

CHAPTER
14

CHEMICAL
KINETICS



FIREWORKS RELY ON RAPID
CHEMICAL reactions both
to propel them skyward
and to produce their colorful
bursts of light.

14.1 Factors that Affect Reaction Rates

We explore four experimental variables that affect reaction rates: concentration, physical states of reactants, temperature, and catalysts. These factors can be understood in terms of the collisions among reactant molecules that lead to reaction.

14.2 Reaction Rates

We consider how to express *reaction rates* and how the rates of disappearance of reactants and the rates of appearance of products are related to the stoichiometry of the reaction.

14.3 Concentration and Rate

We then examine how the effect of concentration on rate is expressed quantitatively by *rate laws* and how rate laws can be determined experimentally.

14.4 The Change of Concentration with Time

We learn that rate equations can be written to express how concentrations change with time. We will look at two simple kinds of such rate equations.

14.5 Temperature and Rate

We next consider the effect of temperature on rate and the fact that reactions require a minimum input of energy called the *activation energy* to occur.

14.6 Reaction Mechanisms

We then examine the *mechanisms* of reactions, the step-by-step molecular pathways leading from reactants to products.

14.7 Catalysis

We end the chapter with a discussion of how *catalysts* speed reaction rates, including a discussion of biological catalysts, called *enzymes*.

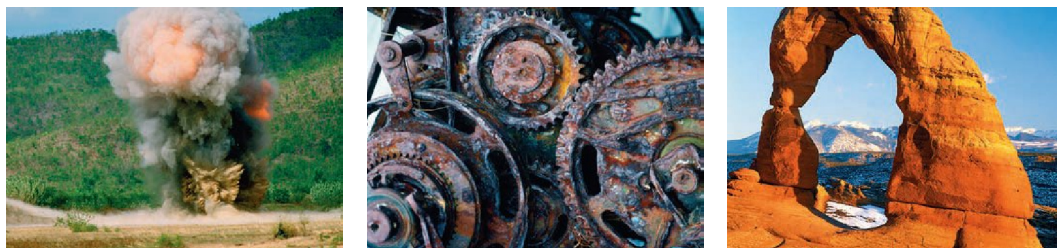
CHEMISTRY IS, BY ITS VERY NATURE, CONCERNED WITH CHANGE.

Chemical reactions convert substances with well-defined properties into other materials with different properties.

Much of our study of chemical reactions concerns the formation of new substances from a given set

of reactants. It is equally important to understand how rapidly chemical reactions occur.

The rates of reactions span an enormous range, from those that are complete within fractions of seconds, such as explosions, to those that take thousands or even millions of years, such as the formation of diamonds or other minerals in Earth's crust (Figure 14.1 ▼). The fireworks shown in this chapter-opening photograph require very rapid reactions, both to propel them skyward and to produce their colorful bursts of light. The chemicals used in the fireworks are chosen both to give the desired colors and to do so very rapidly. The characteristic red, blue, and green colors are produced by salts of strontium, copper, and barium, respectively.



▲ **Figure 14.1 Reaction rates.** The rates of chemical reactions span a range of time scales. For example, explosions are rapid, occurring in seconds or fractions of seconds; corrosion can take years; and the weathering of rocks takes place over thousands or even millions of years.

The area of chemistry that is concerned with the speeds, or rates, of reactions is called **chemical kinetics**. Chemical kinetics is a subject of broad importance. It relates, for example, to how quickly a medicine is able to work, to whether the formation and depletion of ozone in the upper atmosphere are in balance, and to industrial challenges such as the development of catalysts to synthesize new materials.

Our goal in this chapter is to understand how to determine the rates at which reactions occur and to consider the factors that control these rates. For example, what factors determine how rapidly food spoils? How does one design a fast-setting material for dental fillings? What determines the rate at which steel rusts? What controls the rate at which fuel burns in an automobile engine? Although we will not address these specific questions, we will see that the rates of all chemical reactions are subject to the same basic principles.

