag^{+} + 4SCN^- \rightleftharpoons [Ag(SCN)_4]^{3-}$	1.2×10^{10}
$Pb^{2+} + 4I^- \rightleftharpoons [PbI_4]^{2-}$	3.0×10^{4}
$Pt^{2+} + 4Cl^- \rightleftharpoons [PtCl_4]^{2-}$	1×10^{16}

Table K1

Formation Constants for Complex Ions

Equilibrium	K_f
$Cu^{2+} + 4CN \rightleftharpoons [Cu(CN)_4]^{2-}$	1.0×10^{25}
$Co^{2+} + 4SCN^{-} \rightleftharpoons [Co(SCN)_4]^{2-}$	1×10^{3}

Table K1

Appendix L

Standard Electrode (Half-Cell) Potentials

Standard Electrode (Half-Cell) Potentials

Half-Reaction	*E*° (V)
$Ag^{+} + e^{-} \longrightarrow Ag$	+0.7996
$AgCl + e^{-} \longrightarrow Ag + Cl^{-}$	+0.22233
$[Ag(CN)_2]^{-} + e^{-} \longrightarrow Ag + 2CN^{-}$	−0.31
$Ag_2CrO_4 + 2e^{-} \longrightarrow 2Ag + {CrO_4}^{2-}$	+0.45
$[Ag(NH_3)_2]^{+} + e^{-} \longrightarrow Ag + 2NH_3$	+0.373
$[Ag(S_2O_3)_2]^{3+} + e^{-} \longrightarrow Ag + 2{S_2O_3}^{2-}$	+0.017
$[AlF_6]^{3-} + 3e^{-} \longrightarrow Al + 6F^{-}$	−2.07
$Al^{3+} + 3e^{-} \longrightarrow Al$	−1.662
$Am^{3+} + 3e^{-} \longrightarrow Am$	−2.048
$Au^{3+} + 3e^{-} \longrightarrow Au$	+1.498
$Au^{+} + e^{-} \longrightarrow Au$	+1.692
$Ba^{2+} + 2e^{-} \longrightarrow Ba$	−2.912
$Be^{2+} + 2e^{-} \longrightarrow Be$	−1.847
$Br_2(aq) + 2e^{-} \longrightarrow 2Br^{-}$	+1.0873
$Ca^{2+} + 2e^{-} \longrightarrow Ca$	−2.868
$Ce^{3} + 3e^{-} \longrightarrow Ce$	−2.483
$Ce^{4+} + e^{-} \longrightarrow Ce^{3+}$	+1.61
$Cd^{2+} + 2e^{-} \longrightarrow Cd$	−0.4030
$[Cd(CN)_4]^{2-} + 2e^{-} \longrightarrow Cd + 4CN^{-}$	−1.09
$[Cd(NH_3)_4]^{2+} + 2e^{-} \longrightarrow Cd + 4NH_3$	−0.61
$CdS + 2e^{-} \longrightarrow Cd + S^{2-}$	−1.17
$Cl_2 + 2e^{-} \longrightarrow 2Cl^{-}$	+1.35827

Table L1

Standard Electrode (Half-Cell) Potentials

Half-Reaction	*E*° (V)
$\text{ClO}_4{}^- + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{ClO}_3{}^- + 2\text{OH}^-$	+0.36
$\text{ClO}_3{}^- + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{ClO}_2{}^- + 2\text{OH}^-$	+0.33
$\text{ClO}_2{}^- + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{ClO}^- + 2\text{OH}^-$	+0.66
$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{Cl}^- + 2\text{OH}^-$	+0.89
$\text{ClO}_4{}^- + 2\text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow \text{ClO}_3{}^- + 3\text{H}_2\text{O}$	+1.189
$\text{ClO}_3{}^- + 3\text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow \text{HClO}_2 + 4\text{H}_2\text{O}$	+1.21
$\text{HClO} + \text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow \text{Cl}^- + 2\text{H}_2\text{O}$	+1.482
$\text{HClO} + \text{H}_3\text{O}^+ + \text{e}^- \longrightarrow \frac{1}{2}\text{Cl}_2 + 2\text{H}_2\text{O}$	+1.611
$\text{HClO}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^- \longrightarrow \text{HClO} + 3\text{H}_2\text{O}$	+1.628
$\text{Co}^{3+} + \text{e}^- \longrightarrow \text{Co}^{2+}\ (2\text{ mol // H}_2\text{SO}_4)$	+1.83
$\text{Co}^{2+} + 2\text{e}^- \longrightarrow \text{Co}$	−0.28
$[\text{Co(NH}_3)_6]^{3+} + \text{e}^- \longrightarrow [\text{Co(NH}_3)_6]^{2+}$	+0.1
$\text{Co(OH)}_3 + \text{e}^- \longrightarrow \text{Co(OH)}_2 + \text{OH}^-$	+0.17
$\text{Cr}^3 + 3\text{e}^- \longrightarrow \text{Cr}$	−0.744
$\text{Cr}^{3+} + \text{e}^- \longrightarrow \text{Cr}^{2+}$	−0.407
$\text{Cr}^{2+} + 2\text{e}^- \longrightarrow \text{Cr}$	−0.913
$[\text{Cu(CN)}_2]^- + \text{e}^- \longrightarrow \text{Cu} + 2\text{CN}^-$	−0.43
$\text{CrO}_4{}^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \longrightarrow \text{Cr(OH)}_3 + 5\text{OH}^-$	−0.13
$\text{Cr}_2\text{O}_7{}^{2-} + 14\text{H}_3\text{O}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 21\text{H}_2\text{O}$	+1.232
$[\text{Cr(OH)}_4]^- + 3\text{e}^- \longrightarrow \text{Cr} + 4\text{OH}^-$	−1.2
$\text{Cr(OH)}_3 + 3\text{e}^- \longrightarrow \text{Cr} + 3\text{OH}^-$	−1.48
$\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+$	+0.153
$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	+0.34
$\text{Cu}^+ + \text{e}^- \longrightarrow \text{Cu}$	+0.521
$\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$	+2.866
$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}$	−0.447

Table L1

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Standard Electrode (Half-Cell) Potentials

Half-Reaction	*E*° (V)
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.771
$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$	+0.36
$Fe(OH)_2 + 2e^- \longrightarrow Fe + 2OH^-$	−0.88
$FeS + 2e^- \longrightarrow Fe + S^{2-}$	−1.01
$Ga^{3+} + 3e^- \longrightarrow Ga$	−0.549
$Gd^{3+} + 3e^- \longrightarrow Gd$	−2.279
$\frac{1}{2}H_2 + e^- \longrightarrow H^-$	−2.23
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	−0.8277
$H_2O_2 + 2H_3O^+ + 2e^- \longrightarrow 4H_2O$	+1.776
$2H_3O^+ + 2e^- \longrightarrow H_2 + 2H_2O$	0.00
$HO_2{}^- + H_2O + 2e^- \longrightarrow 3OH^-$	+0.878
$Hf^{4+} + 4e^- \longrightarrow Hf$	−1.55
$Hg^{2+} + 2e^- \longrightarrow Hg$	+0.851
$2Hg^{2+} + 2e^- \longrightarrow Hg_2{}^{2+}$	+0.92
$Hg_2{}^{2+} + 2e^- \longrightarrow 2Hg$	+0.7973
$[HgBr_4]^{2-} + 2e^- \longrightarrow Hg + 4Br^-$	+0.21
$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+0.26808
$[Hg(CN)_4]^{2-} + 2e^- \longrightarrow Hg + 4CN^-$	−0.37
$[HgI_4]^{2-} + 2e^- \longrightarrow Hg + 4I^-$	−0.04
$HgS + 2e^- \longrightarrow Hg + S^{2-}$	−0.70
$I_2 + 2e^- \longrightarrow 2I^-$	+0.5355
$In^{3+} + 3e^- \longrightarrow In$	−0.3382
$K^+ + e^- \longrightarrow K$	−2.931
$La^{3+} + 3e^- \longrightarrow La$	−2.52
$Li^+ + e^- \longrightarrow Li$	−3.04
$Lu^{3+} + 3e^- \longrightarrow Lu$	−2.28

Table L1

Standard Electrode (Half-Cell) Potentials

Half-Reaction	*E*° (V)
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.372
$Mn^{2+} + 2e^- \longrightarrow Mn$	−1.185
$MnO_2 + 2H_2O + 2e^- \longrightarrow Mn(OH)_2 + 2OH^-$	−0.05
$MnO_4{}^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$	+0.558
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23
$MnO_4{}^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.507
$Na^+ + e^- \longrightarrow Na$	−2.71
$Nd^{3+} + 3e^- \longrightarrow Nd$	−2.323
$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.257
$[Ni(NH_3)_6]^{2+} + 2e^- \longrightarrow Ni + 6NH_3$	−0.49
$NiO_2 + 4H^+ + 2e^- \longrightarrow Ni^{2+} + 2H_2O$	+1.593
$NiO_2 + 2H_2O + 2e^- \longrightarrow Ni(OH)_2 + 2OH^-$	+0.49
$NiS + 2e^- \longrightarrow Ni + S^{2-}$	+0.76
$NO_3{}^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.957
$NO_3{}^- + 3H^+ + 2e^- \longrightarrow HNO_2 + H_2O$	+0.92
$NO_3{}^- + H_2O + 2e^- \longrightarrow NO_2{}^- + 2OH^-$	+0.10
$Np^{3+} + 3e^- \longrightarrow Np$	−1.856
$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.401
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	+0.695
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.1262
$PbO_2 + SO_4{}^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	+1.69
$PbS + 2e^- \longrightarrow Pb + S^{2-}$	−0.95
$PbSO_4 + 2e^- \longrightarrow Pb + SO_4{}^{2-}$	−0.3505
$Pd^{2+} + 2e^- \longrightarrow Pd$	+0.987
$[PdCl_4]^{2-} + 2e^- \longrightarrow Pd + 4Cl^-$	+0.591

Table L1

Standard Electrode (Half-Cell) Potentials

Half-Reaction	*E*° (V)
$Pt^{2+} + 2e^- \longrightarrow Pt$	+1.20
$[PtBr_4]^{2-} + 2e^- \longrightarrow Pt + 4Br^-$	+0.58
$[PtCl_4]^{2-} + 2e^- \longrightarrow Pt + 4Cl^-$	+0.755
$[PtCl_6]^{2-} + 2e^- \longrightarrow [PtCl_4]^{2-} + 2Cl^-$	+0.68
$Pu^{3} + 3e^- \longrightarrow Pu$	−2.03
$Ra^{2+} + 2e^- \longrightarrow Ra$	−2.92
$Rb^{+} + e^- \longrightarrow Rb$	−2.98
$[RhCl_6]^{3-} + 3e^- \longrightarrow Rh + 6Cl^-$	+0.44
$S + 2e^- \longrightarrow S^{2-}$	−0.47627
$S + 2H^+ + 2e^- \longrightarrow H_2S$	+0.142
$Sc^{3+} + 3e^- \longrightarrow Sc$	−2.09
$Se + 2H^+ + 2e^- \longrightarrow H_2Se$	−0.399
$[SiF_6]^{2-} + 4e^- \longrightarrow Si + 6F^-$	−1.2
$SiO_3{}^{2-} + 3H_2O + 4e^- \longrightarrow Si + 6OH^-$	−1.697
$SiO_2 + 4H^+ + 4e^- \longrightarrow Si + 2H_2O$	−0.86
$Sm^{3+} + 3e^- \longrightarrow Sm$	−2.304
$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.151
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.1375
$[SnF_6]^{2-} + 4e^- \longrightarrow Sn + 6F^-$	−0.25
$SnS + 2e^- \longrightarrow Sn + S^{2-}$	−0.94
$Sr^{2+} + 2e^- \longrightarrow Sr$	−2.89
$TeO_2 + 4H^+ + 4e^- \longrightarrow Te + 2H_2O$	+0.593
$Th^{4+} + 4e^- \longrightarrow Th$	−1.90
$Ti^{2+} + 2e^- \longrightarrow Ti$	−1.630
$U^{3+} + 3e^- \longrightarrow U$	−1.79
$V^{2+} + 2e^- \longrightarrow V$	−1.19

Table L1

Standard Electrode (Half-Cell) Potentials

Half-Reaction	*E*° (V)
$Y^{3+} + 3e^- \longrightarrow Y$	−2.37
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.7618
$[Zn(CN)_4]^{2-} + 2e^- \longrightarrow Zn + 4CN^-$	−1.26
$[Zn(NH_3)_4]^{2+} + 2e^- \longrightarrow Zn + 4NH_3$	−1.04
$Zn(OH)_2 + 2e^- \longrightarrow Zn + 2OH^-$	−1.245
$[Zn(OH)_4]^{2} + 2e^- \longrightarrow Zn + 4OH^-$	−1.199
$ZnS + 2e^- \longrightarrow Zn + S^{2-}$	−1.40
$Zr^{4} + 4e^- \longrightarrow Zr$	−1.539

Table L1

Appendix M

Half-Lives For Several Radioactive Isotopes

Half-Lives for Several Radioactive Isotopes

Isotope	Half-Life[1]	Type of Emission[2]	Isotope	Half-Life[3]	Type of Emission[4]
$^{14}_{6}\text{C}$	5730 y	(β^-)	$^{210}_{83}\text{Bi}$	5.01 d	(β^-)
$^{13}_{7}\text{N}$	9.97 m	(β^+)	$^{212}_{83}\text{Bi}$	60.55 m	$(\alpha \text{ or } \beta^-)$
$^{15}_{9}\text{F}$	4.1×10^{-22} s	(p)	$^{210}_{84}\text{Po}$	138.4 d	(α)
$^{24}_{11}\text{Na}$	15.00 h	(β^-)	$^{212}_{84}\text{Po}$	3×10^{-7} s	(α)
$^{32}_{15}\text{P}$	14.29 d	(β^-)	$^{216}_{84}\text{Po}$	0.15 s	(α)
$^{40}_{19}\text{K}$	1.27×10^{9} y	$(\beta \text{ or } E.C.)$	$^{218}_{84}\text{Po}$	3.05 m	(α)
$^{49}_{26}\text{Fe}$	0.08 s	(β^+)	$^{215}_{85}\text{At}$	1.0×10^{-4} s	(α)
$^{60}_{26}\text{Fe}$	2.6×10^{6} y	(β^-)	$^{218}_{85}\text{At}$	1.6 s	(α)
$^{60}_{27}\text{Co}$	5.27 y	(β^-)	$^{220}_{86}\text{Rn}$	55.6 s	(α)
$^{87}_{37}\text{Rb}$	4.7×10^{10} y	(β^-)	$^{222}_{86}\text{Rn}$	3.82 d	(α)
$^{90}_{38}\text{Sr}$	29 y	(β^-)	$^{224}_{88}\text{Ra}$	3.66 d	(α)
$^{115}_{49}\text{In}$	5.1×10^{15} y	(β^-)	$^{226}_{88}\text{Ra}$	1600 y	(α)
$^{131}_{53}\text{I}$	8.040 d	(β^-)	$^{228}_{88}\text{Ra}$	5.75 y	(β^-)
$^{142}_{58}\text{Ce}$	5×10^{15} y	(α)	$^{228}_{89}\text{Ac}$	6.13 h	(β^-)
$^{208}_{81}\text{Tl}$	3.07 m	(β^-)	$^{228}_{90}\text{Th}$	1.913 y	(α)
$^{210}_{82}\text{Pb}$	22.3 y	(β^-)	$^{232}_{90}\text{Th}$	1.4×10^{10} y	(α)
$^{212}_{82}\text{Pb}$	10.6 h	(β^-)	$^{233}_{90}\text{Th}$	22 m	(β^-)
$^{214}_{82}\text{Pb}$	26.8 m	(β^-)	$^{234}_{90}\text{Th}$	24.10 d	(β^-)

Table M1

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1. y = years, d = days, h = hours, m = minutes, s = seconds
2. *E.C.* = electron capture, *S.F.* = Spontaneous fission
3. y = years, d = days, h = hours, m = minutes, s = seconds
4. *E.C.* = electron capture, *S.F.* = Spontaneous fission

Half-Lives for Several Radioactive Isotopes

Isotope	Half-Life	Type of Emission	Isotope	Half-Life	Type of Emission
${}^{206}_{83}\text{Bi}$	6.243 d	$(E.C.)$	${}^{233}_{91}\text{Pa}$	27 d	(β^-)
${}^{233}_{92}\text{U}$	1.59×10^5 y	(α)	${}^{242}_{96}\text{Cm}$	162.8 d	(α)
${}^{234}_{92}\text{U}$	2.45×10^5 y	(α)	${}^{243}_{97}\text{Bk}$	4.5 h	$(\alpha \text{ or } E.C.)$
${}^{235}_{92}\text{U}$	7.03×10^8 y	(α)	${}^{253}_{99}\text{Es}$	20.47 d	(α)
${}^{238}_{92}\text{U}$	4.47×10^9 y	(α)	${}^{254}_{100}\text{Fm}$	3.24 h	$(\alpha \text{ or } S.F.)$
${}^{239}_{92}\text{U}$	23.54 m	(β^-)	${}^{255}_{100}\text{Fm}$	20.1 h	(α)
${}^{239}_{93}\text{Np}$	2.3 d	(β^-)	${}^{256}_{101}\text{Md}$	76 m	$(\alpha \text{ or } E.C.)$
${}^{239}_{94}\text{Pu}$	2.407×10^4 y	(α)	${}^{254}_{102}\text{No}$	55 s	(α)
${}^{239}_{94}\text{Pu}$	6.54×10^3 y	(α)	${}^{257}_{103}\text{Lr}$	0.65 s	(α)
${}^{241}_{94}\text{Pu}$	14.4 y	$(\alpha \text{ or } \beta^-)$	${}^{260}_{105}\text{Ha}$	1.5 s	$(\alpha \text{ or } S.F.)$
${}^{241}_{95}\text{Am}$	432.2 y	(α)	${}^{263}_{106}\text{Sg}$	0.8 s	$(\alpha \text{ or } S.F.)$

Table M1

Answer Key

Chapter 1

1. Place a glass of water outside. It will freeze if the temperature is below 0 °C.

3. (a) law (states a consistently observed phenomenon, can be used for prediction); (b) theory (a widely accepted explanation of the behavior of matter); (c) hypothesis (a tentative explanation, can be investigated by experimentation)

5. (a) symbolic, microscopic; (b) macroscopic; (c) symbolic, macroscopic; (d) microscopic

7. Macroscopic. The heat required is determined from macroscopic properties.

9. Liquids can change their shape (flow); solids can't. Gases can undergo large volume changes as pressure changes; liquids do not. Gases flow and change volume; solids do not.

11. The mixture can have a variety of compositions; a pure substance has a definite composition. Both have the same composition from point to point.

13. Molecules of elements contain only one type of atom; molecules of compounds contain two or more types of atoms. They are similar in that both are comprised of two or more atoms chemically bonded together.

15. Answers will vary. Sample answer: Gatorade contains water, sugar, dextrose, citric acid, salt, sodium chloride, monopotassium phosphate, and sucrose acetate isobutyrate.

17. (a) element; (b) element; (c) compound; (d) mixture; (e) compound; (f) compound; (g) compound; (h) mixture

19. In each case, a molecule consists of two or more combined atoms. They differ in that the types of atoms change from one substance to the next.

21. Gasoline (a mixture of compounds), oxygen, and to a lesser extent, nitrogen are consumed. Carbon dioxide and water are the principal products. Carbon monoxide and nitrogen oxides are produced in lesser amounts.

23. (a) Increased as it would have combined with oxygen in the air thus increasing the amount of matter and therefore the mass. (b) 0.9 g

25. (a) 200.0 g; (b) The mass of the container and contents would decrease as carbon dioxide is a gaseous product and would leave the container. (c) 102.3 g

27. (a) physical; (b) chemical; (c) chemical; (d) physical; (e) physical

29. physical

31. The value of an extensive property depends upon the amount of matter being considered, whereas the value of an intensive property is the same regardless of the amount of matter being considered.

33. Being extensive properties, both mass and volume are directly proportional to the amount of substance under study. Dividing one extensive property by another will in effect "cancel" this dependence on amount, yielding a ratio that is independent of amount (an intensive property).

35. about a yard

37. (a) kilograms; (b) meters; (c) kilometers/second; (d) kilograms/cubic meter; (e) kelvin; (f) square meters; (g) cubic meters

39. (a) centi-, $\times\ 10^{-2}$; (b) deci-, $\times\ 10^{-1}$; (c) Giga-, $\times\ 10^{9}$; (d) kilo-, $\times\ 10^{3}$; (e) milli-, $\times\ 10^{-3}$; (f) nano-, $\times\ 10^{-9}$; (g) pico-, $\times\ 10^{-12}$; (h) tera-, $\times\ 10^{12}$

41. (a) 8.00 kg, 5.00 L, 1.60 kg/L; (b) 2.00 kg, 5.00 L, 0.400 kg/L; (c) red < green < blue < yellow; (d) If the volumes are the same, then the density is directly proportional to the mass.

43. (a) (b) Answer is one of the following. A/yellow: mass = 65.14 kg, volume = 3.38 L, density = 19.3 kg/L, likely identity = gold. B/blue: mass = 0.64 kg, volume = 1.00 L, density = 0.64 kg/L, likely identity = apple. C/green: mass = 4.08 kg, volume = 5.83 L, density = 0.700 kg/L, likely identity = gasoline. D/red: mass = 3.10 kg, volume = 3.38 L, density = 0.920 kg/L, likely identity = ice; and E/purple: mass = 3.53 kg, volume = 1.00 L, density = 3.53 kg/L, likely identity = diamond. (c) B/blue/apple (0.64 kg/L) < C/green/gasoline (0.700 kg/L) < D/red/ice (0.920 kg/L) < E/purple/diamond (3.53 kg/L) < A/yellow/gold (19.3 kg/L)

45. (a) 7.04×10^2; (b) 3.344×10^{-2}; (c) 5.479×10^2; (d) 2.2086×10^4; (e) 1.00000×10^3; (f) 6.51×10^{-8}; (g) 7.157×10^{-3}

47. (a) exact; (b) exact; (c) uncertain; (d) exact; (e) uncertain; (f) uncertain

49. (a) two; (b) three; (c) five; (d) four; (e) six; (f) two; (g) five

51. (a) 0.44; (b) 9.0; (c) 27; (d) 140; (e) 1.5×10^{-3}; (f) 0.44

53. (a) 2.15×10^5; (b) 4.2×10^6; (c) 2.08; (d) 0.19; (e) 27,440; (f) 43.0

55. (a) Archer X; (b) Archer W; (c) Archer Y

57. (a) $\frac{1.0936\text{ yd}}{1\text{ m}}$; (b) $\frac{0.94635\text{ L}}{1\text{ qt}}$; (c) $\frac{2.2046\text{ lb}}{1\text{ kg}}$

59. $\frac{2.0\text{ L}}{67.6\text{ fl oz}} = \frac{0.030\text{ L}}{1\text{ fl oz}}$
Only two significant figures are justified.

61. 68–71 cm; 400–450 g

63. 355 mL

65. 8×10^{-4} cm

67. yes; weight = 89.4 kg

69. 5.0×10^{-3} mL

71. (a) 1.3×10^{-4} kg; (b) 2.32×10^8 kg; (c) 5.23×10^{-12} m; (d) 8.63×10^{-5} kg; (e) 3.76×10^{-1} m; (f) 5.4×10^{-5} m; (g) 1×10^{12} s; (h) 2.7×10^{-11} s; (i) 1.5×10^{-4} K

73. 45.4 L

75. 1.0160×10^3 kg

77. (a) 394 ft; (b) 5.9634 km; (c) 6.0×10^2; (d) 2.64 L; (e) 5.1×10^{18} kg; (f) 14.5 kg; (g) 324 mg

79. 0.46 m; 1.5 ft/cubit

81. Yes, the acid’s volume is 123 mL.

83. 62.6 in (about 5 ft 3 in.) and 101 lb

85. (a) 3.81 cm × 8.89 cm × 2.44 m; (b) 40.6 cm

87. 2.70 g/cm^3

89. (a) 81.6 g; (b) 17.6 g

91. (a) 5.1 mL; (b) 37 L

93. 5371 °F, 3239 K

95. −23 °C, 250 K

97. −33.4 °C, 239.8 K

99. 113 °F

Chapter 2

1. The starting materials consist of one green sphere and two purple spheres. The products consist of two green spheres and two purple spheres. This violates Dalton’s postulate that that atoms are not created during a chemical change, but are merely redistributed.

3. This statement violates Dalton’s fourth postulate: In a given compound, the numbers of atoms of each type (and thus also the percentage) always have the same ratio.

5. Dalton originally thought that all atoms of a particular element had identical properties, including mass. Thus, the concept of isotopes, in which an element has different masses, was a violation of the original idea. To account for the existence of isotopes, the second postulate of his atomic theory was modified to state that atoms of the same element must have identical chemical properties.

7. Both are subatomic particles that reside in an atom’s nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

9. (a) The Rutherford atom has a small, positively charged nucleus, so most α particles will pass through empty space far from the nucleus and be undeflected. Those α particles that pass near the nucleus will be deflected from their paths due to positive-positive repulsion. The more directly toward the nucleus the α particles are headed, the larger the deflection angle will be. (b) Higher-energy α particles that pass near the nucleus will still undergo deflection, but the faster they travel, the less the expected angle of deflection. (c) If the nucleus is smaller, the positive charge is smaller and the expected deflections are smaller—both in terms of how closely the α particles pass by the nucleus undeflected and the angle of deflection. If the nucleus is larger, the positive charge is larger and the expected deflections are larger—more α particles will be deflected, and the deflection angles will be larger. (d) The paths followed by the α particles match the predictions from (a), (b), and (c).

11. (a) $^{133}Cs^{+}$; (b) $^{127}I^{-}$; (c) $^{31}P^{3-}$; (d) $^{57}Co^{3+}$

13. (a) Carbon-12, ^{12}C; (b) This atom contains six protons and six neutrons. There are six electrons in a neutral ^{12}C atom. The net charge of such a neutral atom is zero, and the mass number is 12. (c) The preceding answers are correct. (d) The atom will be stable since C-12 is a stable isotope of carbon. (e) The preceding answer is correct. Other answers for this exercise are possible if a different element of isotope is chosen.

15. (a) Lithium-6 contains three protons, three neutrons, and three electrons. The isotope symbol is ^{6}Li or ${}^{6}_{3}\text{Li}$. (b) $^{6}Li^{+}$ or ${}^{6}_{3}\text{Li}^{+}$

17. (a) Iron, 26 protons, 24 electrons, and 32 neutrons; (b) iodine, 53 protons, 54 electrons, and 74 neutrons

19. (a) 3 protons, 3 electrons, 4 neutrons; (b) 52 protons, 52 electrons, 73 neutrons; (c) 47 protons, 47 electrons, 62 neutrons; (d) 7 protons, 7 electrons, 8 neutrons; (e) 15 protons, 15 electrons, 16 neutrons

21. Let us use neon as an example. Since there are three isotopes, there is no way to be sure to accurately predict the abundances to make the total of 20.18 amu average atomic mass. Let us guess that the abundances are 9% Ne-22, 91% Ne-20, and only a trace of Ne-21. The average mass would be 20.18 amu. Checking the nature’s mix of isotopes shows that the abundances are 90.48% Ne-20, 9.25% Ne-22, and 0.27% Ne-21, so our guessed amounts have to be slightly adjusted.

