

Chapter 17

Kinetics



Figure 17.1 An agama lizard basks in the sun. As its body warms, the chemical reactions of its metabolism speed up.

Chapter Outline

- 17.1 Chemical Reaction Rates
- 17.2 Factors Affecting Reaction Rates
- 17.3 Rate Laws
- 17.4 Integrated Rate Laws
- 17.5 Collision Theory
- 17.6 Reaction Mechanisms
- 17.7 Catalysis

Introduction

The lizard in the photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. A cold lizard is a slower lizard and an easier meal for predators.

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. Two questions are typically posed when planning to carry out a chemical reaction. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" A third question is often asked when investigating reactions in greater detail: "What specific molecular-level processes take place as the reaction occurs?" Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled.

The study of chemical kinetics concerns the second and third questions—that is, the rate at which a reaction yields products and the molecular-scale means by which a reaction occurs. This chapter examines the factors that influence the rates of chemical reactions, the mechanisms by which reactions proceed, and the quantitative techniques used to

describe the rates at which reactions occur.

17.1 Chemical Reaction Rates

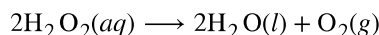
By the end of this section, you will be able to:

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The **rate of reaction** is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. For example, the concentration of hydrogen peroxide, H_2O_2 , in an aqueous solution changes slowly over time as it decomposes according to the equation:



The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned} \text{rate of decomposition of H}_2\text{O}_2 &= - \frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= - \frac{[\text{H}_2\text{O}_2]_{t_2} - [\text{H}_2\text{O}_2]_{t_1}}{t_2 - t_1} \\ &= - \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} \end{aligned}$$

This mathematical representation of the change in species concentration over time is the **rate expression** for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[\text{H}_2\text{O}_2]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1 ; likewise, $[\text{H}_2\text{O}_2]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t_2 ; and $\Delta[\text{H}_2\text{O}_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[\text{H}_2\text{O}_2]$ is a negative quantity. Reaction rates are, by convention, positive quantities, and so this negative change in concentration is multiplied by -1 . **Figure 17.2** provides an example of data collected during the decomposition of H_2O_2 .

Time (h)	[H ₂ O ₂] (mol L ⁻¹)	Δ[H ₂ O ₂] (mol L ⁻¹)	Δt (h)	Rate of Decomposition, (mol L ⁻¹ h ⁻¹)
0.00	1.000	-0.500	6.00	0.0833
6.00	0.500			
12.00	0.250	-0.250	6.00	0.0417
18.00	0.125			
24.00	0.0625	-0.062	6.00	0.010

Figure 17.2 The rate of decomposition of H₂O₂ in an aqueous solution decreases as the concentration of H₂O₂ decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{-(0.500 \text{ mol/L} - 1.000 \text{ mol/L})}{(6.00 \text{ h} - 0.00 \text{ h})} = 0.0833 \text{ mol L}^{-1} \text{ h}^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{-(0.0625 \text{ mol/L} - 0.125 \text{ mol/L})}{(24.00 \text{ h} - 18.00 \text{ h})} = 0.010 \text{ mol L}^{-1} \text{ h}^{-1}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an **average rate** for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its **instantaneous rate**. The instantaneous rate of a reaction at “time zero,” when the reaction commences, is its **initial rate**. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle’s initial rate—analogue to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1 —would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car’s average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. In a plot of the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H₂O₂ at any time t is given by the slope of a straight line that is tangent to the curve at that time (**Figure 17.3**). These tangent line slopes may be evaluated using calculus, but the procedure for doing so is beyond the scope of this chapter.

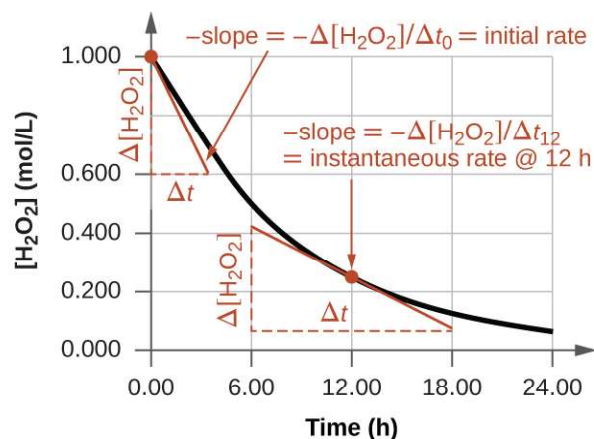


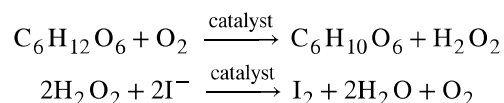
Figure 17.3 This graph shows a plot of concentration versus time for a 1.000 M solution of H_2O_2 . The rate at any time is equal to the negative of the slope of a line tangent to the curve at that time. Tangents are shown at $t = 0$ h (“initial rate”) and at $t = 12$ h (“instantaneous rate” at 12 h).

Chemistry in Everyday Life

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (**Figure 17.4**). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:



The first equation depicts the oxidation of glucose in the urine to yield gluco lactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

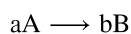
The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.



Figure 17.4 Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)

Relative Rates of Reaction

The rate of a reaction may be expressed as the change in concentration of any reactant or product. For any given reaction, these rate expressions are all related simply to one another according to the reaction stoichiometry. The rate of the general reaction



can be expressed in terms of the decrease in the concentration of A or the increase in the concentration of B. These two rate expressions are related by the stoichiometry of the reaction:

$$\text{rate} = -\left(\frac{1}{a}\right)\left(\frac{\Delta A}{\Delta t}\right) = \left(\frac{1}{b}\right)\left(\frac{\Delta B}{\Delta t}\right)$$

the reaction represented by the following equation:



The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta \text{mol NH}_3}{\Delta t} \times \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} = \frac{\Delta \text{mol N}_2}{\Delta t}$$

This may be represented in an abbreviated format by omitting the units of the stoichiometric factor:

$$-\frac{1}{2} \frac{\Delta \text{mol NH}_3}{\Delta t} = \frac{\Delta \text{mol N}_2}{\Delta t}$$

Note that a negative sign has been included as a factor to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). For homogeneous reactions, both the reactants and products are present in the same solution and thus occupy the same volume, so the molar amounts may be replaced with molar concentrations:

$$-\frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t} = \frac{\Delta[\text{N}_2]}{\Delta t}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 are produced for each mole of N_2 produced.

$$\frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{N}_2]}{\Delta t}$$

Figure 17.5 illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. Slopes of the tangent lines at $t = 500$ s show that the instantaneous rates derived from all three species involved in the reaction are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91 \times 10^{-6} \text{ M/s}}{9.70 \times 10^{-7} \text{ M/s}} \approx 3$$

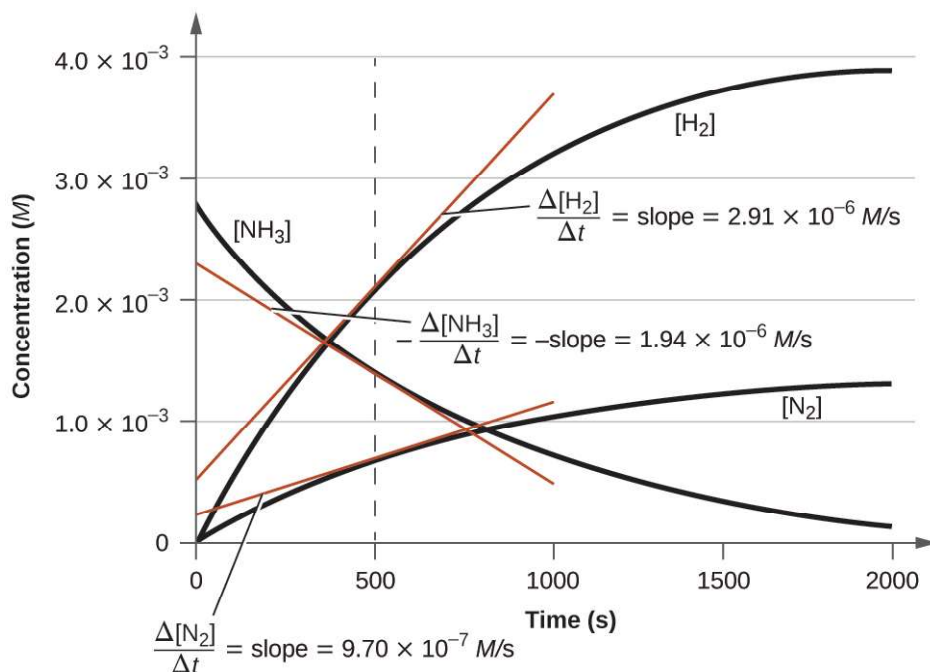
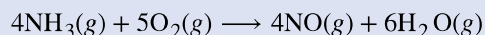


Figure 17.5 Changes in concentrations of the reactant and products for the reaction $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$. The rates of change of the three concentrations are related by the reaction stoichiometry, as shown by the different slopes of the tangents at $t = 500$ s.

Example 17.1

Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:



Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

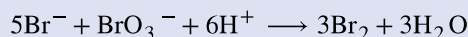
Solution

Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

$$-\frac{1}{4} \frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{1}{5} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

Check Your Learning

The rate of formation of Br_2 is 6.0×10^{-6} mol/L/s in a reaction described by the following net ionic equation:



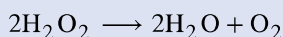
Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

$$\text{Answer: } -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

Example 17.2

Reaction Rate Expressions for Decomposition of H_2O_2

The graph in **Figure 17.3** shows the rate of the decomposition of H_2O_2 over time:



Based on these data, the instantaneous rate of decomposition of H_2O_2 at $t = 11.1$ h is determined to be 3.20×10^{-2} mol/L/h, that is:

$$-\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = 3.20 \times 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1}$$

What is the instantaneous rate of production of H_2O and O_2 ?

Solution

The reaction stoichiometry shows that

$$-\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

and

$$\frac{\Delta[\text{O}_2]}{\Delta t} = 1.60 \times 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1}$$

Check Your Learning

If the rate of decomposition of ammonia, NH_3 , at 1150 K is 2.10×10^{-6} mol/L/s, what is the rate of production of nitrogen and hydrogen?

$$\text{Answer: } 1.05 \times 10^{-6} \text{ mol/L/s, N}_2 \text{ and } 3.15 \times 10^{-6} \text{ mol/L/s, H}_2.$$

17.2 Factors Affecting Reaction Rates

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

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. Five factors typically affecting the rates of chemical reactions will be explored in this section: the chemical nature of

the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

The Physical States of the Reactants

A chemical reaction between two or more substances requires intimate contact between the reactants. When reactants are in different physical states, or phases (solid, liquid, gaseous, dissolved), the reaction takes place only at the interface between the phases. Consider the heterogeneous reaction between a solid phase and either a liquid or gaseous phase. Compared with the reaction rate for large solid particles, the rate for smaller particles will be greater because the surface area in contact with the other reactant phase is greater. For example, large pieces of iron react more slowly with acids than they do with finely divided iron powder (**Figure 17.6**). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



Figure 17.6 (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas: $2\text{Fe}(s) + 6\text{HCl}(aq) \rightarrow 2\text{FeCl}_3(aq) + 3\text{H}_2(g)$. (b) An iron nail reacts more slowly because the surface area exposed to the acid is much less.

Link to Learning

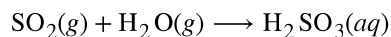
Watch [this video \(http://openstaxcollege.org//16cesium\)](http://openstaxcollege.org//16cesium) to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

Temperature of the Reactants

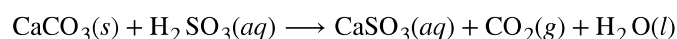
Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. Gas burners, hot plates, and ovens are often used in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. For many chemical processes, reaction rates are approximately doubled when the temperature is raised by 10 °C.

Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate (CaCO_3) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (**Figure 17.7**). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:



Calcium carbonate reacts with sulfurous acid as follows:



In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.



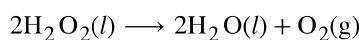
Figure 17.7 Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III)

Link to Learning

Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this [video \(http://openstaxcollege.org/l/16phosphor\)](http://openstaxcollege.org/l/16phosphor) to see an example.

The Presence of a Catalyst

Relatively dilute aqueous solutions of hydrogen peroxide, H_2O_2 , are commonly used as topical antiseptics. Hydrogen peroxide decomposes to yield water and oxygen gas according to the equation:



Under typical conditions, this decomposition occurs very slowly. When dilute $\text{H}_2\text{O}_2(aq)$ is poured onto an open wound, however, the reaction occurs rapidly and the solution foams because of the vigorous production of oxygen gas. This dramatic difference is caused by the presence of substances within the wound's exposed tissues that accelerate the decomposition process. Substances that function to increase the rate of a reaction are called **catalysts**, a topic treated in greater detail later in this chapter.

Link to Learning

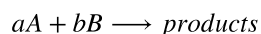
Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the **PhET Reactions & Rates interactive** (<http://openstaxcollege.org//16PHETreaction>) to explore how temperature, concentration, and the nature of the reactants affect reaction rates.

17.3 Rate Laws

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

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

As described in the previous module, the rate of a reaction is often affected by the concentrations of reactants. **Rate laws** (sometimes called *differential rate laws*) or **rate equations** are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. As an example, consider the reaction described by the chemical equation



where a and b are stoichiometric coefficients. The rate law for this reaction is written as:

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

in which $[A]$ and $[B]$ represent the molar concentrations of reactants, and k is the **rate constant**, which is specific for a particular reaction at a particular temperature. The exponents m and n are the **reaction orders** and are typically positive integers, though they can be fractions, negative, or zero. The rate constant k and the reaction orders m and n must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant k is independent of the reactant concentrations, but it does vary with temperature.

The reaction orders in a rate law describe the mathematical dependence of the rate on reactant concentrations. Referring to the generic rate law above, the reaction is m order with respect to A and n order with respect to B . For example, if $m = 1$ and $n = 2$, the reaction is first order in A and second order in B . The **overall reaction order** is simply the sum of orders for each reactant. For the example rate law here, the reaction is third order overall ($1 + 2 = 3$). A few specific examples are shown below to further illustrate this concept.

The rate law:

$$\text{rate} = k[\text{H}_2\text{O}_2]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate} = k[\text{C}_4\text{H}_6]^2$$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

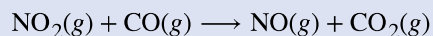
$$\text{rate} = k[\text{H}^+][\text{OH}^-]$$

describes a reaction that is first order in H^+ , first order in OH^- , and second order overall.

Example 17.3

Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:



is second order in NO_2 and zero order in CO at 100°C . What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k[\text{NO}_2]^m[\text{CO}]^n$$

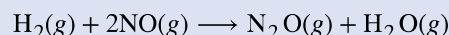
The reaction is second order in NO_2 ; thus $m = 2$. The reaction is zero order in CO ; thus $n = 0$. The rate law is:

$$\text{rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[\text{CO}]^0 = 1$, which is why the CO concentration term may be omitted from the rate law: the rate of reaction is solely dependent on the concentration of NO_2 . A later chapter section on reaction mechanisms will explain how a reactant's concentration can have no effect on a reaction rate despite being involved in the reaction.

Check Your Learning

The rate law for the reaction:

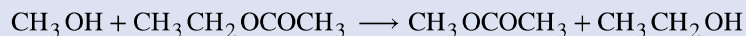


has been determined to be $\text{rate} = k[\text{NO}]^2[\text{H}_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer: order in $\text{NO} = 2$; order in $\text{H}_2 = 1$; overall order = 3

Check Your Learning

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($\text{CH}_3\text{CH}_2\text{OCOCH}_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:



The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, determined to be:

$$\text{rate} = k[\text{CH}_3\text{OH}]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer: order in $\text{CH}_3\text{OH} = 1$; order in $\text{CH}_3\text{CH}_2\text{OCOCH}_3 = 0$; overall order = 1

A common experimental approach to the determination of rate laws is the **method of initial rates**. This method involves measuring reaction rates for multiple experimental trials carried out using different initial reactant concentrations. Comparing the measured rates for these trials permits determination of the reaction orders and, subsequently, the rate constant, which together are used to formulate a rate law. This approach is illustrated in the next two example exercises.

Example 17.4

Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (**Figure 17.8**). One such reaction is the combination of nitric oxide, NO, with ozone, O₃:

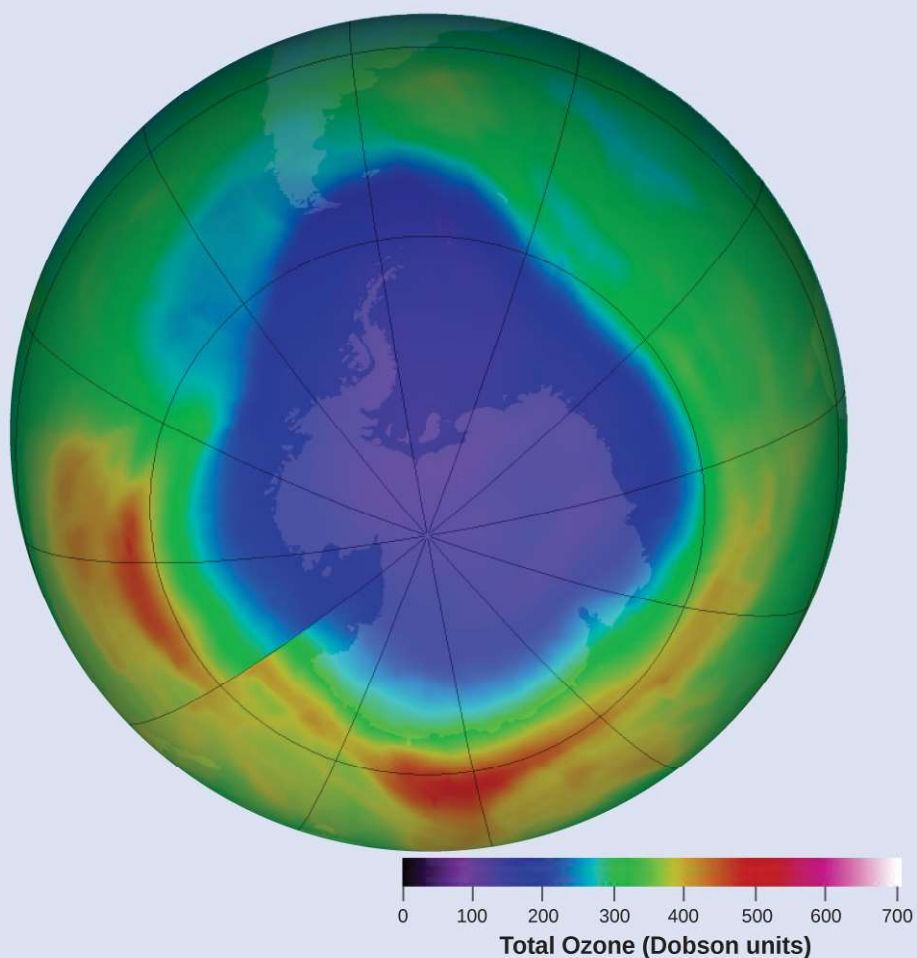
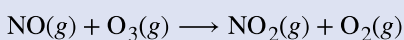


Figure 17.8 A contour map showing stratospheric ozone concentration and the “ozone hole” that occurs over Antarctica during its spring months. (credit: modification of work by NASA)



This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	[O ₃] (mol/L)	$\frac{\Delta[\text{NO}_2]}{\Delta t}$ (mol L ⁻¹ s ⁻¹)
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\text{rate} = k[\text{NO}]^m[\text{O}_3]^n$$

Determine the values of m , n , and k from the experimental data using the following three-part process:

Step 1. Determine the value of m from the data in which [NO] varies and [O₃] is constant. In the last three experiments, [NO] varies while [O₃] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and m in the rate law is equal to 1.

Step 2. Determine the value of n from data in which [O₃] varies and [NO] is constant. In the first three experiments, [NO] is constant and [O₃] varies. The reaction rate changes in direct proportion to the change in [O₃]. When [O₃] doubles from trial 1 to 2, the rate doubles; when [O₃] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O₃], and n is equal to 1. The rate law is thus:

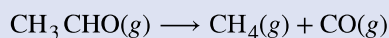
$$\text{rate} = k[\text{NO}]^1[\text{O}_3]^1 = k[\text{NO}][\text{O}_3]$$

Step 3. Determine the value of k from one set of concentrations and the corresponding rate. The data from trial 1 are used below:

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}][\text{O}_3]} \\ &= \frac{6.60 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}}{(1.00 \times 10^{-6} \text{ mol L}^{-1})(3.00 \times 10^{-6} \text{ mol L}^{-1})} \\ &= 2.20 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

Check Your Learning

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:



Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	[CH ₃ CHO] (mol/L)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}$ (mol L ⁻¹ s ⁻¹)
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}

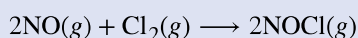
Trial	[CH ₃ CHO] (mol/L)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}$ (mol L ⁻¹ s ⁻¹)
3	7.00×10^{-3}	3.30×10^{-10}

Answer: rate = $k[\text{CH}_3\text{CHO}]^2$ with $k = 6.73 \times 10^{-6}$ L/mol/s

Example 17.5

Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:



Trial	[NO] (mol/L)	[Cl ₂] (mol/L)	$-\frac{\Delta[\text{NO}]}{\Delta t}$ (mol L ⁻¹ s ⁻¹)
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n$$

As in **Example 17.4**, approach this problem in a stepwise fashion, determining the values of m and n from the experimental data and then using these values to determine the value of k . In this example, however, an explicit algebraic approach (vs. the implicit approach of the previous example) will be used to determine the values of m and n :

Step 1. Determine the value of m from the data in which [NO] varies and [Cl₂] is constant. Write the ratios with the subscripts x and y to indicate data from two different trials:

$$\frac{\text{rate}_x}{\text{rate}_y} = \frac{k[\text{NO}]_x^m[\text{Cl}_2]_x^n}{k[\text{NO}]_y^m[\text{Cl}_2]_y^n}$$

Using the third trial and the first trial, in which [Cl₂] does not vary, gives:

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

Canceling equivalent terms in the numerator and denominator leaves:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m}$$

which simplifies to:

$$2.25 = (1.5)^m$$

Use logarithms to determine the value of the exponent m :

$$\begin{aligned}\ln(2.25) &= m\ln(1.5) \\ \frac{\ln(2.25)}{\ln(1.5)} &= m \\ 2 &= m\end{aligned}$$

Confirm the result

$$1.5^2 = 2.25$$

Step 2. Determine the value of n from data in which $[Cl_2]$ varies and $[NO]$ is constant.

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{k(0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

Cancellation gives:

$$\frac{0.0045}{0.0030} = \frac{(0.15)^n}{(0.10)^n}$$

which simplifies to:

$$1.5 = (1.5)^n$$

Thus n must be 1, and the form of the rate law is:

$$\text{rate} = k[NO]^m[Cl_2]^n = k[NO]^2[Cl_2]$$

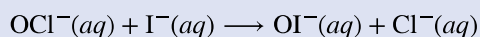
Step 3. Determine the numerical value of the rate constant k with appropriate units. The units for the rate of a reaction are mol/L/s. The units for k are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol³/L³. The units for k should be mol⁻² L²/s so that the rate is in terms of mol/L/s.

To determine the value of k once the rate law expression has been solved, simply plug in values from the first experimental trial and solve for k :

$$\begin{aligned}0.00300 \text{ mol L}^{-1} \text{ s}^{-1} &= k(0.10 \text{ mol L}^{-1})^2(0.10 \text{ mol L}^{-1})^1 \\ k &= 3.0 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}\end{aligned}$$

Check Your Learning

Use the provided initial rate data to derive the rate law for the reaction whose equation is:



Trial	$[OCl^-]$ (mol/L)	$[I^-]$ (mol/L)	Initial Rate (mol/L/s)
1	0.0040	0.0020	0.00184
2	0.0020	0.0040	0.00092
3	0.0020	0.0020	0.00046

Determine the rate law expression and the value of the rate constant k with appropriate units for this reaction.

$$\begin{aligned}\text{Answer: } \frac{\text{rate 2}}{\text{rate 3}} &= \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y} \\ 2.00 &= 2.00^y \\ y &= 1 \\ \frac{\text{rate 1}}{\text{rate 2}} &= \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}\end{aligned}$$

$$2.00 = \frac{2^x}{2^y}$$

$$2.00 = \frac{2^x}{2^1}$$

$$4.00 = 2^x$$

$$x = 2$$

Substituting the concentration data from trial 1 and solving for k yields:

$$\text{rate} = k[\text{OCl}^-]^2[\text{I}^-]^1$$

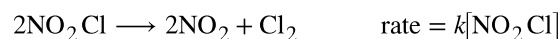
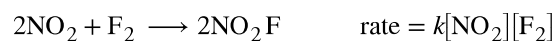
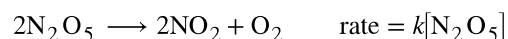
$$0.00184 = k(0.0040)^2(0.0020)^1$$

$$k = 5.75 \times 10^4 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case.

Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:



It is important to note that *rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

The units for a rate constant will vary as appropriate to accommodate the overall order of the reaction. The unit of the rate constant for the second-order reaction described in **Example 17.4** was determined to be $\text{L mol}^{-1} \text{ s}^{-1}$. For the third-order reaction described in **Example 17.5**, the unit for k was derived to be $\text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}$. Dimensional analysis requires the rate constant unit for a reaction whose overall order is x to be $\text{L}^{x-1} \text{ mol}^{1-x} \text{ s}^{-1}$. **Table 17.1** summarizes the rate constant units for common reaction orders.

Rate Constant Units for Common Reaction Orders

Overall Reaction Order (x)	Rate Constant Unit ($\text{L}^{x-1} \text{ mol}^{1-x} \text{ s}^{-1}$)
0 (zero)	$\text{mol L}^{-1} \text{ s}^{-1}$
1 (first)	s^{-1}
2 (second)	$\text{L mol}^{-1} \text{ s}^{-1}$
3 (third)	$\text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}$

Table 17.1

Note that the units in this table were derived using specific units for concentration (mol/L) and time (s), though any valid units for these two properties may be used.

17.4 Integrated Rate Laws

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

- Explain the form and function of an integrated rate law
- Perform integrated rate law calculations for zero-, first-, and second-order reactions
- Define half-life and carry out related calculations
- Identify the order of a reaction from concentration/time data

The rate laws discussed thus far relate the rate and the concentrations of reactants. We can also determine a second form of each rate law that relates the concentrations of reactants and time. These are called **integrated rate laws**. We can use an integrated rate law to determine the amount of reactant or product present after a period of time or to estimate the time required for a reaction to proceed to a certain extent. For example, an integrated rate law is used to determine the length of time a radioactive material must be stored for its radioactivity to decay to a safe level.

Using calculus, the differential rate law for a chemical reaction can be integrated with respect to time to give an equation that relates the amount of reactant or product present in a reaction mixture to the elapsed time of the reaction. This process can either be very straightforward or very complex, depending on the complexity of the differential rate law. For purposes of discussion, we will focus on the resulting integrated rate laws for first-, second-, and zero-order reactions.

First-Order Reactions

Integration of the rate law for a simple first-order reaction (rate = $k[A]$) results in an equation describing how the reactant concentration varies with time:

$$[A]_t = [A]_0 e^{-kt}$$

where $[A]_t$ is the concentration of A at any time t , $[A]_0$ is the initial concentration of A , and k is the first-order rate constant.

For mathematical convenience, this equation may be rearranged to other formats, including direct and indirect proportionalities:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \quad \text{or} \quad \ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

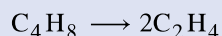
and a format showing a linear dependence of concentration in time:

$$\ln[A]_t = \ln[A]_0 - kt$$

Example 17.6

The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at $500\text{ }^\circ\text{C}$ is $9.2 \times 10^{-3}\text{ s}^{-1}$:



How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

Since the relative change in reactant concentration is provided, a convenient format for the integrated rate law is:

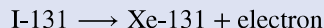
$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

The initial concentration of C_4H_8 , $[A]_0$, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let x be the initial concentration, in which case the concentration after 80.0% decomposition is 20.0% of x or $0.200x$. Rearranging the rate law to isolate t and substituting the provided quantities yields:

$$\begin{aligned} t &= \ln\frac{[x]}{[0.200x]} \times \frac{1}{k} \\ &= \ln 5 \times \frac{1}{9.2 \times 10^{-3} \text{ s}^{-1}} \\ &= 1.609 \times \frac{1}{9.2 \times 10^{-3} \text{ s}^{-1}} \\ &= 1.7 \times 10^2 \text{ s} \end{aligned}$$

Check Your Learning

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:



The decay is first-order with a rate constant of 0.138 d^{-1} . How many days will it take for 90% of the iodine-131 in a 0.500 M solution of this substance to decay to Xe-131?

Answer: 16.7 days

In the next example exercise, a linear format for the integrated rate law will be convenient:

$$\begin{aligned} \ln[A]_t &= (-k)(t) + \ln[A]_0 \\ y &= mx + b \end{aligned}$$

A plot of $\ln[A]_t$ versus t for a first-order reaction is a straight line with a slope of $-k$ and a y -intercept of $\ln[A]_0$. If a set of rate data are plotted in this fashion but do *not* result in a straight line, the reaction is not first order in A .

Example 17.7

Graphical Determination of Reaction Order and Rate Constant

Show that the data in **Figure 17.2** can be represented by a first-order rate law by graphing $\ln[\text{H}_2\text{O}_2]$ versus time. Determine the rate constant for the decomposition of H_2O_2 from these data.

Solution

The data from **Figure 17.2** are tabulated below, and a plot of $\ln[\text{H}_2\text{O}_2]$ is shown in **Figure 17.9**.

Trial	Time (h)	$[\text{H}_2\text{O}_2] \text{ (M)}$	$\ln[\text{H}_2\text{O}_2]$
1	0.00	1.000	0.000
2	6.00	0.500	-0.693
3	12.00	0.250	-1.386
4	18.00	0.125	-2.079
5	24.00	0.0625	-2.772

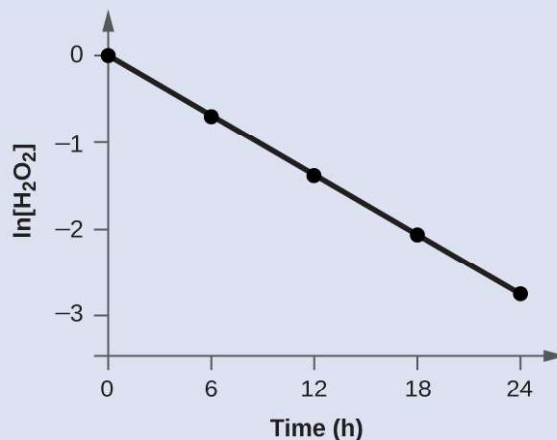


Figure 17.9 A linear relationship between $\ln[\text{H}_2\text{O}_2]$ and time suggests the decomposition of hydrogen peroxide is a first-order reaction.

The plot of $\ln[\text{H}_2\text{O}_2]$ versus time is linear, indicating that the reaction may be described by a first-order rate law.

According to the linear format of the first-order integrated rate law, the rate constant is given by the negative of this plot's slope.

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln[\text{H}_2\text{O}_2]}{\Delta t}$$

The slope of this line may be derived from two values of $\ln[\text{H}_2\text{O}_2]$ at different values of t (one near each end of the line is preferable). For example, the value of $\ln[\text{H}_2\text{O}_2]$ when t is 0.00 h is 0.000; the value when $t = 24.00$ h is -2.772

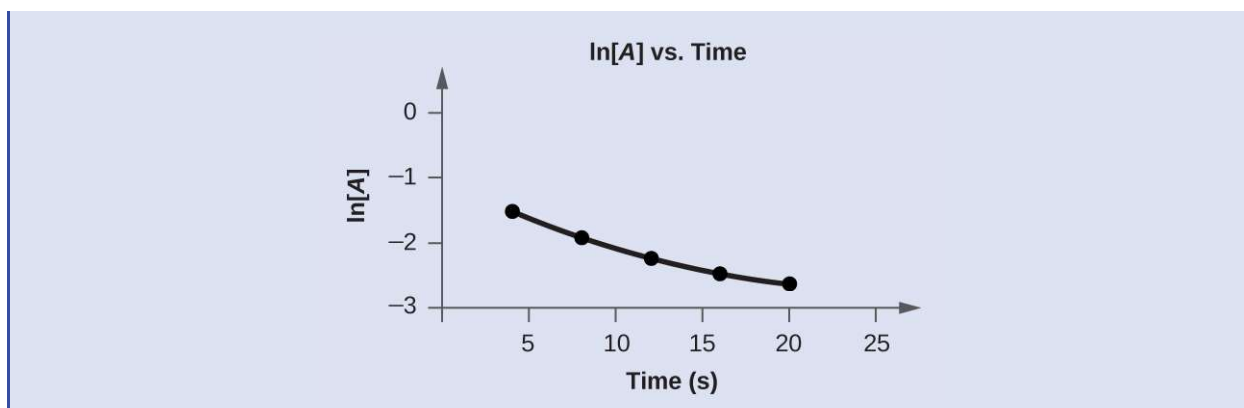
$$\begin{aligned} \text{slope} &= \frac{-2.772 - 0.000}{24.00 - 0.00 \text{ h}} \\ &= \frac{-2.772}{24.00 \text{ h}} \\ &= -0.116 \text{ h}^{-1} \\ k &= -\text{slope} = -(-0.116 \text{ h}^{-1}) = 0.116 \text{ h}^{-1} \end{aligned}$$

Check Your Learning

Graph the following data to determine whether the reaction $A \rightarrow B + C$ is first order.

Trial	Time (s)	[A]
1	4.0	0.220
2	8.0	0.144
3	12.0	0.110
4	16.0	0.088
5	20.0	0.074

Answer: The plot of $\ln[A]_t$ vs. t is not linear, indicating the reaction is not first order:



Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions can be fairly complicated. To illustrate the point with minimal complexity, only the simplest second-order reactions will be described here, namely, those whose rates depend on the concentration of just one reactant. For these types of reactions, the differential rate law is written as:

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

For these second-order reactions, the integrated rate law is:

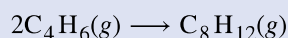
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

where the terms in the equation have their usual meanings as defined earlier.

Example 17.8

The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) to yield C_8H_{12} gas is described by the equation:



This “dimerization” reaction is second order with a rate constant equal to $5.76 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}$ under certain conditions. If the initial concentration of butadiene is 0.200 M , what is the concentration after 10.0 min ?

Solution

For a second-order reaction, the integrated rate law is written

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

We know three variables in this equation: $[A]_0 = 0.200 \text{ mol/L}$, $k = 5.76 \times 10^{-2} \text{ L/mol/min}$, and $t = 10.0 \text{ min}$. Therefore, we can solve for $[A]$, the fourth variable:

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

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)	$\frac{1}{[\text{C}_4\text{H}_6]} (M^{-1})$	$\ln[\text{C}_4\text{H}_6]$
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 $\ln[\text{C}_4\text{H}_6]_t$ versus t is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[\text{C}_4\text{H}_6]_t}$ versus t is linear, indicating that the reaction is second order.

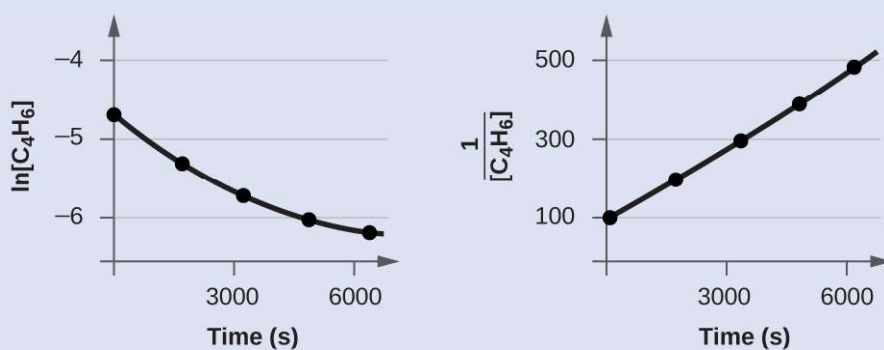


Figure 17.10 These two graphs show first- and second-order plots for the dimerization of C_4H_6 . The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

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:

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

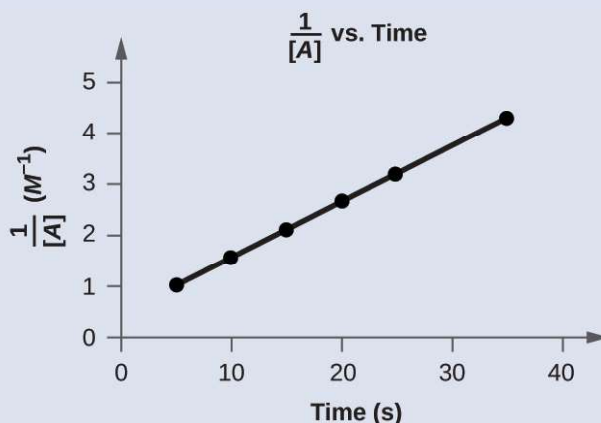
Check Your Learning

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:

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

$$y = mx + b$$

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 $[\text{NH}_3]$ 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 $0.0028 \text{ mol L}^{-1}$ decreasing linearly with time for 1000 s. Assuming no change in this zero-order behavior, at what time (min) will the concentration reach $0.0001 \text{ mol L}^{-1}$?

Answer: 35 min

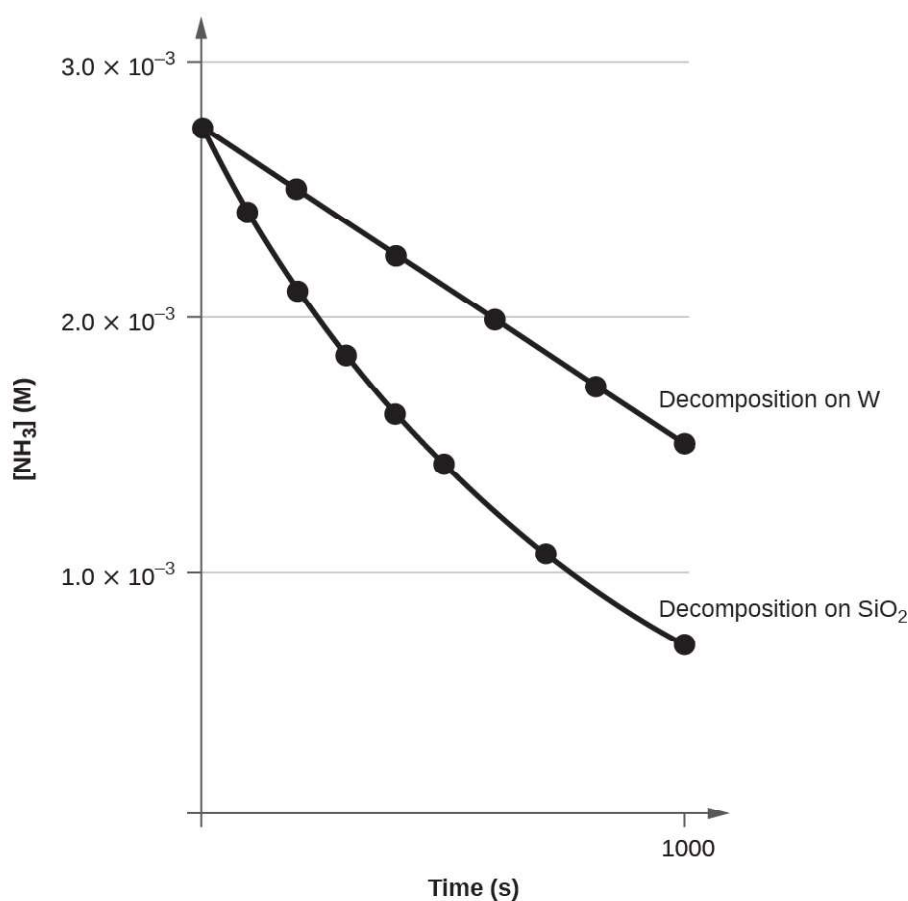


Figure 17.11 The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

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 .

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:

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

$$t = \ln \frac{[A]_0}{[A]_t} \times \frac{1}{k}$$

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: $t = t_{1/2}$, $[A]_t = \frac{1}{2}[A]_0$.

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

$$t_{1/2} = \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k}$$

$$= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k}$$

$$t_{1/2} = \frac{0.693}{k}$$

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**.

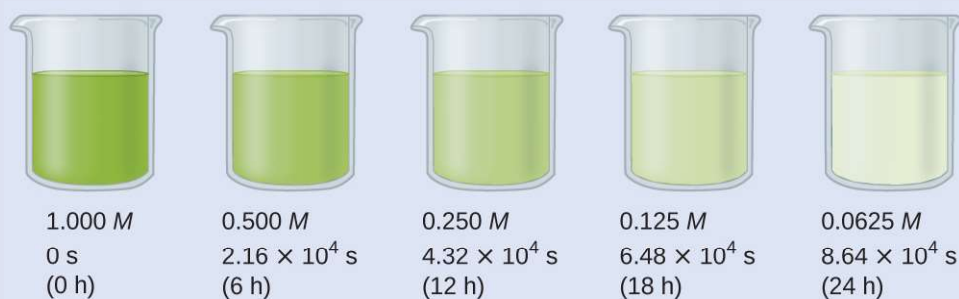


Figure 17.12 The decomposition of H_2O_2 ($2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$) at 40 °C is illustrated. The intensity of the color symbolizes the concentration of H_2O_2 at the indicated times; H_2O_2 is actually colorless.

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:

$$t_{1/2} = \frac{0.693}{k}$$

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

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:

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

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

$$t_{1/2} = \frac{1}{k[A]_0}$$

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:

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

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

$$t_{1/2} = \frac{[A]_0}{2k}$$

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	$M s^{-1}$	s^{-1}	$M^{-1} s^{-1}$
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 $0.0576 \text{ L mol}^{-1} \text{ min}^{-1}$. Substituting these quantities into the second-order half-life equation:

$$t_{1/2} = \frac{1}{[(0.0576 \text{ L mol}^{-1} \text{ min}^{-1})(0.200 \text{ mol L}^{-1})]} = 0.0115 \text{ min}$$

$$t_{1/2} = 0.0115 \text{ min} \left(\frac{60 \text{ s}}{1 \text{ min}}\right) \left(\frac{1000 \text{ ms}}{1 \text{ s}}\right) = 690 \text{ ms}$$

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.

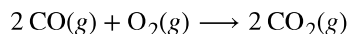
Collision theory is based on the following postulates:

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

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

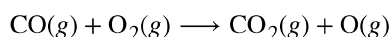
2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form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



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:



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.

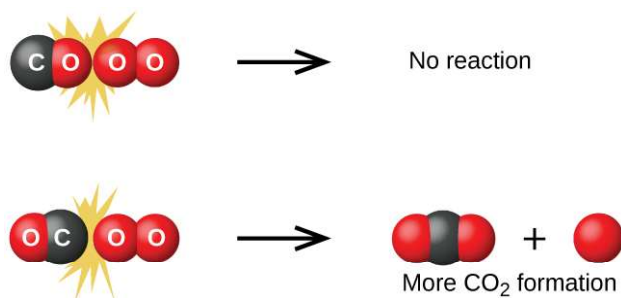


Figure 17.13 Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

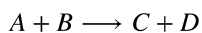
If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. In addition to a proper orientation, the collision must also occur with sufficient energy to result in product formation. When reactant species collide with 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



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.

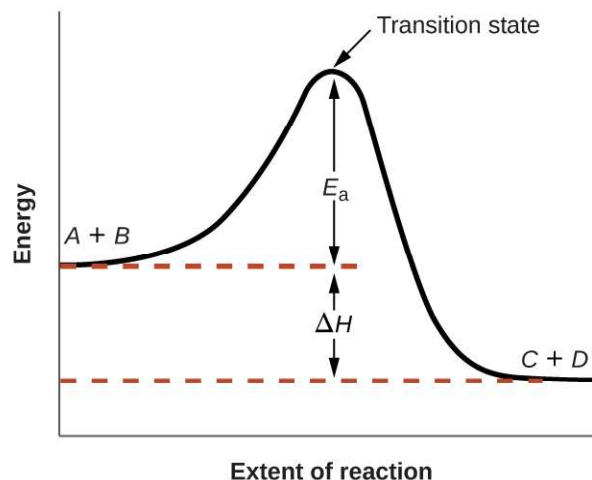


Figure 17.14 Reaction diagram for the exothermic reaction $A + B \rightarrow C + D$.

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, $e^{-E_a/RT}$, 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.

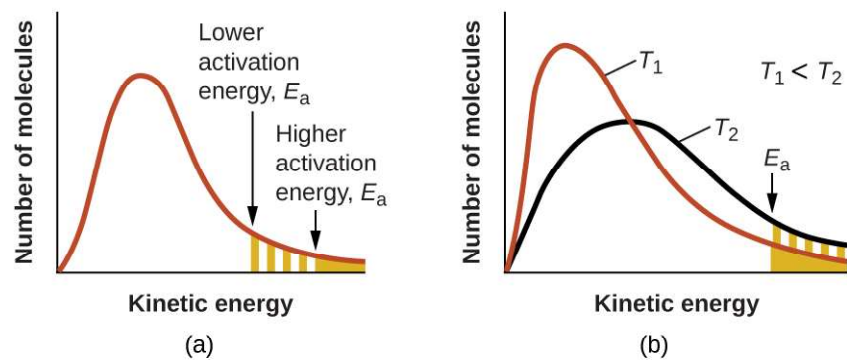


Figure 17.15 Molecular energy distributions showing numbers of molecules with energies exceeding (a) two different activation energies at a given temperature, and (b) a given activation energy at two different temperatures.

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

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

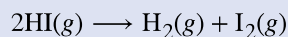
$$y = mx + b$$

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 $\text{HI}(g)$ to $\text{H}_2(g)$ and $\text{I}_2(g)$ is given here. What is the activation energy for the reaction?



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 $\ln k$:

$\frac{1}{T}$ (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.

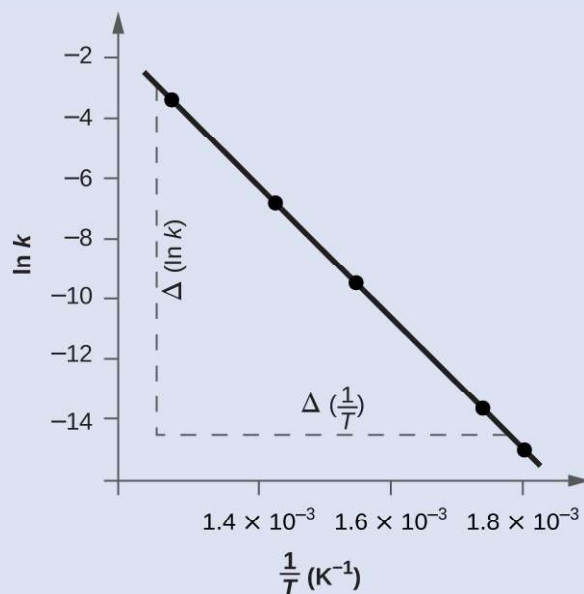


Figure 17.16 This graph shows the linear relationship between $\ln k$ and $\frac{1}{T}$ for the reaction $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ according to the Arrhenius equation.

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

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:

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

Rearranging this equation to isolate activation energy yields:

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

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

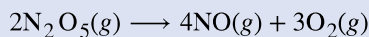
$$E_a = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \left(\frac{-3.231 - (-14.860)}{1.28 \times 10^{-3} \text{ K}^{-1} - 1.80 \times 10^{-3} \text{ K}^{-1}} \right)$$

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



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

Answer: $1.1 \times 10^5 \text{ J mol}^{-1}$ or 110 kJ mol^{-1}

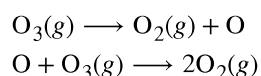
17.6 Reaction Mechanisms

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

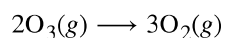
- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

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:



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:



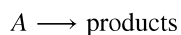
Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called **intermediates**.