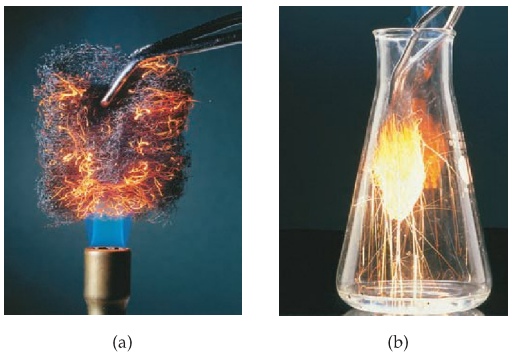
14.1 FACTORS THAT AFFECT REACTION RATES

Before we examine the quantitative aspects of chemical kinetics, such as how rates are measured, let's examine the key factors that influence the rates of reactions. Because reactions involve the breaking and forming of bonds, the speeds of reactions depend on the nature of the reactants themselves. Four factors allow us to change the rates at which particular reactions occur:

1. *The physical state of the reactants.* Reactants must come together to react. The more readily molecules collide with each other, the more rapidly they react. Most of the reactions we consider are homogeneous, involving either gases or liquid solutions. When reactants are in different phases, as when one is a gas and another a solid, the reaction is limited to their area of contact. Thus, reactions that involve solids tend to proceed faster if the surface area of the solid is increased. For example, a medicine in the form of a fine powder will dissolve in the stomach and enter the bloodstream more quickly than the same medicine in the form of a tablet.
2. *The concentrations of the reactants.* Most chemical reactions proceed faster if the concentration of one or more of the reactants is increased. For example, steel wool burns with difficulty in air, which contains 20% O_2 , but bursts into a brilliant white flame in pure oxygen (Figure 14.2 ▶). As concentration increases, the frequency with which the reactant molecules collide increases, leading to increased rates.
3. *The temperature at which the reaction occurs.* The rates of chemical reactions increase as temperature is increased. We refrigerate perishable foods such as milk for this reason. The bacterial reactions that lead to the spoiling of milk proceed much more rapidly at room temperature than they do at the lower temperature of a refrigerator. Increasing temperature increases the kinetic energies of molecules. ∞ (Section 10.7) As molecules move more rapidly, they collide more frequently and also with higher energy, leading to increased reaction rates.

4. *The presence of a catalyst.* Catalysts are agents that increase reaction rates without being used up. They affect the kinds of collisions (the mechanism) that lead to reaction. Catalysts play a crucial role in our lives. The physiology of most living species depends on *enzymes*, protein molecules that act as catalysts, increasing the rates of selected biochemical reactions.

On a molecular level, reaction rates depend on the frequency of collisions between molecules. The greater the frequency of collisions, the greater is the rate of reaction. For a collision to lead to a reaction, however, it must occur with sufficient energy to stretch bonds to a critical length and with suitable orientation for new bonds to form in the proper locations. We will consider these factors as we proceed through this chapter.



▲ **Figure 14.2 Effect of concentration on rate.** (a) When heated in air, steel wool glows red-hot but oxidizes slowly. (b) When the red-hot steel wool is placed in an atmosphere of pure oxygen, it burns vigorously, forming Fe_2O_3 at a much faster rate. The difference in behavior is due to the different concentrations of O_2 in the two environments.

GIVE IT SOME THOUGHT

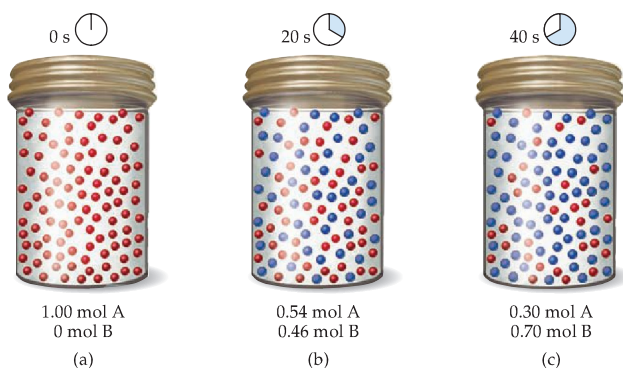
How does increasing the partial pressures of the reactive components of a gaseous mixture affect the rate at which the components react with one another?