23. 79.90 amu

25. Turkey source: 0.264 (of 10.0129 amu isotope); US source: 0.254 (of 10.0129 amu isotope)

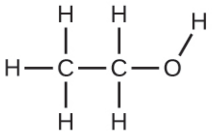
27. The symbol for the element oxygen, O, represents both the element and one atom of oxygen. A molecule of oxygen, O_2, contains two oxygen atoms; the subscript 2 in the formula must be used to distinguish the diatomic molecule from two single oxygen atoms.

29. (a) molecular CO_2, empirical CO_2; (b) molecular C_2H_2, empirical CH; (c) molecular C_2H_4, empirical CH_2; (d) molecular H_2SO_4, empirical H_2SO_4

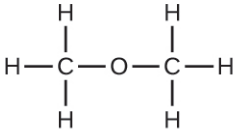
31. (a) $C_4H_5N_2O$; (b) $C_{12}H_{22}O_{11}$; (c) HO; (d) CH_2O; (e) $C_3H_4O_3$

33. (a) CH_2O; (b) C_2H_4O

35. (a) ethanol



(b) methoxymethane, more commonly known as dimethyl ether



(c) These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

37. Use the molecular formula to find the molar mass; to obtain the number of moles, divide the mass of compound by the molar mass of the compound expressed in grams.

39. Formic acid. Its formula has twice as many oxygen atoms as the other two compounds (one each). Therefore, 0.60 mol of formic acid would be equivalent to 1.20 mol of a compound containing a single oxygen atom.

41. The two masses have the same numerical value, but the units are different: The molecular mass is the mass of 1 molecule while the molar mass is the mass of 6.022×10^{23} molecules.

43. (a) 256.528 g/mol; (b) 72.150 g mol^{-1}; (c) 378.103 g mol^{-1}; (d) 58.080 g mol^{-1}; (e) 180.158 g mol^{-1}

45. (a) 197.382 g mol^{-1}; (b) 257.163 g mol^{-1}; (c) 194.193 g mol^{-1}; (d) 60.056 g mol^{-1}; (e) 306.464 g mol^{-1}

47. (a) 0.819 g;
(b) 307 g;
(c) 0.23 g;
(d) 1.235×10^6 g (1235 kg);
(e) 765 g

49. (a) 99.41 g;
(b) 2.27 g;
(c) 3.5 g;
(d) 222 kg;
(e) 160.1 g

51. (a) 9.60 g; (b) 19.2 g; (c) 28.8 g

53. zirconium: 2.038×10^{23} atoms; 30.87 g; silicon: 2.038×10^{23} atoms; 9.504 g; oxygen: 8.151×10^{23} atoms; 21.66 g

55. $AlPO_4$: 1.000 mol
Al_2Cl_6: 1.994 mol
Al_2S_3: 3.00 mol

57. 3.113×10^{25} C atoms

59. 0.865 servings, or about 1 serving.

61. 20.0 g H_2O represents the least number of molecules since it has the least number of moles.

Chapter 3

1. The spectrum consists of colored lines, at least one of which (probably the brightest) is red.

3. 3.15 m

5. 3.233×10^{-19} J; 2.018 eV

7. $v = 4.568 \times 10^{14}\ \text{s}^{-1}$; $\lambda = 656.3$ nm; Energy $\text{mol}^{-1} = 1.823 \times 10^5\ \text{J mol}^{-1}$; red

9. (a) $\lambda = 8.69 \times 10^{-7}$ m; $E = 2.29 \times 10^{-19}$ J; (b) $\lambda = 4.59 \times 10^{-7}$ m; $E = 4.33 \times 10^{-19}$ J; The color of (a) is red; (b) is blue.

11. $E = 9.502 \times 10^{-15}$ J; $v = 1.434 \times 10^{19}\ \text{s}^{-1}$

13. Red: 660 nm; 4.54×10^{14} Hz; 3.01×10^{-19} J. Green: 520 nm; 5.77×10^{14} Hz; 3.82×10^{-19} J. Blue: 440 nm; 6.81×10^{14} Hz; 4.51×10^{-19} J. Somewhat different numbers are also possible.

15. $5.49 \times 10^{14}\ \text{s}^{-1}$; no

17. Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.

19.

$$\begin{aligned} E &= E_2 - E_5 = 2.179 \times 10^{-18}\left(\frac{1}{n_2^2} - \frac{1}{n_5^2}\right)\text{J} \\ &= 2.179 \times 10^{-18}\left(\frac{1}{2^2} - \frac{1}{5^2}\right) = 4.576 \times 10^{-19}\ \text{J} \\ &= \frac{4.576 \times 10^{-19}\ \cancel{\text{J}}}{1.602 \times 10^{-19}\ \cancel{\text{J}}\ \text{eV}^{-1}} = 2.856\ \text{eV} \end{aligned}$$

21. -8.716×10^{-18} J

23. -3.405×10^{-20} J

25. 33.9 Å

27. 1.471×10^{-17} J

29. Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature "solar system" with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic radiation are ignored, such atoms would be stable, having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single quantum number, *n*. The orbiting electron in Bohr's model is assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such "quantum jumps" will produce discrete spectra, in agreement with observations.

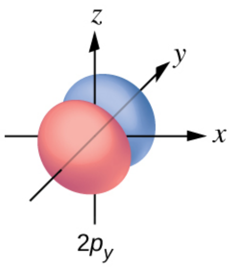
31. Both models have a central positively charged nucleus with electrons moving about the nucleus in accordance with the Coulomb electrostatic potential. The Bohr model *assumes* that the electrons move in circular orbits that have quantized energies, angular momentum, and radii that are specified by a single quantum number, $n = 1, 2, 3, \ldots$, but this quantization is an ad hoc assumption made by Bohr to incorporate quantization into an essentially classical mechanics description of the atom. Bohr also assumed that electrons orbiting the nucleus normally do not emit or absorb electromagnetic radiation, but do so when the electron switches to a different orbit. In the quantum mechanical model, the electrons do not move in precise orbits (such orbits violate the Heisenberg uncertainty principle) and, instead, a probabilistic interpretation of the electron's position at any given instant is used, with a mathematical function ψ called a wavefunction that can be used to determine the electron's spatial probability distribution. These wavefunctions, or orbitals, are three-dimensional stationary waves that can be specified by three quantum numbers that arise naturally from their underlying mathematics (no ad hoc assumptions required): the principal quantum number, *n* (the same one used by Bohr), which specifies shells such that orbitals having the same *n* all have the same energy and approximately the same spatial extent; the angular momentum quantum number *l*, which is a measure of the orbital's angular momentum and corresponds to the orbitals' general shapes, as well as specifying subshells such that orbitals having the same *l* (and *n*) all have the same energy; and the orientation quantum number *m*, which is a measure of the *z* component of the angular momentum and corresponds to the orientations of the orbitals. The Bohr model gives the same expression for the energy as the quantum mechanical expression and, hence, both properly account for hydrogen's discrete spectrum (an example of getting the right answers for the wrong reasons, something that many chemistry students can sympathize with), but gives the wrong expression for the angular momentum (Bohr orbits necessarily all have non-zero angular momentum, but some quantum orbitals [*s* orbitals] can have zero angular momentum).

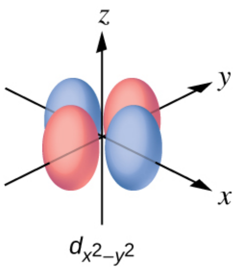
33. *n* determines the general range for the value of energy and the probable distances that the electron can be from the nucleus. *l* determines the shape of the orbital. m_1 determines the orientation of the orbitals of the same *l* value with respect to one another. m_s determines the spin of an electron.

35. (a) 2*p*; (b) 4*d*; (c) 6*s*

37. (a) 3*d;* (b) 1*s;* (c) 4*f*

39.





41. (a) x. 2, y. 2, z. 2; (b) x. 1, y. 3, z. 0; (c) x. 4 0 0 $\frac{1}{2}$, y. 2 1 0 $\frac{1}{2}$, z. 3 2 0 $\frac{1}{2}$; (d) x. 1, y. 2, z. 3; (e) x. $l = 0$, $m_l = 0$, y. $l = 1$, $m_l = –1, 0,$ or $+1$, z. $l = 2$, $m_l = –2, –1, 0, +1, +2$

43. 12

45.

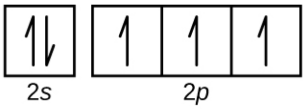
n	l	m_l	s
4	0	0	$+\frac{1}{2}$
4	0	0	$-\frac{1}{2}$
4	1	−1	$+\frac{1}{2}$
4	1	0	$+\frac{1}{2}$
4	1	+1	$+\frac{1}{2}$
4	1	−1	$-\frac{1}{2}$

47. For example, Na^+: $1s^22s^22p^6$; Ca^{2+}: $1s^22s^22p^6$; Sn^{2+}: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^2$; $F^–$: $1s^22s^22p^6$; $O^{2–}$: $1s^22s^22p^6$; $Cl^–$: $1s^22s^22p^63s^23p^6$.

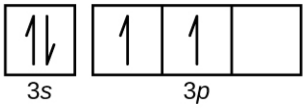
49. (a) $1s^22s^22p^3$; (b) $1s^22s^22p^63s^23p^2$; (c) $1s^22s^22p^63s^23p^64s^23d^6$; (d) $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^4$; (e) $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^9$

51. The charge on the ion.

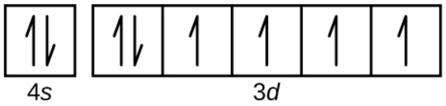
53. (a)



(b)



(c)



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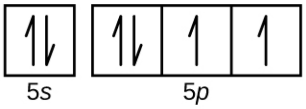
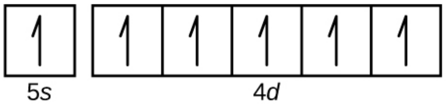


(e)



55. Zr

57. Rb^+, Se^{2-}

59. Although both (b) and (c) are correct, (e) encompasses both and is the best answer.

61. K

63. $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s^24f^{14}5d^{10}$

65. Co has 27 protons, 27 electrons, and 33 neutrons: $1s^22s^22p^63s^23p^64s^23d^7$. I has 53 protons, 53 electrons, and 78 neutrons: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^5$.

67. Cl

69. O

71. Rb < Li < N < F

73. 15 (5A)

75. Mg < Ca < Rb < Cs

77. $Si^{4+} < Al^{3+} < Ca^{2+} < K^+$

79. Se, As^-

81. $Mg^{2+} < K^+ < Br^- < As^{3-}$

83. O, IE_1

85. Ra

87. (a) metal, inner transition metal; (b) nonmetal, representative element; (c) metal, representative element; (d) nonmetal, representative element; (e) metal, transition metal; (f) metal, inner transition metal; (g) metal, transition metal; (h) nonmetal, representative element; (i) nonmetal, representative element; (j) metal, representative element

89. (a) He; (b) Be; (c) Li; (d) O

91. (a) krypton, Kr; (b) calcium, Ca; (c) fluorine, F; (d) tellurium, Te

93. (a) ${}^{23}_{11}\text{Na}$; (b) ${}^{129}_{54}\text{Xe}$; (c) ${}^{73}_{33}\text{As}$; (d) ${}^{226}_{88}\text{Ra}$

95. Ionic: KCl, $MgCl_2$; Covalent: NCl_3, ICl, PCl_5, CCl_4

97. (a) covalent; (b) ionic, Ba^{2+}, O^{2-}; (c) ionic, $NH_4{}^+$, $CO_3{}^{2-}$; (d) ionic, Sr^{2+}, $H_2PO_4{}^-$; (e) covalent; (f) ionic, Na^+, O^{2-}

99. (a) CaS; (b) $(NH_4)_2SO_4$; (c) $AlBr_3$; (d) Na_2HPO_4; (e) $Mg_3(PO_4)_2$

Chapter 4

1. The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

3. P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

5. (a) P^{3-}; (b) Mg^{2+}; (c) Al^{3+}; (d) O^{2-}; (e) Cl^{-}; (f) Cs^{+}

7. (a) $[Ar]4s^2 3d^{10} 4p^6$; (b) $[Kr]4d^{10} 5s^2 5p^6$ (c) $1s^2$ (d) $[Kr]4d^{10}$; (e) $[He]2s^2 2p^6$; (f) $[Ar]3d^{10}$; (g) $1s^2$ (h) $[He]2s^2 2p^6$ (i) $[Kr]4d^{10} 5s^2$ (j) $[Ar]3d^7$ (k) $[Ar]3d^6$, (l) $[Ar]3d^{10} 4s^2$

9. (a) $1s^2 2s^2 2p^6 3s^2 3p^1$; Al^{3+}: $1s^2 2s^2 2p^6$; (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$; Sr^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (d) $1s^2 2s^1$; Li^{+}: $1s^2$; (e) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (f) $1s^2 2s^2 2p^6 3s^2 3p^4$; $1s^2 2s^2 2p^6 3s^2 3p^6$

11. NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

13. ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)

15. (a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N

17. (a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O

19. N, O, F, and Cl

21. (a) HF; (b) CO; (c) OH; (d) PCl; (e) NH; (f) PO; (g) CN

23. (a) cesium chloride; (b) barium oxide; (c) potassium sulfide; (d) beryllium chloride; (e) hydrogen bromide; (f) aluminum fluoride

25. (a) RbBr; (b) MgSe; (c) Na_2O; (d) $CaCl_2$; (e) HF; (f) GaP; (g) $AlBr_3$; (h) $(NH_4)_2SO_4$

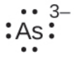
27. (a) ClO_2; (b) N_2O_4; (c) K_3P; (d) Ag_2S; (e) $AlF_3·3H_2O$; (f) SiO_2

29. (a) chromium(III) oxide; (b) iron(II) chloride; (c) chromium(VI) oxide; (d) titanium(IV) chloride; (e) cobalt(II) chloride hexahydrate; (f) molybdenum(IV) sulfide

31. (a) K_3PO_4; (b) $CuSO_4$; (c) $CaCl_2$; (d) TiO_2; (e) NH_4NO_3; (f) $NaHSO_4$

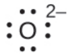
33. (a) manganese(IV) oxide; (b) mercury(I) chloride; (c) iron(III) nitrate; (d) titanium(IV) chloride; (e) copper(II) bromide

34. (a) eight electrons:

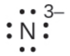


(b) eight electrons:

(c) no electrons Be^{2+}
(d) eight electrons:



(e) no electrons Ga^{3+}
(f) no electrons Li^{+}
(g) eight electrons:



36. (a)

(b)

(c)

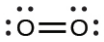
(d)

(e)

(f)

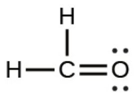
38.

40. (a)

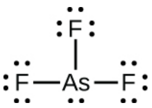


In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

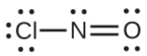
(b)



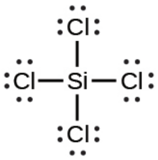
(c)



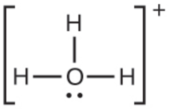
(d)



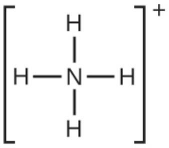
(e)



(f)



(g)



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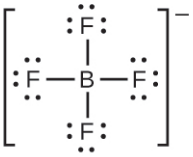
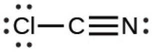


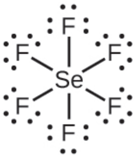
(i)

(j)

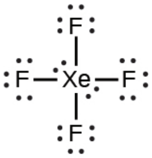


(k)

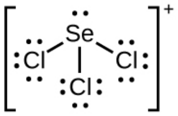
42. (a) SeF_6:



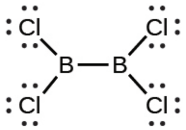
(b) XeF_4:



(c) $SeCl_3{}^+$:

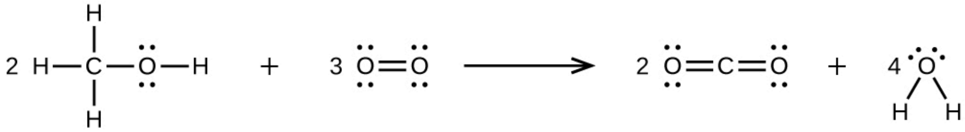


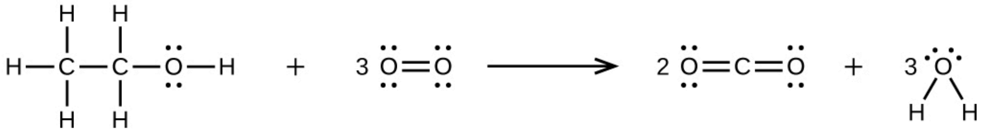
(d) Cl_2BBCl_2:

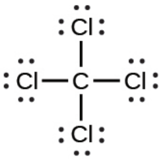


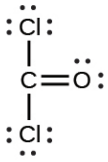
44. Two valence electrons per Pb atom are transferred to Cl atoms; the resulting Pb^{2+} ion has a $6s^2$ valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

46.



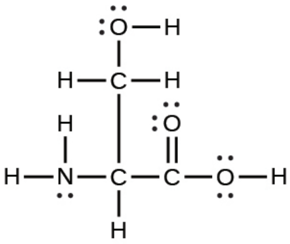




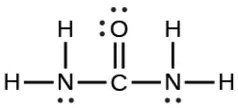


48.

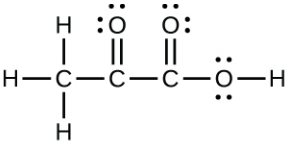
50. (a)



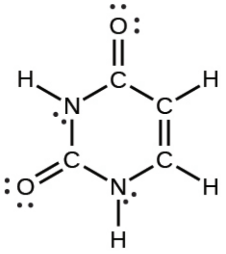
(b)



(c)



(d)



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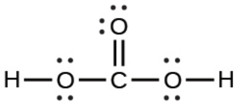
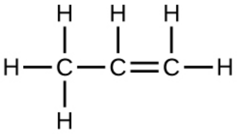
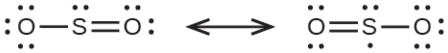




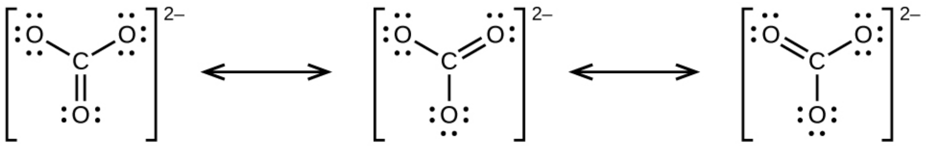
52.

54. Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

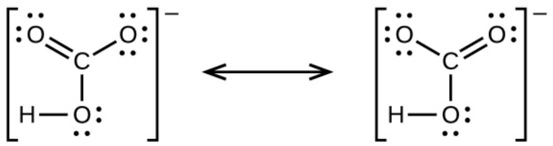
56. (a)



(b)



(c)



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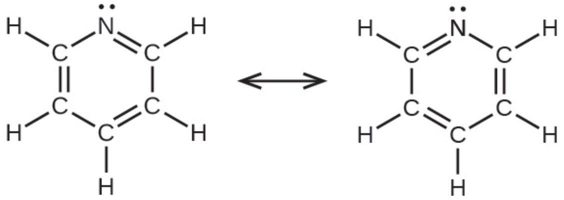
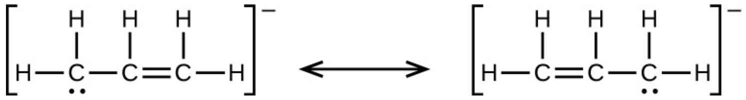
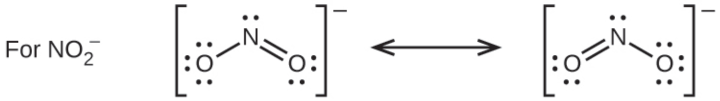


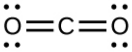
(e)



58.



60. (a)



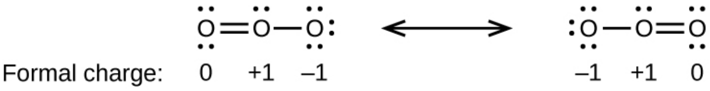
(b)

CO has the strongest carbon-oxygen bond because there is a triple bond joining C and O. CO_2 has double bonds.

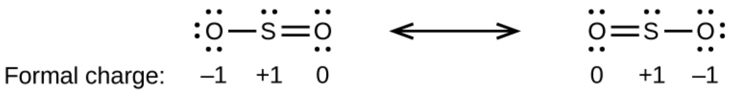
62. (a) H: 0, Cl: 0; (b) C: 0, F: 0; (c) P: 0, Cl 0; (d) P: 0, F: 0

64. Cl in Cl_2: 0; Cl in $BeCl_2$: 0; Cl in ClF_5: 0

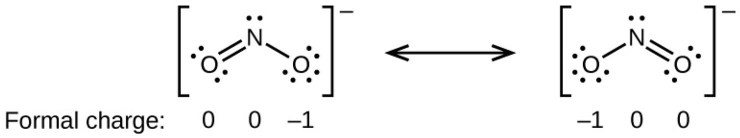
66. (a)



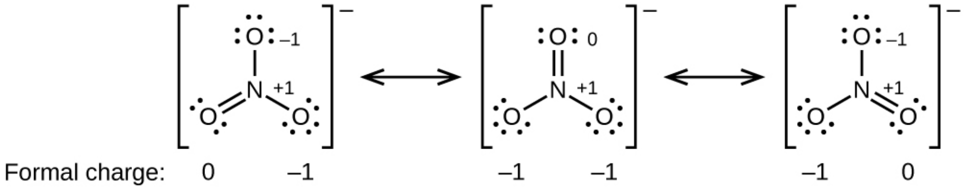
(b)



(c)

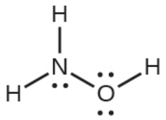


(d)

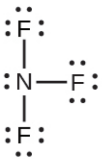


68. HOCl

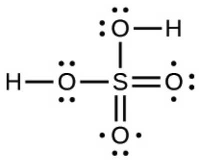
70. The structure that gives zero formal charges is consistent with the actual structure:



72. NF_3;



74.



75. The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

77. Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

79. As long as the polar bonds are compensated (for example. two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

81. (a) Both the electron geometry and the molecular structure are octahedral. (b) Both the electron geometry and the molecular structure are trigonal bipyramid. (c) Both the electron geometry and the molecular structure are linear. (d) Both the electron geometry and the molecular structure are trigonal planar.

83. (a) electron-pair geometry: octahedral, molecular structure: square pyramidal; (b) electron-pair geometry: tetrahedral, molecular structure: bent; (c) electron-pair geometry: octahedral, molecular structure: square planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: trigonal bypyramidal, molecular structure: seesaw; (f) electron-pair geometry: tetrahedral, molecular structure: bent (109°)

85. (a) electron-pair geometry: trigonal planar, molecular structure: bent (120°); (b) electron-pair geometry: linear, molecular structure: linear; (c) electron-pair geometry: trigonal planar, molecular structure: trigonal planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: tetrahedral, molecular structure: tetrahedral; (f) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (g) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

87. All of these molecules and ions contain polar bonds. Only ClF_5, $ClO_2{}^-$, PCl_3, SeF_4, and $PH_2{}^-$ have dipole moments.

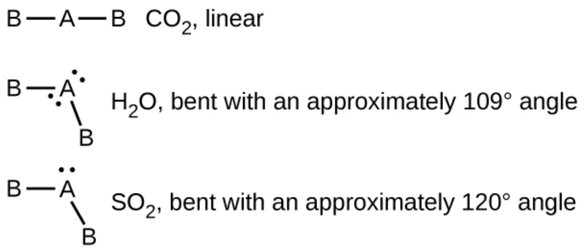
89. SeS_2, CCl_2F_2, PCl_3, and ClNO all have dipole moments.

91. P

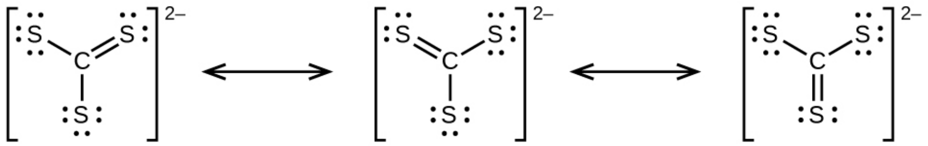
93. nonpolar

95. (a) tetrahedral; (b) trigonal pyramidal; (c) bent (109°); (d) trigonal planar; (e) bent (109°); (f) bent (109°); (g) $\underline{C}H_3CCH$ tetrahedral, $CH_3\underline{CC}H$ linear; (h) tetrahedral; (i) $H_2C\underline{C}CH_2$ linear; $H_2\underline{C}C\underline{C}H_2$ trigonal planar

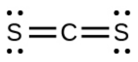
97.



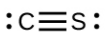
99. (a)



(b)

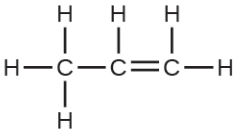


(c)



(d) $CS_3{}^{2-}$ includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar; CS_2 has only two regions of electron density (all bonds with no lone pairs); the shape is linear

101. The Lewis structure is made from three units, but the atoms must be rearranged:



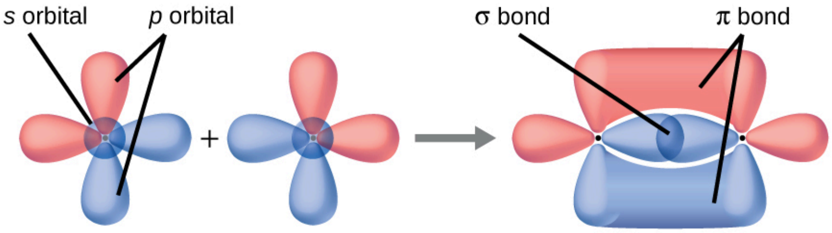
103. The molecular dipole points away from the hydrogen atoms.

105. The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as 109.5°. In the “real” mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of 104.5°.

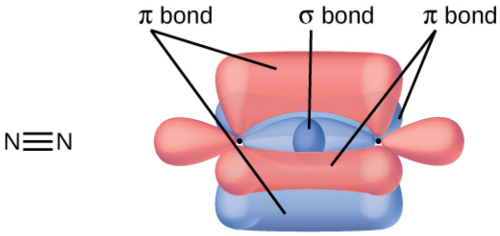
Chapter 5

1. Similarities: Both types of bonds result from overlap of atomic orbitals on adjacent atoms and contain a maximum of two electrons. Differences: σ bonds are stronger and result from end-to-end overlap and all single bonds are σ bonds; π bonds between the same two atoms are weaker because they result from side-by-side overlap, and multiple bonds contain one or more π bonds (in addition to a σ bond).

3. Bonding: One σ bond and one π bond. The *s* orbitals are filled and do not overlap. The *p* orbitals overlap along the axis to form a σ bond and side-by-side to form the π bond.