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

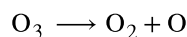
The **molecularity** of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a **unimolecular reaction** involves the reaction of a *single* reactant species to produce one or more molecules of product:



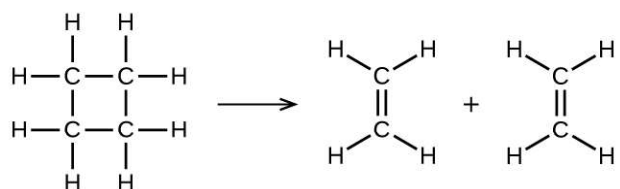
The rate law for a unimolecular reaction is first order:

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

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



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:



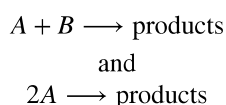
This equation represents the overall reaction observed, and it might also represent a legitimate unimolecular elementary reaction. The rate law predicted from this equation, assuming it is an elementary reaction, turns out to be the same as the rate law derived experimentally for the overall reaction,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



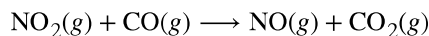
For the first type, in which the two reactant molecules are different, the rate law is first-order in A and first order in B (second-order overall):

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

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:



(see [Figure 17.17](#))

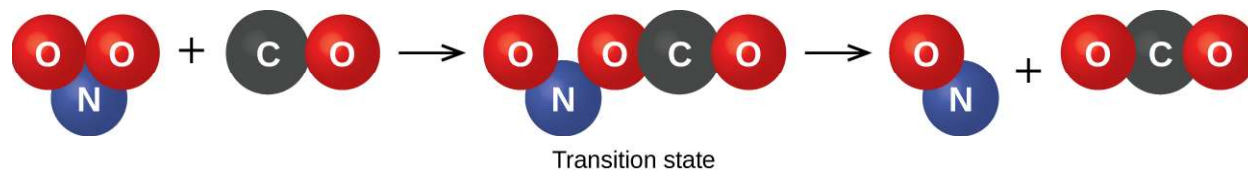
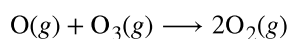


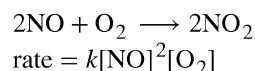
Figure 17.17 The probable mechanism for the reaction between NO_2 and CO to yield NO and CO_2 .

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:

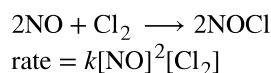


Termolecular Elementary Reactions

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:



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



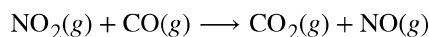
Relating Reaction Mechanisms to Rate Laws

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:



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

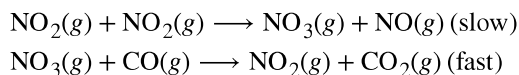
$$\text{rate} = k[\text{NO}_2][\text{CO}]$$

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 :

$$\text{rate} = k[\text{NO}_2]^2$$

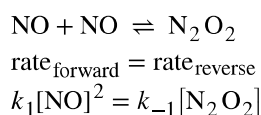
This rate law is not consistent with the single-step mechanism, but is consistent with the following two-step mechanism:



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:



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

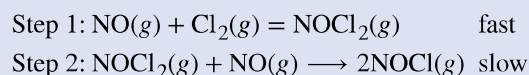
$$\left(\frac{k_1[\text{NO}]^2}{k_{-1}} \right) = [\text{N}_2\text{O}_2]$$

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

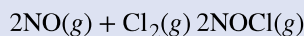
The two-step mechanism below has been proposed for a reaction between nitrogen monoxide and molecular chlorine:



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:



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

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

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, $[\text{NOCl}_2]$. 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:

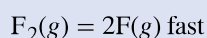
$$\begin{aligned}\text{rate}_1 &= \text{rate}_{-1} \\ k_1[\text{NO}][\text{Cl}_2] &= k_{-1}[\text{NOCl}_2] \\ [\text{NOCl}_2] &= \left(\frac{k_1}{k_{-1}}\right)[\text{NO}][\text{Cl}_2]\end{aligned}$$

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

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

Check Your Learning

The first step of a proposed multistep mechanism is:



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

$$\text{Answer: } [\text{F}] = \left(\frac{k_1[\text{F}_2]}{k_{-1}}\right)^{1/2}$$

17.7 Catalysis

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

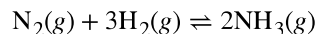
- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

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



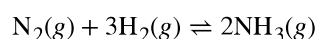
A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year.

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.



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 to 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.

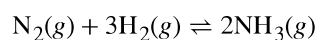
In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, "During peace time 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.

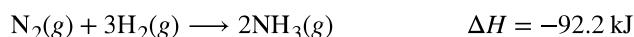
It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

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.



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:



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**).

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.

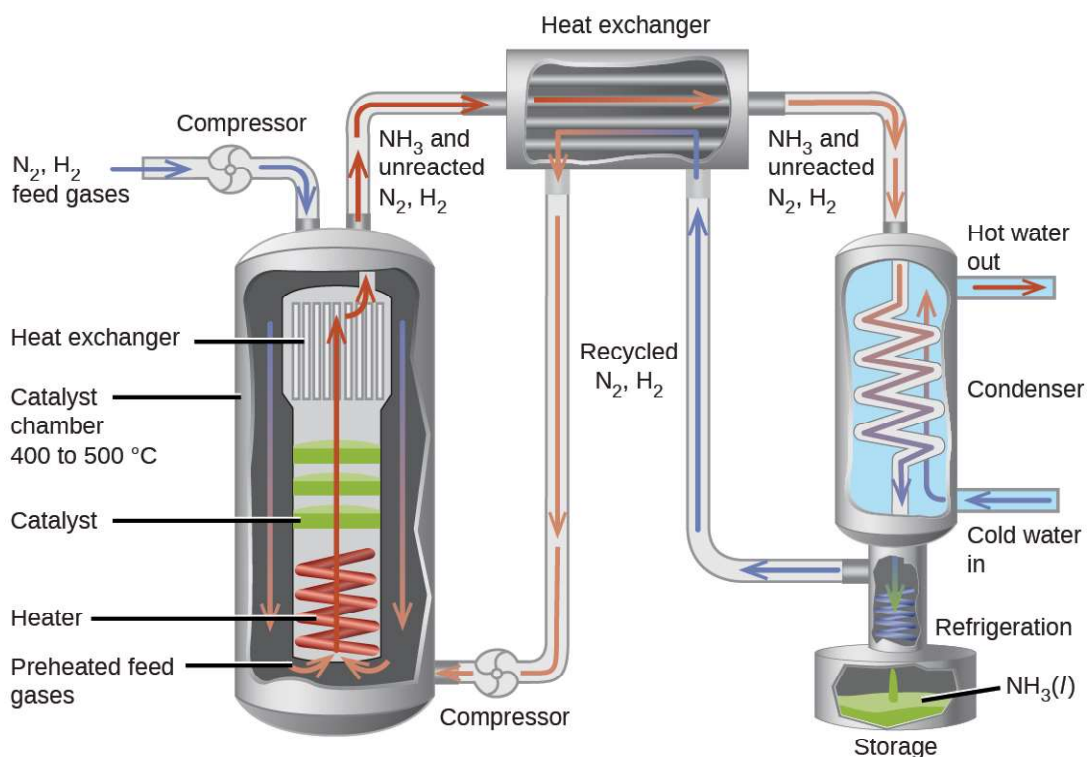


Figure 17.20 Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

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).

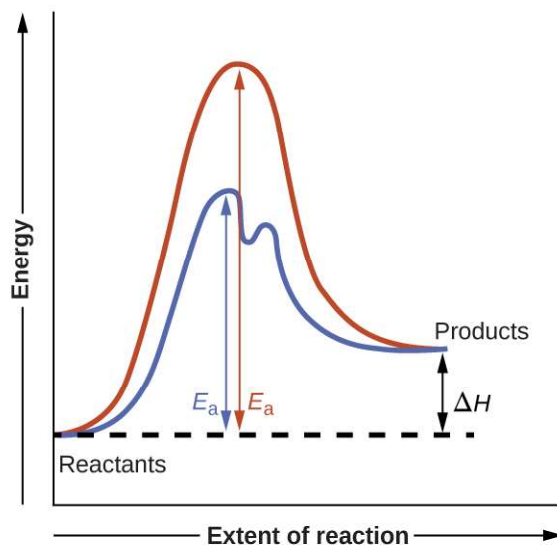
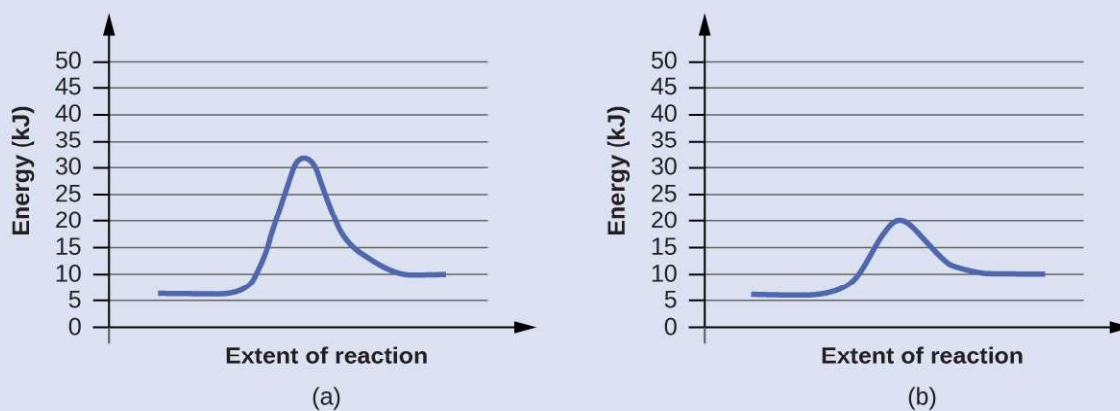


Figure 17.21 Reaction diagrams for an endothermic process in the absence (red curve) and presence (blue curve) of a catalyst. The catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions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

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

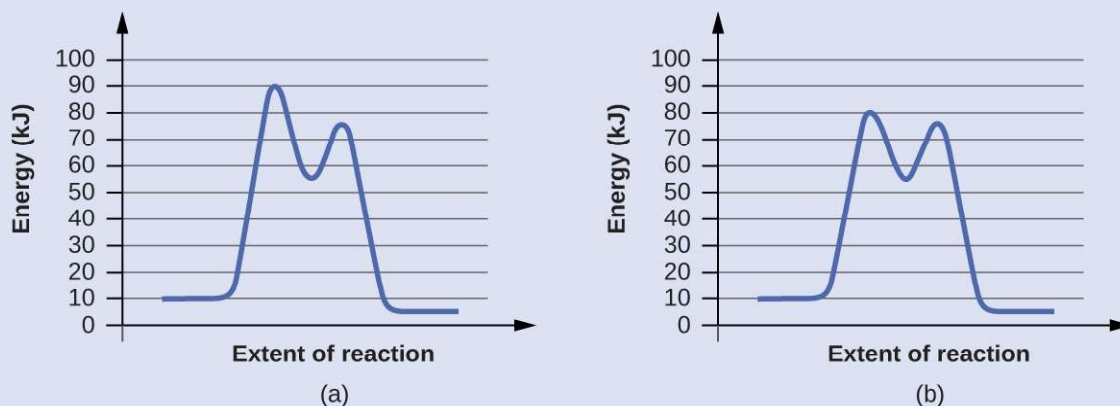
$$\text{diagram (b): } E_a = 20 \text{ kJ} - 6 \text{ kJ} = 14 \text{ kJ}$$

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?

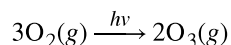


Answer: For the first step, $E_a = 80$ kJ for (a) and 70 kJ for (b), so diagram (b) depicts the catalyzed reaction. Activation energies for the second steps of both mechanisms are the same, 20 kJ.

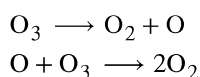
Homogeneous Catalysts

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.

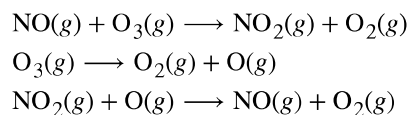
As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:



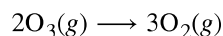
Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following two-step mechanism:



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:



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



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).

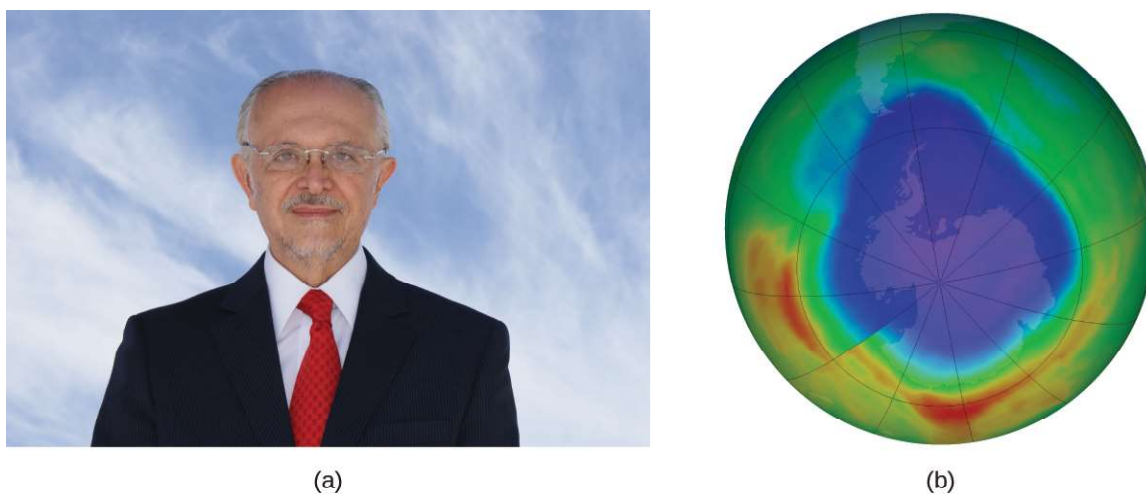
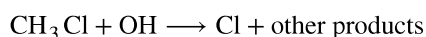


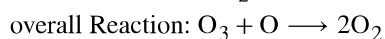
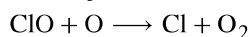
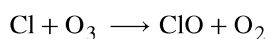
Figure 17.22 (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

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:



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



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**).

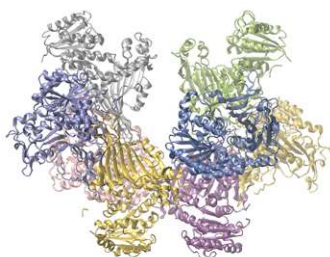


Figure 17.23 Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

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.

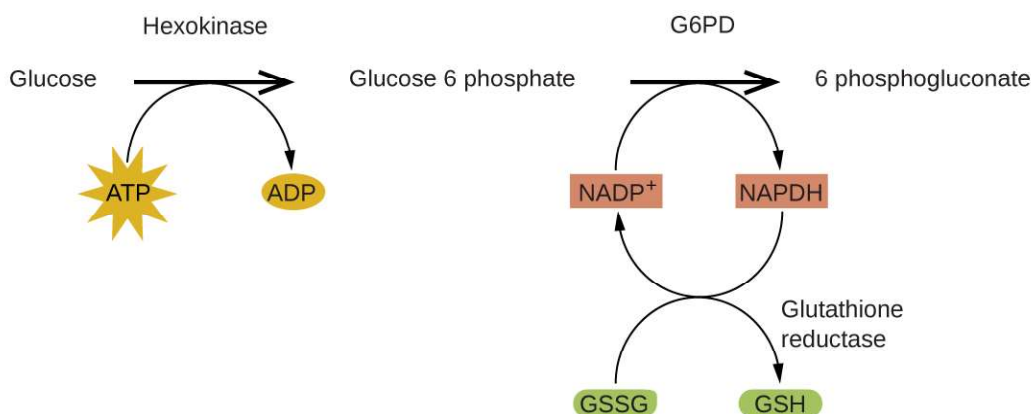


Figure 17.24 In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

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

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).

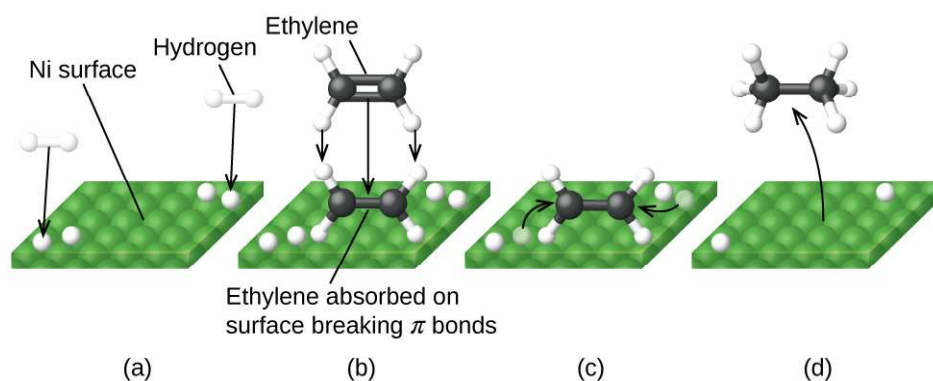


Figure 17.25 Mechanism for the Ni-catalyzed reaction $\text{C}_2\text{H}_4 + \text{H}_2 \longrightarrow \text{C}_2\text{H}_6$. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the C–C π -bond and forming Ni–C bonds. (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**).

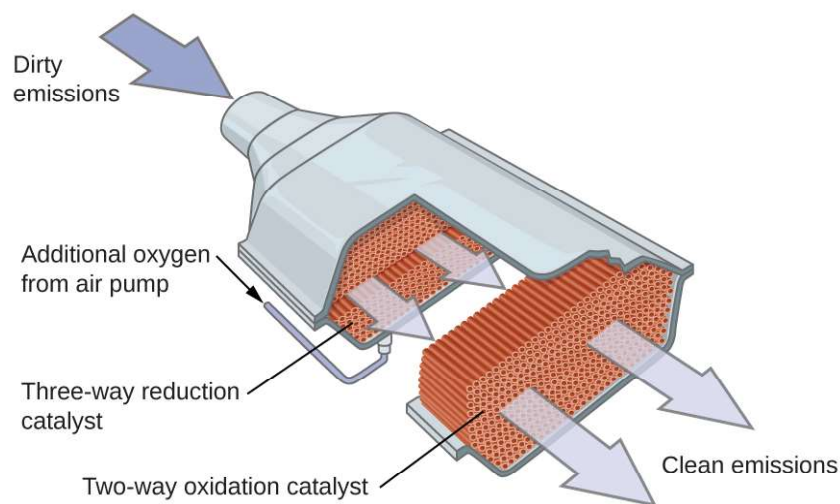
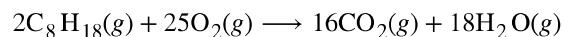
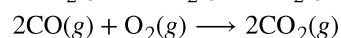
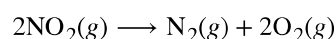


Figure 17.26 A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

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:



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**).

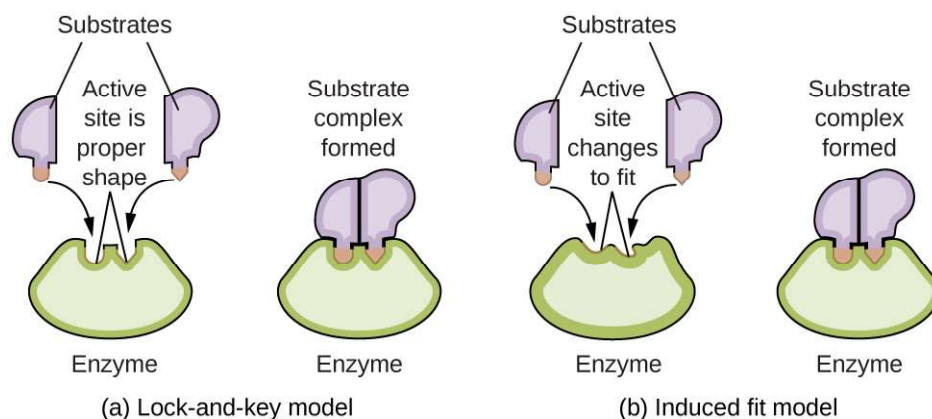


Figure 17.27 (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

Link to Learning

The **Royal Society of Chemistry** (<http://openstax.org//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)



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

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

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 $aA \rightarrow bB = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = \frac{1}{b} \frac{\Delta[B]}{\Delta t}$
- 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 $t_{1/2} = \frac{1}{[A]_0 k}$
- $k = Ae^{-E_a/RT}$
- $\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$
- $\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

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

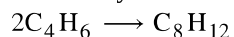
Catalysts affect the rate of a chemical reaction by altering its mechanism to provide a lower activation energy, but they do not affect equilibrium. Catalysts can be homogenous (in the same phase as the reactants) or heterogeneous (a different phase than the reactants).

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 $2\text{O}_3(g) \longrightarrow 3\text{O}_2(g)$. 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 $\text{Cl}_2(g) + 3\text{F}_2(g) \longrightarrow 2\text{ClF}_3(g)$. 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:



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}

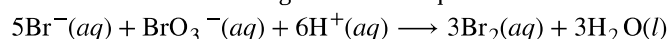
- (a) Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.
- (b) Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus $[C_4H_6]$. What are the units of this rate?
- (c) Determine the average rate of formation of C_8H_{12} at 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:



If the rate of disappearance of $Br^-(aq)$ at a particular moment during the reaction is $3.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, 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//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//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?

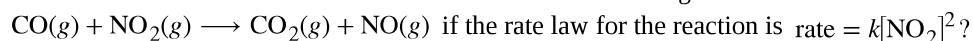
13. Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:

- (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:



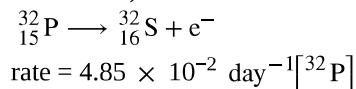
- (a) Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.
- (b) Increasing the concentration of CO from 0.01 M to 0.03 M.

16. How will each of the following affect the rate of the reaction: $\text{CO}(g) + \text{NO}_2(g) \longrightarrow \text{CO}_2(g) + \text{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\text{NO}_2][\text{CO}]$?

- (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.

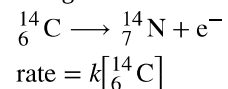
17. Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to depletion of the ozone layer. The reaction $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$ is first order with respect to both NO and O_3 with a rate constant of $2.20 \times 10^7 \text{ L/mol}\cdot\text{s}$. What is the instantaneous rate of disappearance of NO when $[\text{NO}] = 3.3 \times 10^{-6} \text{ M}$ and $[\text{O}_3] = 5.9 \times 10^{-7} \text{ M}$?

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:



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 $1.21 \times 10^{-4} \text{ year}^{-1}$. The products of the decay are nitrogen atoms and electrons (beta particles):



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

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

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:

$[\text{C}_2\text{H}_5\text{OH}] \text{ (M)}$	4.4×10^{-2}	3.3×10^{-2}	2.2×10^{-2}
Rate ($\text{mol L}^{-1} \text{ h}^{-1}$)	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{-2}

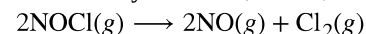
Determine the rate law, the rate constant, and the overall order for this reaction.

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

$[\text{NH}_3] \text{ (M)}$	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
Rate ($\text{mol L}^{-1} \text{ h}^{-1}$)	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 .



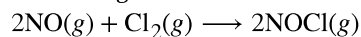
Determine the rate law, the rate constant, and the overall order for this reaction from the following data:

$[\text{NOCl}] \text{ (M)}$	0.10	0.20	0.30
Rate ($\text{mol L}^{-1} \text{ h}^{-1}$)	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 $A \longrightarrow 2C$.

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

25. Nitrogen monoxide reacts with chlorine according to the equation:



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 Cl₂? 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: $\text{H}_2(g) + 2\text{NO}(g) \longrightarrow \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g)$

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?

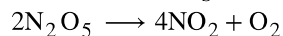
28. For the reaction $Q \longrightarrow W + X$, the following data were obtained at 30 °C:

[Q] _{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?

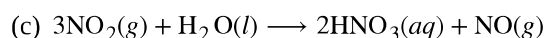
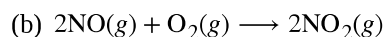
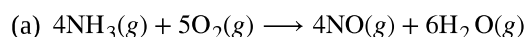
(b) What is the rate constant?

29. The rate constant for the first-order decomposition at 45 °C of dinitrogen pentoxide, N₂O₅, dissolved in chloroform, CHCl₃, is $6.2 \times 10^{-4} \text{ min}^{-1}$.



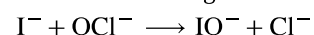
What is the rate of the reaction when $[\text{N}_2\text{O}_5] = 0.40 \text{ M}$?

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.



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 $5.8 \times 10^{-6}\text{ L}^2\text{ mol}^{-2}\text{ s}^{-1}$.