14.2 REACTION RATES

The *speed* of an event is defined as the *change* that occurs in a given interval of *time*: Whenever we talk about speed, we necessarily bring in the notion of time. For example, the speed of a car is expressed as the change in the car's position over a certain period of time. The units of this speed are usually miles per hour (mi/hr)—that is, the quantity that is changing (position, measured in miles) divided by a time interval (hours).

Similarly, the speed of a chemical reaction—its **reaction rate**—is the change in the concentration of reactants or products per unit of time. Thus, the units for reaction rate are usually molarity per second (M/s)—that is, the change in concentration (measured in molarity) divided by a time interval (seconds).

Let's consider a simple hypothetical reaction, $A \longrightarrow B$, depicted in Figure 14.3 ▼. Each red sphere represents 0.01 mol of A, each blue sphere represents 0.01 mol of B, and the container has a volume of 1.00 L. At the beginning of the reaction there is 1.00 mol A, so the concentration is $1.00 \text{ mol/L} = 1.00 M$. After 20 s the concentration of A has fallen to 0.54 M, whereas the concentration of B has risen to 0.46 M. The sum of the concentrations is still 1.00 M because 1 mol



◀ **Figure 14.3 Progress of a hypothetical reaction $A \longrightarrow B$.** Each red sphere represents 0.01 mol A, each blue sphere represents 0.01 mol B, and the vessel has a volume of 1.00 L. (a) At time zero the vessel contains 1.00 mol A (100 red spheres) and 0 mol B (no blue spheres). (b) After 20 s the vessel contains 0.54 mol A and 0.46 mol B. (c) After 40 s the vessel contains 0.30 mol A and 0.70 mol B.

of B is produced for each mole of A that reacts. After 40 s the concentration of A is 0.30 M and that of B is 0.70 M.

The rate of this reaction can be expressed either as the rate of disappearance of reactant A or as the rate of appearance of product B. The *average* rate of appearance of B over a particular time interval is given by the change in concentration of B divided by the change in time:

$$\begin{aligned} \text{Average rate of appearance of B} &= \frac{\text{change in concentration of B}}{\text{change in time}} \\ &= \frac{[\text{B}] \text{ at } t_2 - [\text{B}] \text{ at } t_1}{t_2 - t_1} = \frac{\Delta[\text{B}]}{\Delta t} \end{aligned} \quad [14.1]$$

We use brackets around a chemical formula, as in [B], to indicate the concentration of the substance in molarity. The Greek letter delta, Δ , is read “change in” and is always equal to the final quantity minus the initial quantity. ∞ (Section 5.2) The average rate of appearance of B over the 20-s interval from the beginning of the reaction ($t_1 = 0$ s to $t_2 = 20$ s) is given by

$$\text{Average rate} = \frac{0.46 \text{ M} - 0.00 \text{ M}}{20 \text{ s} - 0 \text{ s}} = 2.3 \times 10^{-2} \text{ M/s}$$

We could equally well express the rate of the reaction with respect to the change of concentration of the reactant, A. In this case we would be describing the rate of disappearance of A, which we express as

$$\text{Average rate of disappearance of A} = -\frac{\Delta[\text{A}]}{\Delta t} \quad [14.2]$$

Notice the minus sign in this equation. By convention, *rates are always expressed as positive quantities*. Because [A] is decreasing with time, $\Delta[\text{A}]$ is a negative number. We use the negative sign to convert the negative $\Delta[\text{A}]$ to a positive rate. Because one molecule of A is consumed for every molecule of B that forms, the average rate of disappearance of A equals the average rate of appearance of B, as calculation shows:

$$\text{Average rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.54 \text{ M} - 1.00 \text{ M}}{20 \text{ s} - 0 \text{ s}} = 2.3 \times 10^{-2} \text{ M/s}$$

SAMPLE EXERCISE 14.1 | Calculating an Average Rate of Reaction

From the data given in the caption of Figure 14.3, calculate the average rate at which A disappears over the time interval from 20 s to 40 s.