5. No, two of the *p* orbitals (one on each N) will be oriented end-to-end and will form a σ bond.

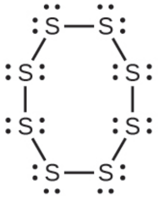


7. Hybridization is introduced to explain the geometry of bonding orbitals in valance bond theory.

9. There are no *d* orbitals in the valence shell of carbon.

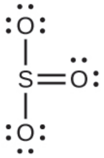
11. trigonal planar, sp^2; trigonal pyramidal (one lone pair on A) sp^3; T-shaped (two lone pairs on A sp^3d, or (three lone pairs on A) sp^3d^2

13. (a) Each S has a bent (109°) geometry, sp^3

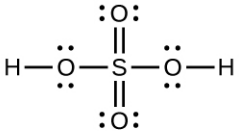


(b) Bent (120°), sp^2

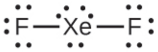
(c) Trigonal planar, sp^2



(d) Tetrahedral, sp^3

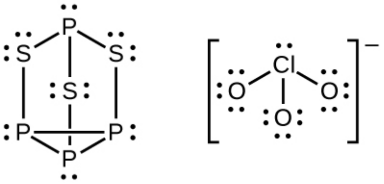


15. (a) XeF_2
(b)



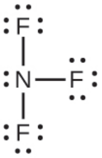
(c) linear (d) sp^3d

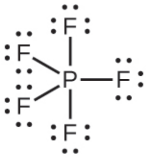
17. (a)



(b) P atoms, trigonal pyramidal; S atoms, bent, with two lone pairs; Cl atoms, trigonal pyramidal; (c) Hybridization about P, S, and Cl is, in all cases, sp^3; (d) Oxidation states P +1, S $-1\frac{1}{3}$, Cl +5, O –2. Formal charges: P 0; S 0; Cl +2: O –1

19.

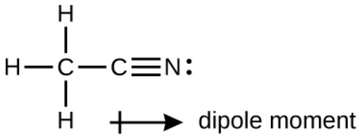




Phosphorus and nitrogen can form sp^3 hybrids to form three bonds and hold one lone pair in PF_3 and NF_3, respectively. However, nitrogen has no valence *d* orbitals, so it cannot form a set of sp^3d hybrid orbitals to bind five fluorine atoms in NF_5. Phosphorus has *d* orbitals and can bind five fluorine atoms with sp^3d hybrid orbitals in PF_5.

21. A triple bond consists of one σ bond and two π bonds. A σ bond is stronger than a π bond due to greater overlap.

23. (a)

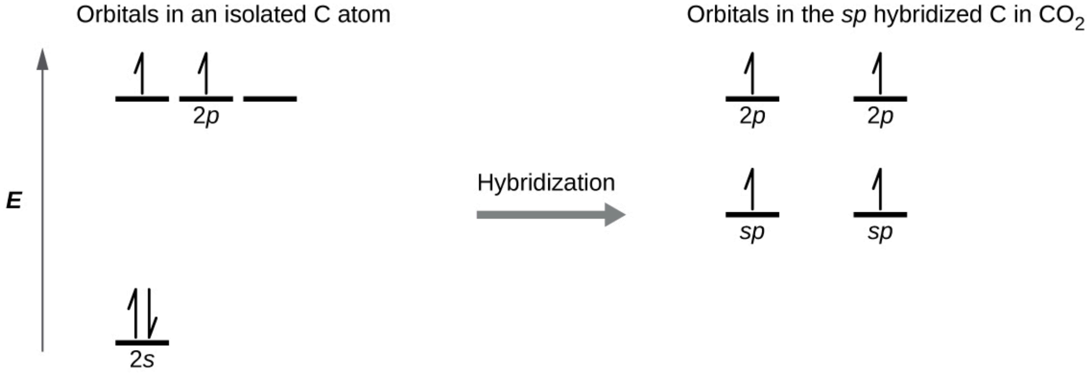


(b) The terminal carbon atom uses sp^3 hybrid orbitals, while the central carbon atom is *sp* hybridized. (c) Each of the two π bonds is formed by overlap of a 2*p* orbital on carbon and a nitrogen 2*p* orbital.

25. (a) sp^2; (b) *sp*; (c) sp^2; (d) sp^3; (e) sp^3; (f) sp^3d; (g) sp^3

27. (a) sp^2, delocalized; (b) *sp*, localized; (c) sp^2, delocalized; (d) sp^3, delocalized

29.



Each of the four electrons is in a separate orbital and overlaps with an electron on an oxygen atom.

31. (a) Similarities: Both are bonding orbitals that can contain a maximum of two electrons. Differences: σ orbitals are end-to-end combinations of atomic orbitals, whereas π orbitals are formed by side-by-side overlap of orbitals. (b) Similarities: Both are quantum-mechanical constructs that represent the probability of finding the electron about the atom or the molecule. Differences: ψ for an atomic orbital describes the behavior of only one electron at a time based on the atom. For a molecule, ψ represents a mathematical combination of atomic orbitals. (c) Similarities: Both are orbitals that can contain two electrons. Differences: Bonding orbitals result in holding two or more atoms together. Antibonding orbitals have the effect of destabilizing any bonding that has occurred.

33. An odd number of electrons can never be paired, regardless of the arrangement of the molecular orbitals. It will always be paramagnetic.

35. Bonding orbitals have electron density in close proximity to more than one nucleus. The interaction between the bonding positively charged nuclei and negatively charged electrons stabilizes the system.

37. The pairing of the two bonding electrons lowers the energy of the system relative to the energy of the nonbonded electrons.

39. (a) H_2 bond order = 1, $H_2{}^+$ bond order = 0.5, $H_2{}^-$ bond order = 0.5, strongest bond is H_2; (b) O_2 bond order = 2, $O_2{}^{2+}$ bond order = 3; $O_2{}^{2-}$ bond order = 1, strongest bond is $O_2{}^{2+}$; (c) Li_2 bond order = 1, $Be_2{}^+$ bond order = 0.5, Be_2 bond order = 0, strongest bond is Li_2; (d) F_2 bond order = 1, $F_2{}^+$ bond order = 1.5, $F_2{}^-$ bond order = 0.5, strongest bond is $F_2{}^+$; (e) N_2 bond order = 3, $N_2{}^+$ bond order = 2.5, $N_2{}^-$ bond order = 2.5, strongest bond is N_2

41. (a) H_2; (b) N_2; (c) O; (d) C_2; (e) B_2

43. Yes, fluorine is a smaller atom than Li, so atoms in the 2*s* orbital are closer to the nucleus and more stable.

45. 2+

47. N_2 has s-p mixing, so the π orbitals are the last filled in $N_2{}^{2+}$. O_2 does not have s-p mixing, so the σ_p orbital fills before the π orbitals.

Chapter 6

1. (a) 12.01 amu; (b) 12.01 amu; (c) 144.12 amu; (d) 60.05 amu

3. (a) 123.896 amu; (b) 18.015 amu; (c) 164.086 amu; (d) 60.052 amu; (e) 342.297 amu

5. (a) 56.107 amu;
(b) 54.091 amu;
(c) 199.9976 amu;
(d) 97.9950 amu

8. (a) % N = 82.24%
% H = 17.76%;
(b) % Na = 29.08%
% S = 40.56%
% O = 30.36%;
(c) % Ca^{2+} = 38.76%

10. % NH_3 = 38.2%

12. (a) CS_2
(b) CH_2O

14. C_6H_6

16. $Mg_3Si_2H_3O_8$ (empirical formula), $Mg_6Si_4H_6O_{16}$ (molecular formula)

18. $C_{15}H_{15}N_3$

20. We need to know the number of moles of sulfuric acid dissolved in the solution and the volume of the solution.

22. (a) 0.679 *M*; (b) 1.00 *M*; (c) 0.06998 *M*; (d) 1.75 *M*; (e) 0.070 *M*; (f) 6.6 *M*

24. (a) determine the number of moles of glucose in 0.500 L of solution; determine the molar mass of glucose; determine the mass of glucose from the number of moles and its molar mass; (b) 27 g

26. (a) 37.0 mol H_2SO_4, 3.63×10^3 g H_2SO_4; (b) 3.8×10^{-6} mol NaCN, 1.9×10^{-4} g NaCN; (c) 73.2 mol H_2CO, 2.20 kg H_2CO; (d) 5.9×10^{-7} mol $FeSO_4$, 8.9×10^{-5} g $FeSO_4$

28. (a) Determine the molar mass of $KMnO_4$; determine the number of moles of $KMnO_4$ in the solution; from the number of moles and the volume of solution, determine the molarity; (b) 1.15×10^{-3} *M*

30. (a) 5.04×10^{-3} *M*; (b) 0.499 *M*; (c) 9.92 *M*; (d) 1.1×10^{-3} *M*

32. 0.025 *M*

34. 0.5000 L

36. 1.9 mL

38. (a) 0.125 *M*; (b) 0.04888 *M*; (c) 0.206 *M*; (d) 0.0056 *M*

40. 11.9 *M*

42. 1.6 L

44. (a) The dilution equation can be used, appropriately modified to accommodate mass-based concentration units: $\%\text{mass}_1 \times \text{mass}_1 = \%\text{mass}_2 \times \text{mass}_2$. This equation can be rearranged to isolate mass_1 and the given quantities substituted into this equation. (b) 58.8 g

46. 114 g

48. 1.75×10^{-3} *M*

50. 95 mg/dL

52. 2.38×10^{-4} mol

54. 0.29 mol

Chapter 7

1. An equation is balanced when the same number of each element is represented on the reactant and product sides.

Equations must be balanced to accurately reflect the law of conservation of matter.

3. (a) $PCl_5(s) + H_2O(l) \longrightarrow POCl_3(l) + 2HCl(aq)$; (b) $3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$; (c) $H_2(g) + I_2(s) \longrightarrow 2HI(s)$; (d) $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$; (e) $2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$; (f) $(NH_4)_2Cr_2O_7(s) \longrightarrow Cr_2O_3(s) + N_2(g) + 4H_2O(g)$; (g) $P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(l)$; (h) $PtCl_4(s) \longrightarrow Pt(s) + 2Cl_2(g)$

5. (a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$; (b) $2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$; (c) $MgC1_2(aq) + 2NaOH(aq) \longrightarrow Mg(OH)_2(s) + 2NaCl(aq)$; (d) $2H_2O(g) + 2Na(s) \longrightarrow 2NaOH(s) + H_2(g)$

7. (a) $Ba(NO_3)_2$, $KClO_3$; (b) $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$; (c) $2Ba(NO_3)_2(s) \longrightarrow 2BaO(s) + 2N_2(g) + 5O_2(g)$; (d) $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$; $4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$; $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$

9. (a) $4HF(aq) + SiO_2(s) \longrightarrow SiF_4(g) + 2H_2O(l)$; (b) complete ionic equation: $2Na^+(aq) + 2F^-(aq) + Ca^{2+}(aq) + 2Cl^-(aq) \longrightarrow CaF_2(s) + 2Na^+(aq) + 2Cl^-(aq)$, net ionic equation: $2F^-(aq) + Ca^{2+}(aq) \longrightarrow CaF_2(s)$

11. (a)

$$2K^+(aq) + C_2O_4{}^{2-}(aq) + Ba^{2+}(aq) + 2OH^-(aq) \longrightarrow 2K^+(aq) + 2OH^-(aq) + BaC_2O_4(s) \qquad \text{(complete)}$$

$$Ba^{2+}(aq) + C_2O_4{}^{2-}(aq) \longrightarrow BaC_2O_4(s) \qquad \text{(net)}$$

(b)

$$Pb^{2+}(aq) + 2NO_3{}^-(aq) + 2H^+(aq) + SO_4{}^{2-}(aq) \longrightarrow PbSO_4(s) + 2H^+(aq) + 2NO_3{}^-(aq) \qquad \text{(complete)}$$

$$Pb^{2+}(aq) + SO_4{}^{2-}(aq) \longrightarrow PbSO_4(s) \qquad \text{(net)}$$

(c)

$$CaCO_3(s) + 2H^+(aq) + SO_4{}^{2-}(aq) \longrightarrow CaSO_4(s) + CO_2(g) + H_2O(l) \qquad \text{(complete)}$$

$$CaCO_3(s) + 2H^+(aq) + SO_4{}^{2-}(aq) \longrightarrow CaSO_4(s) + CO_2(g) + H_2O(l) \qquad \text{(net)}$$

13. (a) oxidation-reduction (addition); (b) acid-base (neutralization); (c) oxidation-reduction (combustion)

15. It is an oxidation-reduction reaction because the oxidation state of the silver changes during the reaction.

17. (a) H +1, P +5, O −2; (b) Al +3, H +1, O −2; (c) Se +4, O −2; (d) K +1, N +3, O −2; (e) In +3, S −2; (f) P +3, O −2

19. (a) acid-base; (b) oxidation-reduction: Na is oxidized, H^+ is reduced; (c) oxidation-reduction: Mg is oxidized, Cl_2 is reduced; (d) acid-base; (e) oxidation-reduction: P^{3-} is oxidized, O_2 is reduced; (f) acid-base

21. (a) $2HCl(g) + Ca(OH)_2(s) \longrightarrow CaCl_2(s) + 2H_2O(l)$; (b) $Sr(OH)_2(aq) + 2HNO_3(aq) \longrightarrow Sr(NO_3)_2(aq) + 2H_2O(l)$

23. (a) $2Al(s) + 3F_2(g) \longrightarrow 2AlF_3(s)$; (b) $2Al(s) + 3CuBr_2(aq) \longrightarrow 3Cu(s) + 2AlBr_3(aq)$; (c) $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$; (d) $Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$

25. (a) $Mg(OH)_2(s) + 2HClO_4(aq) \longrightarrow Mg^{2+}(aq) + 2ClO_4{}^-(aq) + 2H_2O(l)$; (b) $SO_3(g) + 2H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4{}^-(aq)$, (a solution of H_2SO_4); (c) $SrO(s) + H_2SO_4(l) \longrightarrow SrSO_4(s) + H_2O$

27. $H_2(g) + F_2(g) \longrightarrow 2HF(g)$

29. $2NaBr(aq) + Cl_2(g) \longrightarrow 2NaCl(aq) + Br_2(l)$

31. $2LiOH(aq) + CO_2(g) \longrightarrow Li_2CO_3(aq) + H_2O(l)$

33. (a) $Ca(OH)_2(s) + H_2S(g) \longrightarrow CaS(s) + 2H_2O(l)$; (b) $Na_2CO_3(aq) + H_2S(g) \longrightarrow Na_2S(aq) + CO_2(g) + H_2O(l)$

35. (a) step 1: $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, step 2:

$NH_3(g) + HNO_3(aq) \longrightarrow NH_4NO_3(aq) \longrightarrow NH_4NO_3(s)$ (after drying); (b) $H_2(g) + Br_2(l) \longrightarrow 2HBr(g)$; (c) $Zn(s) + S(s) \longrightarrow ZnS(s)$ and $ZnS(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2S(g)$

37. (a) $Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$, (b) $[Ag(NH_3)_2]^+(aq) + e^- \longrightarrow Ag(s) + 2NH_3(aq)$; (c) $Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$; (d) $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$; (e) $6H_2O(l) + 2IO_3{}^-(aq) + 10e^- \longrightarrow I_2(s) + 12OH^-(aq)$; (f) $H_2O(l) + SO_3{}^{2-}(aq) \longrightarrow SO_4{}^{2-}(aq) + 2H^+(aq) + 2e^-$; (g) $8H^+(aq) + MnO_4{}^-(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$; (h) $Cl^-(aq) + 6OH^-(aq) \longrightarrow ClO_3{}^-(aq) + 3H_2O(l) + 6e^-$

39. (a) $Sn^{2+}(aq) + 2Cu^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2Cu^+(aq)$; (b) $H_2S(g) + Hg_2{}^{2+}(aq) + 2H_2O(l) \longrightarrow 2Hg(l) + S(s) + 2H_3O^+(aq)$; (c) $5CN^-(aq) + 2ClO_2(aq) + 3H_2O(l) \longrightarrow 5CNO^-(aq) + 2Cl^-(aq) + 2H_3O^+(aq)$; (d) $Fe^{2+}(aq) + Ce^{4+}(aq) \longrightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$; (e) $2HBrO(aq) + 2H_2O(l) \longrightarrow 2H_3O^+(aq) + 2Br^-(aq) + O_2(g)$

41. (a) $2MnO_4{}^-(aq) + 3NO_2{}^-(aq) + H_2O(l) \longrightarrow 2MnO_2(s) + 3NO_3{}^-(aq) + 2OH^-(aq)$; (b) $3MnO_4{}^{2-}(aq) + 2H_2O(l) \longrightarrow 2MnO_4{}^-(aq) + 4OH^-(aq) + MnO_2(s)$ (in base); (c) $Br_2(l) + SO_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 2Br^-(aq) + SO_4{}^{2-}(aq)$

43. (a) 0.435 mol Na, 0.217 mol Cl_2, 15.4 g Cl_2; (b) 0.005780 mol HgO, 2.890×10^{-3} mol O_2, 9.248×10^{-2} g O_2; (c) 8.00 mol $NaNO_3$, 6.8×10^2 g $NaNO_3$; (d) 1665 mol CO_2, 73.3 kg CO_2; (e) 18.86 mol CuO, 2.330 kg $CuCO_3$; (f) 0.4580 mol $C_2H_4Br_2$, 86.05 g $C_2H_4Br_2$

45. (a) 0.0686 mol Mg, 1.67 g Mg; (b) 2.701×10^{-3} mol O_2, 0.08644 g O_2; (c) 6.43 mol $MgCO_3$, 542 g $MgCO_3$ (d) 713 mol H_2O, 12.8 kg H_2O; (e) 16.31 mol BaO_2, 2762 g BaO_2; (f) 0.207 mol C_2H_4, 5.81 g C_2H_4

47. (a) volume HCl solution $\longrightarrow$ mol HCl $\longrightarrow$ mol $GaCl_3$; (b) 1.25 mol $GaCl_3$, 2.2×10^2 g $GaCl_3$

49. (a) 5.337×10^{22} molecules; (b) 10.41 g $Zn(CN)_2$

51. $SiO_2 + 3C \longrightarrow SiC + 2CO$, 4.50 kg SiO_2

53. 5.00×10^3 kg

55. 1.28×10^5 g CO_2

57. 161.40 mL KI solution

59. 176 g TiO_2

61. The limiting reactant is Cl2.

63. Percent yield = 31%

65. g $CCl_4 \longrightarrow$ mol $CCl_4 \longrightarrow$ mol $CCl_2F_2 \longrightarrow$ g CCl_2F_2, percent yield = 48.3%

67. percent yield = 91.3%

69. Convert mass of ethanol to moles of ethanol; relate the moles of ethanol to the moles of ether produced using the stoichiometry of the balanced equation. Convert moles of ether to grams; divide the actual grams of ether (determined through the density) by the theoretical mass to determine the percent yield; 87.6%

71. The conversion needed is mol Cr $\longrightarrow$ mol H_3PO_4. Then compare the amount of Cr to the amount of acid present. Cr is the limiting reactant.

73. $Na_2C_2O_4$ is the limiting reactant. percent yield = 86.6%

75. Only four molecules can be made.

77. This amount cannot be weighted by ordinary balances and is worthless.

79. 3.4×10^{-3} M H_2SO_4

81. 9.6×10^{-3} *M* Cl^-

83. 22.4%

85. The empirical formula is BH_3. The molecular formula is B_2H_6.

87. 49.6 mL

89. 13.64 mL

91. 0.0122 *M*

93. 34.99 mL KOH

95. The empirical formula is WCl_4.

Chapter 8

1. The cutting edge of a knife that has been sharpened has a smaller surface area than a dull knife. Since pressure is force per unit area, a sharp knife will exert a higher pressure with the same amount of force and cut through material more effectively.

3. Lying down distributes your weight over a larger surface area, exerting less pressure on the ice compared to standing up. If you exert less pressure, you are less likely to break through thin ice.

5. 0.809 atm; 82.0 kPa

7. 2.2×10^2 kPa

9. Earth: 14.7 lb in^{-2}; Venus: 1.31×10^3 lb in^{-2}

11. (a) 101.5 kPa; (b) 51 torr drop

13. (a) 264 torr; (b) 35,200 Pa; (c) 0.352 bar

15. (a) 623 mm Hg; (b) 0.820 atm; (c) 83.1 kPa

17. With a closed-end manometer, no change would be observed, since the vaporized liquid would contribute equal, opposing pressures in both arms of the manometer tube. However, with an open-ended manometer, a higher pressure reading of the gas would be obtained than expected, since $P_{\text{gas}} = P_{\text{atm}} + P_{\text{vol liquid}}$.

19. As the bubbles rise, the pressure decreases, so their volume increases as suggested by Boyle's law.

21. (a) The number of particles in the gas increases as the volume increases. (b) temperature, pressure

23. The curve would be farther to the right and higher up, but the same basic shape.

25. About 12.5 L

27. 3.40×10^3 torr

29. 12.1 L

31. 217 L

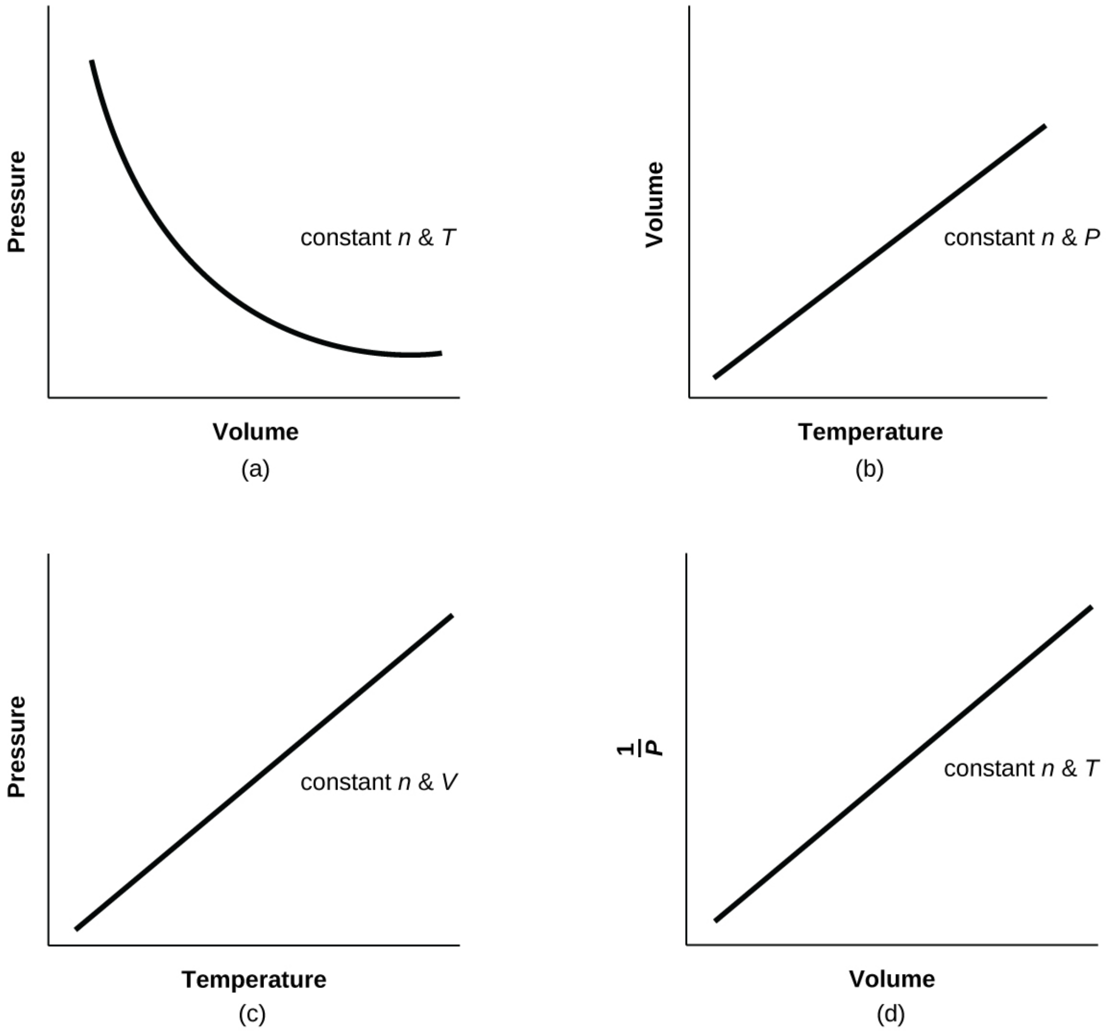
33. 8.190×10^{-2} mol; 5.553 g

35. (a) 7.24×10^{-2} g; (b) 23.1 g; (c) 1.5×10^{-4} g

37. 5561 L

39. 46.4 g

41. For a gas exhibiting ideal behavior:



43. (a) 1.85 L CCl_2F_2; (b) 4.66 L CH_3CH_2F

45. 0.644 atm

47. The pressure decreases by a factor of 3.

49. 4.64 g L^{-1}

51. 38.8 g

53. 72.0 g mol^{-1}

55. 88.1 g mol^{-1}; PF_3

57. 141 atm

59. CH_4: 276 kPa; C_2H_6: 27 kPa; C_3H_8: 3.4 kPa

61. Yes

63. 740 torr

65. (a) Determine the moles of HgO that decompose; using the chemical equation, determine the moles of O_2 produced by decomposition of this amount of HgO; and determine the volume of O_2 from the moles of O_2, temperature, and pressure. (b) 0.308 L

67. (a) Determine the molar mass of CCl_2F_2. From the balanced equation, calculate the moles of H_2 needed for the complete reaction. From the ideal gas law, convert moles of H_2 into volume. (b) 3.72×10^3 L

69. (a) Balance the equation. Determine the grams of CO_2 produced and the number of moles. From the ideal gas law, determine the volume of gas. (b) 7.43×10^5 L

71. 42.00 L

73. (a) 18.0 L; (b) 0.533 atm

75. 10.57 L O_2

77. 5.40×10^5 L

79. XeF_2

81. 4.2 hours

83. Effusion can be defined as the process by which a gas escapes through a pinhole into a vacuum. Graham's law states that with a mixture of two gases A and B: $\left(\frac{\text{rate A}}{\text{rate B}}\right) = \left(\frac{\text{molar mass of B}}{\text{molar mass of A}}\right)^{1/2}$. Both A and B are in the same container at the same temperature, and therefore will have the same kinetic energy:

$$\text{KE}_\text{A} = \text{KE}_\text{B}\ \text{KE} = \frac{1}{2}mv^2$$

Therefore, $\frac{1}{2}m_\text{A}v_\text{A}^2 = \frac{1}{2}m_\text{B}v_\text{B}^2$

$$\frac{v_\text{A}^2}{v_\text{B}^2} = \frac{m_\text{B}}{m_\text{A}}$$

$$\left(\frac{v_\text{A}^2}{v_\text{B}^2}\right)^{1/2} = \left(\frac{m_\text{B}}{m_\text{A}}\right)^{1/2}$$

$$\frac{v_\text{A}}{v_\text{B}} = \left(\frac{m_\text{B}}{m_\text{A}}\right)^{1/2}$$

85. F_2, N_2O, Cl_2, H_2S

87. 1.4; 1.2

89. 51.7 cm

91. Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The average velocity of all the molecules is constant at constant temperature.

93. H_2O. Cooling slows the velocities of the He atoms, causing them to behave as though they were heavier.

95. (a) The number of collisions per unit area of the container wall is constant. (b) The average kinetic energy doubles. (c) The root mean square speed increases to $\sqrt{2}$ times its initial value; u_rms is proportional to $\sqrt{\text{KE}_\text{avg}}$.

97. (a) equal; (b) less than; (c) 29.48 g mol^{-1}; (d) 1.0966 g L^{-1}; (e) 0.129 g/L; (f) 4.01×10^5 g; net lifting capacity = 384 lb; (g) 270 L; (h) 39.1 kJ min^{-1}

99. Gases C, E, and F

101. The gas behavior most like an ideal gas will occur under the conditions in (b). Molecules have high speeds and move through greater distances between collision; they also have shorter contact times and interactions are less likely. Deviations occur with the conditions described in (a) and (c). Under conditions of (a), some gases may liquefy. Under conditions of (c), most gases will liquefy.