31. The following data have been determined for the reaction:



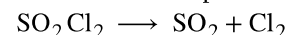
	1	2	3
$[\text{I}^-]_{\text{initial}}\text{ (M)}$	0.10	0.20	0.30
$[\text{OCI}^-]_{\text{initial}}\text{ (M)}$	0.050	0.050	0.010
Rate ($\text{mol L}^{-1}\text{ s}^{-1}$)	3.05×10^{-4}	6.20×10^{-4}	1.83×10^{-4}

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:



Time (s)	0	5.00×10^3	1.00×10^4	1.50×10^4
$[\text{SO}_2\text{Cl}_2]\text{ (M)}$	0.100	0.0896	0.0802	0.0719
Time (s)	2.50×10^4	3.00×10^4	4.00×10^4	
$[\text{SO}_2\text{Cl}_2]\text{ (M)}$	0.0577	0.0517	0.0415	

34. Pure ozone decomposes slowly to oxygen, $2\text{O}_3(g) \longrightarrow 3\text{O}_2(g)$. 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
$[\text{O}_3]\text{ (M)}$	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	
$[\text{O}_3]\text{ (M)}$	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:
 $2X \rightarrow Y + Z$

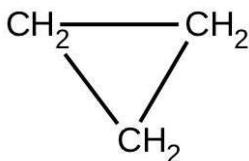
Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
$[X]$ (M)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125

36. What is the half-life for the first-order decay of phosphorus-32? ($^{32}_{15}\text{P} \rightarrow ^{32}_{16}\text{S} + e^{-}$) The rate constant for the decay is $4.85 \times 10^{-2} \text{ day}^{-1}$.
37. What is the half-life for the first-order decay of carbon-14? ($^{14}_6\text{C} \rightarrow ^{14}_7\text{N} + e^{-}$) The rate constant for the decay is $1.21 \times 10^{-4} \text{ year}^{-1}$.
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 $8.0 \times 10^{-8} \text{ L mol}^{-1} \text{ s}^{-1}$.
39. What is the half-life for the decomposition of O_3 when the concentration of O_3 is $2.35 \times 10^{-6} \text{ M}$? The rate constant for this second-order reaction is $50.4 \text{ L mol}^{-1} \text{ h}^{-1}$.
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 $2.42 \text{ L mol}^{-1} \text{ s}^{-1}$. 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 $3 \times 10^4 \text{ g/mol}$ 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 ($0.15 \times 10^{-6} \text{ g}$) of penicillinase, determine the order of the reaction with respect to penicillin and the value of the rate constant.

[Penicillin] (M)	Rate ($\text{mol L}^{-1} \text{ min}^{-1}$)
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 $499\text{ }^\circ\text{C}$, cyclopropane rearranges (isomerizes) and forms propene with a rate constant of $5.95 \times 10^{-4}\text{ s}^{-1}$. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at $499\text{ }^\circ\text{C}$?

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 ${}^{18}_9\text{F} \rightarrow {}^{18}_8\text{O} + {}^0_{+1}\text{e}$) Physicians use ${}^{18}\text{F}$ 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 ${}^{18}\text{F}$ to decay?

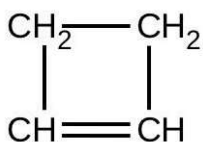
46. Suppose that the half-life of steroids taken by an athlete is 42 days. Assuming that the steroids biodegrade by a first-order process, how long would it take for $\frac{1}{64}$ of the initial dose to remain in the athlete's body?

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 $160\text{ }^\circ\text{C}$ 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 $2.0 \times 10^{-4}\text{ s}^{-1}$ at $150\text{ }^\circ\text{C}$ 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 $150\text{ }^\circ\text{C}$ 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 $\text{C}_4\text{H}_8 \longrightarrow 2\text{C}_2\text{H}_4$ is $6.1 \times 10^{-8} \text{ s}^{-1}$, 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 $1.1 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ at 703 K and $4.95 \text{ L mol}^{-1} \text{ s}^{-1}$ 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, H₂, and iodine, I₂. The value of the rate constant, k , for the reaction was measured at several different temperatures and the data are shown here:

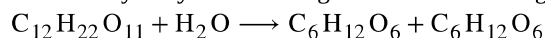
Temperature (K)	k (L mol ⁻¹ s ⁻¹)
555	6.23×10^{-7}
575	2.42×10^{-6}
645	1.44×10^{-4}
700	2.01×10^{-3}

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,



follows a first-order rate law for the disappearance of sucrose: $\text{rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$ (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, $k = 2.1 \times 10^{-11} \text{ s}^{-1}$ at 27 °C and $8.5 \times 10^{-11} \text{ s}^{-1}$ 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 $1.65 \times 10^{-7} M$. 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//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//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 $A + B \rightarrow C$? Can we predict the effect if the reaction is known to be an elementary reaction?

69. Define these terms:

(a) unimolecular reaction

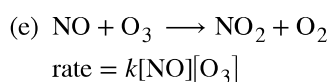
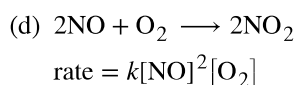
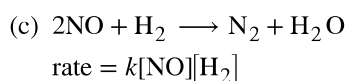
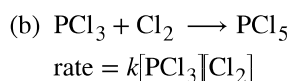
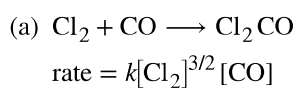
(b) bimolecular reaction

(c) elementary reaction

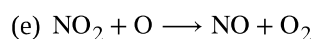
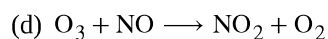
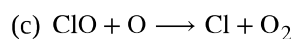
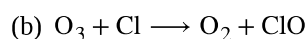
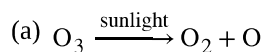
(d) overall reaction

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

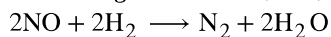
71. Given the following reactions and the corresponding rate laws, in which of the reactions might the elementary reaction and the overall reaction be the same?



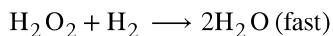
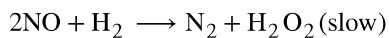
72. Write the rate law for each of the following elementary reactions:



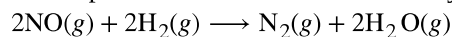
73. Nitrogen monoxide, NO , reacts with hydrogen, H_2 , according to the following equation:



What would the rate law be if the mechanism for this reaction were:



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

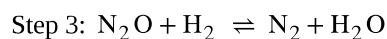
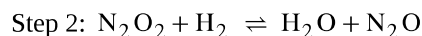
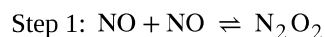


Initial concentrations and rates of reaction are given here.

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}

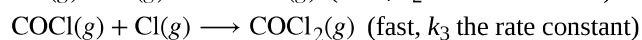
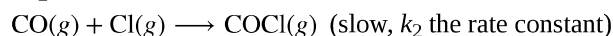
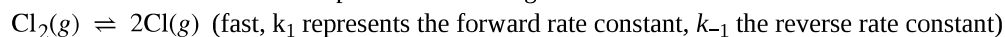
Consider the following questions:

- Determine the order for each of the reactants, NO and H₂, from the data given and show your reasoning.
- Write the overall rate law for the reaction.
- Calculate the value of the rate constant, *k*, for the reaction. Include units.
- For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H₂ had been consumed.
- The following sequence of elementary steps is a proposed mechanism for the reaction.



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 Cl₂ gives phosgene (COCl₂), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:



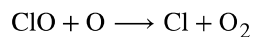
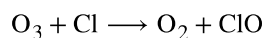
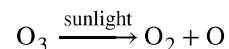
- Write the overall reaction.
- Identify all intermediates.
- Write the rate law for each elementary reaction.
- Write the overall rate law expression.

17.7 Catalysis

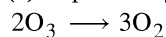
- Account for the increase in reaction rate brought about by a catalyst.
- Compare the functions of homogeneous and heterogeneous catalysts.

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

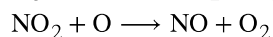
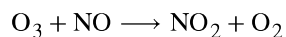
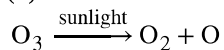
78. Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as CCl_2F_2 , catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:



(a) Explain why chlorine atoms are catalysts in the gas-phase transformation:



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



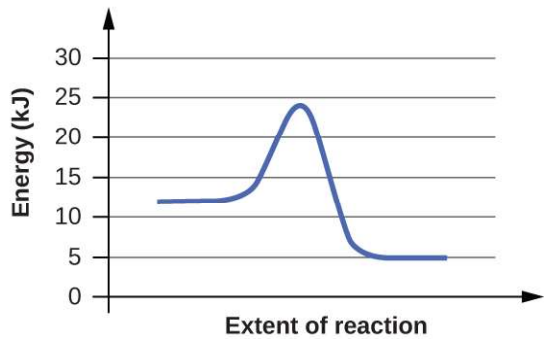
Is NO a catalyst for the decomposition? Explain your answer.

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: $\text{H}_2\text{O}(g) + \text{C}(s) \rightleftharpoons \text{H}_2(g) + \text{CO}(g)$. 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?

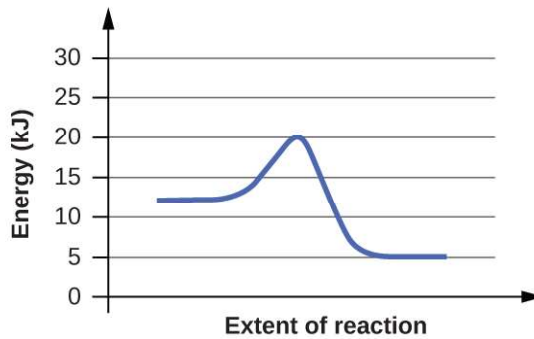
80. Nitrogen and oxygen react at high temperatures. What will happen to the concentrations of N_2 , O_2 , and NO at equilibrium if a catalyst is added?

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

(a)

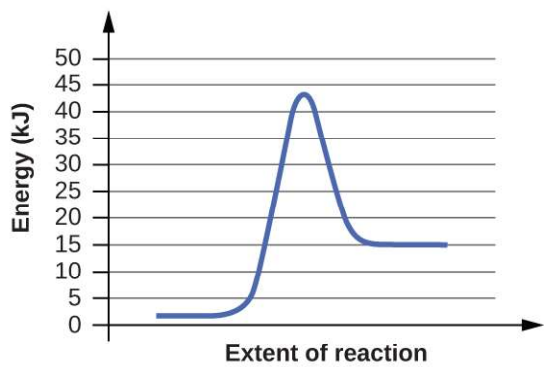


(a)

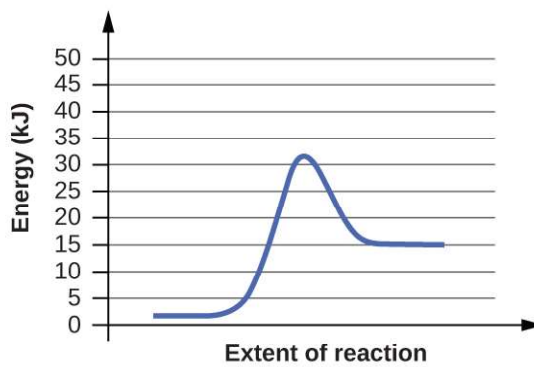


(b)

(b)



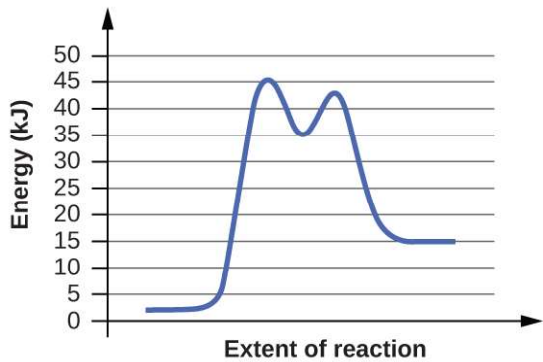
(a)



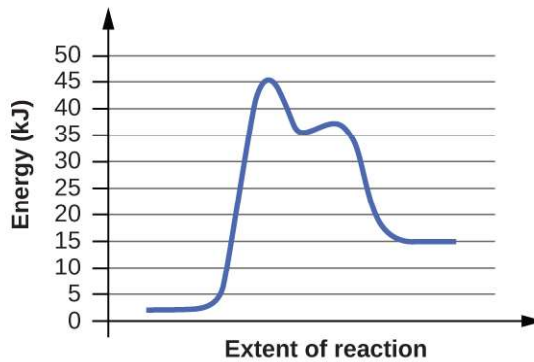
(b)

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

(a)

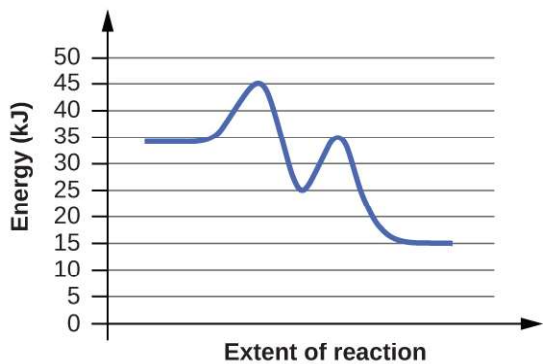


(a)

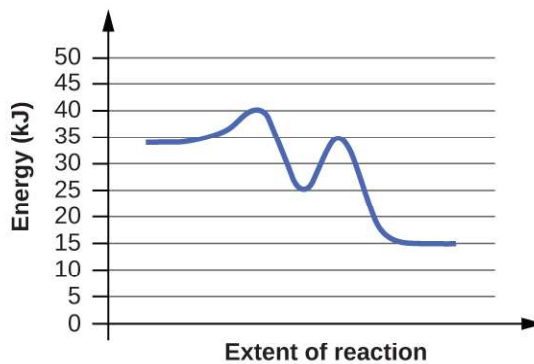


(b)

(b)



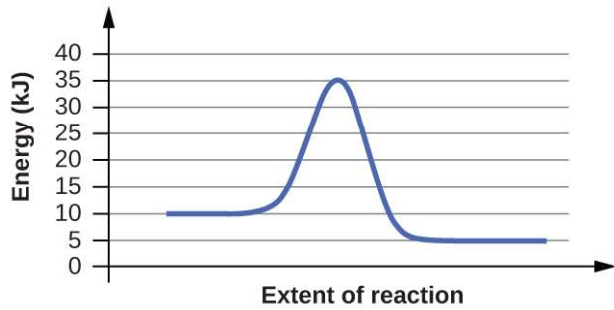
(a)



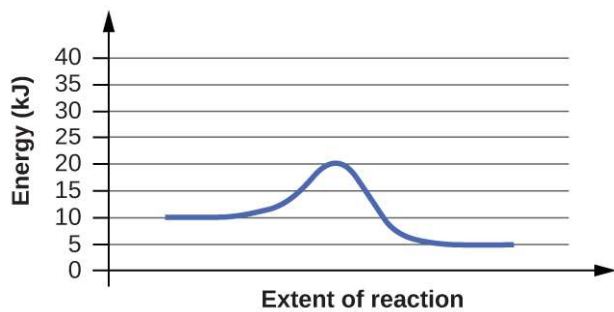
(b)

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

(a)

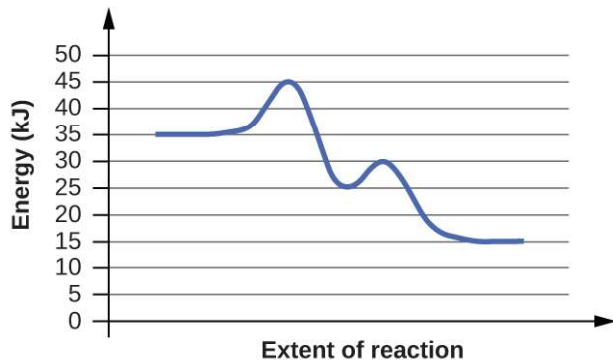


(b)

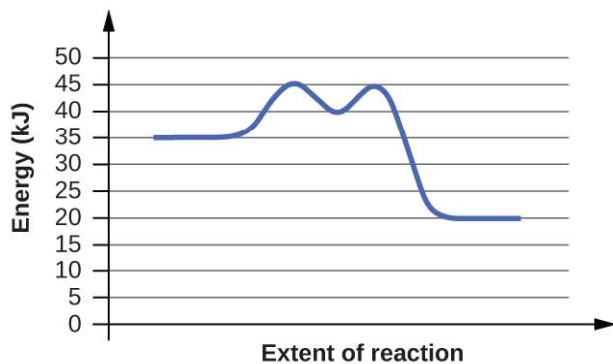


84. For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(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

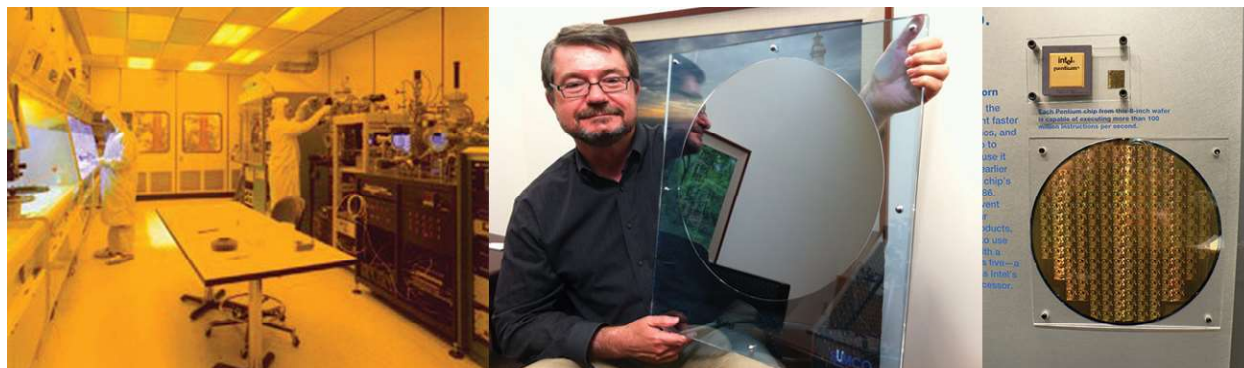


Figure 18.1 Purity is extremely important when preparing silicon wafers. Technicians in a cleanroom prepare silicon without impurities (left). The CEO of VLSI Research, Don Hutcheson, shows off a pure silicon wafer (center). A silicon wafer covered in Pentium chips is an enlarged version of the silicon 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

- 18.1 Periodicity
- 18.2 Occurrence and Preparation of the Representative Metals
- 18.3 Structure and General Properties of the Metalloids
- 18.4 Structure and General Properties of the Nonmetals
- 18.5 Occurrence, Preparation, and Compounds of Hydrogen
- 18.6 Occurrence, Preparation, and Properties of Carbonates
- 18.7 Occurrence, Preparation, and Properties of Nitrogen
- 18.8 Occurrence, Preparation, and Properties of Phosphorus
- 18.9 Occurrence, Preparation, and Compounds of Oxygen
- 18.10 Occurrence, Preparation, and Properties of Sulfur
- 18.11 Occurrence, Preparation, and Properties of Halogens
- 18.12 Occurrence, Preparation, and Properties of the Noble Gases

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 (vertical label on the left)

Group (horizontal label at the top)

1	2										13	14	15	16	17	18	
1 H 1.008 hydrogen											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	
2 Li 6.94 lithium	4 Be 9.012 beryllium											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
3 Na 22.99 sodium	12 Mg 24.31 magnesium	3 Sc	4 Ti	5 V	6 Cr	7 Mn	8 Fe	9 Co	10 Ni	11 Cu	12 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
4 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	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
5 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	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
6 Cs 132.9 cesium	56 Ba 137.3 barium	57-71 La-Lu * lanthanum series	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	113 Nh [285] nihonium	114 Fl [289] flerovium	115 Mc [289] moscovium	116 Lv [293] livermorium	117 Ts [294] tennessine	118 Og [294] oganesson
7 Fr [223] francium	88 Ra [226] radium	89-103 Ac-Lr ** actinide series	104 Rf [267] rutherfordium	105 Db [270] dubnium	106 Sg [271] seaborgium	107 Bh [270] bohrium	108 Hs [271] hassium	109 Mt [276] meitnerium	110 Ds [281] darmstadtium	111 Rg [285] roentgenium	112 Cn [285] copernicium	113 Nh [285] nihonium	114 Fl [289] flerovium	115 Mc [289] 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:

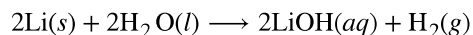


Figure 18.3 Lithium floats in paraffin oil because its density is less than the density of paraffin oil.

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.

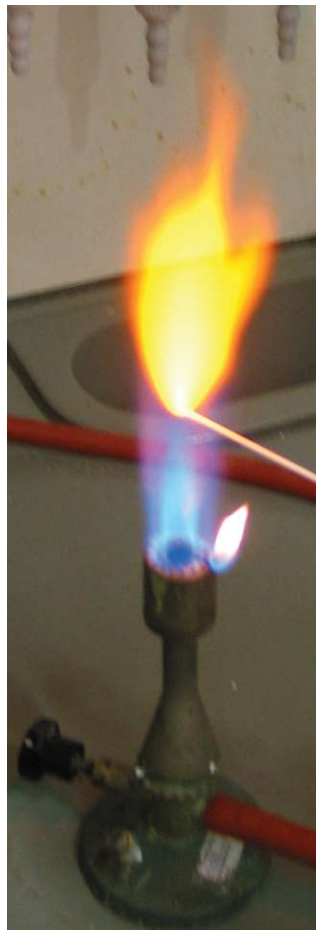


Figure 18.5 Dipping a wire into a solution of a sodium salt and then heating the wire causes emission of a bright yellow light, characteristic of sodium.

Link to Learning

This [video \(http://openstaxcollege.org//16alkalih2o\)](http://openstaxcollege.org//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.

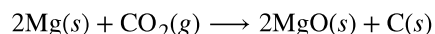
Magnesium is a silver-white metal that is malleable and ductile at high temperatures. Passivation decreases the reactivity of magnesium metal. Upon exposure to air, a tightly adhering layer of magnesium oxycarbonate forms on the surface of the metal and inhibits further reaction. (The carbonate comes 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:



For this reason, a CO₂ 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 Hg₂²⁺ 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:

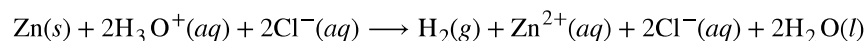


Figure 18.7 Zinc is an active metal. It dissolves in hydrochloric acid, forming a solution of colorless Zn^{2+} ions, Cl^- ions, and hydrogen gas.

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

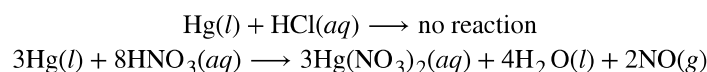
A sacrificial anode, or galvanic anode, is a means of providing cathodic protection of various metals. Cathodic protection refers to the prevention of corrosion by converting the corroding metal into a cathode. As a cathode, the metal resists corrosion, which is an oxidation process. Corrosion occurs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



The clear NO initially formed quickly undergoes further oxidation to the reddish brown NO₂.



Figure 18.8 From left to right: Hg(*l*), Hg + concentrated HCl, Hg + concentrated HNO₃. (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 Hg₂²⁺ 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.

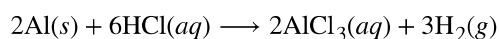
Dentists use amalgams containing silver and other metals to fill cavities. There are several reasons to use an amalgam including low cost, ease of manipulation, and longevity compared to alternate materials. Dental amalgams are approximately 50% mercury by weight, which, in recent years, has become a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

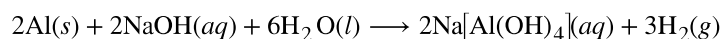
Group 13

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:



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



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 $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, 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 \(http://openstaxcollege.org//16aluminumhg\)](http://openstaxcollege.org//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.



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.

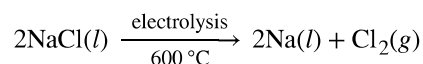
These metals primarily occur in minerals, with lithium found in silicate or phosphate minerals, and sodium and potassium found in salt deposits from evaporation of ancient seas and in silicates. The alkaline earth metals occur as silicates and, with the exception of beryllium, as carbonates and sulfates. Beryllium occurs as the mineral beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, 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.

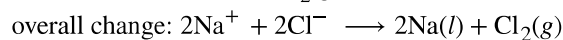
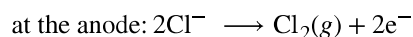
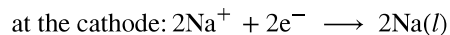
The Preparation of Sodium

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:



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:



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.