SOLUTION

Analyze: We are given the concentration of A at 20 s (0.54 M) and at 40 s (0.30 M) and asked to calculate the average rate of reaction over this time interval.

Plan: The average rate is given by the change in concentration, $\Delta[\text{A}]$, divided by the corresponding change in time, Δt . Because A is a reactant, a minus sign is used in the calculation to make the rate a positive quantity.

Solve: Average rate = $-\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.30 \text{ M} - 0.54 \text{ M}}{40 \text{ s} - 20 \text{ s}} = 1.2 \times 10^{-2} \text{ M/s}$

PRACTICE EXERCISE

For the reaction pictured in Figure 14.3, calculate the average rate of appearance of B over the time interval from 0 to 40 s.

Answer: $1.8 \times 10^{-2} \text{ M/s}$

TABLE 14.1 ■ Rate Data for Reaction of C_4H_9Cl with Water

Time, t (s)	$[C_4H_9Cl](M)$	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

Change of Rate with Time

Now, let's consider an actual chemical reaction, one that occurs when butyl chloride (C_4H_9Cl) is placed in water. The products formed are butyl alcohol (C_4H_9OH) and hydrochloric acid:



Suppose that we prepare a 0.1000 M aqueous solution of C_4H_9Cl and then measure the concentration of C_4H_9Cl at various times after time zero (the time the reactants are mixed, thereby initiating the reaction). The resultant data are shown in the first two columns of Table 14.1. We can use these data to calculate the average rate of disappearance of C_4H_9Cl over the intervals between measurements; these rates are given in the third column. Notice that the average rate decreases over each 50-s interval for the first several measurements and continues to decrease over even larger intervals through the remaining measurements. *It is typical for rates to decrease as a reaction proceeds, because the concentration of reactants decreases.* The change in rate as the reaction proceeds is also seen in a graph of the concentration of C_4H_9Cl versus time (Figure 14.4). Notice how the steepness of the curve decreases with time, indicating a decreasing rate of reaction.

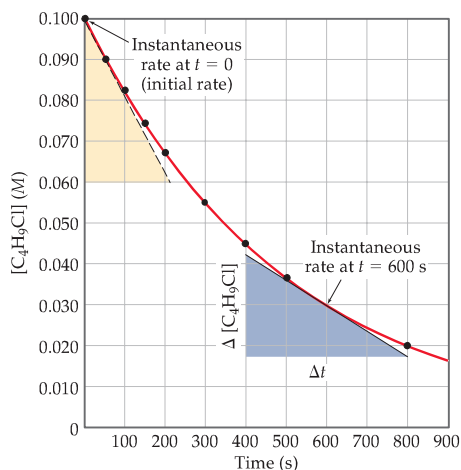
GIVE IT SOME THOUGHT

Why do the rates of reactions decrease as concentrations decrease?

Instantaneous Rate

Graphs showing how the concentration of a reactant or product changes with time, such as the graph in Figure 14.4, allow us to evaluate the **instantaneous rate**, the rate at a particular moment in the reaction. The instantaneous rate is determined from the slope (or tangent) of this curve at the point of interest. We have drawn two tangents in Figure 14.4, one at $t = 0$ and the other at $t = 600$ s. The slopes of these tangents give the instantaneous rates at these times.* For example, to determine the instantaneous rate at 600 s, we draw the tangent to the curve at this time, then construct horizontal and vertical lines to

*You may wish to review briefly the idea of graphical determination of slopes by referring to Appendix A. If you are familiar with calculus, you may recognize that the average rate approaches the instantaneous rate as the time interval approaches zero. This limit, in the notation of calculus, is represented as $-d[C_4H_9Cl]/dt$.