103. SF_6

105. (a) A straight horizontal line at 1.0; (b) When real gases are at low pressures and high temperatures, they behave close enough to ideal gases that they are approximated as such; however, in some cases, we see that at a high pressure and temperature, the ideal gas approximation breaks down and is significantly different from the pressure calculated by the ideal gas equation. (c) The greater the compressibility, the more the volume matters. At low pressures, the correction factor for intermolecular attractions is more significant, and the effect of the volume of the gas molecules on Z would be a small lowering compressibility. At higher pressures, the effect of the volume of the gas molecules themselves on Z would increase compressibility (see **Figure 8.35**). (d) Once again, at low pressures, the effect of intermolecular attractions on Z would be more important than the correction factor for the volume of the gas molecules themselves, though perhaps still small. At higher pressures and low temperatures, the effect of intermolecular attractions would be larger. See **Figure 8.35** . (e) Low temperatures

Chapter 9

1. The temperature of 1 gram of burning wood is approximately the same for both a match and a bonfire. This is an intensive property and depends on the material (wood). However, the overall amount of produced heat depends on the amount of material; this is an extensive property. The amount of wood in a bonfire is much greater than that in a match; the total amount of produced heat is also much greater, which is why we can sit around a bonfire to stay warm, but a match would not provide enough heat to keep us from getting cold.

3. Heat capacity refers to the heat required to raise the temperature of the mass of the substance 1 degree; specific heat refers to the heat required to raise the temperature of 1 gram of the substance 1 degree. Thus, heat capacity is an extensive property, and specific heat is an intensive one.

5. (a) 47.6 J/°C; 11.38 cal $°C^{-1}$; (b) 407 J/°C; 97.3 cal $°C^{-1}$

7. 1310 J; 313 cal

9. 7.15 °C

11. (a) 0.390 J/g °C; (b) Copper is a likely candidate.

13. We assume that the density of water is 1.0 g/cm^3(1 g/mL) and that it takes as much energy to keep the water at 85 °F as to heat it from 72 °F to 85 °F. We also assume that only the water is going to be heated. Energy required = 7.47 kWh

15. lesser; more heat would be lost to the coffee cup and the environment and so ΔT for the water would be lesser and the calculated q would be lesser

17. greater, since taking the calorimeter's heat capacity into account will compensate for the thermal energy transferred to the solution from the calorimeter; this approach includes the calorimeter itself, along with the solution, as "surroundings": $q_{\text{rxn}} = -(q_{\text{solution}} + q_{\text{calorimeter}})$; since both q_{solution} and $q_{\text{calorimeter}}$ are negative, including the latter term (q_{rxn}) will yield a greater value for the heat of the dissolution

19. The temperature of the coffee will drop 1 degree.

21. 5.7×10^2 kJ

23. 38.5 °C

25. −2.2 kJ; The heat produced shows that the reaction is exothermic.

27. 1.4 kJ

29. 22.6. Since the mass and the heat capacity of the solution is approximately equal to that of the water, the two-fold increase in the amount of water leads to a two-fold decrease of the temperature change.

31. 11.7 kJ

33. 30%

35. 0.24 g

37. 1.4×10^2 Calories

39. The enthalpy change of the indicated reaction is for exactly 1 mol HCL and 1 mol NaOH; the heat in the example is produced by 0.0500 mol HCl and 0.0500 mol NaOH.

41. 25 kJ mol^{-1}

43. 81 kJ mol^{-1}

45. 5204.4 kJ

47. 1.83×10^{-2} mol

49. –802 kJ mol^{-1}

51. 15.5 kJ/ºC

53. 7.43 g

55. Yes.

57. 459.6 kJ

59. −495 kJ/mol

61. 44.01 kJ/mol

63. −394 kJ

65. 265 kJ

67. 90.3 kJ/mol

69. (a) −1615.0 kJ mol^{-1}; (b) −484.3 kJ mol^{-1}; (c) 164.2 kJ; (d) −232.1 kJ

71. −54.04 kJ mol^{-1}

73. −2660 kJ mol^{-1}

75. 67.1 kJ

77. −122.8 kJ

79. 3.7 kg

81. On the assumption that the best rocket fuel is the one that gives off the most heat, B_2H_6 is the prime candidate.

83. −88.2 kJ

85. (a) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$; (b) 330 L; (c) −104.5 kJ mol^{-1}; (d) 75.4 °C

88. (a) −114 kJ;
(b) 30 kJ;
(c) −1055 kJ

91. The specific average bond distance is the distance with the lowest energy. At distances less than the bond distance, the positive charges on the two nuclei repel each other, and the overall energy increases.

92. The greater bond energy is in the figure on the left. It is the more stable form.

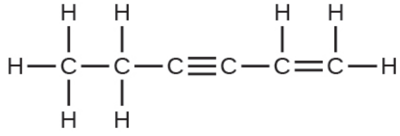
94.

$$\begin{array}{ll}
\text{HCl}(g) \longrightarrow \frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{Cl}_2(g) & \Delta H_1^\circ = -\Delta H^\circ_{\text{f[HCl}(g)]} \\
\frac{1}{2}\text{H}_2(g) \longrightarrow \text{H}(g) & \Delta H_2^\circ = \Delta H^\circ_{\text{f[H}(g)]} \\
\frac{1}{2}\text{Cl}_2(g) \longrightarrow \text{Cl}(g) & \Delta H_3^\circ = \Delta H^\circ_{\text{f[Cl}(g)]} \\
\hline
\text{HCl}(g) \longrightarrow \text{H}(g) + \text{Cl}(g) & \Delta H^\circ_{298} = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ
\end{array}$$

$$\begin{aligned}
D_{\text{HCl}} = \Delta H^\circ_{298} &= \Delta H^\circ_{\text{f[HCl}(g)]} + \Delta H^\circ_{\text{f[H}(g)]} + \Delta H^\circ_{\text{f[Cl}(g)]} \\
&= -(-92.307\text{ kJ}) + 217.97\text{ kJ} + 121.3\text{ kJ} \\
&= 431.6\text{ kJ}
\end{aligned}$$

96. The S–F bond in SF_4 is stronger.

98.



The C–C single bonds are longest.

100. (a) When two electrons are removed from the valence shell, the Ca radius loses the outermost energy level and reverts to the lower *n* = 3 level, which is much smaller in radius. (b) The +2 charge on calcium pulls the oxygen much closer compared with K, thereby increasing the lattice energy relative to a less charged ion. (c) Removal of the 4*s* electron in Ca requires more energy than removal of the 4*s* electron in K because of the stronger attraction of the nucleus and the extra energy required to break the pairing of the electrons. The second ionization energy for K requires that an electron be removed from a lower energy level, where the attraction is much stronger from the nucleus for the electron. In addition, energy is required to unpair two electrons in a full orbital. For Ca, the second ionization potential requires removing only a lone electron in the exposed outer energy level. (d) In Al, the removed electron is relatively unprotected and unpaired in a *p* orbital. The higher energy for Mg mainly reflects the unpairing of the 2*s* electron.

102. (d)

104. 4008 kJ/mol; both ions in MgO have twice the charge of the ions in LiF; the bond length is very similar and both have the same structure; a quadrupling of the energy is expected based on the equation for lattice energy

106. (a) Na_2O; Na^+ has a smaller radius than K^+; (b) BaS; Ba has a larger charge than K; (c) BaS; Ba and S have larger charges; (d) BaS; S has a larger charge

108. (e)

Chapter 10

1. Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.

3. They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.

5. All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.

7. (a) Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (e.g., Ar). (b) A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (e.g., ICI molecules attract one another by dipole-dipole interaction). (c) Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, or nitrogen atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (e.g., $\text{HF}\cdots\text{HF}$).

9. The London forces typically increase as the number of electrons increase.

11. (a) $SiH_4 < HCl < H_2O$; (b) $F_2 < Cl_2 < Br_2$; (c) $CH_4 < C_2H_6 < C_3H_8$; (d) $N_2 < O_2 < NO$

13. Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction, therefore, is stronger, leading to a higher boiling point.

15. −85 °C. Water has stronger hydrogen bonds, so it melts at a higher temperature.

17. The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.

19. H-bonding is the principle IMF holding the protein strands together. The H-bonding is between the $\text{N}-\text{H}$ and $\text{C}=\text{O}$.

21. (a) hydrogen bonding, dipole-dipole attraction, and dispersion forces; (b) dispersion forces; (c) dipole-dipole attraction and dispersion forces

23. The water molecules have strong intermolecular forces of hydrogen bonding. The water molecules are thus attracted strongly to one another and exhibit a relatively large surface tension, forming a type of “skin” at its surface. This skin can support a bug or paper clip if gently placed on the water.

25. Temperature has an effect on intermolecular forces: The higher the temperature, the greater the kinetic energies of the molecules and the greater the extent to which their intermolecular forces are overcome, and so the more fluid (less viscous) the liquid. The lower the temperature, the less the intermolecular forces are overcome, and so the less viscous the liquid.

27. (a) As the water reaches higher temperatures, the increased kinetic energies of its molecules are more effective in overcoming hydrogen bonding, and so its surface tension decreases. Surface tension and intermolecular forces are directly related. (b) The same trend in viscosity is seen as in surface tension, and for the same reason.

29. 1.7×10^{-4} m

31. The heat is absorbed by the ice, providing the energy required to partially overcome intermolecular attractive forces in the solid and causing a phase transition to liquid water. The solution remains at 0 °C until all the ice is melted. Only the amount of water existing as ice changes until the ice disappears. Then the temperature of the water can rise.

33. We can see the amount of liquid in an open container decrease and we can smell the vapor of some liquids.

35. The vapor pressure of a liquid decreases as the strength of its intermolecular forces increases.

37. As the temperature increases, the average kinetic energy of the molecules of gasoline increases and so a greater fraction of molecules have sufficient energy to escape from the liquid than at lower temperatures.

39. They are equal when the pressure of gas above the liquid is exactly 1 atm.

41. approximately 95 °C

43. (a) At 5000 feet, the atmospheric pressure is lower than at sea level, and water will therefore boil at a lower temperature. This lower temperature will cause the physical and chemical changes involved in cooking the egg to proceed more slowly, and a longer time is required to fully cook the egg. (b) As long as the air surrounding the body contains less water vapor than the maximum that air can hold at that temperature, perspiration will evaporate, thereby cooling the body by removing the heat of vaporization required to vaporize the water.

45. Dispersion forces increase with molecular mass or size. As the number of atoms composing the molecules in this homologous series increases, so does the extent of intermolecular attraction via dispersion forces and, consequently, the energy required to overcome these forces and vaporize the liquids.

47. The boiling point of CS_2 is higher than that of CO_2 partially because of the higher molecular weight of CS_2; consequently, the attractive forces are stronger in CS_2. It would be expected, therefore, that the heat of vaporization would be greater than that of 9.8 kJ/mol for CO_2. A value of 28 kJ/mol would seem reasonable. A value of −8.4 kJ/mol would indicate a release of energy upon vaporization, which is clearly implausible.

49. The thermal energy (heat) needed to evaporate the liquid is removed from the skin.

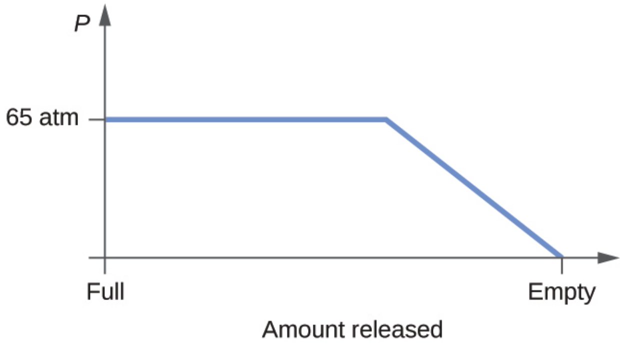
51. 1130 kJ

53. (a) 13.0 kJ; (b) It is likely that the heat of vaporization will have a larger magnitude since in the case of vaporization the intermolecular interactions have to be completely overcome, while melting weakens or destroys only some of them.

55. At low pressures and 0.005 °C, the water is a gas. As the pressure increases to 4.6 torr, the water becomes a solid; as the pressure increases still more, it becomes a liquid. At 40 °C, water at low pressure is a vapor; at pressures higher than about 75 torr, it converts into a liquid. At −40 °C, water goes from a gas to a solid as the pressure increases above very low values.

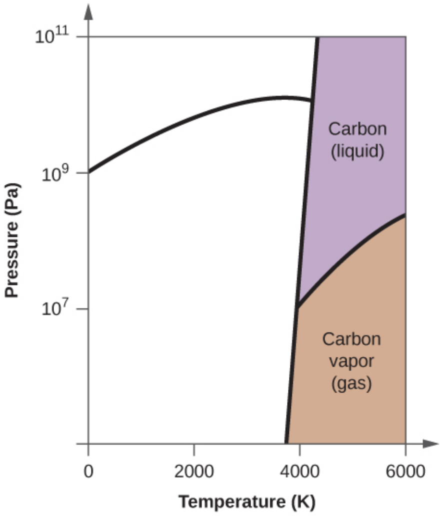
57. (a) gas; (b) gas; (c) gas; (d) gas; (e) solid; (f) gas

59.

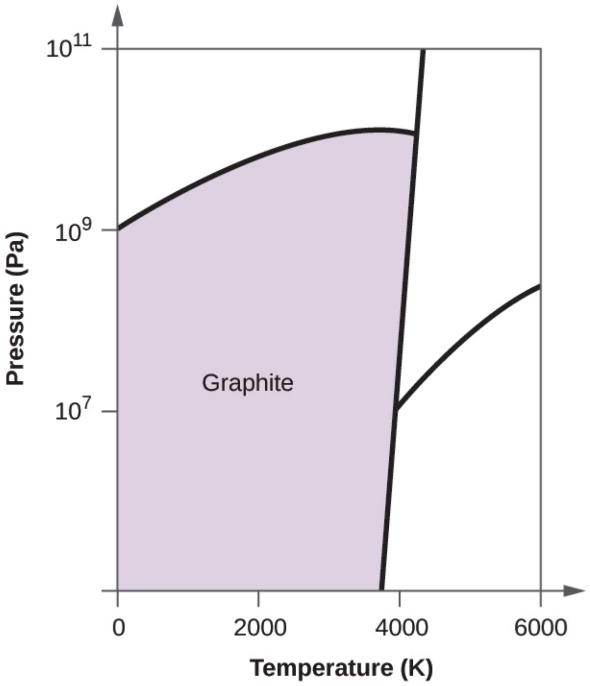


61. Yes, ice will sublime, although it may take it several days. Ice has a small vapor pressure, and some ice molecules form gas and escape from the ice crystals. As time passes, more and more solid converts to gas until eventually the clothes are dry.

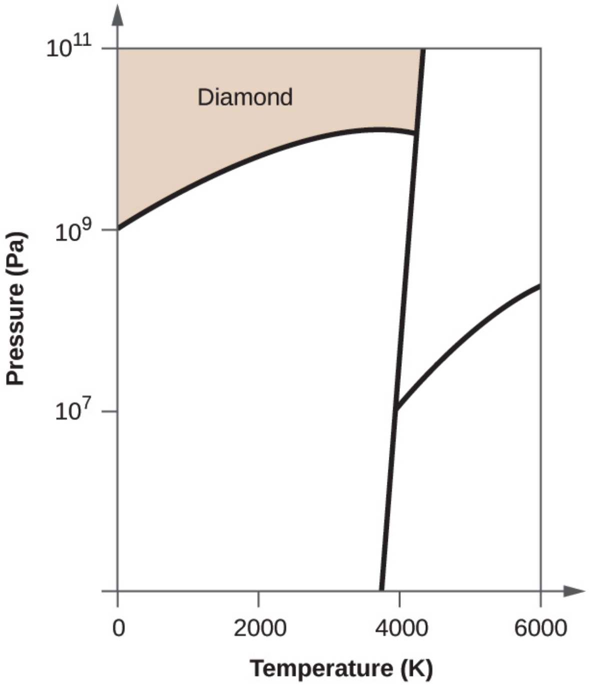
63. (a)



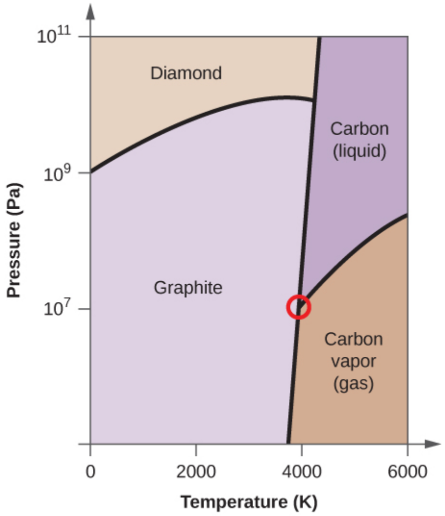
(b)


10^11
10^9
10^7
Pressure (Pa)
Graphite
0
2000
4000
6000
Temperature (K)

(c)


10^11
10^9
10^7
Pressure (Pa)
Diamond
0
2000
4000
6000
Temperature (K)

(d)



(e) liquid phase (f) sublimation

65. (e) molecular crystals

67. Ice has a crystalline structure stabilized by hydrogen bonding. These intermolecular forces are of comparable strength and thus require the same amount of energy to overcome. As a result, ice melts at a single temperature and not over a range of temperatures. The various, very large molecules that compose butter experience varied van der Waals attractions of various strengths that are overcome at various temperatures, and so the melting process occurs over a wide temperature range.

69. (a) ionic; (b) covalent network; (c) molecular; (d) metallic; (e) covalent network; (f) molecular; (g) molecular; (h) ionic; (i) ionic

71. X = ionic; Y = metallic; Z = covalent network

73. (b) metallic solid

75. The structure of this low-temperature form of iron (below 910 °C) is body-centered cubic. There is one-eighth atom at each of the eight corners of the cube and one atom in the center of the cube.

77. eight

79. 12

81. (a) 1.370 Å; (b) 19.26 g/cm

83. (a) 2.176 Å; (b) 3.595 g/cm^3

85. The crystal structure of Si shows that it is less tightly packed (coordination number 4) in the solid than Al (coordination number 12).

87. In a closest-packed array, two tetrahedral holes exist for each anion. If only half the tetrahedral holes are occupied, the numbers of anions and cations are equal. The formula for cadmium sulfide is CdS.

89. Co_3O_4

91. In a simple cubic array, only one cubic hole can be occupied be a cation for each anion in the array. The ratio of thallium to iodide must be 1:1; therefore, the formula for thallium is TlI.

93. 59.95%; The oxidation number of titanium is +4.

95. Both ions are close in size: Mg, 0.65; Li, 0.60. This similarity allows the two to interchange rather easily. The difference in charge is generally compensated by the switch of Si^{4+} for Al^{3+}.

97. Mn_2O_3

99. 1.48 Å

101. 2.874 Å

103. 20.2°

105. 1.74×10^4 eV

Chapter 11

1. A solution can vary in composition, while a compound cannot vary in composition. Solutions are homogeneous at the molecular level, while other mixtures are heterogeneous.

3. (a) The process is endothermic as the solution is consuming heat. (b) Attraction between the K^+ and $NO_3{}^-$ ions is stronger than between the ions and water molecules (the ion-ion interactions have a lower, more negative energy). Therefore, the dissolution process increases the energy of the molecular interactions, and it consumes the thermal energy of the solution to make up for the difference. (c) No, an ideal solution is formed with no appreciable heat release or consumption.

5. (a) ion-dipole forces; (b) dipole-dipole forces; (c) dispersion forces; (d) dispersion forces; (e) hydrogen bonding

7. Heat is released when the total intermolecular forces (IMFs) between the solute and solvent molecules are stronger than the total IMFs in the pure solute and in the pure solvent: Breaking weaker IMFs and forming stronger IMFs releases heat. Heat is absorbed when the total IMFs in the solution are weaker than the total of those in the pure solute and in the pure solvent: Breaking stronger IMFs and forming weaker IMFs absorbs heat.

9. Crystals of NaCl dissolve in water, a polar liquid with a very large dipole moment, and the individual ions become strongly solvated. Hexane is a nonpolar liquid with a dipole moment of zero and, therefore, does not significantly interact with the ions of the NaCl crystals.

11. (a) $Fe(NO_3)_3$ is a strong electrolyte, thus it should completely dissociate into Fe^{3+} and $NO_3{}^-$ ions. Therefore, (z) best represents the solution. (b) $\text{Fe(NO}_3)_3(s) \longrightarrow \text{Fe}^{3+}(aq) + 3\text{NO}_3{}^-(aq)$

13. (a) high conductivity (solute is an ionic compound that will dissociate when dissolved); (b) high conductivity (solute is a strong acid and will ionize completely when dissolved); (c) nonconductive (solute is a covalent compound, neither acid nor base, unreactive towards water); (d) low conductivity (solute is a weak base and will partially ionize when dissolved)

15. (a) ion-dipole; (b) hydrogen bonds; (c) dispersion forces; (d) dipole-dipole attractions; (e) dispersion forces

17. The solubility of solids usually decreases upon cooling a solution, while the solubility of gases usually decreases upon heating.

19. 40%

21. 2.8 g

23. 2.9 atm

25. 102 L HCl

27. The strength of the bonds between like molecules is stronger than the strength between unlike molecules. Therefore, some regions will exist in which the water molecules will exclude oil molecules and other regions will exist in which oil molecules will exclude water molecules, forming a heterogeneous region.

29. Both form homogeneous solutions; their boiling point elevations are the same, as are their lowering of vapor pressures. Osmotic pressure and the lowering of the freezing point are also the same for both solutions.

31. (a) Find number of moles of HNO_3 and H_2O in 100 g of the solution. Find the mole fractions for the components. (b) The mole fraction of HNO_3 is 0.378. The mole fraction of H_2O is 0.622.

33. (a) $X_{\text{Na}_2\text{CO}_3} = 0.0119;$ $X_{\text{H}_2\text{O}} = 0.988;$ (b) $X_{\text{NH}_4\text{NO}_3} = 0.0928;$ $X_{\text{H}_2\text{O}} = 0.907;$ (c) $X_{\text{Cl}_2} = 0.192;$ $X_{\text{CH}_2\text{CI}_2} = 0.808;$ (d) $X_{\text{C}_5\text{H}_9\text{N}} = 0.00426;$ $X_{\text{CHCl}_3} = 0.997$

35. In a 1 *M* solution, the mole is contained in exactly 1 L of solution. In a 1 *m* solution, the mole is contained in exactly 1 kg of solvent.

37. (a) Determine the molar mass of HNO_3. Determine the number of moles of acid in the solution. From the number of moles and the mass of solvent, determine the molality. (b) 33.7 *m*

39. (a) 6.70×10^{-1} *m*; (b) 5.67 *m*; (c) 2.8 *m*; (d) 0.0358 *m*

41. 1.08 *m*

43. (a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the boiling point of water and the boiling point of the solution; determine the new boiling point. (b) 100.5 °C

45. (a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the freezing temperature of water and the freezing temperature of the solution; determine the new freezing temperature. (b) −1.8 °C

47. (a) Determine the molar mass of $Ca(NO_3)_2$; determine the number of moles of $Ca(NO_3)_2$ in the solution; determine the number of moles of ions in the solution; determine the molarity of ions, then the osmotic pressure. (b) 2.67 atm

49. (a) Determine the molal concentration from the change in boiling point and K_b; determine the moles of solute in the solution from the molal concentration and mass of solvent; determine the molar mass from the number of moles and the mass of solute. (b) 2.1×10^2 g mol^{-1}

51. No. Pure benzene freezes at 5.5 °C, and so the observed freezing point of this solution is depressed by $\Delta T_f = 5.5 - 0.4 = 5.1$ °C. The value computed, assuming no ionization of HCl, is $\Delta T_f = (1.0\text{ m})(5.14\text{ °C}/m) = 5.1$ °C. Agreement of these values supports the assumption that HCl is not ionized.

53. 144 g mol^{-1}

55. 0.870 °C

57. S_8

59. 1.39×10^4 g mol^{-1}

61. 54 g

63. 100.26 °C

65. (a) $X_{CH_3OH} = 0.590;\ X_{C_2H_5OH} = 0.410;$ (b) Vapor pressures are: CH_3OH: 55 torr; C_2H_5OH: 18 torr; (c) CH_3OH: 0.75; C_2H_5OH: 0.25

67. The ions and compounds present in the water in the beef lower the freezing point of the beef below −1 °C.

69. $$\Delta\text{bp} = K_b m = (1.20\ \text{°C}/m)\left(\frac{9.41\text{g} \times \frac{1\text{mol HgCl}_2}{271.496\text{ g}}}{0.03275\text{ kg}}\right) = 1.27\ \text{°C}$$

The observed change equals the theoretical change; therefore, no dissociation occurs.

71.

Colloidal System	Dispersed Phase	Dispersion Medium
starch dispersion	starch	water
smoke	solid particles	air
fog	water	air
pearl	water	calcium carbonate ($CaCO_3$)
whipped cream	air	cream
floating soap	air	soap

Colloidal System	Dispersed Phase	Dispersion Medium
jelly	fruit juice	pectin gel
milk	butterfat	water
ruby	chromium(III) oxide (Cr_2O_3)	aluminum oxide (Al_2O_3)

73. Colloidal dispersions consist of particles that are much bigger than the solutes of typical solutions. Colloidal particles are either very large molecules or aggregates of smaller species that usually are big enough to scatter light. Colloids are homogeneous on a macroscopic (visual) scale, while solutions are homogeneous on a microscopic (molecular) scale.

75. If they are placed in an electrolytic cell, dispersed particles will move toward the electrode that carries a charge opposite to their own charge. At this electrode, the charged particles will be neutralized and will coagulate as a precipitate.

Chapter 12

1. A reaction has a natural tendency to occur and takes place without the continual input of energy from an external source.

3. (a) spontaneous; (b) nonspontaneous; (c) spontaneous; (d) nonspontaneous; (e) spontaneous; (f) spontaneous

5. Although the oxidation of plastics is spontaneous, the rate of oxidation is very slow. Plastics are therefore kinetically stable and do not decompose appreciably even over relatively long periods of time.

7. There are four initial microstates and four final microstates.

$$\Delta S = k \ln \frac{W_\text{f}}{W_\text{i}} = 1.38 \times 10^{-23}\ \text{J/K} \times \ln \frac{4}{4} = 0$$

9. The probability for all the particles to be on one side is $\frac{1}{32}$. This probability is noticeably lower than the $\frac{1}{8}$ result for the four-particle system. The conclusion we can make is that the probability for all the particles to stay in only one part of the system will decrease rapidly as the number of particles increases, and, for instance, the probability for all molecules of gas to gather in only one side of a room at room temperature and pressure is negligible since the number of gas molecules in the room is very large.

11. There is only one initial state. For the final state, the energy can be contained in pairs A-C, A-D, B-C, or B-D. Thus, there are four final possible states.

$$\Delta S = k\ \ln\left(\frac{W_\text{f}}{W_\text{i}}\right) = 1.38 \times 10^{-23}\ \text{J/K} \times \ln\left(\frac{4}{1}\right) = 1.91 \times 10^{-23}\ \text{J/K}$$

13. The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

15. (a) $C_3H_7OH(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature. (b) $C_2H_5OH(g)$ as it is in the gaseous state. (c) $2H(g)$, since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

17. (a) Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution. (b) Negative. There is a net loss of three moles of gas from reactants to products. (c) Positive. There is a net increase of seven moles of gas from reactants to products.