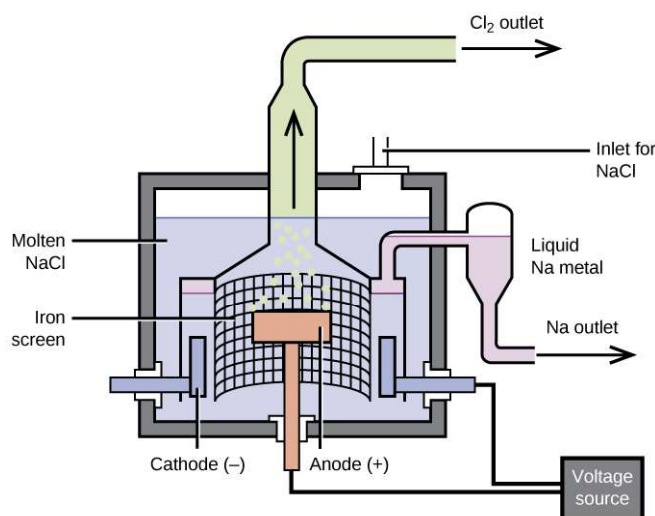
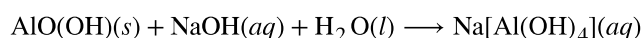


Figure 18.10 Pure sodium metal is isolated by electrolysis of molten sodium chloride using a Downs cell. It is not possible to isolate sodium by electrolysis of aqueous solutions of sodium salts because hydrogen ions are more easily reduced than are sodium ions; as a result, hydrogen gas forms at the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

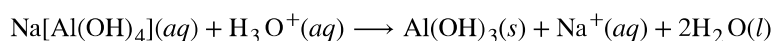
The Preparation of Aluminum

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, $\text{AlO}(\text{OH})$, with hot sodium hydroxide forms soluble sodium aluminate, while clay and other impurities remain undissolved:



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



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.

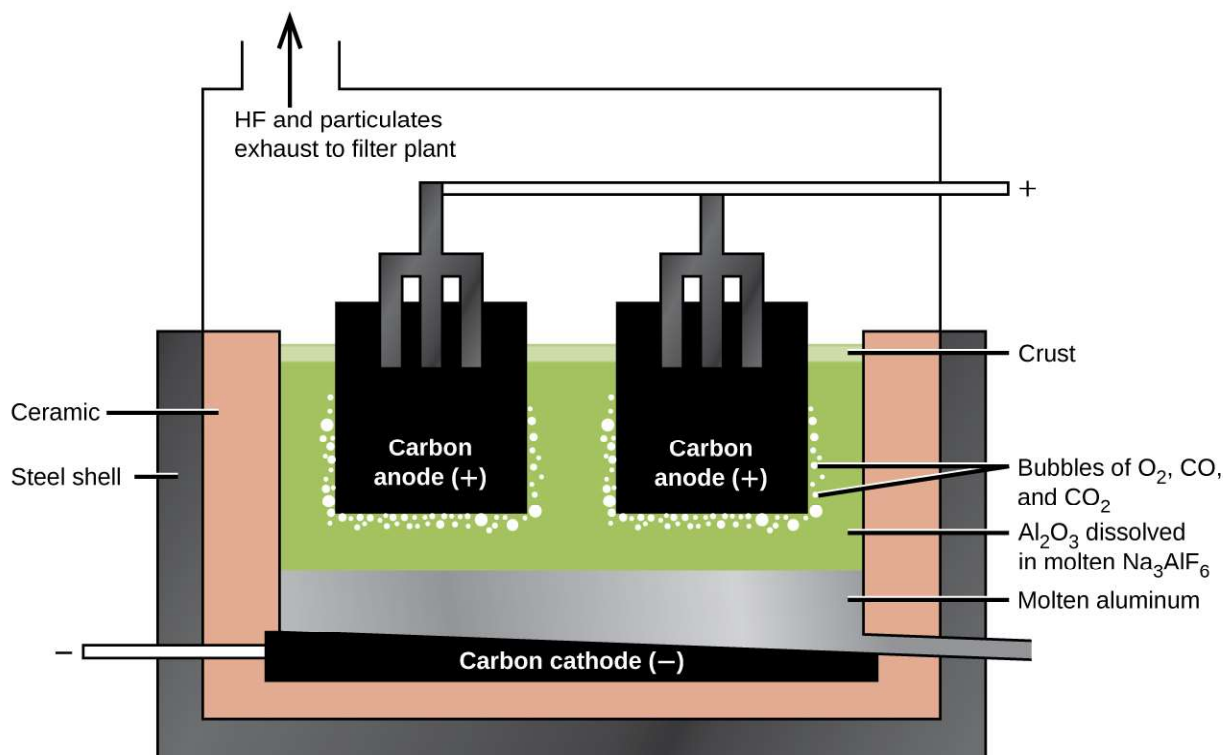
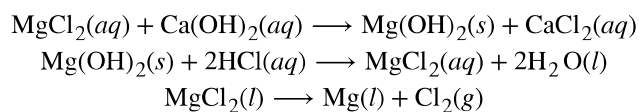


Figure 18.11 An electrolytic cell is used for the production of aluminum. The electrolysis of a solution of cryolite and calcium fluoride results in aluminum metal at the cathode, and oxygen, carbon monoxide, and carbon dioxide at the anode.

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:



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

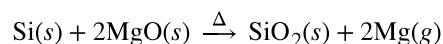
It is possible to isolate many of the representative metals by **chemical reduction** using other elements as reducing agents. In general, chemical reduction is much less expensive than electrolysis, and for this reason, chemical reduction is the method of choice for the isolation of these elements. 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

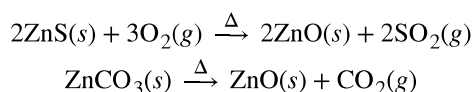
The **Pidgeon process** involves the reaction of magnesium oxide with elemental silicon at high temperatures to form pure magnesium:



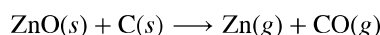
Although this reaction is unfavorable in terms of thermodynamics, the removal of the magnesium vapor produced takes advantage of Le Châtelier's principle to continue the forward progress of the reaction. Over 75% of the world's production of magnesium, primarily in China, comes from this process.

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:



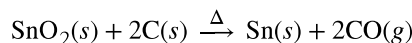
Carbon, in the form of coal, reduces the zinc oxide to form zinc vapor:



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:



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 $3d$ 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.

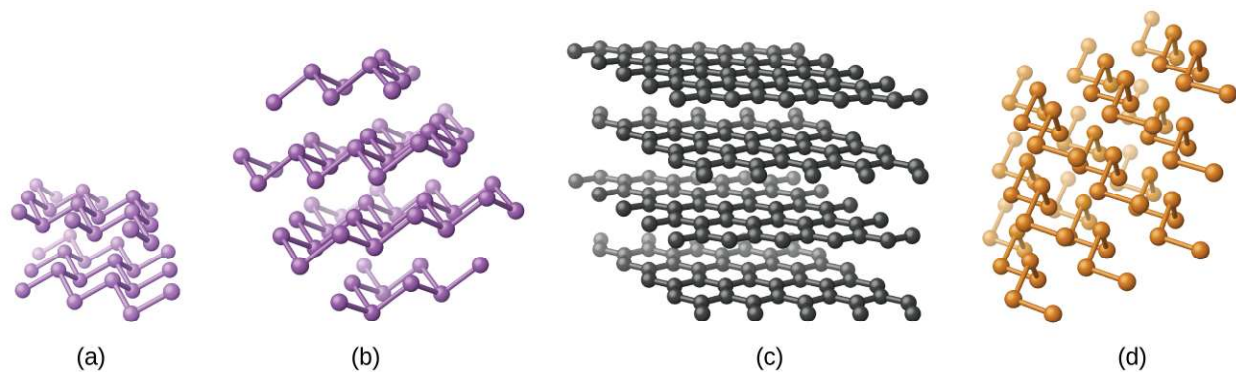


Figure 18.12 (a) Arsenic and (b) antimony have a layered structure similar to that of (c) graphite, except that the layers are puckered rather than planar. (d) Elemental tellurium forms spiral chains.

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.

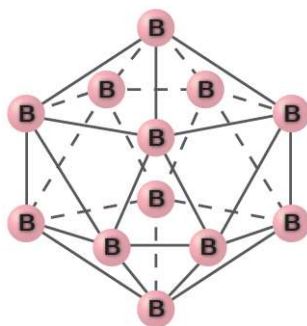


Figure 18.13 An icosahedron is a symmetrical, solid shape with 20 faces, each of which is an equilateral triangle. The faces meet at 12 corners.

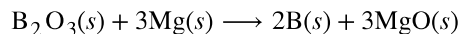
The name silicon is derived from the Latin word for flint, *silex*. The metalloid silicon readily forms compounds containing Si-O-Si bonds, which are of prime importance in the mineral world. This bonding capability is in contrast to the nonmetal carbon, whose ability to form carbon-carbon bonds gives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

Occurrence, Preparation, and Compounds of Boron and Silicon

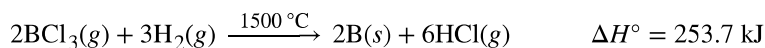
Boron constitutes less than 0.001% by weight of the earth's crust. In nature, it only occurs in compounds with oxygen. Boron is widely distributed in volcanic regions as boric acid, $B(OH)_3$, and in dry lake regions, including the desert areas of California, as borates and salts of boron oxyacids, such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

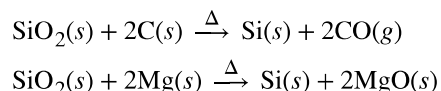


An **amorphous** substance is a material that appears to be a solid, but does not have a long-range order like a true solid. Treatment with hydrochloric acid removes the magnesium oxide. Further purification of the boron begins with conversion of the impure boron into boron trichloride. The next step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



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:



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.

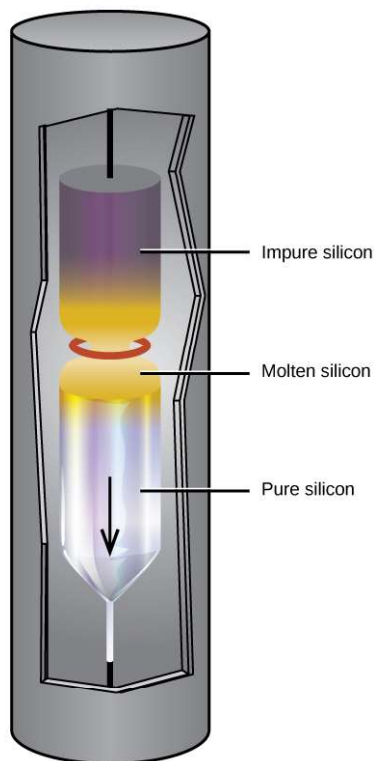
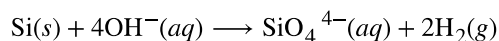


Figure 18.14 A zone-refining apparatus used to purify silicon.

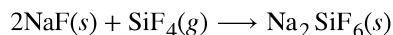
This highly purified silicon, containing no more than one part impurity per million parts of silicon, is the most important element in the computer industry. Pure silicon is necessary in semiconductor electronic devices such as transistors, computer chips, and solar cells.

Like some metals, passivation of silicon occurs due to 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:



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 $\text{Na}_2[\text{SiF}_6]$, which contains the octahedral $[\text{SiF}_6]^{2-}$ ion in which silicon is sp^3d^2 hybridized:



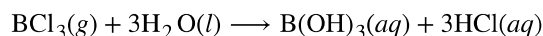
Antimony reacts readily with stoichiometric amounts of fluorine, chlorine, bromine, or iodine, yielding trihalides or, with excess fluorine or chlorine, forming the pentahalides SbF_5 and SbCl_5 . Depending on the stoichiometry, it forms antimony(III) sulfide, Sb_2S_3 , or antimony(V) sulfide when heated 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

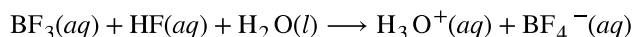
Boron trihalides— BF_3 , BCl_3 , BBr_3 , and BI_3 —can be prepared by the direct reaction of the elements. These nonpolar molecules contain boron with sp^2 hybridization and a trigonal planar molecular geometry. The fluoride and chloride

compounds are colorless gasses, the bromide is a liquid, and the iodide is a white crystalline solid.

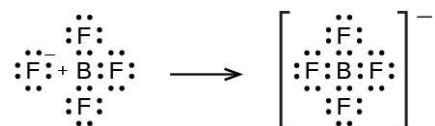
Except for boron trifluoride, the boron trihalides readily hydrolyze in water to form boric acid and the corresponding hydrohalic acid. Boron trichloride reacts according to the equation:



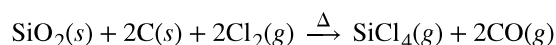
Boron trifluoride reacts with hydrofluoric acid, to yield a solution of fluoroboric acid, HBF_4 :



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:

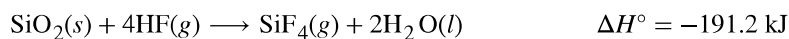


All the tetrahalides of silicon, SiX_4 , have been prepared. Silicon tetrachloride can be prepared by direct chlorination at elevated temperatures or by heating silicon dioxide with chlorine and carbon:



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:



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, $\text{Si}(\text{OH})_4$ 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, $\text{B}(\text{OH})_3$:

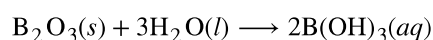


Figure 18.15 Laboratory glassware, such as Pyrex and Kimax, is made of borosilicate glass because it does not break when heated. The inclusion of borates in the glass helps to mediate the effects of thermal expansion and contraction. This reduces the likelihood of thermal shock, which causes silicate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

The boron atom in $\text{B}(\text{OH})_3$ is sp^2 hybridized and is located at the center of an equilateral triangle with oxygen atoms at the corners. In solid $\text{B}(\text{OH})_3$, 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^- :

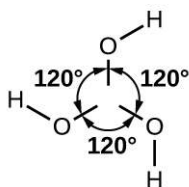
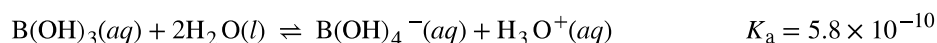


Figure 18.16 Boric acid has a planar structure with three $-\text{OH}$ groups spread out equally at 120° angles from each other.

Heating boric acid to 100°C causes molecules of water to split out between pairs of adjacent $-\text{OH}$ 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, $\text{H}_2\text{B}_4\text{O}_7$. 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 , $\text{K}[\text{B}_5\text{O}_6(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ (commonly written $\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$) and $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ (commonly written $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) are shown in **Figure 18.17**. Commercially, the most important borate is borax, $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$, 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, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$.

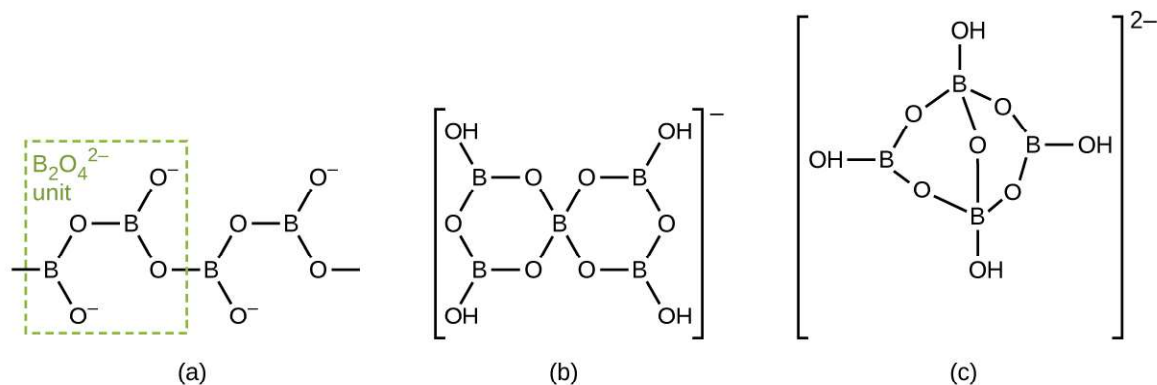


Figure 18.17 The borate anions are (a) CaB_2O_4 , (b) $\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$, and (c) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. The anion in CaB_2O_4 is an “infinite” chain.

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 reflects 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.



dry ice



quartz

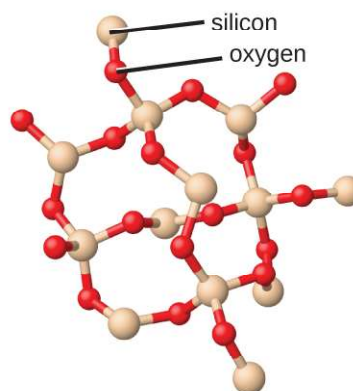
CO₂
(a)SiO₂
(b)

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 SiO₄ 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.

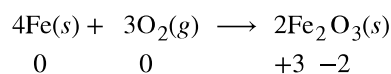
The first member of each nonmetal group exhibits different behaviors, in many respects, from the other group members. The reasons for this include smaller size, greater ionization energy, and (most important) the fact that the first member of each group has only four valence orbitals (one $2s$ and three $2p$) 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.

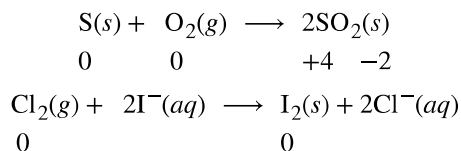
The variety of oxidation states displayed by most of the nonmetals means that many of their chemical reactions

involve changes in oxidation state through oxidation-reduction reactions. There are five general aspects of the oxidation-reduction chemistry:

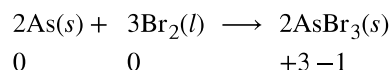
1. Nonmetals oxidize most metals. The oxidation state of the metal becomes positive as it undergoes oxidation and that of the nonmetal becomes negative as it undergoes reduction. For example:



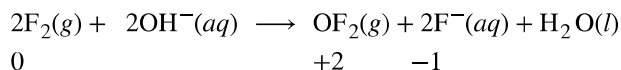
2. With the exception of nitrogen and carbon, which are poor oxidizing agents, a more electronegative nonmetal oxidizes a less electronegative nonmetal or the anion of the nonmetal:



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:

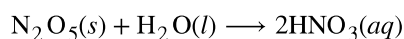
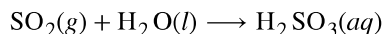


4. The stronger a nonmetal is as an oxidizing agent, the more difficult it is to oxidize the anion formed by the nonmetal. This means that the most stable negative ions are formed by elements at the top of the group or in group 17 of the period.
5. Fluorine and oxygen are the strongest oxidizing elements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

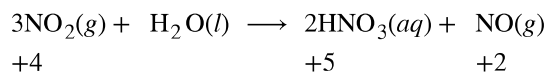


With the exception of most of the noble gases, all nonmetals form compounds with oxygen, yielding covalent oxides. Most of these oxides are acidic, that is, they react with water to form oxyacids. Recall from the acid-base chapter that an oxyacid is an acid consisting of hydrogen, oxygen, and some other element. Notable exceptions are carbon monoxide, CO, nitrous oxide, N₂O, and nitric oxide, NO. There are three characteristics of these acidic oxides:

1. Oxides such as SO₂ and N₂O₅, 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:



2. Those oxides such as NO₂ and ClO₂, 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:



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, NH₃, is a weaker acid than is water, H₂O, which is weaker than

is hydrogen fluoride, HF. Water, H₂O, is also a weaker acid than is hydrogen sulfide, H₂S, which is weaker than is hydrogen selenide, H₂Se. 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 H₂, N₂, O₂, F₂, and Cl₂. The other halogens are also diatomic; Br₂ is a liquid and I₂ 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: O₂, dioxygen, and O₃, 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).

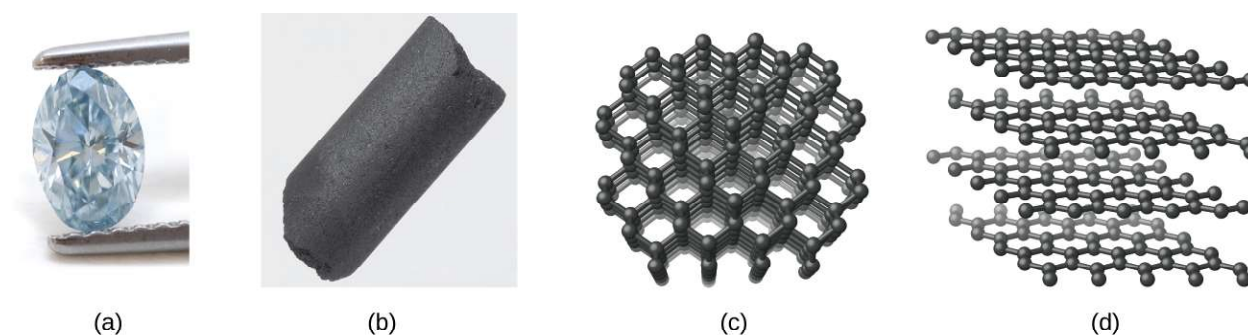


Figure 18.20 (a) Diamond and (b) graphite are two forms of carbon. (c) In the crystal structure of diamond, the covalent bonds form three-dimensional tetrahedrons. (d) In the crystal structure of graphite, each planar layer is composed of six-membered rings. (credit a: modification of work by “Fancy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

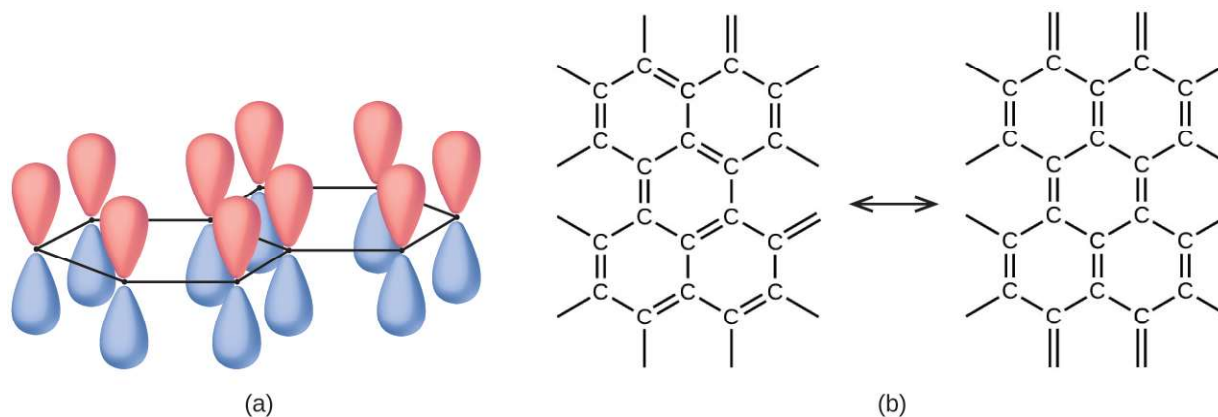


Figure 18.21 (a) Carbon atoms in graphite have unhybridized p orbitals. Each p orbital is perpendicular to the plane of carbon atoms. (b) These are two of the many resonance forms of graphite necessary to describe its electronic structure as a resonance hybrid.

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**).

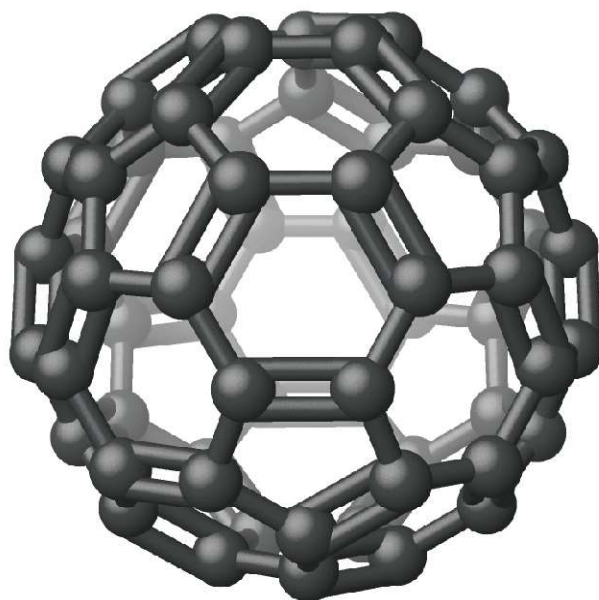


Figure 18.22 The molecular structure of C_{60} , buckminsterfullerene, is icosahedral.

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**.