▲ **Figure 14.4** Concentration of butyl chloride (C_4H_9Cl) as a function of time. The dots represent the experimental data from the first two columns of Table 14.1, and the red curve is drawn to connect the data points smoothly. Lines are drawn that are tangent to the curve at $t = 0$ and $t = 600$ s. The slope of each tangent is defined as the vertical change divided by the horizontal change: $\Delta[C_4H_9Cl]/\Delta t$. The reaction rate at any time is related to the slope of the tangent to the curve at that time. Because C_4H_9Cl is disappearing, the rate is equal to the negative of the slope.

form the right triangle shown. The slope is the ratio of the height of the vertical side to the length of the horizontal side:

$$\begin{aligned}\text{Instantaneous rate} &= -\frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = -\frac{(0.017 - 0.042) \text{ M}}{(800 - 400)\text{s}} \\ &= 6.3 \times 10^{-5} \text{ M/s}\end{aligned}$$

In discussions that follow, the term “rate” means “instantaneous rate,” unless indicated otherwise. The instantaneous rate at $t = 0$ is called the *initial rate* of the reaction.

To understand better the difference between average rate and instantaneous rate, imagine that you have just driven 98 mi in 2.0 hr. Your average speed is 49 mi/hr, whereas your instantaneous speed at any moment is the speedometer reading at that time.

SAMPLE EXERCISE 14.2 | Calculating an Instantaneous Rate of Reaction

Using Figure 14.4, calculate the instantaneous rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$ at $t = 0$ (the initial rate).

SOLUTION

Analyze: We are asked to determine an instantaneous rate from a graph of concentration versus time.

Plan: To obtain the instantaneous rate at $t = 0$, we must determine the slope of the curve at $t = 0$. The tangent is drawn on the graph. The slope of this straight line equals the change in the vertical axis divided by the corresponding change in the horizontal axis (that is, change in molarity over change in time).

Solve: The straight line falls from $[\text{C}_4\text{H}_9\text{Cl}] = 0.100 \text{ M}$ to 0.060 M in the time change from 0 s to 210 s, as indicated by the tan triangle shown in Figure 14.4. Thus, the initial rate is

$$\text{Rate} = -\frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = -\frac{(0.060 - 0.100) \text{ M}}{(210 - 0) \text{ s}} = 1.9 \times 10^{-4} \text{ M/s}$$

PRACTICE EXERCISE

Using Figure 14.4, determine the instantaneous rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$ at $t = 300 \text{ s}$.

Answer: $1.1 \times 10^{-4} \text{ M/s}$

GIVE IT SOME THOUGHT

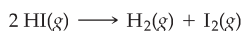
Figure 14.4 shows two triangles that are used to determine the slope of the curve at two different times. How do you determine how large a triangle to draw when determining the slope of a curve at a particular point?

Reaction Rates and Stoichiometry

During our earlier discussion of the hypothetical reaction $\text{A} \longrightarrow \text{B}$, we saw that the stoichiometry requires that the rate of disappearance of A equals the rate of appearance of B. Likewise, the stoichiometry of Equation 14.3 indicates that 1 mol of $\text{C}_4\text{H}_9\text{OH}$ is produced for each mole of $\text{C}_4\text{H}_9\text{Cl}$ consumed. Therefore, the rate of appearance of $\text{C}_4\text{H}_9\text{OH}$ equals the rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$:

$$\text{Rate} = -\frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = \frac{\Delta[\text{C}_4\text{H}_9\text{OH}]}{\Delta t}$$

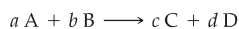
What happens when the stoichiometric relationships are not one to one? For example, consider this reaction:



We can measure the rate of disappearance of HI or the rate of appearance of either H_2 or I_2 . Because 2 mol of HI disappear for each mole of H_2 or I_2 that forms, the rate of disappearance of HI is twice the rate of appearance of either H_2 or I_2 . To equate the rates, we must therefore divide the rate of disappearance of HI by 2 (its coefficient in the balanced chemical equation):

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

In general, for the reaction



the rate is given by

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b} \frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c} \frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d} \frac{\Delta[\text{D}]}{\Delta t} \quad [14.4]$$

When we speak of the rate of a reaction without specifying a particular reactant or product, we will mean it in this sense.*

SAMPLE EXERCISE 14.3 | Relating Rates at Which Products Appear and Reactants Disappear

- (a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction $2 \text{O}_3(g) \longrightarrow 3 \text{O}_2(g)$?
 (b) If the rate at which O_2 appears, $\Delta[\text{O}_2]/\Delta t$, is $6.0 \times 10^{-5} \text{ M/s}$ at a particular instant, at what rate is O_3 disappearing at this same time, $-\Delta[\text{O}_3]/\Delta t$?