19. $C_6H_6(l) + 7.5O_2(g) \longrightarrow 3H_2O(g) + 6CO_2(g)$

There are 7.5 moles of gas initially, and 3 + 6 = 9 moles of gas in the end. Therefore, it is likely that the entropy increases as a result of this reaction, and ΔS is positive.

21. (a) 107 J/K; (b) −86.4 J/K; (c) 133.2 J/K; (d) 118.8 J/K; (e) −326.6 J/K; (f) −171.9 J/K; (g) −7.2 J/K

23. 100.6 J/K

25. (a) −198.1 J/K; (b) −348.9 J/K

27. As $\Delta S_{\text{univ}} < 0$ at each of these temperatures, melting is not spontaneous at either of them. The given values for entropy and enthalpy are for NaCl at 298 K. It is assumed that these do not change significantly at the higher temperatures used in the problem.

29. (a) 2.86 J/K; (b) 24.8 J/K; (c) −113.2 J/K; (d) −24.7 J/K; (e) 15.5 J/K; (f) 290.0 J/K

31. The reaction is nonspontaneous at room temperature.
Above 400 K, ΔG will become negative, and the reaction will become spontaneous.

33. (a) 465.1 kJ nonspontaneous; (b) −106.86 kJ spontaneous; (c) −53.6 kJ spontaneous; (d) −83.4 kJ spontaneous; (e) −406.7 kJ spontaneous; (f) −30.0 kJ spontaneous

35. (a) The standard free energy of formation is –1124.3 kJ/mol. (b) The calculation agrees with the value in **Appendix G** because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

37. (a) The reaction is nonspontaneous; (b) Above 566 °C the process is spontaneous.

39. (a) 1.5×10^2 kJ; (b) −21.9 kJ; (c) −5.34 kJ; (d) −0.383 kJ; (e) 18 kJ; (f) 71 kJ

41. (a) $K = 41$; (b) $K = 0.053$; (c) $K = 6.9 \times 10^{13}$; (d) $K = 1.9$; (e) $K = 0.04$

42. (a) 22.1 kJ;
(b) 61.6 kJ/mol

44. 90 kJ/mol

46. (a) Under standard thermodynamic conditions, the evaporation is nonspontaneous; (b) $K_p = 0.031$; (c) The evaporation of water is spontaneous; (d) $P_{\text{H}_2\text{O}}$ must always be less than K_p or less than 0.031 atm. 0.031 atm represents air saturated with water vapor at 25 °C, or 100% humidity.

48. (a) Nonspontaneous as $\Delta G° > 0$; (b) $\Delta G° = \Delta G° + RT \ln Q$,
$\Delta G = 1.7 \times 10^3 + \left(8.314 \times 335 \times \ln \frac{28}{128}\right) = -2.5 \text{ kJ}.$ The forward reaction to produce F6P is spontaneous under these conditions.

50. ΔG is negative as the process is spontaneous. ΔH is positive as with the solution becoming cold, the dissolving must be endothermic. ΔS must be positive as this drives the process, and it is expected for the dissolution of any soluble ionic compound.

52. (a) Increasing P_{O_2} will shift the equilibrium toward the products, which increases the value of K. $\Delta G°$ therefore becomes more negative.
(b) Increasing P_{O_2} will shift the equilibrium toward the products, which increases the value of K. $\Delta G°$ therefore becomes more negative.
(c) Increasing P_{O_2} will shift the equilibrium the reactants, which decreases the value of K. $\Delta G°$ therefore becomes more positive.

Chapter 13

1. The reaction can proceed in both the forward and reverse directions.

3. When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the forward and reverse reactions continue to proceed, but at equal rates.

5. Not necessarily. A system at equilibrium is characterized by *constant* reactant and product concentrations, but the values of the reactant and product concentrations themselves need not be equal.

7. Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

9. (a) $K_c = [\text{Ag}^+][\text{Cl}^-] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than 1 M; (b)

$K_c = \frac{1}{[Pb^{2+}][Cl^-]^2}$ > 1 because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level (<1 *M*).

11. Since $K_c = \frac{[C_6H_6]}{[C_2H_2]^3}$, a value of $K_c \approx 10$ means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

13. $K_c > 1$

15. (a) $Q_c = \frac{[CH_3Cl][HCl]}{[CH_4][Cl_2]}$; (b) $Q_c = \frac{[NO]^2}{[N_2][O_2]}$; (c) $Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$; (d) $Q_c = [SO_2]$; (e) $Q_c = \frac{1}{[P_4][O_2]^5}$; (f) $Q_c = \frac{[Br]^2}{[Br_2]}$; (g) $Q_c = \frac{[CO_2]}{[CH_4][O_2]^2}$; (h) $Q_c = [H_2O]^5$

17. (a) Q_c 25 proceeds left; (b) Q_P 0.22 proceeds right; (c) Q_c undefined proceeds left; (d) Q_P 1.00 proceeds right; (e) Q_P 0 proceeds right; (f) Q_c 4 proceeds left

19. The system will shift toward the reactants to reach equilibrium.

21. (a) homogenous; (b) homogenous; (c) homogenous; (d) heterogeneous; (e) heterogeneous; (f) homogenous; (g) heterogeneous; (h) heterogeneous

23. This situation occurs in (a) and (b).

25. (a) $K_P = 1.6 \times 10^{-4}$; (b) $K_P = 50.2$; (c) $K_c = 5.34 \times 10^{-39}$; (d) $K_c = 4.60 \times 10^{-3}$

27. $K_P = P_{H_2O} = 0.042$.

29. $Q_c = \frac{[NH_4{}^+][OH^-]}{[HN_3]}$

31. The amount of $CaCO_3$ must be so small that P_{CO_2} is less than K_P when the $CaCO_3$ has completely decomposed. In other words, the starting amount of $CaCO_3$ cannot completely generate the full P_{CO_2} required for equilibrium.

33. The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

34. No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

36. Add N_2; add H_2; decrease the container volume; heat the mixture.

38. (a) *T* increase = shift right, *V* decrease = shift left; (b) *T* increase = shift right, *V* = no effect; (c) *T* increase = shift left, *V* decrease = shift left; (d) *T* increase = shift left, *V* decrease = shift right.

40. (a) $K_c = \frac{[CH_3OH]}{[H_2]^2[CO]}$; (b) $[H_2]$ increases, [CO] decreases, $[CH_3OH]$ increases; (c), $[H_2]$ increases, [CO] decreases, $[CH_3OH]$ decreases; (d), $[H_2]$ increases, [CO] increases, $[CH_3OH]$ increases; (e), $[H_2]$ increases, [CO] increases, $[CH_3OH]$ decreases

42. (a) $K_c = \frac{[CO][H_2]}{[H_2O]}$; (b) $[H_2O]$ no change, [CO] no change, $[H_2]$ no change; (c) $[H_2O]$ decreases, [CO] decreases, $[H_2]$ decreases; (d) $[H_2O]$ increases, [CO] increases, $[H_2]$ decreases; (f) $[H_2O]$ decreases, [CO] increases, $[H_2]$ increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

44. Only (b)

46. Add NaCl or some other salt that produces Cl^- to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(*s*).

48. (a)

50. $K_c = \frac{[C]^2}{[A][B]^2}$. [A] = 0.1 *M*, [B] = 0.1 *M*, [C] = 1 *M*; and [A] = 0.01, [B] = 0.250, [C] = 0.791.

52. $K_c = 6.00 \times 10^{-2}$

54. $K_c = 0.50$

56. $K_P = 1.9 \times 10^3$

58. $K_P = 3.06$

60. (a) −2*x*, 2*x*, −0.250 *M*, 0.250 *M*; (b) 4*x*, −2*x*, −6*x*, 0.32 *M*, −0.16 *M*, −0.48 *M*; (c) −2*x*, 3*x*, −50 torr, 75 torr; (d) *x*, − *x*, −3*x*, 5 atm, −5 atm, −15 atm; (e) *x*, 1.03×10^{-4} *M*; (f) *x*, 0.1 atm.

62. Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.

64. $[NH_3] = 9.1 \times 10^{-2}$ *M*

66. $P_{BrCl} = 4.9 \times 10^{-2}$ atm

68. $[CO] = 2.04 \times 10^{-4}$ *M*

70. $P_{H_2O} = 3.64 \times 10^{-3}$ atm

72. Calculate *Q* based on the calculated concentrations and see if it is equal to K_c. Because *Q* does equal 4.32, the system must be at equilibrium.

74. (a) $[NO_2] = 1.17 \times 10^{-3}$ *M*
$[N_2O_4] = 0.128$ *M*
(b) The assumption that *x* is negligibly small compared to 0.129 is confirmed by comparing the initial concentration of the N_2O_4 to its concentration at equilibrium (they differ by just 1 in the least significant digit's place).

76. (a) $[H_2S] = 0.810$ atm
$[H_2] = 0.014$ atm
$[S_2] = 0.0072$ atm
(b) The assumption that 2*x* is negligibly small compared to 0.824 is confirmed by comparing the initial concentration of the H_2S to its concentration at equilibrium (0.824 atm versus 0.810 atm, a difference of less than 2%).

78. 507 g

80. 330 g

83. (a) 0.33 mol.
(b) $[CO]_2 = 0.50$ *M*. Added H_2 forms some water as a result of a shift to the left after H_2 is added.

85. (a) $K_c = \frac{[NH_3]^4 [O_2]^7}{[NO_2]^4 [H_2O]^6}$. (b) $[NH_3]$ must increase for Q_c to reach K_c. (c) The increase in system volume would lower the partial pressures of all reactants (including NO_2). (d) $P_{O_2} = 49$ torr

87. $P_{N_2O_3} = 1.90$ atm and $P_{NO} = P_{NO_2} = 1.90$ atm

90. In each of the following, the value of Δ*G* is not given at the temperature of the reaction. Therefore, we must calculate Δ*G* from the values Δ*H*° and Δ*S* and then calculate Δ*G* from the relation $\Delta G = \Delta H° - T\Delta S°$.
(a) $K = 1.29$;
(b) $K = 2.51 \times 10^{-3}$;
(c) $K = 4.83 \times 10^3$;
(d) $K = 0.219$;
(e) $K = 16.1$

92. The standard free energy change is $\Delta G°_{298} = -RT \ln K = 4.84$ kJ/mol. When reactants and products are in their standard states (1 bar or 1 atm), *Q* = 1. As the reaction proceeds toward equilibrium, the reaction shifts left (the amount of products drops while the amount of reactants increases): $Q < 1$, and ΔG_{298} becomes less positive as it approaches zero. At equilibrium, $Q = K$, and $\Delta G = 0$.

94. The reaction will be spontaneous at temperatures greater than 287 K.

96. $K = 5.35 \times 10^{15}$
The process is exothermic.

98. 1.0×10^{-8} atm. This is the maximum pressure of the gases under the stated conditions.

100. $x = 1.29 \times 10^{-5}\ \text{atm} = P_{O_2}$

102. −0.16 kJ

Chapter 14

1. One example for NH_3 as a conjugate acid: $NH_2^- + H^+ \longrightarrow NH_3$; as a conjugate base: $NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$

3. (a) $H_3O^+(aq) \longrightarrow H^+(aq) + H_2O(l)$; (b) $HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$; (c) $NH_3(aq) \longrightarrow H^+(aq) + NH_2^-(aq)$; (d) $CH_3CO_2H(aq) \longrightarrow H^+(aq) + CH_3CO_2^-(aq)$; (e) $NH_4^+(aq) \longrightarrow H^+(aq) + NH_3(aq)$; (f) $HSO_4^-(aq) \longrightarrow H^+(aq) + SO_4^{2-}(aq)$

5. (a) $H_2O(l) + H^+(aq) \longrightarrow H_3O^+(aq)$; (b) $OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)$; (c) $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$; (d) $CN^-(aq) + H^+(aq) \longrightarrow HCN(aq)$; (e) $S^{2-}(aq) + H^+(aq) \longrightarrow HS^-(aq)$; (f) $H_2PO_4^-(aq) + H^+(aq) \longrightarrow H_3PO_4(aq)$

7. (a) H_2O, O^{2-}; (b) H_3O^+, OH^-; (c) H_2CO_3, CO_3^{2-}; (d) NH_4^+, NH_2^-; (e) H_2SO_4, SO_4^{2-}; (f) $H_3O_2^+$, HO_2^-; (g) H_2S; S^{2-}; (h) $H_6N_2^{2+}$, H_4N_2

9. The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. (a) HNO_3(BA), H_2O(BB), H_3O^+(CA), NO_3^-(CB); (b) CN^-(BB), H_2O(BA), HCN(CA), OH^-(CB); (c) H_2SO_4(BA), Cl^-(BB), HCl(CA), HSO_4^-(CB); (d) HSO_4^-(BA), OH^-(BB), SO_4^{2-}(CB), H_2O(CA); (e) O^{2-}(BB), H_2O(BA) OH^-(CB and CA); (f) $[Cu(H_2O)_3(OH)]^+$(BB), $[Al(H_2O)_6]^{3+}$(BA), $[Cu(H_2O)_4]^{2+}$(CA), $[Al(H_2O)_5(OH)]^{2+}$(CB); (g) H_2S(BA), NH_2^-(BB), HS^-(CB), NH_3(CA)

11. Amphiprotic species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is H_2O. As an acid: $H_2O(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$. As a base: $H_2O(aq) + HCl(aq) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

13. amphiprotic: (a) $NH_3 + H_3O^+ \longrightarrow NH_4OH + H_2O$, $NH_3 + OCH_3^- \longrightarrow NH_2^- + CH_3OH$; (b) $HPO_4^{2-} + OH^- \longrightarrow PO_4^{3-} + H_2O$, $HPO_4^{2-} + HClO_4 \longrightarrow H_2PO_4^- + ClO_4^-$; not amphiprotic: (c) Br^-; (d) NH_4^+; (e) AsO_4^{3-}

15. In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C, $[H_3O^+] = [OH^-] = (2.910^{-14})^{1/2} = 1.7 \times 10^{-7}$.

17. $x = 3.051 \times 10^{-7}\ M = [H_3O^+] = [OH^-]$; pH = $-\log 3.051 \times 10^{-7} = -(-6.5156) = 6.5156$; pOH = pH = 6.5156

19. (a) pH = 3.587; pOH = 10.413; (b) pH = 0.68; pOH = 13.32; (c) pOH = 3.85; pH = 10.15; (d) pH = −0.40; pOH = 14.4

21. $[H_3O^+] = 3.0 \times 10^{-7}\ M$; $[OH^-] = 3.3 \times 10^{-8}\ M$

23. $[H_3O^+] = 1 \times 10^{-2}\ M$; $[OH^-] = 1 \times 10^{-12}\ M$

25. $[OH^-] = 3.1 \times 10^{-12}\ M$

27. The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms OH^-, which causes the solution to be basic.

29. $[H_2O] > [CH_3CO_2H] > [H_3O^+] \approx [CH_3CO_2^-] > [OH^-]$

31. The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3.

33. $\underset{\text{BB}}{Mg(OH)_2(s)} + \underset{\text{BA}}{2HCl(aq)} \longrightarrow \underset{\text{CB}}{Mg^{2+}(aq)} + \underset{\text{CA}}{2Cl^{-}(aq)} + 2H_2O(l)$

35. $K_a = 2.3 \times 10^{-11}$

37. The stronger base or stronger acid is the one with the larger K_b or K_a, respectively. In these two examples, they are $(CH_3)_2NH$ and $CH_3NH_3{}^{+}$.

39. triethylamine

41. (a) $HSO_4{}^{-}$; higher electronegativity of the central ion. (b) H_2O; NH_3 is a base and water is neutral, or decide on the basis of K_a values. (c) HI; PH_3 is weaker than HCl; HCl is weaker than HI. Thus, PH_3 is weaker than HI. (d) PH_3; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group. (e) HBr; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S, so HBr is the stronger acid.

43. (a) $NaHSeO_3 < NaHSO_3 < NaHSO_4$; in polyoxy acids, the more electronegative central element—S, in this case—forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner. (b) $ClO_2{}^{-} < BrO_2{}^{-} < IO_2{}^{-}$; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (c) HOI < HOBr < HOCl; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (d) $HOCl < HOClO < HOClO_2 < HOClO_3$; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases). (e) $HTe^{-} < HS^{-} << PH_2{}^{-} < NH_2{}^{-}$; $PH_2{}^{-}$ and $NH_2{}^{-}$ are anions of weak bases, so they act as strong bases toward H^+. HTe^{-} and HS^{-} are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion. (f) $BrO_4{}^{-} < BrO_3{}^{-} < BrO_2{}^{-} < BrO^{-}$; with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.

45. $[H_2O] > [C_6H_4OH(CO_2H)] > [H^+]\,0 > [C_6H_4OH(CO_2)^{-}] \gg [C_6H_4O(CO_2H)^{-}] > [OH^{-}]$

47. 1. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration. 2. Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+.

48. (b) The addition of HCl

50. (a) Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2, and decreasing the concentration of $NO_2{}^{-}$ ions. (b) Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of $NO_2{}^{-}$ ions and decreasing the concentration of OH^- ions. (c) Adding NaOH adds OH^- ions, which shifts the equilibrium to the left, increasing the concentration of $NO_2{}^{-}$ ions and decreasing the concentrations of HNO_2. (d) Adding NaCl has no effect on the concentrations of the ions. (e) Adding KNO_2 adds $NO_2{}^{-}$ ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.

52. This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[H_3O^+]$ produced by the stronger acid.

54. (a) $K_b = 1.8 \times 10^{-5}$; (b) $K_a = 4.5 \times 10^{-4}$; (c) $K_b = 7.4 \times 10^{-5}$; (d) $K_a = 5.6 \times 10^{-10}$

56. $K_a = 1.2 \times 10^{-2}$

58. (a) $K_b = 4.3 \times 10^{-12}$ (b) $K_a = 1.6 \times 10^{-8}$ (c) $K_b = 5.9 \times 10^{-7}$ (d) $K_b = 4.2 \times 10^{-3}$ (e) $K_b = 2.3 \times 10^{-3}$ (f) $K_b = 6.3 \times 10^{-13}$

60. (a) $\frac{[H_3O^+][ClO^-]}{[HClO]} = \frac{(x)(x)}{(0.0092 - x)} \approx \frac{(x)(x)}{0.0092} = 2.9 \times 10^{-8}$

Solving for x gives 1.63×10^{-5} M. This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:
$[H_3O^+] = [ClO] = 5.8 \times 10^{-5}$ M
$[HClO] = 0.00092$ M
$[OH^-] = 6.1 \times 10^{-10}$ M;
(b) $\frac{[C_6H_5NH_3{}^+][OH^-]}{[C_6H_5NH_2]} = \frac{(x)(x)}{(0.0784 - x)} \approx \frac{(x)(x)}{0.0784} = 4.3 \times 10^{-10}$
Solving for x gives 5.81×10^{-6} M. This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:
$[CH_3CO_2{}^-] = [OH^-] = 5.8 \times 10^{-6}$ M
$[C_6H_5NH_2] = 0.00784$
$[H_3O^+] = 1.7 \times 10^{-9}$ M;
(c) $\frac{[H_3O^+][CN^-]}{[HCN]} = \frac{(x)(x)}{(0.0810 - x)} \approx \frac{(x)(x)}{0.0810} = 4.9 \times 10^{-10}$
Solving for x gives 6.30×10^{-6} M. This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:
$[H_3O^+] = [CN^-] = 6.3 \times 10^{-6}$ M
$[HCN] = 0.0810$ M
$[OH^-] = 1.6 \times 10^{-9}$ M;
(d) $\frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{(0.11 - x)} \approx \frac{(x)(x)}{0.11} = 6.3 \times 10^{-5}$
Solving for x gives 2.63×10^{-3} M. This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:
$[(CH_3)_3NH^+] = [OH^-] = 2.6 \times 10^{-3}$ M
$[(CH_3)_3N] = 0.11$ M
$[H_3O^+] = 3.8 \times 10^{-12}$ M;
(e) $\frac{[Fe(H_2O)_5(OH)^+][H_3O^+]}{[Fe(H_2O)_6{}^{2+}]} = \frac{(x)(x)}{(0.120 - x)} \approx \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$
Solving for x gives 1.39×10^{-4} M. This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:
$[Fe(H_2O)_5(OH)^+] = [H_3O^+] = 1.4 \times 10^{-4}$ M
$[Fe(H_2O)_6{}^{2+}] = 0.120$ M
$[OH^-] = 7.2 \times 10^{-11}$ M

62. pH = 2.41

64. $[C_{10}H_{14}N_2] = 0.049$ M; $[C_{10}H_{14}N_2H^+] = 1.9 \times 10^{-4}$ M; $[C_{10}H_{14}N_2H_2{}^{2+}] = 1.4 \times 10^{-11}$ M; $[OH^-] = 1.9 \times 10^{-4}$ M; $[H_3O^+] = 5.3 \times 10^{-11}$ M

66. $K_a = 1.2 \times 10^{-2}$

68. $K_b = 1.77 \times 10^{-5}$

70. (a) acidic; (b) basic; (c) acidic; (d) neutral

72. $[H_3O^+]$ and $[HCO_3{}^-]$ are practically equal

74. $[C_6H_4(CO_2H)_2]$ 7.2×10^{-3} M, $[C_6H_4(CO_2H)(CO_2)^-] = [H_3O^+]$ 2.8×10^{-3} M, $[C_6H_4(CO_2)_2{}^{2-}]$ 3.9×10^{-6} M, $[OH^-]$ 3.6×10^{-12} M

76. (a) $K_{a2} = 1.5 \times 10^{-11}$;

(b) $K_b = 4.3 \times 10^{-12}$;

(c) $\frac{[\mathrm{Te}^{2-}][\mathrm{H_3O^+}]}{[\mathrm{HTe}^-]} = \frac{(x)(0.0141 + x)}{(0.0141 - x)} \approx \frac{(x)(0.0141)}{0.0141} = 1.5 \times 10^{-11}$

Solving for x gives 1.5×10^{-11} *M*. Therefore, compared with 0.014 *M*, this value is negligible (1.1×10^{-7}%).

78. Excess H_3O^+ is removed primarily by the reaction: $\mathrm{H_3O^+}(aq) + \mathrm{H_2PO_4{}^-}(aq) \longrightarrow \mathrm{H_3PO_4}(aq) + \mathrm{H_2O}(l)$
Excess base is removed by the reaction: $\mathrm{OH^-}(aq) + \mathrm{H_3PO_4}(aq) \longrightarrow \mathrm{H_2PO_4{}^-}(aq) + \mathrm{H_2O}(l)$

80. $[H_3O^+] = 1.5 \times 10^{-4}$ *M*

82. $[OH^-] = 4.2 \times 10^{-4}$ *M*

84. (a) The added HCl will increase the concentration of H_3O^+ slightly, which will react with $\mathrm{CH_3CO_2{}^-}$ and produce CH_3CO_2H in the process. Thus, $[\mathrm{CH_3CO_2{}^-}]$ decreases and $[CH_3CO_2H]$ increases. (b) The added KCH_3CO_2 will increase the concentration of $[\mathrm{CH_3CO_2{}^-}]$ which will react with H_3O^+ and produce CH_3CO_2 H in the process. Thus, $[H_3O^+]$ decreases slightly and $[CH_3CO_2H]$ increases. (c) The added NaCl will have no effect on the concentration of the ions. (d) The added KOH will produce OH^- ions, which will react with the H_3O^+, thus reducing $[H_3O^+]$. Some additional CH_3CO_2H will dissociate, producing $[\mathrm{CH_3CO_2{}^-}]$ ions in the process. Thus, $[CH_3CO_2H]$ decreases slightly and $[\mathrm{CH_3CO_2{}^-}]$ increases. (e) The added CH_3CO_2H will increase its concentration, causing more of it to dissociate and producing more $[\mathrm{CH_3CO_2{}^-}]$ and H_3O^+ in the process. Thus, $[H_3O^+]$ increases slightly and $[\mathrm{CH_3CO_2{}^-}]$ increases.

86. pH = 8.95

88. 37 g (0.27 mol)

90. (a) pH = 5.222; (b) The solution is acidic. (c) pH = 5.221

92. At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example.

94. (a) pH = 2.50; (b) pH = 4.01; (c) pH = 5.60; (d) pH = 8.35; (e) pH = 11.08

Chapter 15

1. (a) $$\mathrm{AgI}(s) \rightleftharpoons \underset{x}{\mathrm{Ag^+}(aq)} + \underset{x}{\mathrm{I^-}(aq)}$$

(b) $$\mathrm{CaCO_3}(s) \rightleftharpoons \underset{x}{\mathrm{Ca^{2+}}(aq)} + \underset{x}{\mathrm{CO_3{}^{2-}}(aq)}$$

(c) $$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \underset{x}{\mathrm{Mg^{2+}}(aq)} + \underset{2x}{\mathrm{2OH^-}(aq)}$$

(d) $$\mathrm{Mg_3(PO_4)_2}(s) \rightleftharpoons \underset{3x}{\mathrm{3Mg^{2+}}(aq)} + \underset{2x}{\mathrm{2PO_4{}^{3-}}(aq)}$$

(e) $$\mathrm{Ca_5(PO_4)_3OH}(s) \rightleftharpoons \underset{5x}{\mathrm{5Ca^{2+}}(aq)} + \underset{3x}{\mathrm{3PO_4{}^{3-}}(aq)} + \underset{x}{\mathrm{OH^-}(aq)}$$

3. There is no change. A solid has an activity of 1 whether there is a little or a lot.

5. The solubility of silver bromide at the new temperature must be known. Normally the solubility increases and some of the solid silver bromide will dissolve.

7. CaF_2, $MnCO_3$, and ZnS

9. (a) $\mathrm{LaF_3}(s) \rightleftharpoons \mathrm{La^{3+}}(aq) + \mathrm{3F^-}(aq)$ $K_{sp} = [\mathrm{La^{3+}}][\mathrm{F^-}]^3$;

(b) $\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3{}^{2-}}(aq)$ $K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{CO_3{}^{2-}}]$;

(c) $\mathrm{Ag_2SO_4}(s) \rightleftharpoons \mathrm{2Ag^+}(aq) + \mathrm{SO_4{}^{2-}}(aq)$ $K_{sp} = [\mathrm{Ag^+}]^2[\mathrm{SO_4{}^{2-}}]$;

(d) $\text{Pb(OH)}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{OH}^-(aq) \qquad K_{\text{sp}} = [\text{Pb}^{2+}][\text{OH}^-]^2$

11. (a)1.77×10^{-7}; (b) 1.6×10^{-6}; (c) 2.2×10^{-9}; (d) 7.91×10^{-22}

13. (a) 2×10^{-2} *M*; (b) 1.5×10^{-3} *M*; (c) 2.27×10^{-9} *M*; (d) 2.2×10^{-10} *M*

15. (a) 6.4×10^{-9} *M* = $[\text{Ag}^+]$, $[\text{Cl}^-]$ = 0.025 *M*. Check: $\frac{6.4 \times 10^{-9}\ M}{0.025\ M} \times 100\% = 2.6 \times 10^{-5}\,\%,$ an insignificant change;

(b) 2.2×10^{-5} *M* = $[\text{Ca}^{2+}]$, $[\text{F}^-]$ = 0.0013 *M*. Check: $\frac{2.26 \times 10^{-5}\ M}{0.00133\ M} \times 100\% = 1.70\%.$ This value is less than 5% and can be ignored.