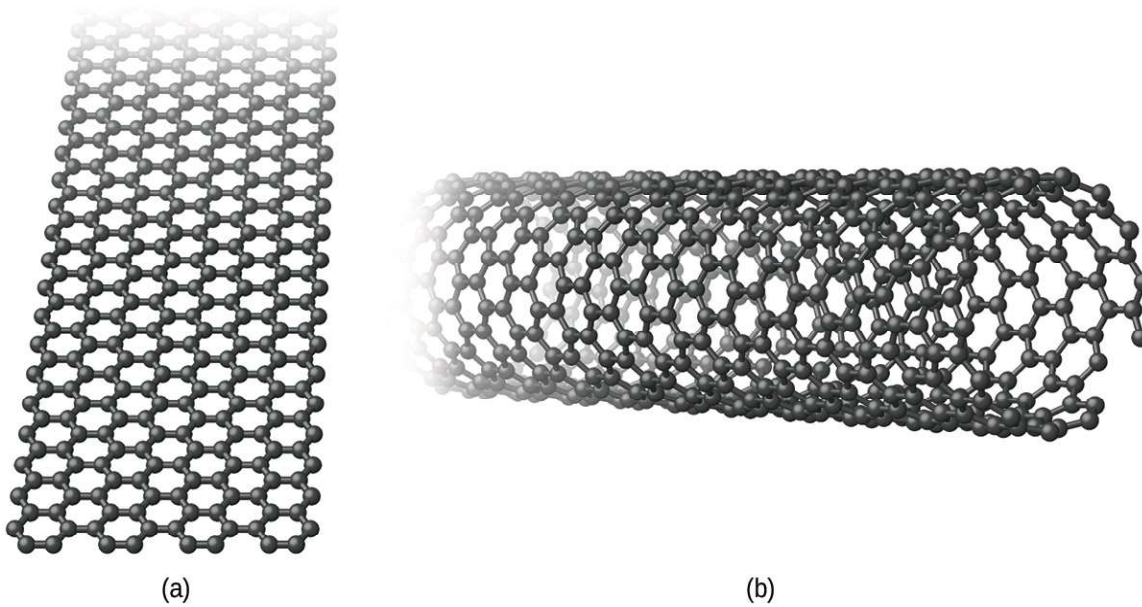


Figure 18.23 (a) Graphene and (b) carbon nanotubes are both allotropes of carbon.

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.

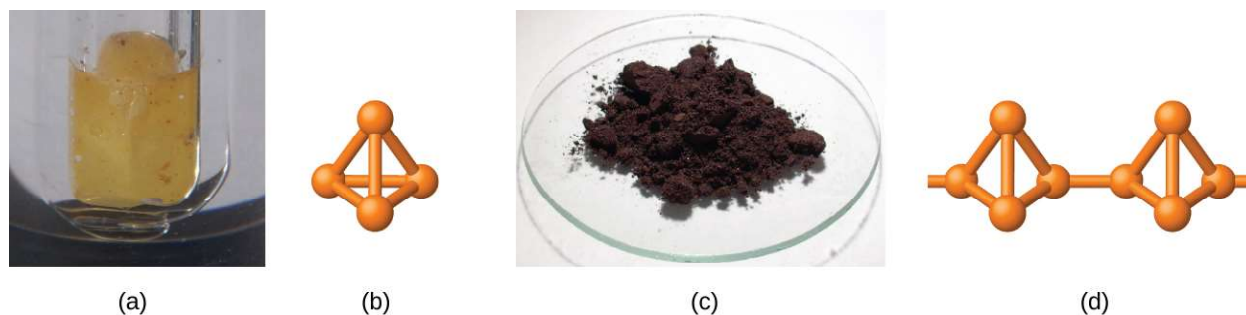


Figure 18.24 (a) Because white phosphorus bursts into flame in air, it is stored in water. (b) The structure of white phosphorus consists of P₄ molecules arranged in a tetrahedron. (c) Red phosphorus is much less reactive than is white phosphorus. (d) The structure of red phosphorus consists of networks of P₄ 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 P₄ tetrahedra joined by P-P single bonds. Red phosphorus is insoluble in solvents that dissolve white phosphorus. When red phosphorus is heated, P₄ 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 S₈ 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.

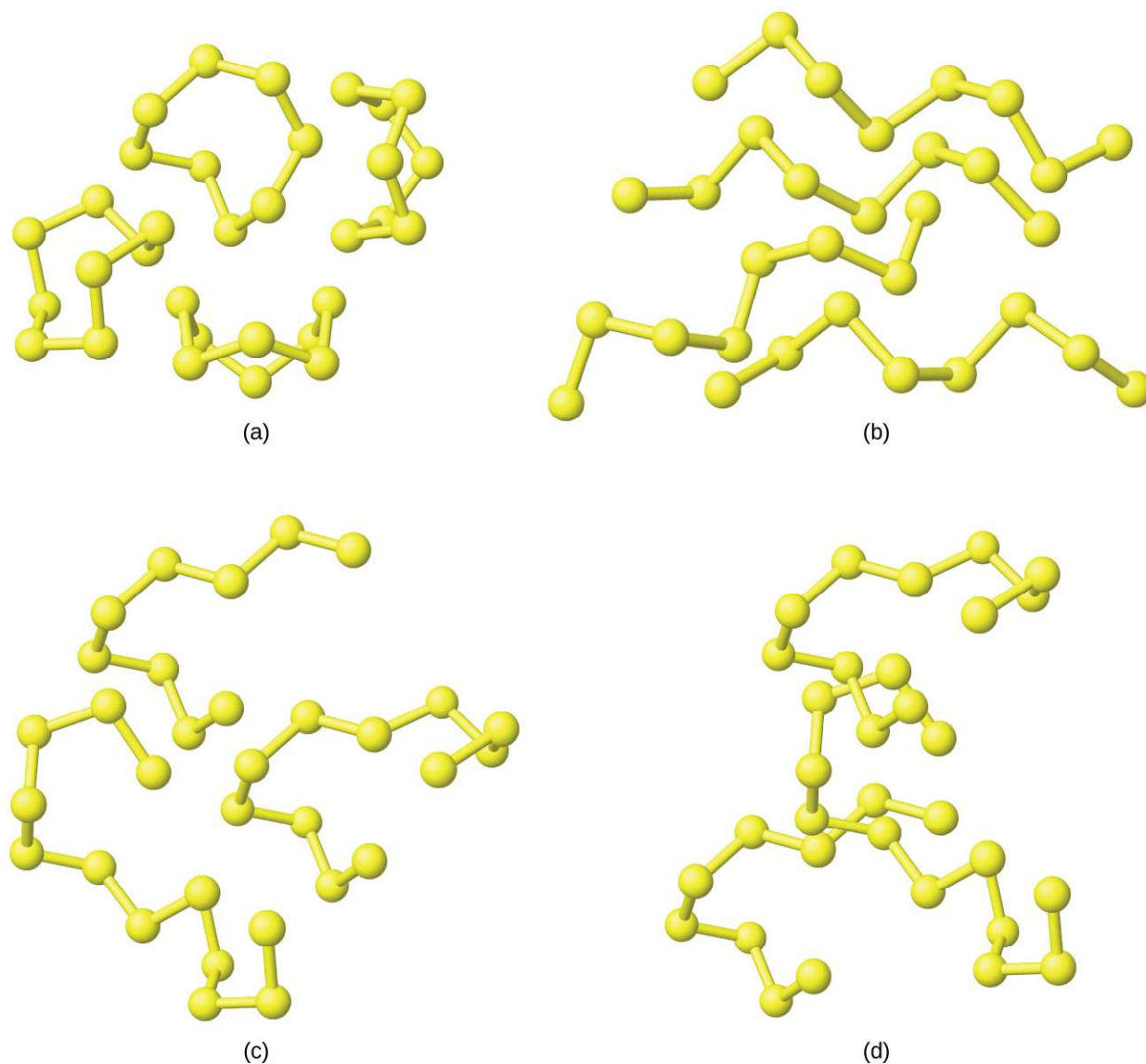


Figure 18.25 These four sulfur allotropes show eight-membered, puckered rings. Each sulfur atom bonds to each of its two neighbors in the ring by covalent S-S single bonds. Here are (a) individual S_8 rings, (b) S_8 chains formed when the rings open, (c) longer chains formed by adding sulfur atoms to 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 $230\text{ }^\circ\text{C}$) 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 $445\text{ }^\circ\text{C}$ and forms a vapor consisting of S_2 , S_6 , and S_8 molecules; at about $1000\text{ }^\circ\text{C}$, 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.

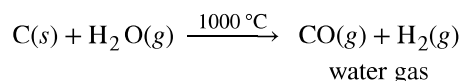
At ordinary temperatures, hydrogen is a colorless, odorless, tasteless, and nonpoisonous gas consisting of the diatomic molecule H_2 . Hydrogen is composed of three isotopes, and unlike other elements, these isotopes have different names and chemical symbols: protium, ^1H , deuterium, ^2H (or “D”), and 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.

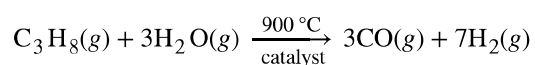
From Steam and Carbon or Hydrocarbons

Water is the cheapest and most abundant source of hydrogen. Passing steam over coke (an impure form of elemental carbon) at $1000\text{ }^\circ\text{C}$ produces a mixture of carbon monoxide and hydrogen known as 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:



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:

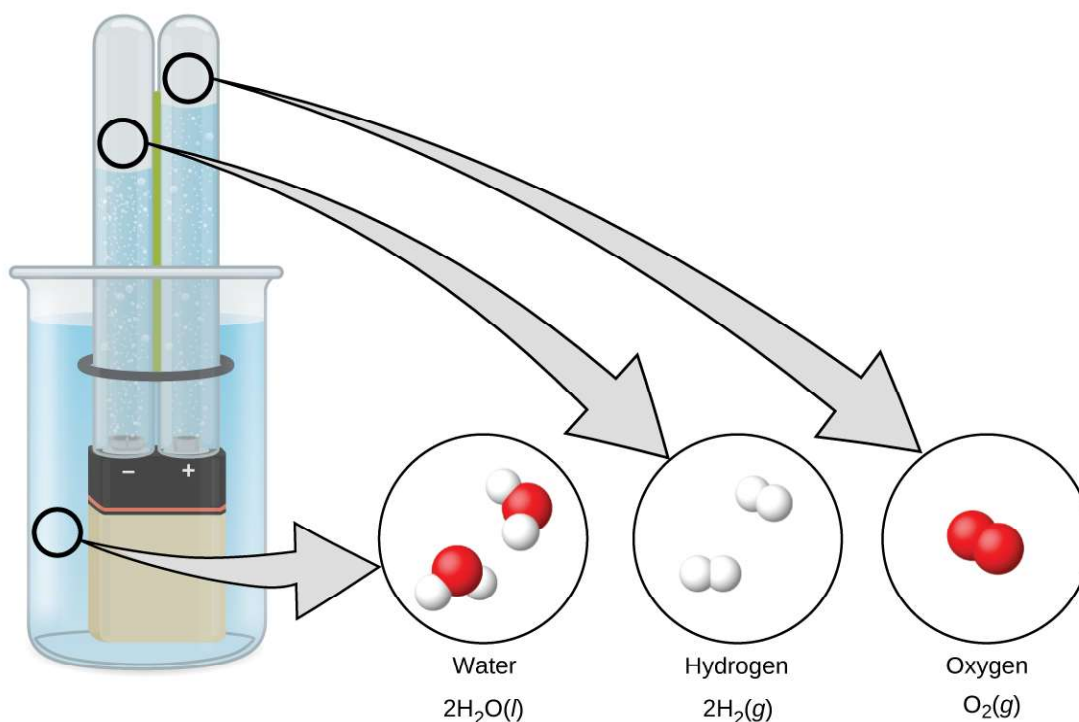
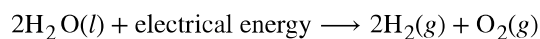


Figure 18.26 The electrolysis of water produces hydrogen and oxygen. Because there are twice as many hydrogen atoms as oxygen atoms and both elements are diatomic, there is twice the volume of hydrogen produced at the cathode as there is oxygen produced at the anode.

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:

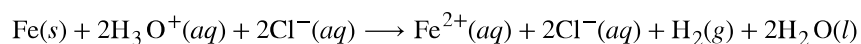
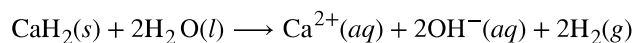


Figure 18.27 The reaction of iron with an acid produces hydrogen. Here, iron reacts with hydrochloric acid. (credit: Mark Ott)

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:



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: "reynnermedia"/Flickr)

An uncombined hydrogen atom consists of a nucleus and one valence electron in the 1s 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 or $MH_2 \longrightarrow MOH$ or $M(OH)_2 + H_2$	ionic hydrides with group 1 and Ca, Sr, and Ba
$H_2 + C \longrightarrow$ (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

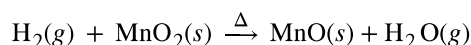
General Equation	Comments
$H_2 + X_2 \longrightarrow 2HX$	X = F, Cl, Br, and I; explosive with F ₂ ; low yield with I ₂

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:

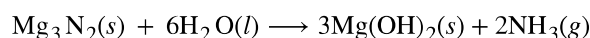


Hydrogen Compounds

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, NH₃, 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:



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

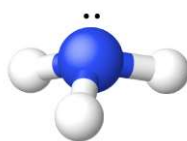
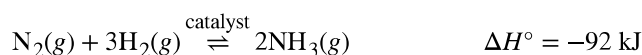


Figure 18.29 The structure of ammonia is shown with a central nitrogen atom and three hydrogen atoms.

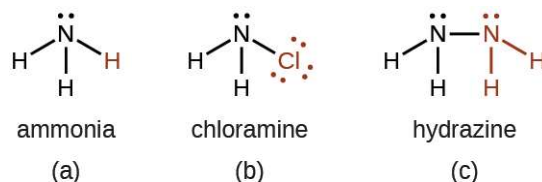
Ammonia is a colorless gas with a sharp, pungent odor. Smelling salts utilize this powerful odor. Gaseous ammonia readily liquefies to give a colorless liquid that boils at -33°C . Due to intermolecular hydrogen bonding, the enthalpy of vaporization of liquid ammonia is higher than that of any other liquid except water, so ammonia is useful as a refrigerant. Ammonia is quite soluble in water (658 L at STP dissolves in 1 L H₂O).

The chemical properties of ammonia are as follows:

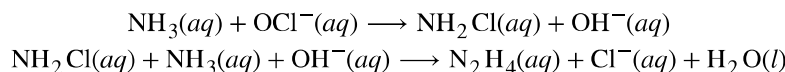
1. Ammonia acts as a Brønsted base, as discussed in the chapter on acid-base chemistry. The ammonium ion is similar in size to the potassium ion; compounds of the two ions exhibit many similarities in their structures and solubilities.
2. Ammonia can display acidic behavior, although it is a much weaker 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.

- 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 .
- 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 :



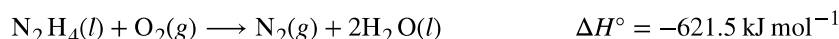
Chloramine, NH_2Cl , results from the reaction of sodium hypochlorite, NaOCl , with ammonia in basic solution. In the presence of a large excess of ammonia at low temperature, the chloramine reacts further to produce hydrazine, N_2H_4 :



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



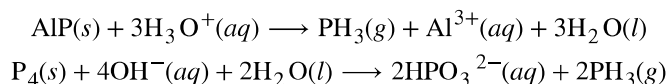
Hydrazine is a fuming, colorless liquid that has some physical properties remarkably similar to those of H_2O (it melts at 2°C , boils at 113.5°C , and has a density at 25°C of 1.00 g/mL). It burns rapidly and completely in air with substantial evolution of heat:



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 $\text{N}_2\text{H}_6^{2+}$ 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:



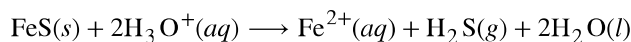
Phosphine is a colorless, very poisonous gas, which has an odor like that of decaying fish. Heat easily decomposes phosphine ($4\text{PH}_3 \longrightarrow \text{P}_4 + 6\text{H}_2$), and the compound burns in air. The major uses of phosphine are as a fumigant for grains and in semiconductor processing. 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

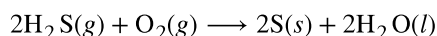
Hydrogen sulfide, H_2S , is a colorless gas that is responsible for the offensive odor of rotten eggs and of many hot

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 ($\text{H}_2 + \text{S}$) 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:

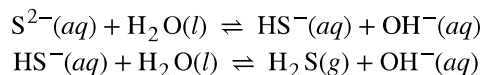


It is easy to oxidize the sulfur in metal sulfides and in hydrogen sulfide, making metal sulfides and H_2S good reducing agents. In acidic solutions, hydrogen sulfide reduces Fe^{3+} to Fe^{2+} , MnO_4^- to Mn^{2+} , $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} , and HNO_3 to NO_2 . The sulfur in H_2S usually oxidizes to elemental sulfur, unless a large excess of the oxidizing agent is present. In which case, the sulfide may oxidize to SO_3^{2-} or SO_4^{2-} (or to SO_2 or SO_3 in the absence of water):



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:

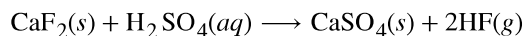


Halogen Hydrogen Compounds

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.

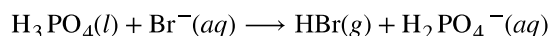
In general, it is possible to prepare the halides by the general techniques used to prepare other acids. Fluorine, chlorine, and bromine react directly with hydrogen to form the respective hydrogen halide. This is a commercially important reaction for preparing hydrogen chloride and hydrogen bromide.

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:



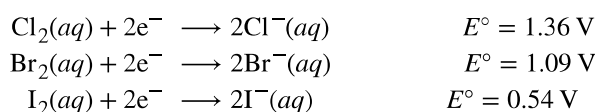
Gaseous hydrogen fluoride is also a by-product in the preparation of phosphate fertilizers by the reaction of fluoroapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, with sulfuric acid. The reaction of concentrated sulfuric acid with a chloride salt produces hydrogen chloride both commercially and in the 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:

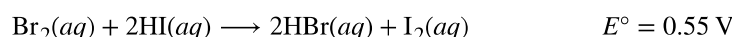


All of the hydrogen halides are very soluble in water, forming hydrohalic acids. With the exception of hydrogen fluoride, which has a strong hydrogen-fluoride bond, they are strong acids. Reactions of hydrohalic acids with metals, metal hydroxides, oxides, or carbonates produce salts of the halides.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

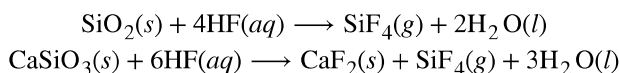
The halide ions give the substances the properties associated with $\text{X}^-(aq)$. The heavier halide ions (Cl^- , Br^- , and I^-) can act as reducing agents, and the lighter halogens or other oxidizing agents will oxidize them:



For example, bromine oxidizes iodine:



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



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.

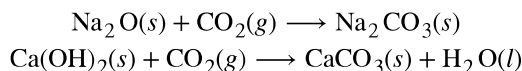
18.6 Occurrence, Preparation, and Properties of Carbonates

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

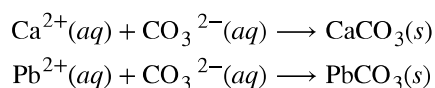
- Describe the preparation, properties, and uses of some representative metal carbonates

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:

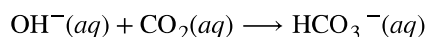


The carbonates of the alkaline earth metals of group 12 and lead(II) are not soluble. These carbonates precipitate upon mixing a solution of soluble alkali metal carbonate with a solution of soluble salts of these metals. Examples of net ionic equations for the reactions are:



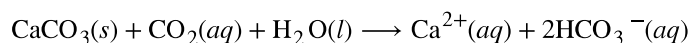
Pearls and the shells of most mollusks are calcium carbonate. Tin(II) or one of the trivalent or tetravalent ions such as Al^{3+} or Sn^{4+} behave differently in this reaction as carbon dioxide and the corresponding oxide form instead of the carbonate.

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:



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:



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.

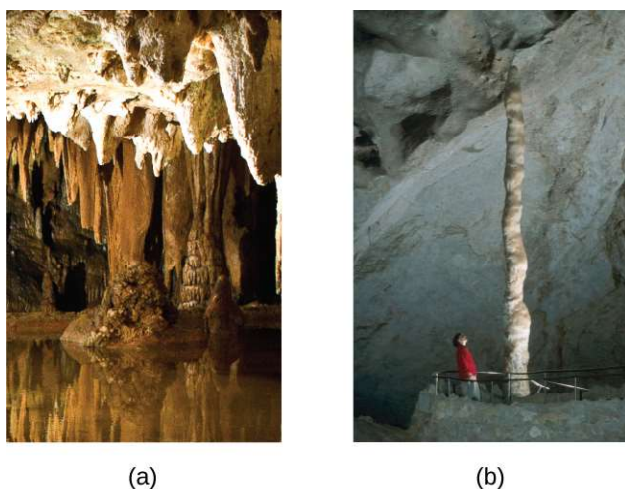
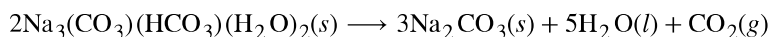
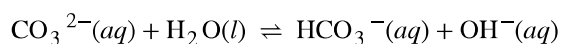


Figure 18.30 (a) Stalactites and (b) stalagmites are cave formations of calcium carbonate. (credit a: modification of work by Arvind Govindaraj; credit b: modification of work by the National Park Service.)

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, $\text{Na}_3(\text{CO}_3)(\text{HCO}_3)(\text{H}_2\text{O})_2$. Following recrystallization to remove clay and other impurities, heating the recrystallized trona produces Na_2CO_3 :



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



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:

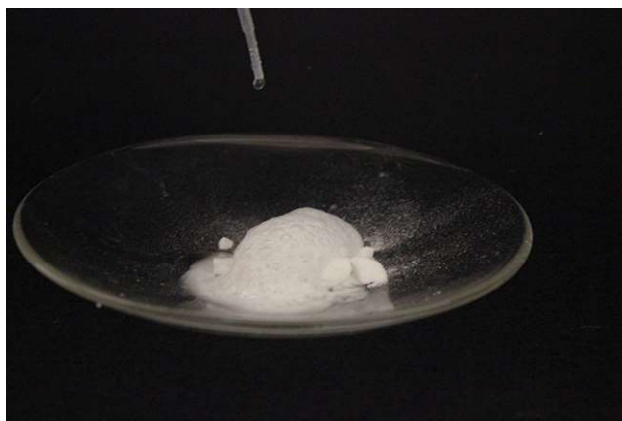
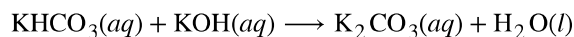


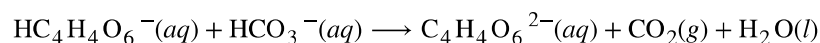
Figure 18.31 The reaction of calcium carbonate with hydrochloric acid is shown. (credit: Mark Ott)

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:



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), $\text{KHC}_4\text{H}_4\text{O}_6$. 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:



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 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**.