SOLUTION

Analyze: We are given a balanced chemical equation and asked to relate the rate of appearance of the product to the rate of disappearance of the reactant.

Plan: We can use the coefficients in the chemical equation as shown in Equation 14.4 to express the relative rates of reactions.

Solve: (a) Using the coefficients in the balanced equation and the relationship given by Equation 14.4, we have:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t}$$

(b) Solving the equation from part (a) for the rate at which O_3 disappears, $-\Delta[\text{O}_3]/\Delta t$ we have:

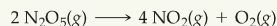
$$-\frac{\Delta[\text{O}_3]}{\Delta t} = \frac{2}{3} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{2}{3} (6.0 \times 10^{-5} \text{ M/s}) = 4.0 \times 10^{-5} \text{ M/s}$$

Check: We can directly apply a stoichiometric factor to convert the O_2 formation rate to the rate at which the O_3 disappears:

$$-\frac{\Delta[\text{O}_3]}{\Delta t} = \left(6.0 \times 10^{-5} \frac{\text{mol O}_2/\text{L}}{\text{s}} \right) \left(\frac{2 \text{ mol O}_3}{3 \text{ mol O}_2} \right) = 4.0 \times 10^{-5} \frac{\text{mol O}_3/\text{L}}{\text{s}} = 4.0 \times 10^{-5} \text{ M/s}$$

PRACTICE EXERCISE

The decomposition of N_2O_5 proceeds according to the following equation:



If the rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is $4.2 \times 10^{-7} \text{ M/s}$, what is the rate of appearance of (a) NO_2 , (b) O_2 ?

Answers: (a) $8.4 \times 10^{-7} \text{ M/s}$, (b) $2.1 \times 10^{-7} \text{ M/s}$

*Equation 14.4 does not hold true if substances other than C and D are formed in significant amounts during the course of the reaction. For example, sometimes intermediate substances build in concentration before forming the final products. In that case, the relationship between the rate of disappearance of reactants and the rate of appearance of products will not be given by Equation 14.4. All reactions whose rates we consider in this chapter obey Equation 14.4.

A Closer Look

USING SPECTROSCOPIC METHODS TO MEASURE REACTION RATES

A variety of techniques can be used to monitor the concentration of a reactant or product during a reaction. Spectroscopic methods, which rely on the ability of substances to absorb (or emit) electromagnetic radiation, are some of the most useful. Spectroscopic kinetic studies are often performed with the reaction mixture in the sample compartment of the spectrometer. The spectrometer is set to measure the light absorbed at a wavelength characteristic of one of the reactants or products. In the decomposition of HI(g) into H₂(g) and I₂(g) for example, both HI and H₂ are colorless, whereas I₂ is violet. During the course of the reaction, the color increases in intensity as I₂ forms. Thus, visible light of appropriate wavelength can be used to monitor the reaction.

Figure 14.5 shows the basic components of a spectrometer. The spectrometer measures the amount of light absorbed by the sample by comparing the intensity of the light emitted

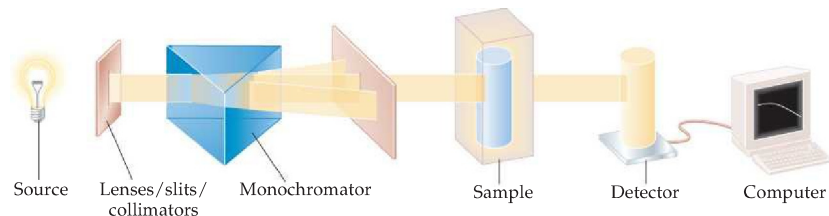
from the light source with the intensity of the light that emerges from the sample. As the concentration of I₂ increases and its color becomes more intense, the amount of light absorbed by the reaction mixture increases, causing less light to reach the detector.