(c) 0.2238 *M* = $[\text{SO}_4{}^{2-}]$; $[\text{Ag}^+]$ = 7.4×10^{-3} *M*. Check: $\frac{3.7 \times 10^{-3}}{0.2238} \times 100\% = 1.64 \times 10^{-2};$ the condition is satisfied.

(d) $[\text{OH}^-]$ = 2.8×10^{-3} *M*; 5.7×10^{-12} *M* = $[\text{Zn}^{2+}]$. Check: $\frac{5.7 \times 10^{-12}}{2.8 \times 10^{-3}} \times 100\% = 2.0 \times 10^{-7}\,\%;$ *x* is less than 5% of $[\text{OH}^-]$ and is, therefore, negligible.

17. (a) $[\text{Cl}^-]$ = 7.6×10^{-3} *M*

Check: $\frac{7.6 \times 10^{-3}}{0.025} \times 100\% = 30\%$

This value is too large to drop *x*. Therefore solve by using the quadratic equation:

$[\text{Ti}^+]$ = 3.1×10^{-2} *M*

$[\text{Cl}^-]$ = 6.1×10^{-3}

(b) $[\text{Ba}^{2+}]$ = 7.7×10^{-4} *M*

Check: $\frac{7.7 \times 10^{-4}}{0.0313} \times 100\% = 2.4\%$

Therefore, the condition is satisfied.

$[\text{Ba}^{2+}]$ = 7.7×10^{-4} *M*

$[\text{F}^-]$ = 0.0321 *M*;

(c) $\text{Mg(NO}_3)_2$ = 0.02444 *M*

$[\text{C}_2\text{O}_4{}^{2-}] = 2.9 \times 10^{-5}$

Check: $\frac{2.9 \times 10^{-5}}{0.02444} \times 100\% = 0.12\%$

The condition is satisfied; the above value is less than 5%.

$[\text{C}_2\text{O}_4{}^{2-}] = 2.9 \times 10^{-5}\ M$

$[\text{Mg}^{2+}]$ = 0.0244 *M*

(d) $[\text{OH}^-]$ = 0.0501 *M*

$[\text{Ca}^{2+}]$ = 3.15×10^{-3}

Check: $\frac{3.15 \times 10^{-3}}{0.050} \times 100\% = 6.28\%$

This value is greater than 5%, so a more exact method, such as successive approximations, must be used.

$[\text{Ca}^{2+}]$ = 2.8×10^{-3} *M*

$[\text{OH}^-]$ = 0.053×10^{-2} *M*

19. The changes in concentration are greater than 5% and thus exceed the maximum value for disregarding the change.

21. $\text{CaSO}_4{\cdot}2\text{H}_2\text{O}$ is the most soluble Ca salt in mol/L, and it is also the most soluble Ca salt in g/L.

23. 4.8×10^{-3} *M* = $[\text{SO}_4{}^{2-}]$ = $[\text{Ca}^{2+}]$; Since this concentration is higher than 2.60×10^{-3} *M*, “gyp” water does not meet the standards.

25. Mass ($\text{CaSO}_4{\cdot}2\text{H}_2\text{O}$) = 0.72 g/L

27. (a) $[\text{Ag}^+]$ = $[\text{I}^-]$ = 1.3×10^{-5} *M*; (b) $[\text{Ag}^+]$ = 2.88×10^{-2} *M*, $[\text{SO}_4{}^{2-}]$ = 1.44×10^{-2} *M*; (c) $[\text{Mn}^{2+}]$ = 3.7×10^{-5} *M*, $[\text{OH}^-]$ = 7.4×10^{-5} *M*; (d) $[\text{Sr}^{2+}]$ = 4.3×10^{-2} *M*, $[\text{OH}^-]$ = 8.6×10^{-2} *M*; (e) $[\text{Mg}^{2+}]$ = 1.3×10^{-4} *M*, $[\text{OH}^-]$ = 2.6×10^{-4} *M*.

29. (a) 1.7×10^{-4}; (b) 8.2×10^{-55}; (c) 1.35×10^{-4}; (d) 1.18×10^{-5}; (e) 1.08×10^{-10}

31. (a) $CaCO_3$ does precipitate. (b) The compound does not precipitate. (c) The compound does not precipitate. (d) The compound precipitates.

33. 3.03×10^{-7} M

35. 9.2×10^{-13} M

37. $[Ag^+] = 1.8 \times 10^{-3}$ M

39. 6.3×10^{-4}

41. (a) 2.25 L; (b) 7.2×10^{-7} g

43. 100% of it is dissolved

45. (a) $Hg_2{}^{2+}$ and Cu^{2+}: Add $SO_4{}^{2-}$. (b) $SO_4{}^{2-}$ and Cl^-: Add Ba^{2+}. (c) Hg^{2+} and Co^{2+}: Add S^{2-}. (d) Zn^{2+} and Sr^{2+}: Add OH^- until $[OH^-] = 0.050$ M. (e) Ba^{2+} and Mg^{2+}: Add $SO_4{}^{2-}$. (f) $CO_3{}^{2-}$ and OH^-: Add Ba^{2+}.

47. AgI will precipitate first.

49. 1.5×10^{-12} M

51. 3.99 kg

53. (a) 3.1×10^{-11}; (b) $[Cu^{2+}] = 2.6 \times 10^{-3}$; $[IO_3{}^-] = 5.3 \times 10^{-3}$

55. 1.8×10^{-5} g $Pb(OH)_2$

57. $Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^-$ $\qquad K_{sp} = [Mg^{2+}][OH^-]^2$
1.23×10^{-3} g $Mg(OH)_2$

59. $MnCO_3$ will form first, since it has the smallest K_{sp} value it is the least soluble. $MnCO_3$ will be the last to precipitate, it has the largest K_{sp} value.

62. when the amount of solid is so small that a saturated solution is not produced

64. 8×10^{-5} M

66. 5×10^{23}

	$[Cd(CN)_4{}^{2-}]$	$[CN^-]$	$[Cd^{2+}]$
Initial concentration (M)	0.250	0	0
Equilibrium (M)	$0.250 - x$	$4x$	x

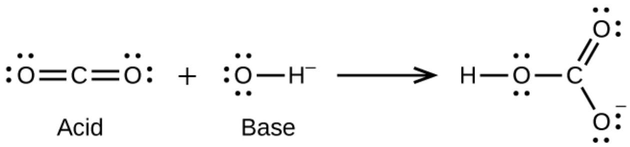
68.
$[Cd^{2+}] = 9.5 \times 10^{-5}$ M; $[CN^-] = 3.8 \times 10^{-4}$ M

70. $[Co^{3+}] = 3.0 \times 10^{-6}$ M; $[NH_3] = 1.8 \times 10^{-5}$ M

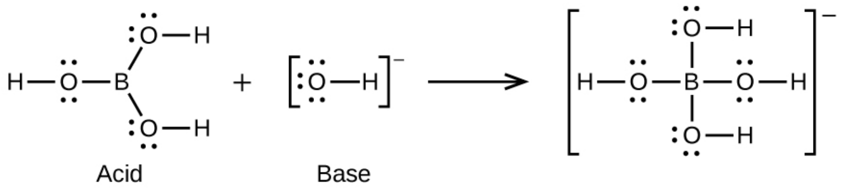
72. 1.3 g

74. 0.79 g

76. (a)



(b)



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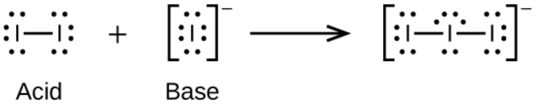

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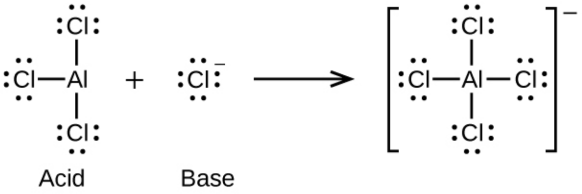
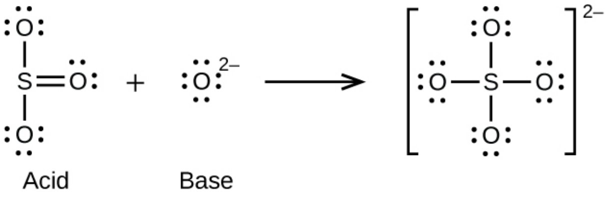
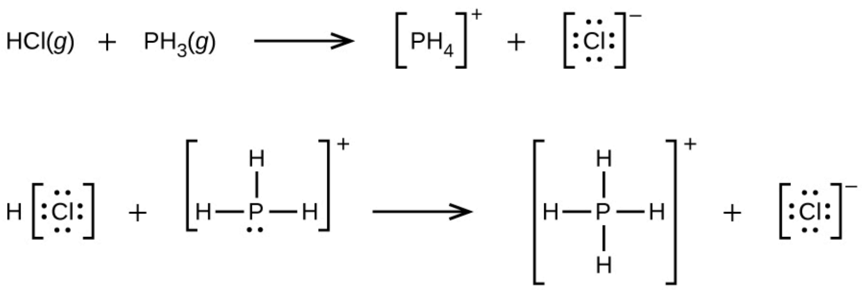


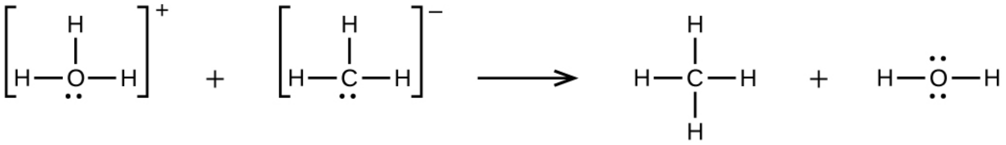
(e)



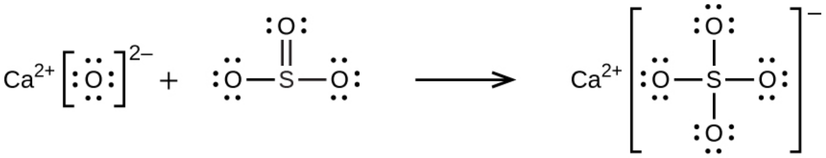
78. (a)



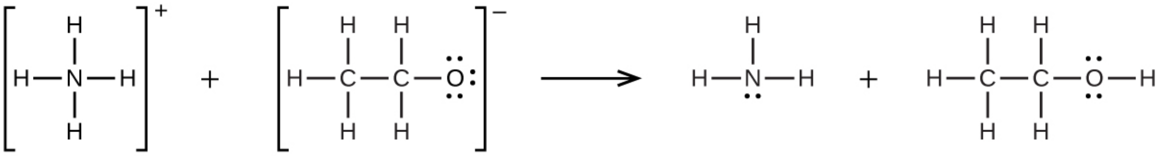
(b) $H_3O^+ + CH_3^- \longrightarrow CH_4 + H_2O$



(c) $CaO + SO_3 \longrightarrow CaSO4$



(d) $NH_4{}^+ + C_2H_5O^- \longrightarrow C_2H_5OH + NH_3$



80. 0.0281 g

82. $HNO_3(l) + HF(l) \longrightarrow H_2NO_3{}^+ + F^-;\ \ HF(l) + BF_3(g) \longrightarrow H^+ + BF_4$

84. (a) $H_3BO_3 + H_2O \longrightarrow H_4BO_4{}^- + H^+;$ (b) The electronic and molecular shapes are the same—both tetrahedral. (c) The tetrahedral structure is consistent with sp^3 hybridization.

86. 0.014 M

88. 7.2×10^{-15} M

90. 4.4×10^{-22} M

93. $[OH^-] = 4.5 \times 10^{-5}$; $[Al^{3+}] = 2.2 \times 10^{-20}$ (molar solubility)

95. $[SO_4{}^{2-}] = 0.049\ M$; $[Ba^{2+}] = 4.7 \times 10^{-7}$ (molar solubility)

97. $[OH^-] = 7.6 \times 10^{-3}$ M; $[Pb^{2+}] = 2.1 \times 10^{-11}$ (molar solubility)

99. 7.66

101. (a) $K_{sp} = [Mg^{2+}][F^-]^2 = (1.21 \times 10^{-3})(2 \times 1.21 \times 10^{-3})^2 = 7.09 \times 10^{-9}$
(b) 7.09×10^{-7} M
(c) Determine the concentration of Mg^{2+} and F^- that will be present in the final volume. Compare the value of the ion product $[Mg^{2+}][F^-]^2$ with K_{sp}. If this value is larger than K_{sp}, precipitation will occur.
$0.1000\ L \times 3.00 \times 10^{-3}\ M\ Mg(NO_3)_2 = 0.3000\ L \times M\ Mg(NO_3)_2$
$M\ Mg(NO_3)_2 = 1.00 \times 10^{-3}\ M$
$0.2000\ L \times 2.00 \times 10^{-3}\ M\ NaF = 0.3000\ L \times M\ NaF$
$M\ NaF = 1.33 \times 10^{-3}\ M$
ion product = $(1.00 \times 10^{-3})(1.33 \times 10^{-3})^2 = 1.77 \times 10^{-9}$ This value is smaller than K_{sp}, so no precipitation will occur.
(d) MgF_2 is less soluble at 27 °C than at 18 °C. Because added heat acts like an added reagent, when it appears on the product side, the Le Châtelier's principle states that the equilibrium will shift to the reactants' side to counter the stress. Consequently, less reagent will dissolve. This situation is found in our case. Therefore, the reaction is exothermic.

103. BaF_2, $Ca_3(PO_4)_2$, ZnS; each is a salt of a weak acid, and the $[H_3O^+]$ from perchloric acid reduces the equilibrium concentration of the anion, thereby increasing the concentration of the cations

105. Effect on amount of solid $CaHPO_4$, $[Ca^{2+}]$, $[OH^-]$: (a) increase, increase, decrease; (b) decrease, increase, decrease; (c) no effect, no effect, no effect; (d) decrease, increase, decrease; (e) increase, no effect, no effect

Chapter 16

1. (a) reduction; (b) oxidation; (c) oxidation; (d) reduction

3. (a) $F_2 + Ca \longrightarrow 2F^- + Ca^{2+}$; (b) $Cl_2 + 2Li \longrightarrow 2Li^+ + 2Cl^-$; (c) $3Br_2 + 2Fe \longrightarrow 2Fe^{3+} + 6Br^-$; (d) $MnO_4 + 4H^+ + 3Ag \longrightarrow 3Ag^+ + MnO_2 + 2H_2O$

5. Oxidized: (a) Sn^{2+}; (b) Hg; (c) Al; reduced: (a) H_2O_2; (b) PbO_2; (c) ${Cr_2O_7}^{2-}$; oxidizing agent: (a) H_2O_2; (b) PbO_2; (c) ${Cr_2O_7}^{2-}$; reducing agent: (a) Sn^{2+}; (b) Hg; (c) Al

7. Oxidized = reducing agent: (a) ${SO_3}^{2-}$; (b) $Mn(OH)_2$; (c) H_2; (d) Al; reduced = oxidizing agent: (a) $Cu(OH)_2$; (b) O_2; (c) ${NO_3}^-$; (d) ${CrO_4}^{2-}$

9. In basic solution, $[OH^-] > 1 \times 10^{-7}\,M > [H^+]$. Hydrogen ion cannot appear as a reactant because its concentration is essentially zero. If it were produced, it would instantly react with the excess hydroxide ion to produce water. Thus, hydrogen ion should *not* appear as a reactant or product in basic solution.

11. (a) $Mg(s) \mid Mg^{2+}(aq) \parallel Ni^{2+}(aq) \mid Ni(s)$; (b) $Cu(s) \mid Cu^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$; (c) $Mn(s) \mid Mn^{2+}(aq) \parallel Sn^{2+}(aq) \mid Sn(s)$; (d) $Pt(s) \mid Cu^+(aq), Cu^{2+}(aq) \parallel Au^{3+}(aq) \mid Au(s)$

13. (a) $Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$; (b) $2Ag^+(aq) + Ni(s) \longrightarrow Ni^{2+}(aq) + 2Ag(s)$

15. Species oxidized = reducing agent: (a) Al(*s*); (b) NO(*g*); (c) Mg(*s*); and (d) $MnO_2(s)$; Species reduced = oxidizing agent: (a) $Zr^{4+}(aq)$; (b) $Ag^+(aq)$; (c) ${SiO_3}^{2-}(aq)$; and (d) ${ClO_3}^-(aq)$

17. Without the salt bridge, the circuit would be open (or broken) and no current could flow. With a salt bridge, each half-cell remains electrically neutral and current can flow through the circuit.

19. Active electrodes participate in the oxidation-reduction reaction. Since metals form cations, the electrode would lose mass if metal atoms in the electrode were to oxidize and go into solution. Oxidation occurs at the anode.

21. (a) +2.115 V (spontaneous); (b) +0.4626 V (spontaneous); (c) +1.0589 V (spontaneous); (d) +0.727 V (spontaneous)

23. $3Cu(s) + 2Au^{3+}(aq) \longrightarrow 3Cu^{2+}(aq) + 2Au(s)$; +1.16 V; spontaneous

25. $3Cd(s) + 2Al^{3+}(aq) \longrightarrow 3Cd^{2+}(aq) + 2Al(s)$; −1.259 V; nonspontaneous

27. (a) 0 kJ/mol; (b) −83.7 kJ/mol; (c) +235.3 kJ/mol

29. (a) standard cell potential: 1.50 V, spontaneous; cell potential under stated conditions: 1.43 V, spontaneous; (b) standard cell potential: 1.405 V, spontaneous; cell potential under stated conditions: 1.423 V, spontaneous; (c) standard cell potential: −2.749 V, nonspontaneous; cell potential under stated conditions: −2.757 V, nonspontaneous

31. (a) 1.7×10^{-10}; (b) 2.6×10^{-21}; (c) 8.9×10^{19}; (d) 1.0×10^{-14}

33. (a) $\begin{array}{ll} \text{anode: } Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^- & E^\circ_{\text{anode}} = 0.34\text{ V} \\ \text{cathode: } 2 \times \left(Ag^+(aq) + e^- \longrightarrow Ag(s)\right) & E^\circ_{\text{cathode}} = 0.7996\text{ V} \end{array}$; (b) 3.5×10^{15}; (c) $5.6 \times 10^{-9}\,M$

34. Batteries are self-contained and have a limited supply of reagents to expend before going dead. Alternatively, battery reaction byproducts accumulate and interfere with the reaction. Because a fuel cell is constantly resupplied with reactants and products are expelled, it can continue to function as long as reagents are supplied.

36. E_{cell}, as described in the Nernst equation, has a term that is directly proportional to temperature. At low temperatures, this term is decreased, resulting in a lower cell voltage provided by the battery to the device—the same effect as a battery running dead.

38. Mg and Zn

40. Both examples involve cathodic protection. The (sacrificial) anode is the metal that corrodes (oxidizes or reacts). In the case of iron (−0.447 V) and zinc (−0.7618 V), zinc has a more negative standard reduction potential and so serves as the anode. In the case of iron and copper (0.34 V), iron has the smaller standard reduction potential and so corrodes (serves as the anode).

42. While the reduction potential of lithium would make it capable of protecting the other metals, this high potential is also indicative of how reactive lithium is; it would have a spontaneous reaction with most substances. This means that the lithium would react quickly with other substances, even those that would not oxidize the metal it is attempting to protect. Reactivity like this means the sacrificial anode would be depleted rapidly and need to be replaced frequently. (Optional additional reason: fire hazard in the presence of water.)

46. (a) $\begin{array}{l}\text{mass Ca} = 69.1\text{ g}\\ \text{mass Cl}_2 = 122\text{ g}\end{array}$; (b) $\begin{array}{l}\text{mass Li} = 23.9\text{ g}\\ \text{mass H}_2 = 3.48\text{ g}\end{array}$; (c) $\begin{array}{l}\text{mass Al} = 31.0\text{ g}\\ \text{mass Cl}_2 = 122\text{ g}\end{array}$; (d) $\begin{array}{l}\text{mass Cr} = 59.8\text{ g}\\ \text{mass Br}_2 = 276\text{ g}\end{array}$

48. 0.79 L

Chapter 17

1. The instantaneous rate is the rate of a reaction at any particular point in time, a period of time that is so short that the concentrations of reactants and products change by a negligible amount. The initial rate is the instantaneous rate of reaction as it starts (as product just begins to form). Average rate is the average of the instantaneous rates over a time period.

3. $\text{rate} = +\frac{1}{2}\frac{\Delta[\text{ClF}_3]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[\text{F}_2]}{\Delta t}$

5. (a) average rate, 0 − 10 s = 0.0375 mol L^{-1} s^{-1}; average rate, 10 − 20 s = 0.0265 mol L^{-1} s^{-1}; (b) instantaneous rate, 15 s = 0.023 mol L^{-1} s^{-1}; (c) average rate for B formation = 0.0188 mol L^{-1} s^{-1}; instantaneous rate for B formation = 0.012 mol L^{-1} s^{-1}

7. Higher molarity increases the rate of the reaction. Higher temperature increases the rate of the reaction. Smaller pieces of magnesium metal will react more rapidly than larger pieces because more reactive surface exists.

9. (a) Depending on the angle selected, the atom may take a long time to collide with the molecule and, when a collision does occur, it may not result in the breaking of the bond and the forming of the other. (b) Particles of reactant must come into contact with each other before they can react.

11. (a) very slow; (b) As the temperature is increased, the reaction proceeds at a faster rate. The amount of reactants decreases, and the amount of products increases. After a while, there is a roughly equal amount of *BC*, *AB*, and *C* in the mixture and a slight excess of *A*.

13. (a) 2; (b) 1

15. (a) The process reduces the rate by a factor of 4. (b) Since CO does not appear in the rate law, the rate is not affected.

17. 4.3×10^{-5} mol/L/s

19. 7.9×10^{-13} mol/L/year

21. rate = k; $k = 2.0 \times 10^{-2}$ mol L^{-1} h^{-1} (about 0.9 g L^{-1} h^{-1} for the average male); The reaction is zero order.

23. rate = $k[\text{NOCl}]^2$; $k = 8.0 \times 10^{-8}$ L/mol/h; second order

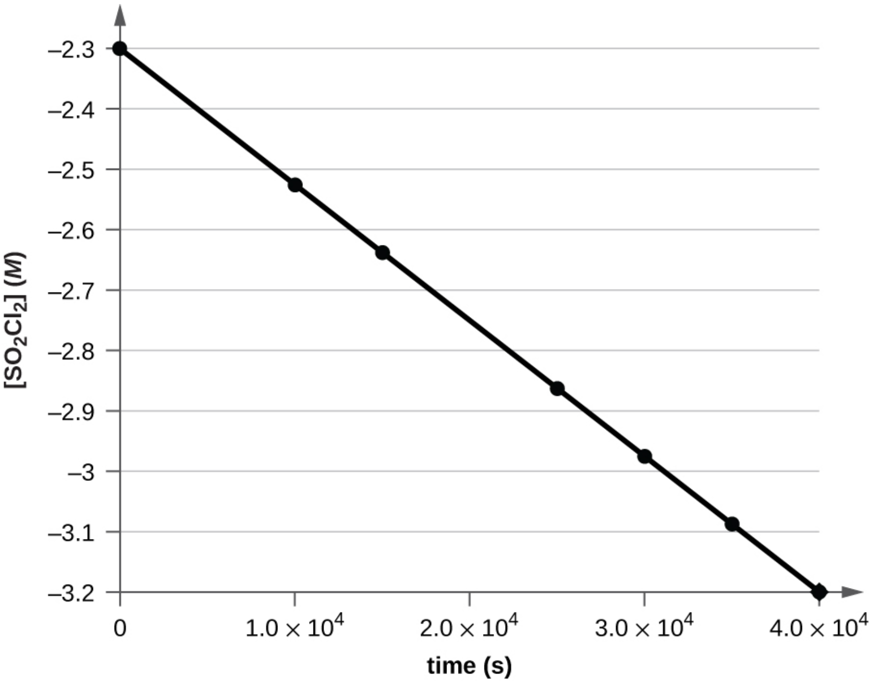
25. rate = $k[\text{NO}]^2[\text{Cl}_2]$; $k = 9.1$ L^2 mol^{-2} h^{-1}; second order in NO; first order in Cl_2

27. (a) The rate law is second order in A and is written as rate = $k[A]^2$. (b) $k = 7.88 \times 10^{-3}$ L mol^{-1} s^{-1}

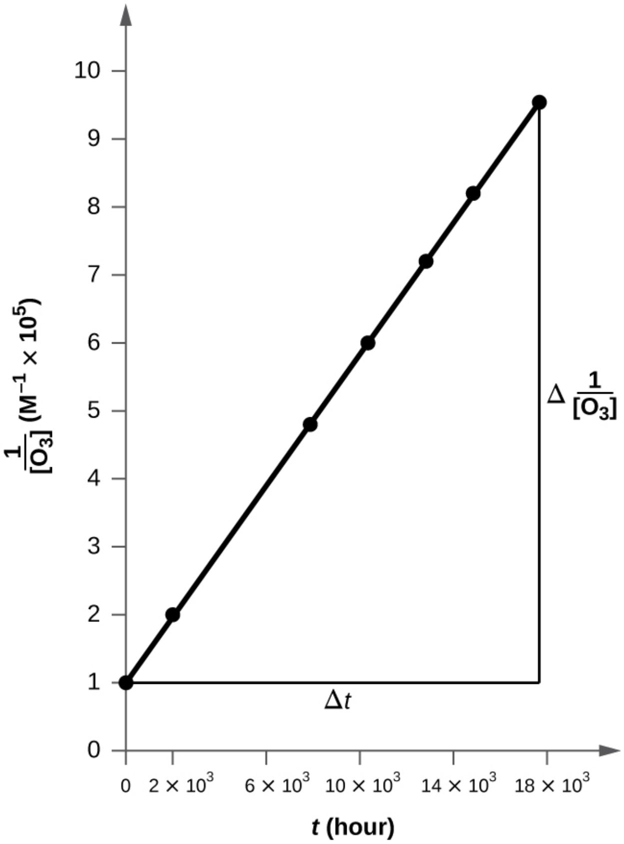
29. (a) 2.5×10^{-4} mol/L/min

31. rate = $k[\text{I}^-][\text{OCl}^-]$; $k = 6.1 \times 10^{-2}$ L mol^{-1} s^{-1}

33. Plotting a graph of $\ln[\text{SO}_2\text{Cl}_2]$ versus t reveals a linear trend; therefore we know this is a first-order reaction:



$k = -2.20 \times 10^5\ s^{-1}$



34.

The plot is nicely linear, so the reaction is second order. $k = 50.1\ L\ mol^{-1}\ h^{-1}$

36. 14.3 d

38. 8.3×10^7 s

40. 0.826 s

42. The reaction is first order. $k = 1.0 \times 10^7$ L mol^{-1} min^{-1}

44. 1.67×10^3 s ; 20% remains

46. 252 days

48.

$[A]_0$ (M)	$k \times 10^3$ (s^{-1})
4.88	2.45
3.52	2.51
2.29	2.53
1.81	2.58
5.33	2.36
4.05	2.47
2.95	2.48
1.72	2.43

50. The reactants either may be moving too slowly to have enough kinetic energy to exceed the activation energy for the reaction, or the orientation of the molecules when they collide may prevent the reaction from occurring.

52. The activation energy is the minimum amount of energy necessary to form the activated complex in a reaction. It is usually expressed as the energy necessary to form one mole of activated complex.