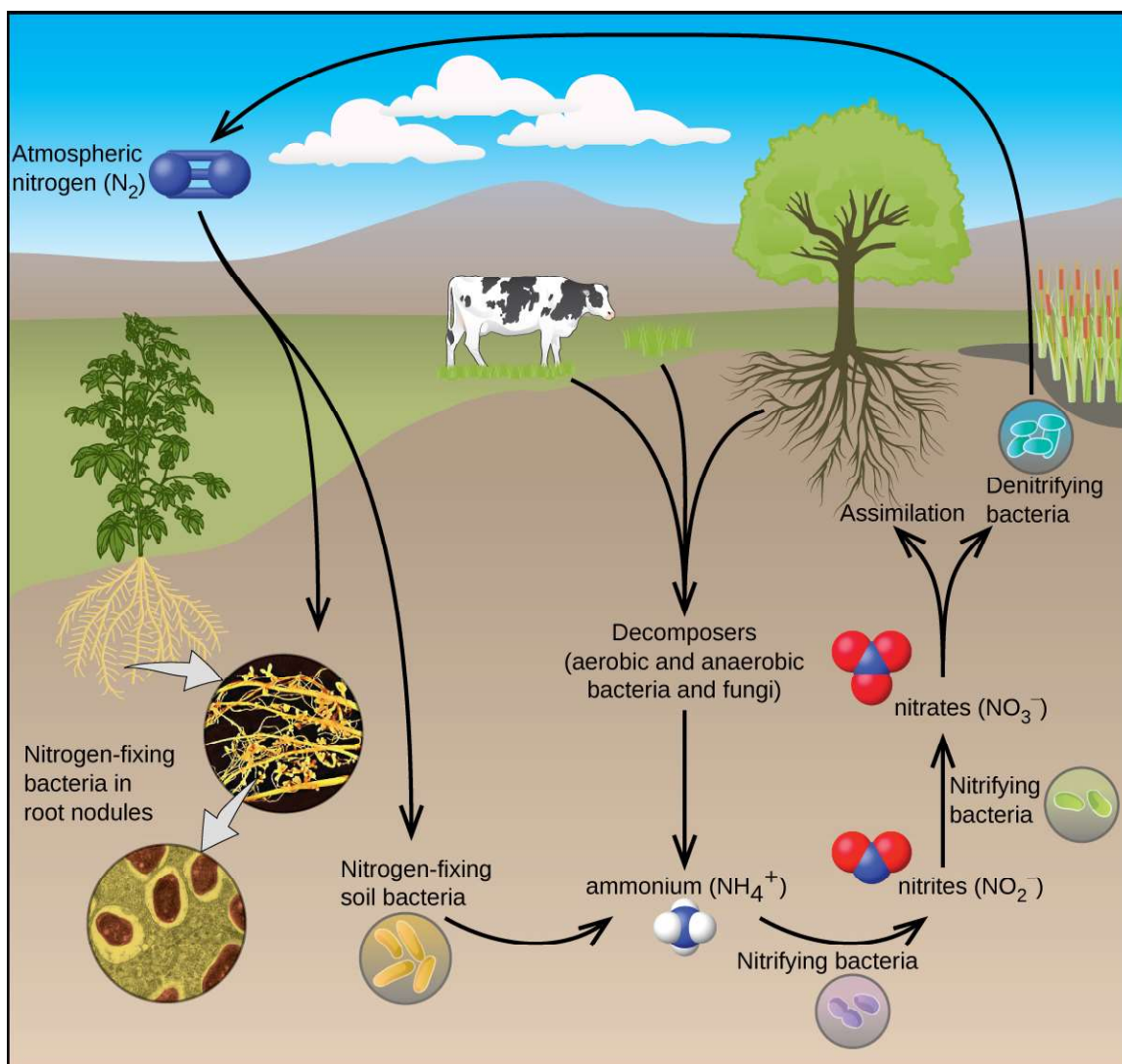


Figure 18.32 All living organisms require nitrogen. A few microorganisms are able to process atmospheric nitrogen using nitrogen fixation. (credit “roots”: modification of work by the United States Department of Agriculture; credit “root nodules”: modification of work by Louisa Howard)

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.”

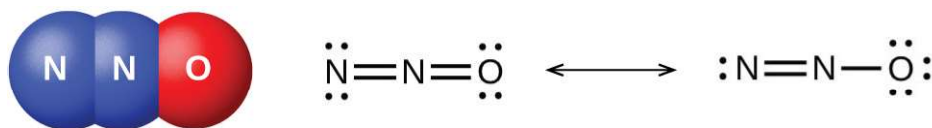
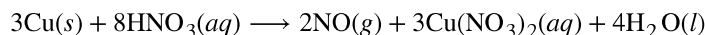


Figure 18.33 Nitrous oxide, N_2O , is an anesthetic that has these molecular (left) and resonance (right) structures.

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:



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.

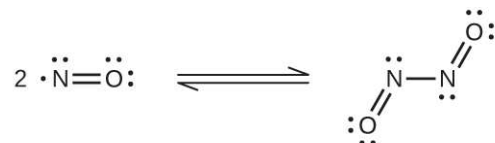


Figure 18.34 This shows the equilibrium between NO and N₂O₂. The molecule, N₂O₂, absorbs light.

Cooling a mixture of equal parts nitric oxide and nitrogen dioxide to -21 °C produces dinitrogen trioxide, a blue liquid consisting of N₂O₃ 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 NO₂.

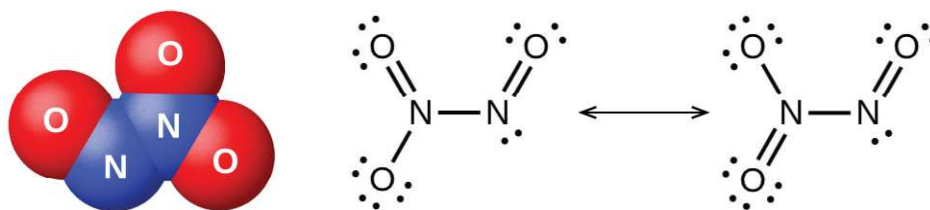


Figure 18.35 Dinitrogen trioxide, N₂O₃, only exists in liquid or solid states and has these molecular (left) and resonance (right) structures.

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.

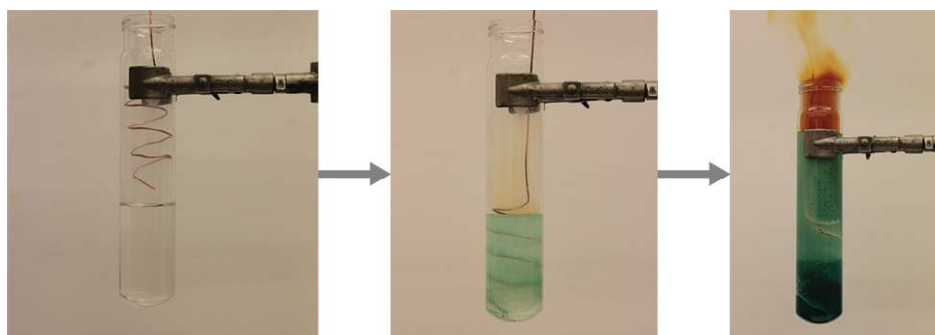


Figure 18.36 The reaction of copper metal with concentrated HNO₃ produces a solution of Cu(NO₃)₂ and brown fumes of NO₂. (credit: modification of work by Mark Ott)

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 NO₂. At low pressures or at high temperatures, nitrogen dioxide has a deep brown color that is due to the presence of the NO₂ molecule. At low temperatures, the color almost entirely disappears as dinitrogen tetraoxide, N₂O₄, forms. At room temperature, an equilibrium exists:

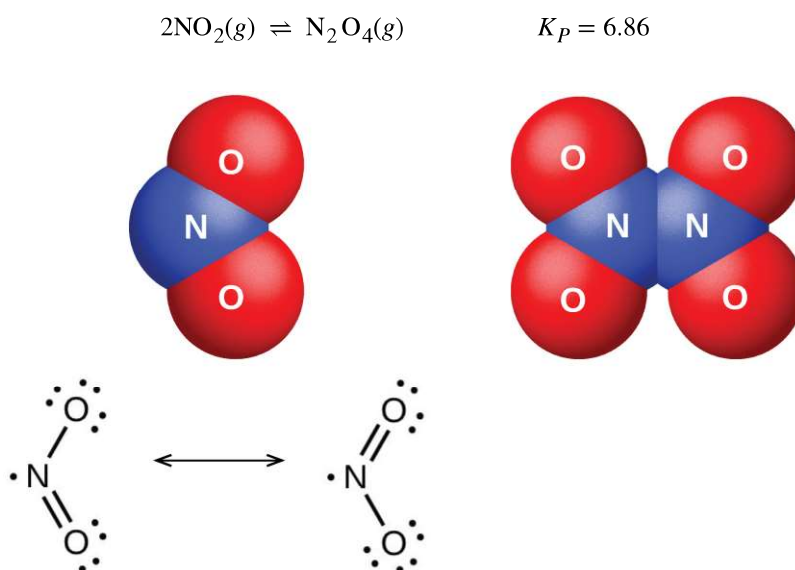
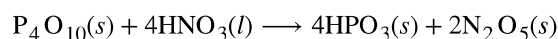


Figure 18.37 The molecular and resonance structures for nitrogen dioxide (NO_2 , left) and dinitrogen tetroxide (N_2O_4 , right) are shown.

Dinitrogen pentoxide, 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):



It is unstable above room temperature, decomposing to N_2O_4 and O_2 .

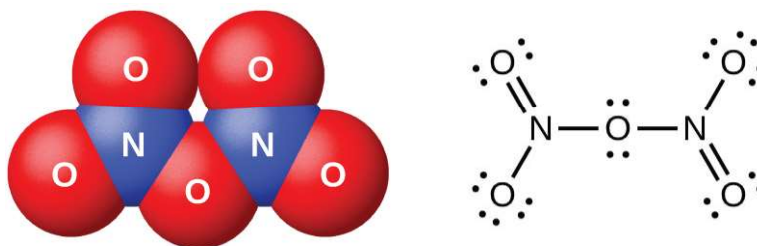
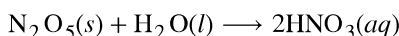
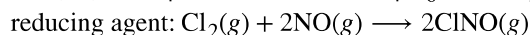


Figure 18.38 This image shows the molecular structure and one resonance structure of a molecule of dinitrogen pentoxide, N_2O_5 .

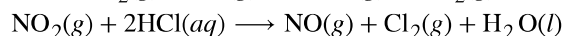
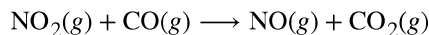
The oxides of nitrogen(III), nitrogen(IV), and nitrogen(V) react with water and form nitrogen-containing oxyacids. Nitrogen(III) oxide, N_2O_3 , is the anhydride of nitrous acid; HNO_2 forms when N_2O_3 reacts with water. There are no stable oxyacids containing nitrogen with an oxidation state of 4+; 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:



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:



Nitrogen dioxide (or dinitrogen tetraoxide) is a good oxidizing agent. For example:

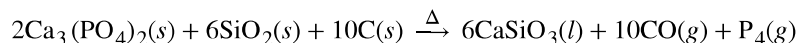


18.8 Occurrence, Preparation, and Properties of Phosphorus

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:



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, $\text{H}_2\text{P-PH}_2$, and tetraphosphorus trisulfide, P_4S_3 , illustrated in [Figure 18.39](#).

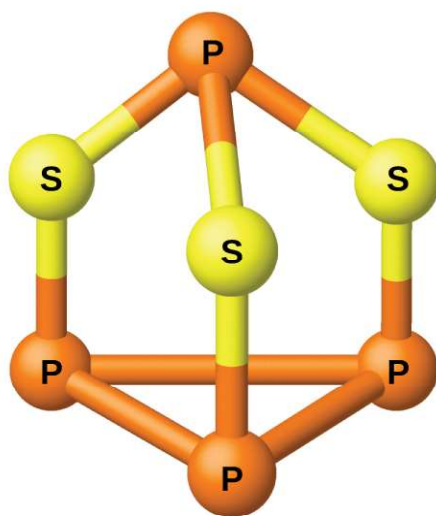


Figure 18.39 P_4S_3 is a component of the heads of strike-anywhere matches.

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 .

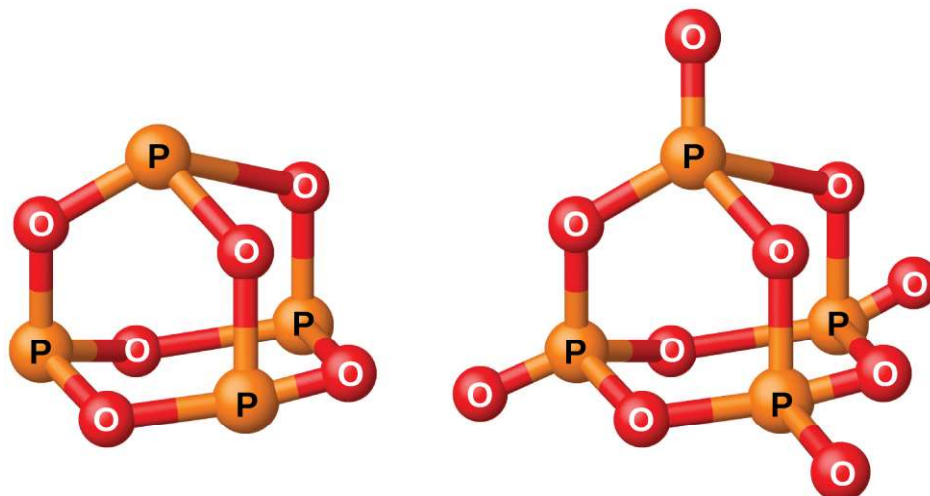
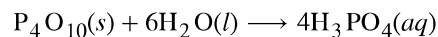


Figure 18.40 This image shows the molecular structures of P_4O_6 (left) and P_4O_{10} (right).

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:



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 sublimates when warmed and forms an equilibrium with the trichloride and chlorine when heated.

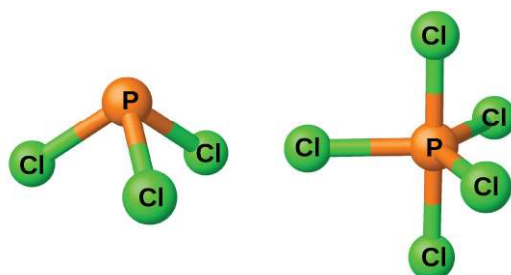


Figure 18.41 This image shows the molecular structure of PCl_3 (left) and PCl_5 (right) in the gas phase.

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.

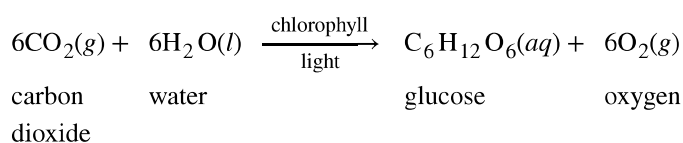
Oxygen is essential in combustion processes such as the burning of fuels. Plants and animals use the oxygen from the air in respiration. The administration of oxygen-enriched air is an important medical practice when a patient is receiving an inadequate supply of oxygen because of shock, pneumonia, or 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.

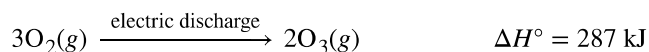
As we know, oxygen is very important to life. The energy required for the maintenance of normal body functions in human beings and in other organisms comes from the slow oxidation of chemical compounds. Oxygen is the final oxidizing agent in these reactions. In humans, oxygen passes from the lungs into 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:



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:



The sharp odor associated with sparking electrical equipment is due, in part, to ozone.

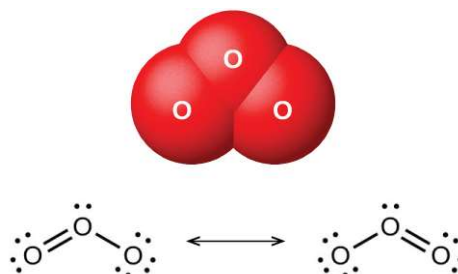
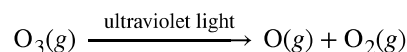


Figure 18.42 The image shows the bent ozone (O_3) molecule and the resonance structures necessary to describe its bonding.

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:



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.

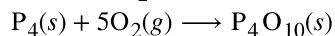
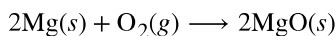
The uses of ozone depend on its reactivity with other substances. It can be used as a bleaching agent for oils, waxes, fabrics, and starch: It oxidizes the colored compounds in these substances to colorless compounds. It is an alternative to chlorine as a disinfectant for water.

Reactions

Elemental oxygen is a strong oxidizing agent. It reacts with most other elements and many compounds.

Reaction with Elements

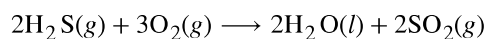
Oxygen reacts directly at room temperature or at elevated temperatures with all other elements except the noble gases, the halogens, and few second- and third-row transition metals of low reactivity (those with higher reduction potentials than copper). Rust is an example of the reaction of oxygen with iron. The more active metals form peroxides or superoxides. Less active metals and the nonmetals give oxides. Two examples of these reactions are:



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:



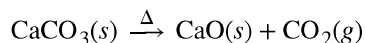
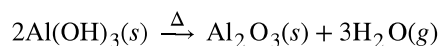
It is also possible to oxidize oxides such as CO and P_4O_6 that contain an element with a lower oxidation state. The ease with which elemental oxygen picks up electrons is mirrored by the difficulty of removing electrons from oxygen in most oxides. Of the elements, only the very reactive fluorine can oxidize oxides to form oxygen gas.

Oxides, Peroxides, and Hydroxides

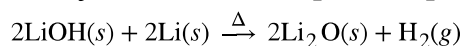
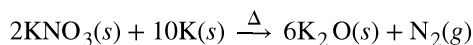
Compounds of the representative metals with oxygen fall into three categories: (1) **oxides**, containing oxide ions, O^{2-} ; (2) **peroxides**, containing peroxide ions, O_2^{2-} , with oxygen-oxygen covalent single bonds and a very limited number of **superoxides**, containing superoxide ions, O_2^- , 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:



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:

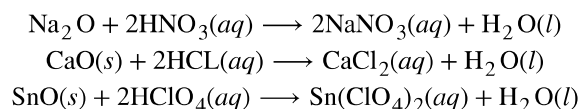


With the exception of mercury(II) oxide, it is possible to produce the oxides of the metals of groups 2–15 by burning the corresponding metal in air. The heaviest member of each group, the member for which the inert pair effect is most pronounced, forms an oxide in which the oxidation state of the metal 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.

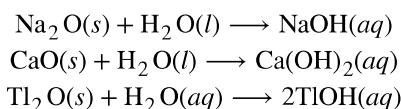
The oxides of the lighter members of each group exhibit the group oxidation state. For example, SnO_2 forms from burning tin. Mercury(II) oxide, HgO , forms slowly when mercury is warmed below $500\text{ }^\circ\text{C}$; it decomposes at higher temperatures.

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:



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:



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.”

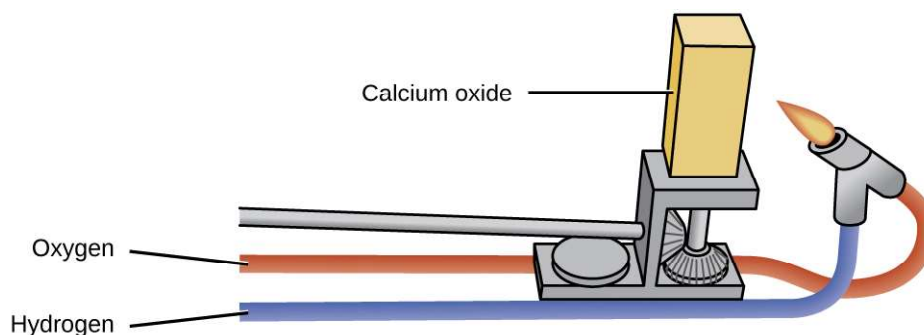
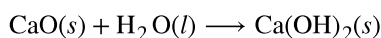


Figure 18.43 Calcium oxide has many industrial uses. When it is heated at high temperatures, it emits an intense white light.

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:



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:



Both CaO and Ca(OH)₂ are useful as bases; they accept protons and neutralize acids.

Alumina (Al₂O₃) 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.

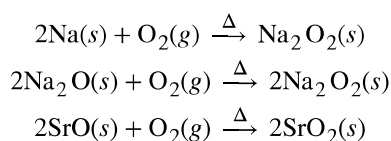
Zinc oxide, ZnO, was a useful white paint pigment; however, pollutants tend to discolor the compound. The compound is also important in the manufacture of automobile tires and other rubber goods, and in the preparation of medicinal ointments. For example, zinc-oxide-based sunscreens, as shown in **Figure 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.



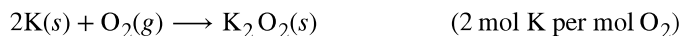
Figure 18.44 Zinc oxide protects exposed skin from sunburn. (credit: modification of work by "osseous"/Flickr)

Peroxides and Superoxides

Peroxides and superoxides are strong oxidizers and are important in chemical processes. Hydrogen peroxide, H₂O₂, 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:



The peroxides of potassium, rubidium, and cesium can be prepared by heating the metal or its oxide in a carefully controlled amount of oxygen:



With an excess of oxygen, the superoxides KO₂, RbO₂, and CsO₂ form. For example:



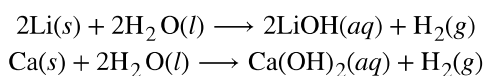
The stability of the peroxides and superoxides of the alkali metals increases as the size of the cation increases.

Hydroxides

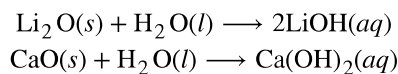
Hydroxides are compounds that contain the OH⁻ ion. It is possible to prepare these compounds by two general types of reactions. Soluble metal hydroxides can be produced by the reaction of the metal or metal oxide with water.

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:

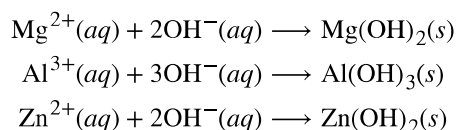


However, these reactions can be violent and dangerous; therefore, it is preferable to produce soluble metal hydroxides by the reaction of the respective oxide with water:



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:



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: Al(OH)_4^{-} , Ga(OH)_4^{-} , Zn(OH)_4^{2-} , and 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.

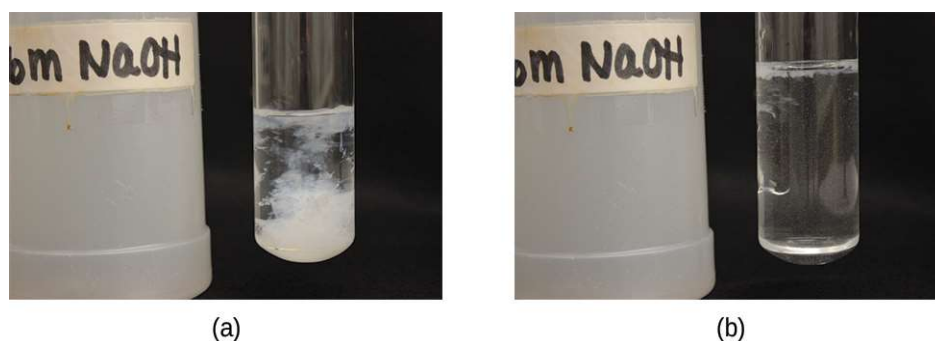


Figure 18.45 (a) Mixing solutions of NaOH and $\text{Zn(NO}_3)_2$ produces a white precipitate of Zn(OH)_2 . (b) Addition of an excess of NaOH results in dissolution of the precipitate. (credit: modification of work by Mark Ott)

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

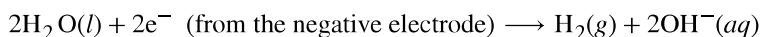
The Chlor-Alkali Process

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.

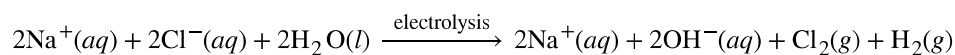
Passing a direct current of electricity through a solution of NaCl causes the chloride ions to migrate to the positive electrode where oxidation to gaseous chlorine occurs when the ion gives up an electron to the electrode:



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:



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 :



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.

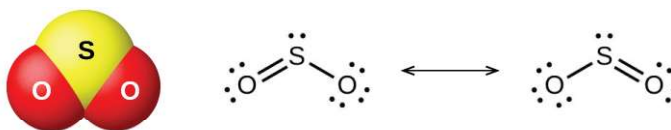
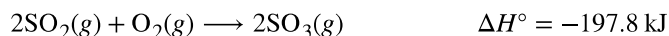


Figure 18.47 This image shows the molecular structure (left) and resonance forms (right) of sulfur dioxide.

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:



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.

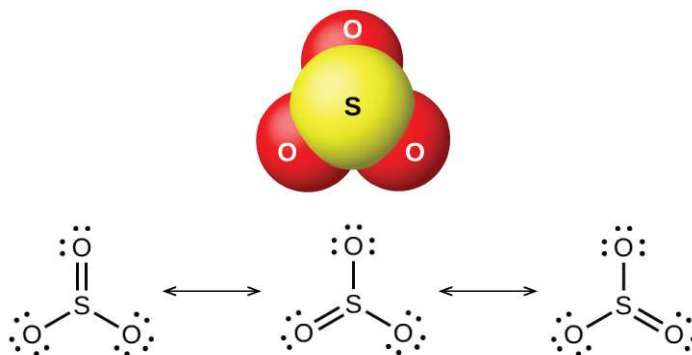


Figure 18.48 This image shows the structure (top) of sulfur trioxide in the gas phase and its resonance forms (bottom).

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.

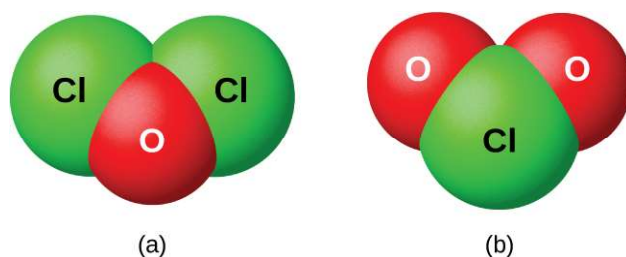


Figure 18.49 This image shows the structures of the (a) Cl_2O and (b) ClO_2 molecules.