Beer's law relates the amount of light being absorbed to the concentration of the substance absorbing the light:

$$A = abc \quad [14.5]$$

In this equation, A is the measured absorbance, a is the molar absorptivity constant (a characteristic of the substance being monitored), b is the path length through which the radiation must pass, and c is the molar concentration of the absorbing substance. Thus, the concentration is directly proportional to absorbance.

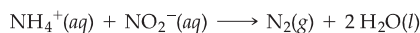
Related Exercise: 14.92



◀ **Figure 14.5**
Basic components of a spectrometer.

14.3 THE RATE LAW: THE EFFECT OF CONCENTRATION ON RATE

One way of studying the effect of concentration on reaction rate is to determine the way in which the rate at the beginning of a reaction (the initial rate) depends on the starting concentrations. To illustrate this approach, consider the following reaction:



We might study the rate of this reaction by measuring the concentration of NH₄⁺ or NO₂⁻ as a function of time or by measuring the volume of N₂ collected. Because the stoichiometric coefficients on NH₄⁺, NO₂⁻, and N₂ are all the same, all of these rates will be equal.

Table 14.2 shows the initial reaction rate for various starting concentrations of NH₄⁺ and NO₂⁻. These data indicate that changing either [NH₄⁺] or

TABLE 14.2 ■ Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C

Experiment Number	Initial NH ₄ ⁺ Concentration (M)	Initial NO ₂ ⁻ Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4 × 10 ⁻⁷
2	0.0200	0.200	10.8 × 10 ⁻⁷
3	0.0400	0.200	21.5 × 10 ⁻⁷
4	0.200	0.0202	10.8 × 10 ⁻⁷
5	0.200	0.0404	21.6 × 10 ⁻⁷
6	0.200	0.0808	43.3 × 10 ⁻⁷

$[\text{NO}_2^-]$ changes the reaction rate. Notice that if we double $[\text{NH}_4^+]$ while holding $[\text{NO}_2^-]$ constant, the rate doubles (compare experiments 1 and 2). If $[\text{NH}_4^+]$ is increased by a factor of 4 with $[\text{NO}_2^-]$ left unchanged (compare experiments 1 and 3), the rate changes by a factor of 4, and so forth. These results indicate that the rate is proportional to $[\text{NH}_4^+]$. When $[\text{NO}_2^-]$ is similarly varied while $[\text{NH}_4^+]$ is held constant, the rate is affected in the same manner. Thus, the rate is also directly proportional to the concentration of NO_2^- . We can express the way in which the rate depends on the concentrations of the reactants, NH_4^+ and NO_2^- , in terms of the following equation:

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-] \quad [14.6]$$

An equation such as Equation 14.6, which shows how the rate depends on the concentrations of reactants, is called a **rate law**. For a general reaction,



the rate law generally has the form

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n \quad [14.7]$$

The constant k in the rate law is called the **rate constant**. The magnitude of k changes with temperature and therefore determines how temperature affects rate, as we will see in Section 14.5. The exponents m and n are typically small whole numbers (usually 0, 1, or 2). We will consider these exponents more closely very shortly.

If we know the rate law for a reaction and its rate for a set of reactant concentrations, we can calculate the value of the rate constant, k . For example, using the data in Table 14.2 and the results from experiment 1, we can substitute into Equation 14.6

$$5.4 \times 10^{-7} \text{ M/s} = k(0.0100 \text{ M})(0.200 \text{ M})$$

Solving for k gives

$$k = \frac{5.4 \times 10^{-7} \text{ M/s}}{(0.0100 \text{ M})(0.200 \text{ M})} = 2.7 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

You may wish to verify that this same value of k is obtained using any of the other experimental results given in Table 14.2.