54. After finding k at several different temperatures, a plot of ln k versus $\frac{1}{T}$, gives a straight line with the slope $\frac{-E_a}{R}$ from which E_a may be determined.

56. (a) 4-times faster (b) 128-times faster

58. 3.9×10^{15} s^{-1}

60. 43.0 kJ/mol

62. 177 kJ/mol

64. E_a = 108 kJ; $A = 2.0 \times 10^8$ s^{-1}; $k = 3.2 \times 10^{-10}$ s^{-1}; (b) 1.81×10^8 h or 7.6×10^6 day; (c) Assuming that the reaction is irreversible simplifies the calculation because we do not have to account for any reactant that, having been converted to product, returns to the original state.

66. The A atom has enough energy to react with BC; however, the different angles at which it bounces off of BC without reacting indicate that the orientation of the molecule is an important part of the reaction kinetics and determines whether a reaction will occur.

68. No. In general, for the overall reaction, we cannot predict the effect of changing the concentration without knowing the rate law. Yes. If the reaction is an elementary reaction, then doubling the concentration of A doubles the rate.

70. Rate = $k[A][B]^2$; Rate = $k[A]^3$

72. (a) Rate$_1$ = $k[O_3]$; (b) Rate$_2$ = $k[O_3][Cl]$; (c) Rate$_3$ = $k[ClO][O]$; (d) Rate$_2$ = $k[O_3][NO]$; (e) Rate$_3$ = $k[NO_2][O]$

74. (a) Doubling $[H_2]$ doubles the rate. $[H_2]$ must enter the rate law to the first power. Doubling [NO] increases the rate by a factor of 4. [NO] must enter the rate law to the second power. (b) Rate = $k\,[NO]^2[H_2]$; (c) $k = 5.0 \times 10^3$

$mol^{-2}\ L^{-2}\ min^{-1}$; (d) 0.0050 mol/L; (e) Step II is the rate-determining step. If step I gives N_2O_2 in adequate amount, steps 1 and 2 combine to give $2NO + H_2 \longrightarrow H_2O + N_2O$. This reaction corresponds to the observed rate law. Combine steps 1 and 2 with step 3, which occurs by supposition in a rapid fashion, to give the appropriate stoichiometry.

76. The general mode of action for a catalyst is to provide a mechanism by which the reactants can unite more readily by taking a path with a lower reaction energy. The rates of both the forward and the reverse reactions are increased, leading to a faster achievement of equilibrium.

78. (a) Chlorine atoms are a catalyst because they react in the second step but are regenerated in the third step. Thus, they are not used up, which is a characteristic of catalysts. (b) NO is a catalyst for the same reason as in part (a).

79. no changes.

82. The lowering of the transition state energy indicates the effect of a catalyst. (a) B; (b) B

84. The energy needed to go from the initial state to the transition state is (a) 10 kJ; (b) 10 kJ

86. Both diagrams describe two-step, exothermic reactions, but with different changes in enthalpy, suggesting the diagrams depict two different overall reactions.

Chapter 18

1. The alkali metals all have a single *s* electron in their outermost shell. In contrast, the alkaline earth metals have a completed *s* subshell in their outermost shell. In general, the alkali metals react faster and are more reactive than the corresponding alkaline earth metals in the same period.

3.

$$Na + I_2 \longrightarrow 2NaI$$
$$2Na + Se \longrightarrow Na_2Se$$
$$2Na + O_2 \longrightarrow Na_2O_2$$
$$Sr + I_2 \longrightarrow SrI_2$$
$$Sr + Se \longrightarrow SrSe$$
$$2Sr + O_2 \longrightarrow 2SrO$$
$$2Al + 3I_2 \longrightarrow 2AlI_3$$
$$2Al + 3Se \longrightarrow Al_2Se_3$$
$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

5. The possible ways of distinguishing between the two include infrared spectroscopy by comparison of known compounds, a flame test that gives the characteristic yellow color for sodium (strontium has a red flame), or comparison of their solubilities in water. At 20 °C, NaCl dissolves to the extent of $\frac{35.7\ g}{100\ mL}$ compared with $\frac{53.8\ g}{100\ mL}$ for $SrCl_2$. Heating to 100 °C provides an easy test, since the solubility of NaCl is $\frac{39.12\ g}{100\ mL}$, but that of $SrCl_2$ is $\frac{100.8\ g}{100\ mL}$. Density determination on a solid is sometimes difficult, but there is enough difference (2.165 g/mL NaCl and 3.052 g/mL $SrCl_2$) that this method would be viable and perhaps the easiest and least expensive test to perform.

7. (a) $2Sr(s) + O_2(g) \longrightarrow 2SrO(s)$; (b) $Sr(s) + 2HBr(g) \longrightarrow SrBr_2(s) + H_2(g)$; (c) $Sr(s) + H_2(g) \longrightarrow SrH_2(s)$; (d) $6Sr(s) + P_4(s) \longrightarrow 2Sr_3P_2(s)$; (e) $Sr(s) + 2H_2O(l) \longrightarrow Sr(OH)_2(aq) + H_2(g)$

9. 11 lb

11. Yes, tin reacts with hydrochloric acid to produce hydrogen gas.

13. In $PbCl_2$, the bonding is ionic, as indicated by its melting point of 501 °C. In $PbCl_4$, the bonding is covalent, as evidenced by it being an unstable liquid at room temperature.

15.

$$2CsCl(l) + Ca(g) \xrightarrow{\substack{\text{countercurrent}\\ \text{fractionating}\\ \text{tower}}} 2Cs(g) + CaCl_2(l)$$

17. Cathode (reduction): $2Li^+ + 2e^- \longrightarrow 2Li(l)$; Anode (oxidation): $2Cl^- \longrightarrow Cl_2(g) + 2e^-$; Overall reaction: $2Li^+ + 2Cl^- \longrightarrow 2Li(l) + Cl_2(g)$

19. 0.5035 g H_2

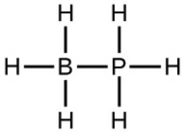
21. Despite its reactivity, magnesium can be used in construction even when the magnesium is going to come in contact with a flame because a protective oxide coating is formed, preventing gross oxidation. Only if the metal is finely subdivided or present in a thin sheet will a high-intensity flame cause its rapid burning.

23. Extract from ore: $AlO(OH)(s) + NaOH(aq) + H_2O(l) \longrightarrow Na[Al(OH)_4](aq)$
Recover: $2Na[Al(OH)_4](s) + H_2SO_4(aq) \longrightarrow 2Al(OH)_3(s) + Na_2SO_4(aq) + 2H_2O(l)$
Sinter: $2Al(OH)_3(s) \longrightarrow Al_2O_3(s) + 3H_2O(g)$
Dissolve in $Na_3AlF_6(l)$ and electrolyze: $Al^{3+} + 3e^- \longrightarrow Al(s)$

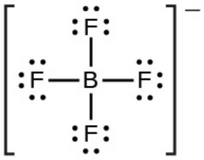
25. 25.83%

27. 39 kg

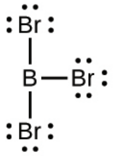
29. (a) H_3BPH_3:



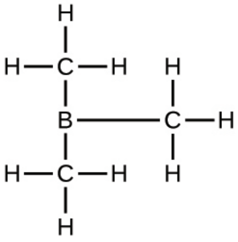
(b) $BF_4{}^-$:



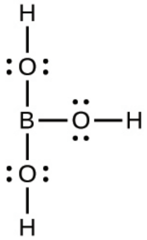
(c) BBr_3:



(d) $B(CH_3)_3$:



(e) $B(OH)_3$:



31. $1s^22s^22p^63s^23p^23d^0$.

33. (a) $(CH_3)_3SiH$: sp^3 bonding about Si; the structure is tetrahedral; (b) $SiO_4{}^{4-}$: sp^3 bonding about Si; the structure is tetrahedral; (c) Si_2H_6: sp^3 bonding about each Si; the structure is linear along the Si-Si bond; (d) $Si(OH)_4$: sp^3 bonding about Si; the structure is tetrahedral; (e) $SiF_6{}^{2-}$: sp^3d^2 bonding about Si; the structure is octahedral

35. (a) nonpolar; (b) nonpolar; (c) polar; (d) nonpolar; (e) polar

37. (a) tellurium dioxide or tellurium(IV) oxide; (b) antimony(III) sulfide; (c) germanium(IV) fluoride; (d) silane or silicon(IV) hydride; (e) germanium(IV) hydride

39. Boron has only *s* and *p* orbitals available, which can accommodate a maximum of four electron pairs. Unlike silicon, no *d* orbitals are available in boron.

41. (a) $\Delta H° = 87$ kJ; $\Delta G° = 44$ kJ; (b) $\Delta H° = -109.9$ kJ; $\Delta G° = -154.7$ kJ; (c) $\Delta H° = -510$ kJ; $\Delta G° = -601.5$ kJ

43. A mild solution of hydrofluoric acid would dissolve the silicate and would not harm the diamond.

45. In the N_2 molecule, the nitrogen atoms have an σ bond and two π bonds holding the two atoms together. The presence of three strong bonds makes N_2 a very stable molecule. Phosphorus is a third-period element, and as such, does not form π bonds efficiently; therefore, it must fulfill its bonding requirement by forming three σ bonds.

47. (a) H = 1+, C = 2+, and N = 3−; (b) O = 2+ and F = 1−; (c) As = 3+ and Cl = 1−

49. S < Cl < O < F

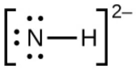
51. The electronegativity of the nonmetals is greater than that of hydrogen. Thus, the negative charge is better represented on the nonmetal, which has the greater tendency to attract electrons in the bond to itself.

53. Hydrogen has only one orbital with which to bond to other atoms. Consequently, only one two-electron bond can form.

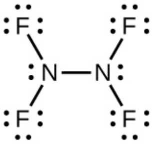
55. 0.43 g H_2

57. (a) $Ca(OH)_2(aq) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l)$; (b) $CaO(s) + SO_2(g) \longrightarrow CaSO_3(s)$;
(c) $2NaHCO_3(s) + NaH_2PO_4(aq) \longrightarrow Na_3PO_4(aq) + 2CO_2(g) + 2H_2O(l)$

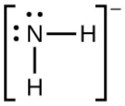
59. (a) NH^{2-}:



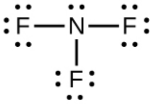
(b) N_2F_4:



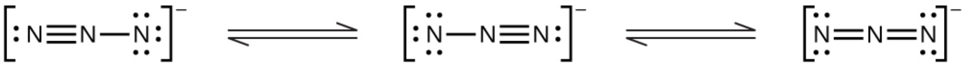
(c) $NH_2{}^-$:



(d) NF_3:



(e) $N_3{}^-$:

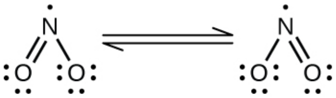


61. Ammonia acts as a Brønsted base because it readily accepts protons and as a Lewis base in that it has an electron pair to donate.

Brønsted base: $NH_3 + H_3O^+ \longrightarrow NH_4{}^+ + H_2O$

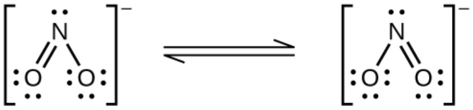
Lewis base: $2NH_3 + Ag^+ \longrightarrow [H_3N - Ag - NH_3]^+$

63. (a) NO_2:



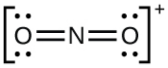
Nitrogen is sp^2 hybridized. The molecule has a bent geometry with an ONO bond angle of approximately 120°.

(b) $NO_2{}^-$:



Nitrogen is sp^2 hybridized. The molecule has a bent geometry with an ONO bond angle slightly less than 120°.

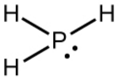
(c) $NO_2{}^+$:



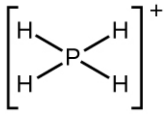
Nitrogen is sp hybridized. The molecule has a linear geometry with an ONO bond angle of 180°.

65. Nitrogen cannot form a NF_5 molecule because it does not have *d* orbitals to bond with the additional two fluorine atoms.

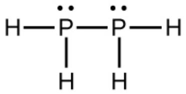
67. (a)



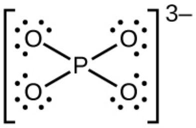
(b)



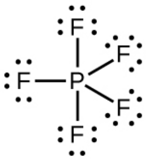
(c)



(d)



(e)

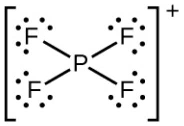


69. (a) $P_4(s) + 4Al(s) \longrightarrow 4AlP(s)$; (b) $P_4(s) + 12Na(s) \longrightarrow 4Na_3P(s)$; (c) $P_4(s) + 10F_2(g) \longrightarrow 4PF_5(l)$; (d) $P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(l)$ or $P_4(s) + 10Cl_2(g) \longrightarrow 4PCl_5(l)$; (e) $P_4(s) + 3O_2(g) \longrightarrow P_4O_6(s)$ or $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$; (f) $P_4O_6(s) + 2O_2(g) \longrightarrow P_4O_{10}(s)$

71. 291 mL

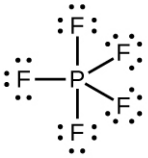
73. 28 tons

75. (a)



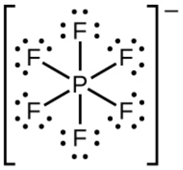
Tetrahedral

(b)



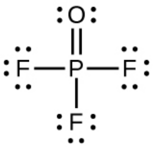
Trigonal bipyramid

(c)



Octahedral

(d)



Tetrahedral

77. (a) P = 3+; (b) P = 5+; (c) P = 3+; (d) P = 5+; (e) P = 3−; (f) P = 5+

79. FrO_2

81. (a) $2Zn(s) + O_2(g) \longrightarrow 2ZnO(s)$; (b) $ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$; (c) $ZnCO_3(s) + 2CH_3COOH(aq) \longrightarrow Zn(CH_3COO)_2(aq) + CO_2(g) + H_2O(l)$; (d) $Zn(s) + 2HBr(aq) \longrightarrow ZnBr_2(aq) + H_2(g)$

83. $Al(OH)_3(s) + 3H^+(aq) \longrightarrow Al^{3+} + 3H_2O(l)$; $Al(OH)_3(s) + OH^- \longrightarrow [Al(OH)_4]^-(aq)$

85. (a) $Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$; (b) $Cs_2CO_3(s) + 2HF(aq) \longrightarrow 2CsF(aq) + CO_2(g) + H_2O(l)$; (c) $Al_2O_3(s) + 6HClO_4(aq) \longrightarrow 2Al(ClO_4)_3(aq) + 3H_2O(l)$; (d) $Na_2CO_3(aq) + Ba(NO_3)_2(aq) \longrightarrow 2NaNO_3(aq) + BaCO_3(s)$; (e) $TiCl_4(l) + 4Na(s) \longrightarrow Ti(s) + 4NaCl(s)$

87. $HClO_4$ is the stronger acid because, in a series of oxyacids with similar formulas, the higher the electronegativity of the central atom, the stronger is the attraction of the central atom for the electrons of the oxygen(s). The stronger attraction of the oxygen electron results in a stronger attraction of oxygen for the electrons in the O-H bond, making the hydrogen more easily released. The weaker this bond, the stronger the acid.

89. As H_2SO_4 and H_2SeO_4 are both oxyacids and their central atoms both have the same oxidation number, the acid strength depends on the relative electronegativity of the central atom. As sulfur is more electronegative than selenium, H_2SO_4 is the stronger acid.

91. SO_2, sp^2 4+; SO_3, sp^2, 6+; H_2SO_4, sp^3, 6+

93. SF_6: S = 6+; SO_2F_2: S = 6+; KHS: S = 2−

95. Sulfur is able to form double bonds only at high temperatures (substantially endothermic conditions), which is not the case for oxygen.

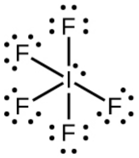
97. There are many possible answers including: $Cu(s) + 2H_2SO_4(l) \longrightarrow CuSO_4(aq) + SO_2(g) + 2H_2O(l)$ and $C(s) + 2H_2SO_4(l) \longrightarrow CO_2(g) + 2SO_2(g) + 2H_2O(l)$

99. 5.1×10^4 g

101. $SnCl_4$ is not a salt because it is covalently bonded. A salt must have ionic bonds.

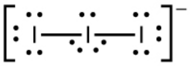
103. In oxyacids with similar formulas, the acid strength increases as the electronegativity of the central atom increases. $HClO_3$ is stronger than $HBrO_3$; Cl is more electronegative than Br.

105. (a)



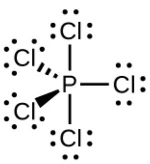
Square pyramidal

(b)



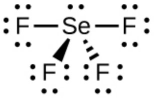
Linear

(c)



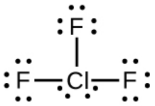
Trigonal bipyramidal

(d)



Seesaw

(e)



T-shaped

107. (a) bromine trifluoride; (b) sodium bromate; (c) phosphorus pentabromide; (d) sodium perchlorate; (e) potassium hypochlorite

109. (a) I: 7+; (b) I: 7+; (c) Cl: 4+; (d) I: 3+; Cl: 1−; (e) F: 0

111. (a) sp^3d hybridized; (b) sp^3d^2 hybridized; (c) sp^3 hybridized; (d) sp^3 hybridized; (e) sp^3d^2 hybridized;

113. (a) nonpolar; (b) nonpolar; (c) polar; (d) nonpolar; (e) polar

115. The empirical formula is XeF_6, and the balanced reactions are:

$$\text{Xe}(g) + 3\text{F}_2(g) \xrightarrow{\Delta} \text{XeF}_6(s)$$
$$\text{XeF}_6(s) + 3\text{H}_2(g) \longrightarrow 6\text{HF}(g) + \text{Xe}(g)$$

Chapter 19

1. (a) Sc: $[\text{Ar}]4s^23d^1$; (b) Ti: $[\text{Ar}]4s^23d^2$; (c) Cr: $[\text{Ar}]4s^13d^5$; (d) Fe: $[\text{Ar}]4s^23d^6$; (e) Ru: $[\text{Kr}]5s^24d^6$

3. (a) La: $[\text{Xe}]6s^25d^1$, La^{3+}: [Xe]; (b) Sm: $[\text{Xe}]6s^24f^6$, Sm^{3+}: $[\text{Xe}]4f^5$; (c) Lu: $[\text{Xe}]6s^24f^{14}5d^1$, Lu^{3+}: $[\text{Xe}]4f^{14}$

5. Al is used because it is the strongest reducing agent and the only option listed that can provide sufficient driving force to convert La(III) into La.

7. Mo

9. The $CaSiO_3$ slag is less dense than the molten iron, so it can easily be separated. Also, the floating slag layer creates a barrier that prevents the molten iron from exposure to O_2, which would oxidize the Fe back to Fe_2O_3.

11. 2.57%

13. 0.167 V

15. $E° = −0.6$ V, $E°$ is negative so this reduction is not spontaneous. $E° = +1.1$ V

17. (a) $Fe(s) + 2H_3O^+(aq) + SO_4{}^{2-}(aq) \longrightarrow Fe^{2+}(aq) + SO_4{}^{2-}(aq) + H_2(g) + 2H_2O(l)$; (b) $FeCl_3(aq) + 3Na^+(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s) + 3Na^+(aq) + 3Cl^+(aq)$; (c) $Mn(OH)_2(s) + 2H_3O^+(aq) + 2Br^-(aq) \longrightarrow Mn^{2+}(aq) + 2Br^-(aq) + 4H_2O(l)$; (d) $4Cr(s) + 3O_2(g) \longrightarrow 2Cr_2O_3(s)$; (e) $Mn_2O_3(s) + 6H_3O^+(aq) + 6Cl^-(aq) \longrightarrow 2MnCl_3(s) + 9H_2O(l)$; (f) $Ti(s) + xsF_2(g) \longrightarrow TiF_4(g)$

19. (a) $Cr_2(SO_4)_3(aq) + 2Zn(s) + 2H_3O^+(aq) \longrightarrow 2Zn^{2+}(aq) + H_2(g) + 2H_2O(l) + 2Cr^{2+}(aq) + 3SO_4{}^{2-}(aq)$; (b) $4TiCl_3(s) + CrO_4{}^{2-}(aq) + 8H^+(aq) \longrightarrow 4Ti^{4+}(aq) + Cr(s) + 4H_2O(l) + 12Cl^-(aq)$; (c) In acid solution between pH 2 and pH 6, $CrO_4{}^{2-}$ forms $HCrO_4{}^-$, which is in equilibrium with dichromate ion. The reaction is $2HCrO_4{}^-(aq) \longrightarrow Cr_2O_7{}^{2-}(aq) + H_2O(l)$. At other acidic pHs, the reaction is $3Cr^{2+}(aq) + CrO_4{}^{2-}(aq) + 8H_3O^+(aq) \longrightarrow 4Cr^{3+}(aq) + 12H_2O(l)$; (d) $8CrO_3(s) + 9Mn(s) \xrightarrow{\Delta} 4Cr_2O_3(s) + 3Mn_3O_4(s)$; (e) $CrO(s) + 2H_3O^+(aq) + 2NO_3{}^-(aq) \longrightarrow Cr^{2+}(aq) + 2NO_3{}^-(aq) + 3H_2O(l)$; (f) $CrCl_3(s) + 3NaOH(aq) \longrightarrow Cr(OH)_3(s) + 3Na^+(aq) + 3Cl^-(aq)$

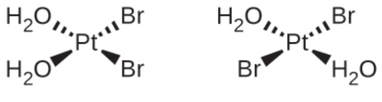
21. (a) $3Fe(s) + 4H_2O(g) \longrightarrow Fe_3O_4(s) + 4H_2(g)$; (b) $3NaOH(aq) + Fe(NO_3)_3(aq) \xrightarrow{H_2O} Fe(OH)_3(s) + 3Na^+(aq) + 3NO_3{}^-(aq)$; (c) $MnO^{4-} + 5Fe2+ + 8H+ \longrightarrow Mn^{2+} + 5Fe_3 + 4H_2O$; (d) $Fe(s) + 2H_3O^+(aq) + SO_4{}^{2-}(aq) \longrightarrow Fe^{2+}(aq) + SO_4{}^{2-}(aq) + H_2(g) + 2H_2O(l)$; (e) $4Fe^{2+}(aq) + O_2(g) + 4HNO_3(aq) \longrightarrow 4Fe^{3+}(aq) + 2H_2O(l) + 4NO_3{}^-(aq)$; (f) $FeCO_3(s) + 2HClO_4(aq) \longrightarrow Fe(ClO_4)_2(aq) + H_2O(l) + CO_2(g)$; (g) $3Fe(s) + 2O_2(g) \xrightarrow{\Delta} Fe_3O_4(s)$

23. As CN^- is added,
$Ag^+(aq) + CN^-(aq) \longrightarrow AgCN(s)$
As more CN^- is added,
$Ag^+(aq) + 2CN^-(aq) \longrightarrow [Ag(CN)_2]^-(aq)$
$AgCN(s) + CN^-(aq) \longrightarrow [Ag(CN)_2]^-(aq)$

25. (a) Sc^{3+}; (b) Ti^{4+}; (c) V^{5+}; (d) Cr^{6+}; (e) Mn^{4+}; (f) Fe^{2+} and Fe^{3+}; (g) Co^{2+} and Co^{3+}; (h) Ni^{2+}; (i) Cu^+

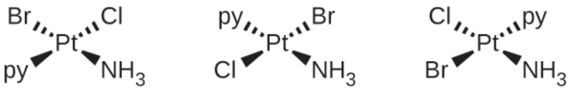
27. (a) 4, $[Zn(OH)_4]^{2-}$; (b) 6, $[Pd(CN)_6]^{2-}$; (c) 2, $[AuCl_2]^-$; (d) 4, $[Pt(NH_3)_2Cl_2]$; (e) 6, $K[Cr(NH_3)_2Cl_4]$; (f) 6, $[Co(NH_3)_6][Cr(CN)_6]$; (g) 6, $[Co(en)_2Br_2]NO_3$

29. (a) $[Pt(H_2O)_2Br_2]$:

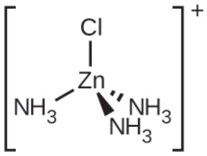


cis *trans*

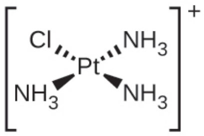
(b) $[Pt(NH_3)(py)(Cl)(Br)]$:



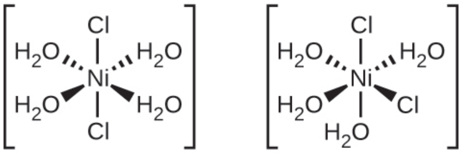
(c) $[Zn(NH_3)_3Cl]^+$:



(d) $[Pt(NH_3)_3Cl]^+$:

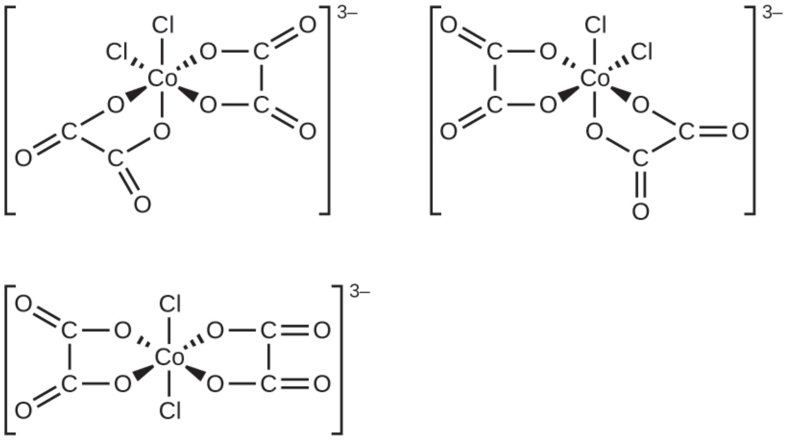


(e) $[Ni(H_2O)_4Cl_2]$:



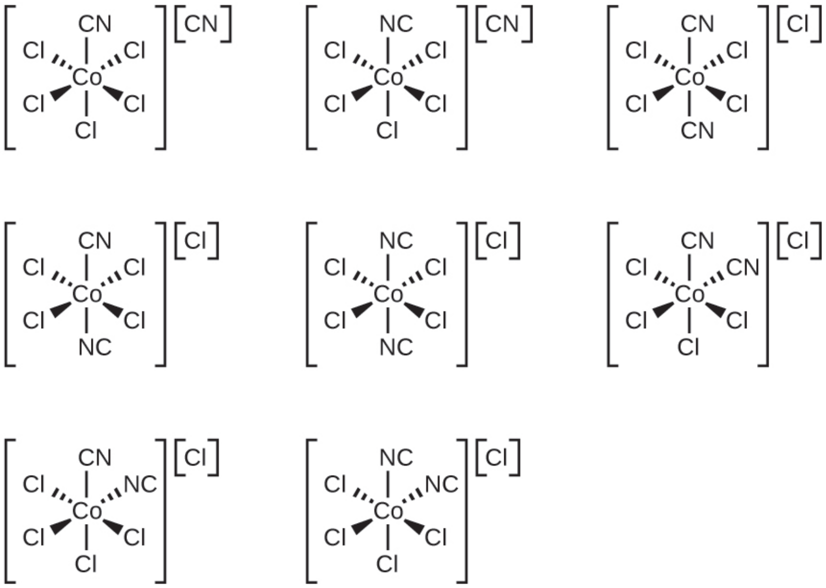
trans *cis*

(f) $[Co(C_2O_4)_2Cl_2]^{3-}$:



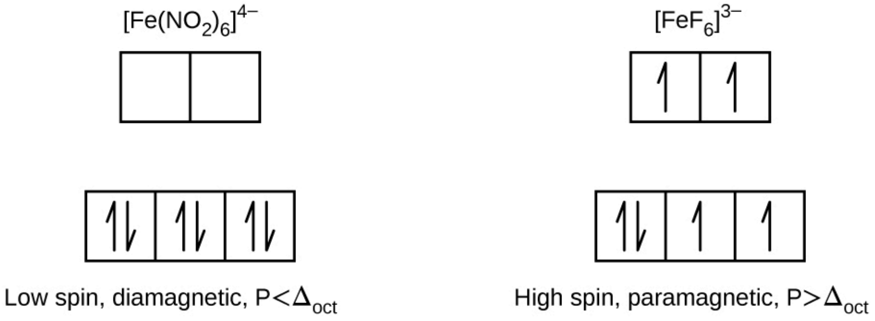
31. (a) tricarbonatocobaltate(III) ion; (b) tetraaminecopper(II) ion; (c) tetraaminedibromocobalt(III) sulfate; (d) tetraamineplatinum(II) tetrachloroplatinate(II); (e) *tris*-(ethylenediamine)chromium(III) nitrate; (f) diaminedibromopalladium(II); (g) potassium pentachlorocuprate(II); (h) diaminedichlorozinc(II)

33. (a) none; (b) none; (c) The two Cl ligands can be *cis* or *trans*. When they are *cis*, there will also be an optical isomer.