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 pentoxide, 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.

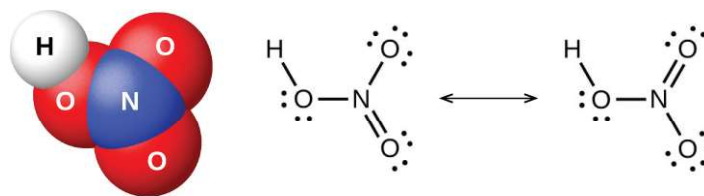
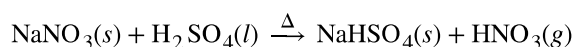
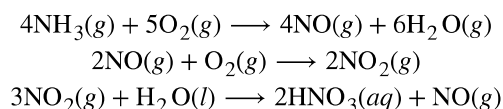


Figure 18.50 This image shows the molecular structure (left) of nitric acid, HNO_3 and its resonance forms (right).

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:



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:



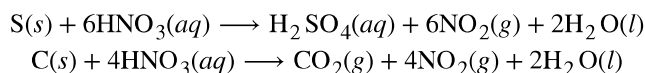
Or



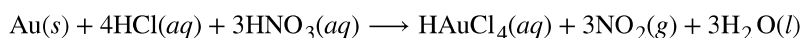
Pure nitric acid is a colorless liquid. However, it is often yellow or brown in color because NO_2 forms as the acid decomposes. Nitric acid is stable in aqueous solution; solutions containing 68% of the acid are commercially available concentrated nitric acid. It is both a strong oxidizing agent and 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 :



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:



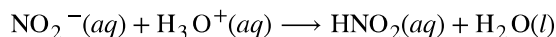
Link to Learning

Although gold is generally unreactive, you can watch a [video \(http://openstaxcollege.org/l/16gold\)](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:



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.

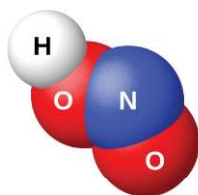


Figure 18.51 This image shows the molecular structure of a molecule of nitrous acid, HNO_2 .

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:

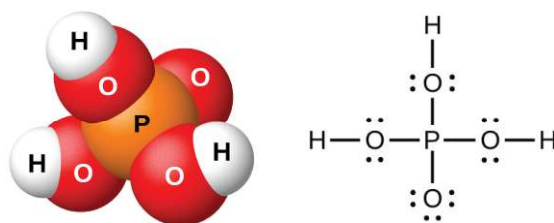
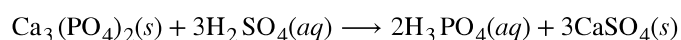
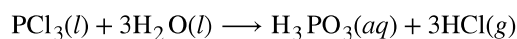


Figure 18.52 Orthophosphoric acid, H_3PO_4 , is colorless when pure and has this molecular (left) and Lewis structure (right).

Dilution of the products with water, followed by filtration to remove calcium sulfate, gives a dilute acid solution contaminated with calcium dihydrogen phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, 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:



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 $70.1\text{ }^\circ\text{C}$ and decomposes at about $200\text{ }^\circ\text{C}$ by disproportionation into phosphine and orthophosphoric acid:

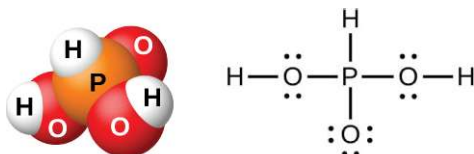


Figure 18.53 In a molecule of phosphorous acid, H_3PO_3 , only the two hydrogen atoms bonded to an oxygen atom are acidic.

Phosphorous acid forms only two series of salts, which contain the dihydrogen phosphite ion, H_2PO_3^- , or the hydrogen phosphate ion, 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 $10.5\text{ }^\circ\text{C}$. 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 $338\text{ }^\circ\text{C}$ 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.

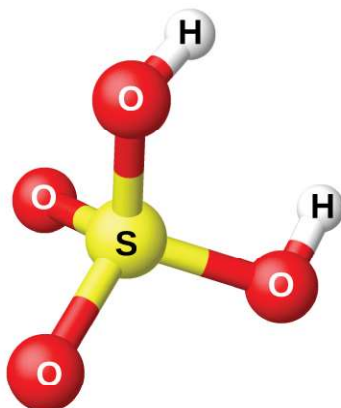


Figure 18.54 Sulfuric acid has a tetrahedral molecular structure.

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: $K_a = 1.2 \times 10^{-2}$).

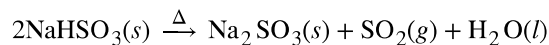
Being a diprotic acid, sulfuric acid forms both sulfates, such as Na_2SO_4 , and hydrogen sulfates, such as NaHSO_4 . Most sulfates are soluble in water; however, the sulfates of barium, strontium, calcium, and lead are only slightly soluble in water.

Among the important sulfates are $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and Epsom salts, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. 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.

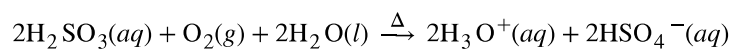
Hot, concentrated sulfuric acid is an oxidizing agent. Depending on its concentration, the temperature, and the strength of the reducing agent, sulfuric acid oxidizes many compounds and, in the process, undergoes reduction to SO_2 , HSO_3^- , SO_3^{2-} , S , H_2S , or S^{2-} .

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:



Strong oxidizing agents can oxidize sulfurous acid. Oxygen in the air oxidizes it slowly to the more stable sulfuric acid:



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

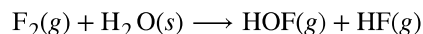
The compounds HXO , HXO_2 , HXO_3 , and HXO_4 , where X represents Cl, Br, or I, are the hypohalous, halous, halic, and perhalic acids, respectively. The strengths of these acids increase from the hypohalous acids, which are very weak acids, to the perhalic acids, which are very strong. **Table 18.2** 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 ₅ IO ₆ (1.6)

Table 18.2

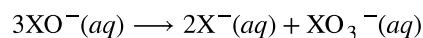
The only known oxyacid of fluorine is the very unstable hypofluorous acid, HOF, which is prepared by the reaction of gaseous fluorine with ice:



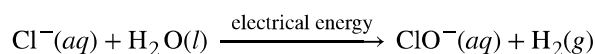
The compound is very unstable and decomposes above -40°C . This compound does not ionize in water, and there are no known salts. It is uncertain whether the name hypofluorous acid is even appropriate for HOF; a more appropriate name might be hydrogen hypofluorite.

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.

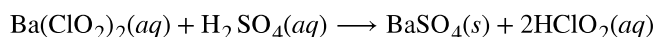
The addition of base to solutions of the hypohalous acids produces solutions of salts containing the basic hypohalite ions, OX^- . It is possible to isolate these salts as solids. All of the hypohalites are unstable with respect to disproportionation in solution, but the reaction is slow for hypochlorite. Hypobromite and hypoiodite disproportionate rapidly, even in the cold:



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:



The only definitely known halous acid is chlorous acid, HClO_2 , obtained by the reaction of barium chlorite with dilute sulfuric acid:



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.

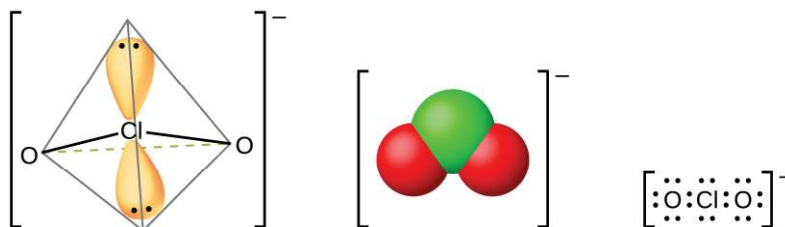


Figure 18.55 Chlorite ions, ClO_2^- , are produced when chlorous acid reacts with bases.

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 :



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.

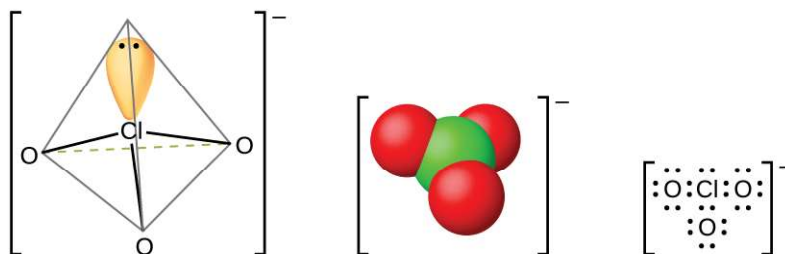
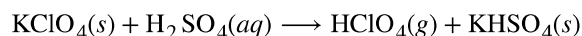


Figure 18.56 Chlorate ions, ClO_3^- , are produced when halic acids react with bases.

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:



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.

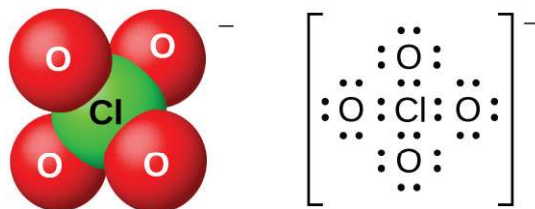


Figure 18.57 Perchlorate ions, ClO_4^- , can be produced when perchloric acid reacts with a base or by electrolysis of hot solutions of their chlorides.

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.

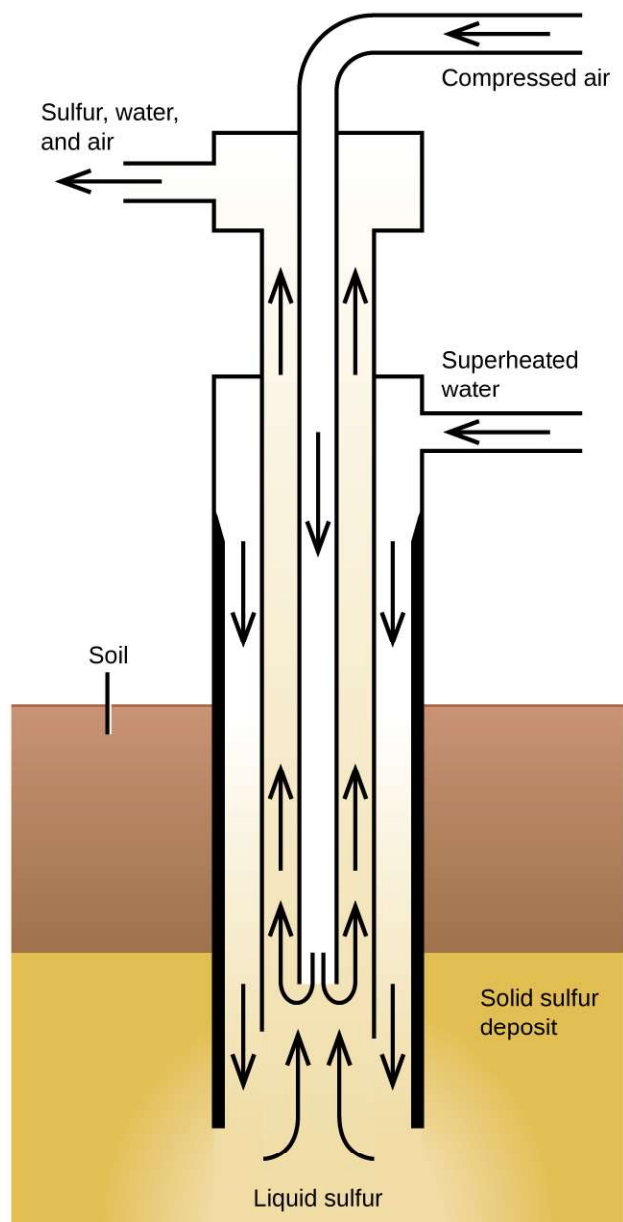


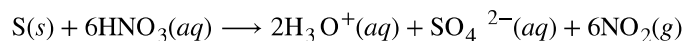
Figure 18.59 The Frasch process is used to mine sulfur from underground deposits.

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:



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.

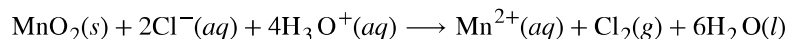
Occurrence and Preparation

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 CaF_2 , $\text{Ca}(\text{PO}_4)_3\text{F}$, and 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 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.

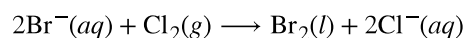
The best sources of halogens (except iodine) are halide salts. It is possible to oxidize the halide ions to free diatomic halogen molecules by various methods, depending on the ease of oxidation of the halide ion. Fluoride is the most difficult to oxidize, whereas iodide is the easiest.

The major method for preparing fluorine is electrolytic oxidation. The most common electrolysis procedure is to use a molten mixture of potassium hydrogen fluoride, 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 (MnO_2) or sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$). The reaction with manganese dioxide is:

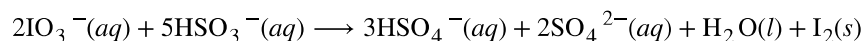


The commercial preparation of bromine involves the oxidation of bromide ion by chlorine:



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:



Properties of the Halogens

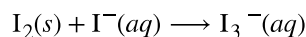
Fluorine is a pale yellow gas, chlorine is a greenish-yellow gas, bromine is a deep reddish-brown liquid, and iodine is a grayish-black crystalline solid. Liquid bromine has a high vapor pressure, and the reddish vapor is readily visible in **Figure 18.60**. Iodine crystals have a noticeable vapor pressure. 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:



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

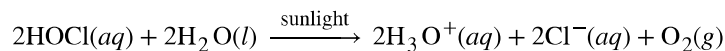
O₂, OF₂, H₂O₂, O₃, and HF. Wood and asbestos ignite and burn in fluorine gas. Most hot metals burn vigorously in fluorine. However, it is possible to handle fluorine in copper, iron, or nickel containers because an adherent film of the fluoride salt passivates their surfaces. Fluorine is the only element 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, N₂, and O₂ 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.

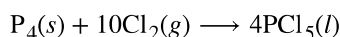
In cold water, chlorine undergoes a disproportionation reaction:



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:



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:



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.

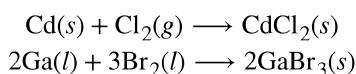
Compared with the other halogens, iodine reacts only slightly with water. Traces of iodine in water react with a mixture of starch and iodide ion, forming a deep blue color. This reaction is a very sensitive test for the presence of iodine in water.

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.

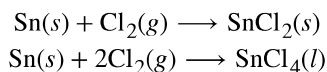
The direct reaction of a metal and a halogen produce the halide of the metal. Examples of these oxidation-reduction reactions include:



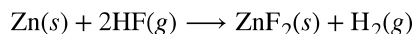
Link to Learning

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//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.

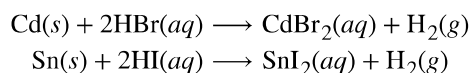
If a metal can exhibit two oxidation states, it may be necessary to control the stoichiometry in order to obtain the halide with the lower oxidation state. For example, preparation of tin(II) chloride requires a 1:1 ratio of Sn to Cl₂, whereas preparation of tin(IV) chloride requires a 1:2 ratio:



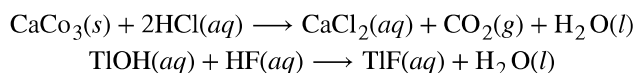
The active representative metals—those that are easier to oxidize than hydrogen—react with gaseous hydrogen halides to produce metal halides and hydrogen. The reaction of zinc with hydrogen fluoride is:



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:



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:



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 $\text{Hg}(\text{NO}_3)_2$ 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**.

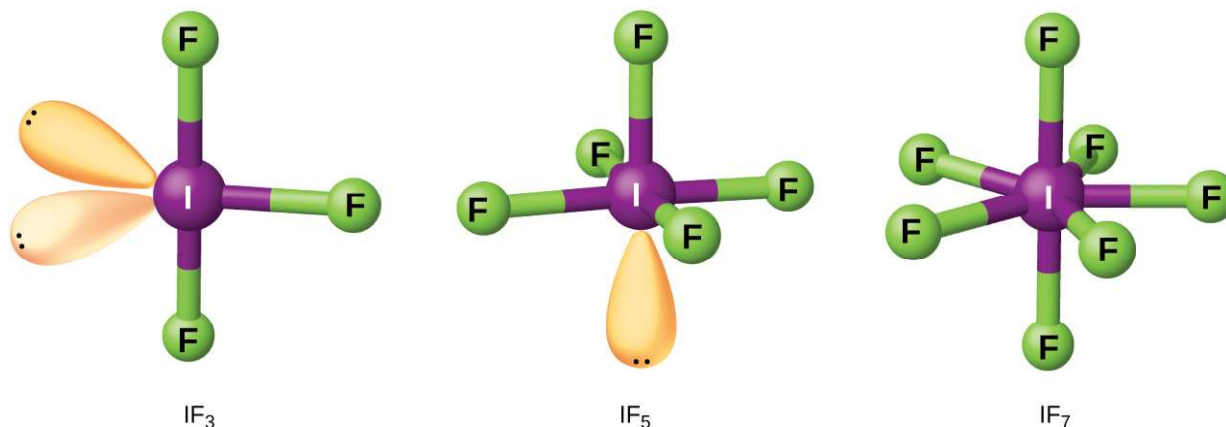


Figure 18.63 The structure of IF_3 is T-shaped (left), IF_5 is square pyramidal (center), and IF_7 is pentagonal bipyramidal (right).

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
$\text{ClF}(g)$	$\text{ClF}_3(g)$	$\text{ClF}_5(g)$	
$\text{BrF}(g)$	$\text{BrF}_3(l)$	$\text{BrF}_5(l)$	
$\text{BrCl}(g)$			
$\text{IF}(s)$	$\text{IF}_3(s)$	$\text{IF}_5(l)$	$\text{IF}_7(g)$
$\text{ICl}(l)$	$\text{ICl}_3(s)$		
$\text{IBr}(s)$			

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 $-\text{CF}_2\text{CF}_2-$ 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 $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ into $\text{Ca}_5(\text{PO}_4)_3\text{F}$.

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 ($\text{C}_2\text{H}_5\text{Cl}$), 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.

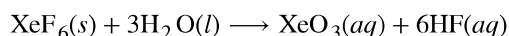
Argon was useful in the manufacture of gas-filled electric light bulbs, where its lower heat conductivity and chemical

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:



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, XeO_6^{4-} , in which xenon reaches its maximum oxidation state 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 $-\text{OH}$

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 $-\text{O}-$ or $=\text{O}$

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 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 $\text{N}\equiv\text{N}$ 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 an 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

- How do alkali metals differ from alkaline earth metals in atomic structure and general properties?
- Why does the reactivity of the alkali metals decrease from cesium to lithium?
- 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.

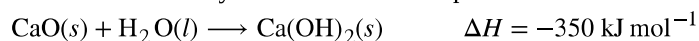
1	2
Na	I
Sr	Se
Al	O

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, CaCl₂, and BeCl₂
- (c) the lowest first ionization energy among the elements Rb, K, and Li
- (d) the smallest among Al, Al⁺, and Al³⁺
- (e) the largest among Cs⁺, Ba²⁺, 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:



- (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 HgCl₂.) 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 PbCl₂ to that of the bonds in PbCl₄.

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) $\text{Te}(\text{OH})_6$

(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) $\text{B}(\text{CH}_3)_3$

(e) $\text{B}(\text{OH})_3$

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) $\text{B}(\text{CH}_3)_3$
- (e) $\text{B}(\text{OH})_3$

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) $(\text{CH}_3)_3\text{SiH}$
- (b) SiO_4^{4-}
- (c) Si_2H_6
- (d) $\text{Si}(\text{OH})_4$
- (e) SiF_6^{2-}

33. Describe the hybridization of silicon and the molecular structure of the following molecules and ions:

- (a) $(\text{CH}_3)_3\text{SiH}$
- (b) SiO_4^{4-}
- (c) Si_2H_6
- (d) $\text{Si}(\text{OH})_4$
- (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:



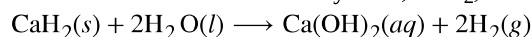
49. Arrange the following in order of increasing electronegativity: F; Cl; O; and S.

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?

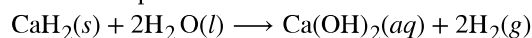
52. The reaction of calcium hydride, CaH_2 , with water can be characterized as a Lewis acid-base reaction:



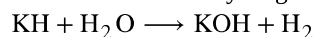
Identify the Lewis acid and the Lewis base among the reactants. The reaction is also an oxidation-reduction reaction. Identify the oxidizing agent, the reducing agent, and the changes in oxidation number that occur in the reaction.

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:



55. What mass of hydrogen gas results from the reaction of 8.5 g of KH with water?

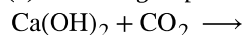


18.6 Occurrence, Preparation, and Properties of Carbonates

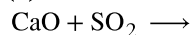
56. Carbon forms the CO_3^{2-} ion, yet silicon does not form an analogous SiO_3^{2-} ion. Why?

57. Complete and balance the following chemical equations:

(a) hardening of plaster containing slaked lime



(b) removal of sulfur dioxide from the flue gas of power plants



(c) the reaction of baking powder that produces carbon dioxide gas and causes bread to rise



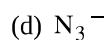
58. Heating a sample of $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ weighing 4.640 g until the removal of the water of hydration leaves 1.720 g of anhydrous Na_2CO_3 . What is the formula of the hydrated compound?

18.7 Occurrence, Preparation, and Properties of Nitrogen

59. Write the Lewis structures for each of the following:

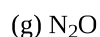
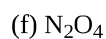
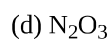
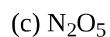
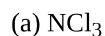


60. For each of the following, indicate the hybridization of the nitrogen atom (for N_3^- , the central nitrogen).

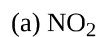


61. Explain how ammonia can function both as a Brønsted base and as a Lewis base.

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.



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.



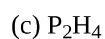
64. How many grams of gaseous ammonia will the reaction of 3.0 g hydrogen gas and 3.0 g of nitrogen gas produce?

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.



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) $\text{P}_4 + \text{Al} \longrightarrow$
- (b) $\text{P}_4 + \text{Na} \longrightarrow$
- (c) $\text{P}_4 + \text{F}_2 \longrightarrow$
- (d) $\text{P}_4 + \text{Cl}_2 \longrightarrow$
- (e) $\text{P}_4 + \text{O}_2 \longrightarrow$
- (f) $\text{P}_4\text{O}_6 + \text{O}_2 \longrightarrow$

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 $\text{Ca}_3(\text{PO}_4)_2$ 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) $\text{Na}_4\text{P}_2\text{O}_7$

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, $\text{CH}_3\text{CO}_2\text{H}$
- (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, $\text{CH}_3\text{CO}_2\text{H}$

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) C₂H₂
- (e) CO

89. Which is the stronger acid, H₂SO₄ or H₂SeO₄? 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 SO₂, in SO₃, and in H₂SO₄.

92. Which is the stronger acid, NaHSO₃ or NaHSO₄?

93. Determine the oxidation state of sulfur in SF₆, SO₂F₂, and KHS.

94. Which is a stronger acid, sulfurous acid or sulfuric acid? Why?

95. Oxygen forms double bonds in O₂, but sulfur forms single bonds in S₈. Why?

96. Give the Lewis structure of each of the following:

- (a) SF₄
- (b) K₂SO₄
- (c) SO₂Cl₂
- (d) H₂SO₃
- (e) SO₃

97. Write two balanced chemical equations in which sulfuric acid acts as an oxidizing agent.

98. Explain why sulfuric acid, H₂SO₄, which is a covalent molecule, dissolves in water and produces a solution that contains ions.

99. How many grams of Epsom salts (MgSO₄·7H₂O) 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?

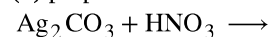
101. Why is SnCl₄ not classified as a salt?

102. The following reactions are all similar to those of the industrial chemicals. Complete and balance the equations for these reactions:

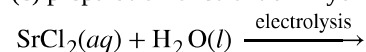
(a) reaction of a weak base and a strong acid



(b) preparation of a soluble silver salt for silver plating



(c) preparation of strontium hydroxide by electrolysis of a solution of strontium chloride



103. Which is the stronger acid, HClO₃ or HBrO₃? Why?

104. What is the hybridization of iodine in IF₃ and IF₅?

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 $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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?