35.

37.



39. $[Co(H_2O)_6]Cl_2$ with three unpaired electrons.

41. (a) 4; (b) 2; (c) 1; (d) 5; (e) 0

43. (a) $[Fe(CN)_6]^{4-}$; (b) $[Co(NH_3)_6]^{3+}$; (c) $[Mn(CN)_6]^{4-}$

45. The complex does not have any unpaired electrons. The complex does not have any geometric isomers, but the mirror image is nonsuperimposable, so it has an optical isomer.

47. No. Au^+ has a complete 5*d* sublevel.

Chapter 20

1. (a) sodium-24; (b) aluminum-29; (c) krypton-73; (d) iridium-194

3. (a) $^{34}_{14}\text{Si}$; (b) $^{36}_{15}\text{P}$; (c) $^{57}_{25}\text{Mn}$; (d) $^{121}_{56}\text{Ba}$

5. (a) $^{45}_{25}\text{Mn}^{+1}$; (b) $^{69}_{45}\text{Rh}^{+2}$; (c) $^{142}_{53}\text{I}^{-1}$; (d) $^{243}_{97}\text{Bk}$

7. Nuclear reactions usually change one type of nucleus into another; chemical changes rearrange atoms. Nuclear reactions involve much larger energies than chemical reactions and have measureable mass changes.

9. (a), (b), (c), (d), and (e)

11. (a) A nucleon is any particle contained in the nucleus of the atom, so it can refer to protons and neutrons. (b) An α particle is one product of natural radioactivity and is the nucleus of a helium atom. (c) A β particle is a product of natural radioactivity and is a high-speed electron. (d) A positron is a particle with the same mass as an electron but with a positive charge. (e) Gamma rays compose electromagnetic radiation of high energy and short wavelength. (f) Nuclide is a term used when referring to a single type of nucleus. (g) The mass number is the sum of the number of protons and the number of neutrons in an element. (h) The atomic number is the number of protons in the nucleus of an element.

13. (a) ${}^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \longrightarrow {}^{30}_{15}\text{P} + {}^{1}_{0}\text{n}$; (b) ${}^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$; (c) ${}^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$; (d) ${}^{235}_{92}\text{U} \longrightarrow {}^{96}_{37}\text{Rb} + {}^{135}_{55}\text{Cs} + 4{}^{1}_{0}\text{n}$

15. (a) ${}^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$; (b) ${}^{14}_{7}\text{C} + {}^{1}_{0}\text{n} \longrightarrow {}^{14}_{6}\text{C} + {}^{1}_{1}\text{H}$; (c) ${}^{232}_{90}\text{Th} + {}^{1}_{0}\text{n} \longrightarrow {}^{233}_{90}\text{Th}$; (d) ${}^{238}_{92}\text{U} + {}^{2}_{1}\text{H} \longrightarrow {}^{239}_{92}\text{U} + {}^{1}_{1}\text{H}$

17. (a) 148.8 MeV per atom; (b) 7.808 MeV/nucleon

19. α (helium nuclei), β (electrons), β^{+} (positrons), and η (neutrons) may be emitted from a radioactive element, all of which are particles; γ rays also may be emitted.

21. (a) conversion of a neutron to a proton: ${}^{1}_{0}\text{n} \longrightarrow {}^{1}_{1}\text{p} + {}^{0}_{+1}\text{e}$; (b) conversion of a proton to a neutron; the positron has the same mass as an electron and the same magnitude of positive charge as the electron has negative charge; when the n:p ratio of a nucleus is too low, a proton is converted into a neutron with the emission of a positron: ${}^{1}_{1}\text{p} \longrightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\text{e}$; (c) In a proton-rich nucleus, an inner atomic electron can be absorbed. In simplest form, this changes a proton into a neutron: ${}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \longrightarrow {}^{1}_{0}\text{p}$

23. The electron pulled into the nucleus was most likely found in the 1*s* orbital. As an electron falls from a higher energy level to replace it, the difference in the energy of the replacement electron in its two energy levels is given off as an X-ray.

25. Manganese-51 is most likely to decay by positron emission. The n:p ratio for Cr-53 is $\frac{29}{24}$ = 1.21; for Mn-51, it is $\frac{26}{25}$ = 1.04; for Fe-59, it is $\frac{33}{26}$ = 1.27. Positron decay occurs when the n:p ratio is low. Mn-51 has the lowest n:p ratio and therefore is most likely to decay by positron emission. Besides, ${}^{53}_{24}\text{Cr}$ is a stable isotope, and ${}^{59}_{26}\text{Fe}$ decays by beta emission.

27. (a) β decay; (b) α decay; (c) positron emission; (d) β decay; (e) α decay

29. ${}^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$; ${}^{234}_{90}\text{Th} \longrightarrow {}^{234}_{91}\text{Pa} + {}^{0}_{-1}\text{e}$; ${}^{234}_{91}\text{Pa} \longrightarrow {}^{234}_{92}\text{U} + {}^{0}_{-1}\text{e}$; ${}^{234}_{92}\text{U} \longrightarrow {}^{230}_{90}\text{Th} + {}^{4}_{2}\text{He}$ ${}^{230}_{90}\text{Th} \longrightarrow {}^{226}_{88}\text{Ra} + {}^{4}_{2}\text{He}$ ${}^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$; ${}^{222}_{86}\text{Rn} \longrightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He}$

31. Half-life is the time required for half the atoms in a sample to decay. Example (answers may vary): For C-14, the half-life is 5770 years. A 10-g sample of C-14 would contain 5 g of C-14 after 5770 years; a 0.20-g sample of C-14 would contain 0.10 g after 5770 years.

33. $\left(\frac{1}{2}\right)^{0.04} = 0.973$ or 97.3%

35. 2×10^{3} y

37. 0.12 h^{-1}

39. (a) 3.8 billion years; (b) The rock would be younger than the age calculated in part (a). If Sr was originally in the rock, the amount produced by radioactive decay would equal the present amount minus the initial amount. As this amount would be smaller than the amount used to calculate the age of the rock and the age is proportional to the amount of Sr, the rock would be younger.

41. $c = 0$; This shows that no Pu-239 could remain since the formation of the earth. Consequently, the plutonium now present could not have been formed with the uranium.

43. 17.5 MeV

45. (a) ${}^{212}_{83}\text{Bi} \longrightarrow {}^{212}_{84}\text{Po} + {}^{0}_{-1}\text{e}$; (b) ${}^{8}_{5}\text{B} \longrightarrow {}^{8}_{4}\text{Be} + {}^{0}_{-1}\text{e}$; (c) ${}^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\text{Np}$,

$^{239}_{93}\text{Np} \longrightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\text{e}$; (d) $^{90}_{38}\text{Sr} \longrightarrow {}^{90}_{39}\text{Y} + {}^{0}_{-1}\text{e}$

47. (a) $^{241}_{95}\text{Am} + {}^{4}_{2}\text{He} \longrightarrow {}^{244}_{97}\text{Bk} + {}^{1}_{0}\text{n}$; (b) $^{239}_{94}\text{Pu} + 15{}^{1}_{0}\text{n} \longrightarrow {}^{254}_{100}\text{Fm} + 6{}^{0}_{-1}\text{e}$; (c) $^{250}_{98}\text{Cf} + {}^{11}_{5}\text{B} \longrightarrow {}^{257}_{103}\text{Lr} + 4{}^{1}_{0}\text{n}$; (d) $^{249}_{98}\text{Cf} + {}^{15}_{7}\text{N} \longrightarrow {}^{260}_{105}\text{Db} + 4{}^{1}_{0}\text{n}$

49. Two nuclei must collide for fusion to occur. High temperatures are required to give the nuclei enough kinetic energy to overcome the very strong repulsion resulting from their positive charges.

51. A nuclear reactor consists of the following:

1. A nuclear fuel. A fissionable isotope must be present in large enough quantities to sustain a controlled chain reaction. The radioactive isotope is contained in tubes called fuel rods.
2. A moderator. A moderator slows neutrons produced by nuclear reactions so that they can be absorbed by the fuel and cause additional nuclear reactions.
3. A coolant. The coolant carries heat from the fission reaction to an external boiler and turbine where it is transformed into electricity.
4. A control system. The control system consists of control rods placed between fuel rods to absorb neutrons and is used to adjust the number of neutrons and keep the rate of the chain reaction at a safe level.
5. A shield and containment system. The function of this component is to protect workers from radiation produced by the nuclear reactions and to withstand the high pressures resulting from high-temperature reactions.

53. The fission of uranium generates heat, which is carried to an external steam generator (boiler). The resulting steam turns a turbine that powers an electrical generator.

55. Introduction of either radioactive Ag^{+} or radioactive Cl^{-} into the solution containing the stated reaction, with subsequent time given for equilibration, will produce a radioactive precipitate that was originally devoid of radiation.

57. (a) $^{133}_{53}\text{I} \longrightarrow {}^{133}_{54}\text{Xe} + {}^{0}_{-1}\text{e}$; (b) 37.6 days

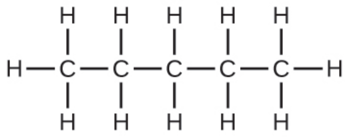
59. Alpha particles can be stopped by very thin shielding but have much stronger ionizing potential than beta particles, X-rays, and γ-rays. When inhaled, there is no protective skin covering the cells of the lungs, making it possible to damage the DNA in those cells and cause cancer.

61. (a) 7.64×10^{9} Bq; (b) 2.06×10^{-2} Ci

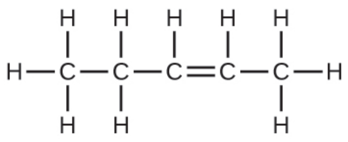
Chapter 21

1. There are several sets of answers; one is:

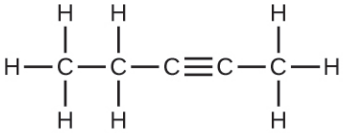
(a) C_5H_{12}



(b) C_5H_{10}



(c) C_5H_8

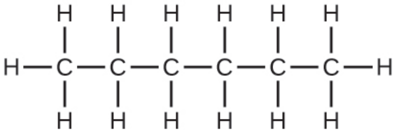


3. Both reactions result in bromine being incorporated into the structure of the product. The difference is the way in which that incorporation takes place. In the saturated hydrocarbon, an existing C–H bond is broken, and a bond between the C and the Br can then be formed. In the unsaturated hydrocarbon, the only bond broken in the hydrocarbon is the π bond whose electrons can be used to form a bond to one of the bromine atoms in Br_2 (the electrons from the Br–Br bond form the other C–Br bond on the other carbon that was part of the π bond in the starting unsaturated hydrocarbon).

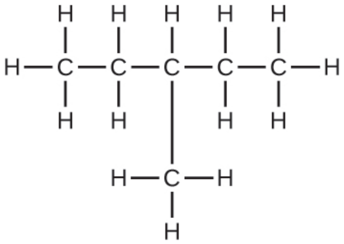
5. Unbranched alkanes have free rotation about the C–C bonds, yielding all orientations of the substituents about these bonds equivalent, interchangeable by rotation. In the unbranched alkenes, the inability to rotate about the $\text{C}=\text{C}$ bond results in fixed (unchanging) substituent orientations, thus permitting different isomers. Since these concepts pertain to phenomena at the molecular level, this explanation involves the microscopic domain.

7. They are the same compound because each is a saturated hydrocarbon containing an unbranched chain of six carbon atoms.

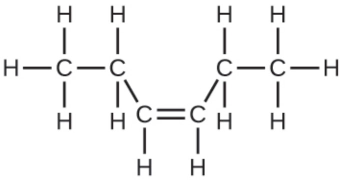
9. (a) C_6H_{14}



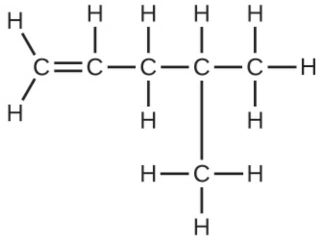
(b) C_6H_{14}



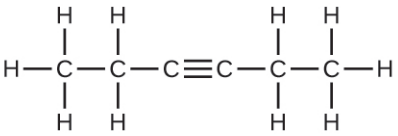
(c) C_6H_{12}



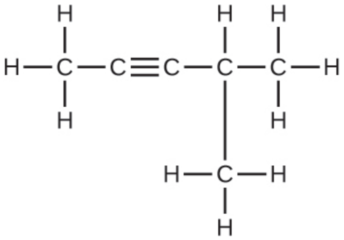
(d) C_6H_{12}



(e) C_6H_{10}

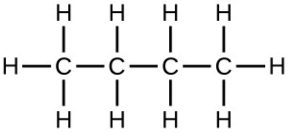


(f) C_6H_{10}

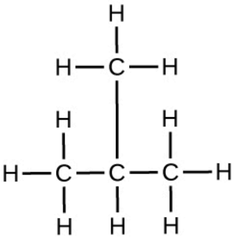


11. (a) 2,2-dibromobutane; (b) 2-chloro-2-methylpropane; (c) 2-methylbutane; (d) 1-butyne; (e) 4-fluoro-4-methyl-1-octyne; (f) *trans*-1-chloropropene; (g) 5-methyl-1-pentene

13.

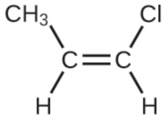


n-butane

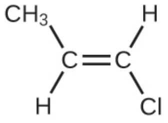


2-methylpropane

15.

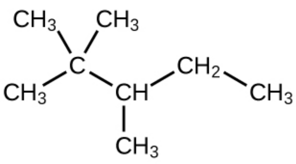


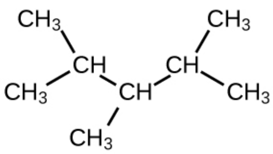
cis-

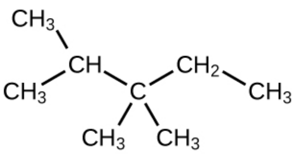


trans-

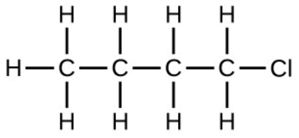
17. (a) 2,2,4-trimethylpentane; (b) 2,2,3-trimethylpentane, 2,3,4-trimethylpentane, and 2,3,3-trimethylpentane:



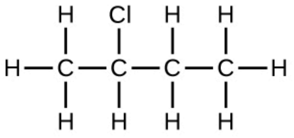




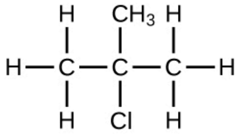
19.



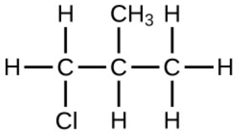
1-chlorobutane



2-chlorobutane

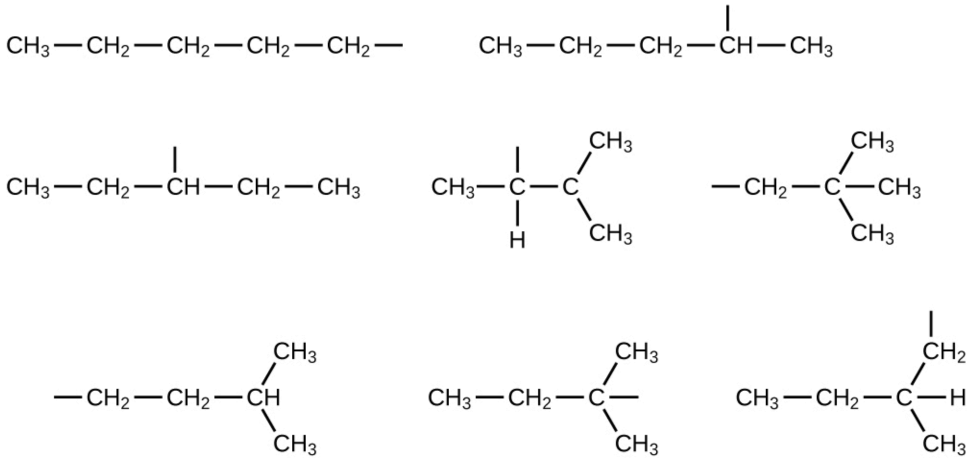


2-chloro-2-methylpropane

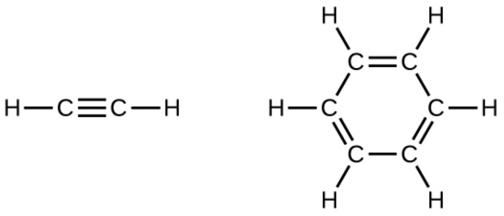


1-chloro-2-methylpropane
(1-chloro-2-methylpropane)

21. In the following, the carbon backbone and the appropriate number of hydrogen atoms are shown in condensed form:

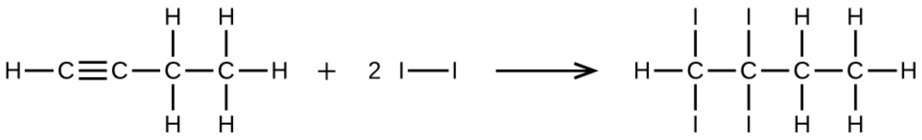


23.

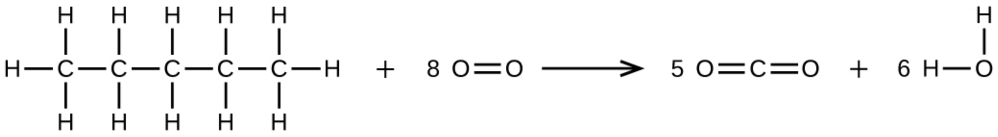


In acetylene, the bonding uses *sp* hybrids on carbon atoms and *s* orbitals on hydrogen atoms. In benzene, the carbon atoms are sp^2 hybridized.

25. (a) $\mathrm{CH}\equiv\mathrm{CCH_2CH_3}+2\mathrm{I_2}\longrightarrow\mathrm{CHI_2CI_2CH_2CH_3}$



(b) $\mathrm{CH_3CH_2CH_2CH_2CH_3}+8\mathrm{O_2}\longrightarrow 5\mathrm{CO_2}+6\mathrm{H_2O}$



27. 65.2 g

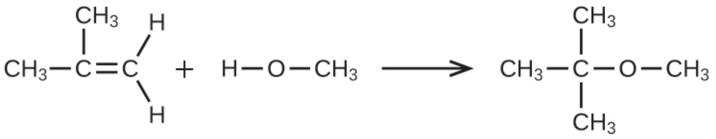
29. 9.328 $\times$ 10^2 kg

31. (a) ethyl alcohol, ethanol: CH_3CH_2OH; (b) methyl alcohol, methanol: CH_3OH; (c) ethylene glycol, ethanediol: $HOCH_2CH_2OH$; (d) isopropyl alcohol, 2-propanol: $CH_3CH(OH)CH_3$; (e) glycerine, l,2,3-trihydroxypropane: $HOCH_2CH(OH)CH_2OH$

33. (a) 1-ethoxybutane, butyl ethyl ether; (b) 1-ethoxypropane, ethyl propyl ether; (c) 1-methoxypropane, methyl propyl ether

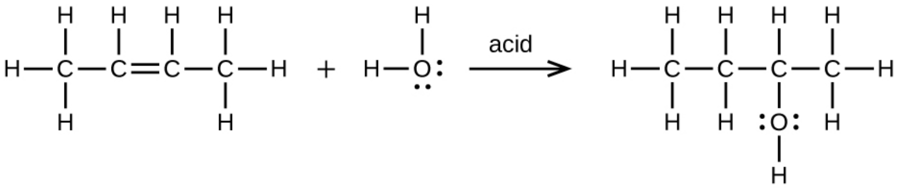
35. $HOCH_2CH_2OH$, two alcohol groups; CH_3OCH_2OH, ether and alcohol groups

37. (a)

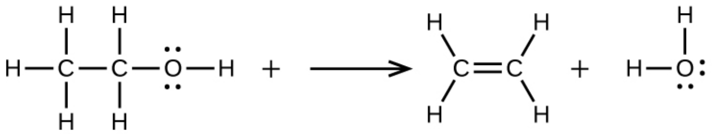


(b) 4.593 $\times$ 10^2 L

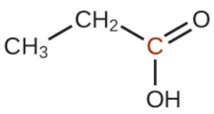
39. (a) $CH_3CH = CHCH_3 + H_2O \longrightarrow CH_3CH_2CH(OH)CH_3$



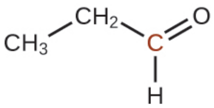
(b) $CH_3CH_2OH \longrightarrow CH_2 = CH_2 + H_2O$



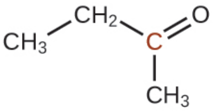
41. (a)



(b)



(c)

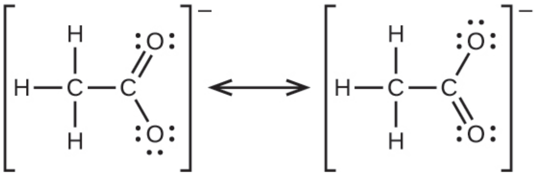


43. A ketone contains a group bonded to two additional carbon atoms; thus, a minimum of three carbon atoms are needed.

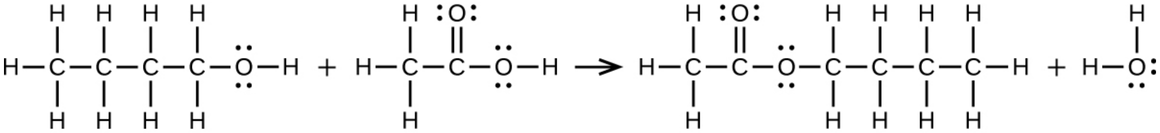
45. Since they are both carboxylic acids, they each contain the –COOH functional group and its characteristics. The difference is the hydrocarbon chain in a saturated fatty acid contains no double or triple bonds, whereas the hydrocarbon chain in an unsaturated fatty acid contains one or more multiple bonds.

47. (a) $CH_3CH(OH)CH_3$: all carbons are tetrahedral; (b) CH_3COCH_3: the end carbons are tetrahedral and the central carbon is trigonal planar; (c) CH_3OCH_3: all are tetrahedral; (d) CH_3COOH: the methyl carbon is tetrahedral and the acid carbon is trigonal planar; (e) $CH_3CH_2CH_2CH(CH_3)CHCH_2$: all are tetrahedral except the right-most two carbons, which are trigonal planar

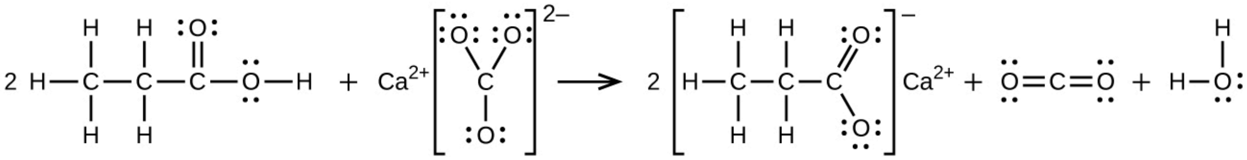
49.



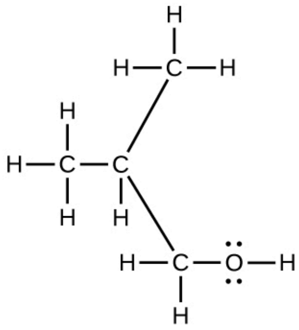
51. (a) $CH_3CH_2CH_2CH_2OH + CH_3C(O)OH \longrightarrow CH_3C(O)OCH_2CH_2CH_2CH_3 + H_2O$:



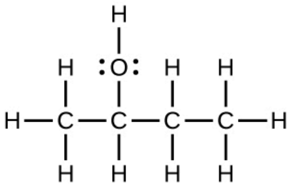
(b) $2CH_3CH_2COOH + CaCO_3 \longrightarrow (CH_3CH_2COO)_2Ca + CO_2 + H_2O$:



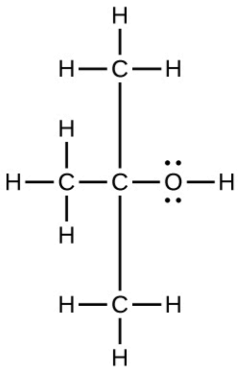
53.



Compound A



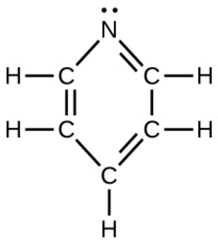
Compound B



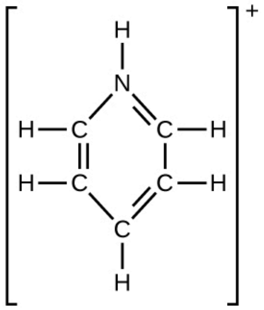
Compound C

55. Trimethyl amine: trigonal pyramidal, *sp*^{3}; trimethyl ammonium ion: tetrahedral, *sp*^{3}

57.

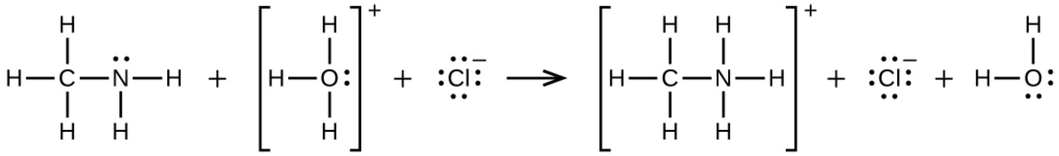


pyridine,
trigonal planar, *sp*^{2}



pyridinium ion,
trigonal planar, *sp*^{2}

59. $CH_3NH_2 + H_3O^+ \longrightarrow CH_3NH_3{}^+ + H_2O$



61. $CH_3\underline{C}H = \underline{C}HCH_3(sp^2) + Cl \longrightarrow CH_3\underline{C}H(Cl)H(Cl)CH_3(sp^3)$; $2\underline{C}_6H_6(sp^2) + 15O_2 \longrightarrow 12\underline{C}O_2(sp) + 6H_2O$

63. The carbon in $CO_3{}^{2-}$, initially at *sp*^{2}, changes hybridization to *sp* in CO_2.

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