Once we have both the rate law and the value of the rate constant for a reaction, we can calculate the rate of reaction for any set of concentrations. For example, using Equation 14.6 and $k = 2.7 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, we can calculate the rate for $[\text{NH}_4^+] = 0.100 \text{ M}$ and $[\text{NO}_2^-] = 0.100 \text{ M}$:

$$\text{Rate} = (2.7 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1})(0.100 \text{ M})(0.100 \text{ M}) = 2.7 \times 10^{-6} \text{ M/s}$$

GIVE IT SOME THOUGHT

(a) What is a rate law? (b) What is the name of the quantity k in any rate law?

Reaction Orders: The Exponents in the Rate Law

The rate laws for most reactions have the general form

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \dots \quad [14.8]$$

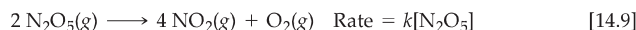
The exponents m and n in a rate law are called **reaction orders**. For example, consider again the rate law for the reaction of NH_4^+ with NO_2^- :

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

Because the exponent of $[\text{NH}_4^+]$ is 1, the rate is *first order* in NH_4^+ . The rate is also first order in NO_2^- . (The exponent “1” is not shown explicitly in rate laws.) The **overall reaction order** is the sum of the orders with respect to each reactant in the rate law. Thus, the rate law has an overall reaction order of $1 + 1 = 2$, and the reaction is *second order overall*.

The exponents in a rate law indicate how the rate is affected by the concentration of each reactant. Because the rate at which NH_4^+ reacts with NO_2^- depends on $[\text{NH}_4^+]$ raised to the first power, the rate doubles when $[\text{NH}_4^+]$ doubles, triples when $[\text{NH}_4^+]$ triples, and so forth. Doubling or tripling $[\text{NO}_2^-]$ likewise doubles or triples the rate. If a rate law is second order with respect to a reactant, $[\text{A}]^2$, then doubling the concentration of that substance causes the reaction rate to quadruple ($[2]^2 = 4$), whereas tripling the concentration causes the rate to increase ninefold ($[3]^2 = 9$).

The following are some additional examples of rate laws:



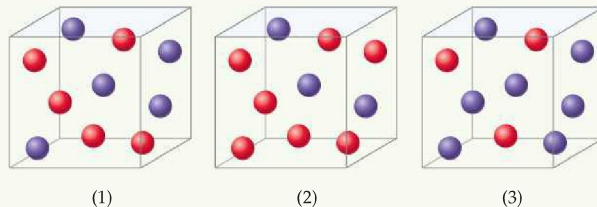
Although the exponents in a rate law are sometimes the same as the coefficients in the balanced equation, this is not necessarily the case, as seen in Equations 14.9 and 14.10. *The values of these exponents must be determined experimentally.* In most rate laws, reaction orders are 0, 1, or 2. However, we also occasionally encounter rate laws in which the reaction order is fractional (such as Equation 14.10) or even negative.

GIVE IT SOME THOUGHT

The experimentally determined rate law for the reaction $2 \text{NO}(\text{g}) + 2 \text{H}_2(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$ is $\text{rate} = k[\text{NO}]^2[\text{H}_2]$. (a) What are the reaction orders in this rate law? (b) Does doubling the concentration of NO have the same effect on rate as doubling the concentration of H_2 ?

SAMPLE EXERCISE 14.4 | Relating a Rate Law to the Effect of Concentration on Rate

Consider a reaction $\text{A} + \text{B} \longrightarrow \text{C}$ for which $\text{rate} = k[\text{A}][\text{B}]^2$. Each of the following boxes represents a reaction mixture in which A is shown as red spheres and B as purple ones. Rank these mixtures in order of increasing rate of reaction.



SOLUTION

Analyze: We are given three boxes containing different numbers of spheres representing mixtures containing different reactant concentrations. We are asked to use the given rate law and the compositions of the boxes to rank the mixtures in order of increasing reaction rates.

Plan: Because all three boxes have the same volume, we can put the number of spheres of each kind into the rate law and calculate the rate for each box.

Solve: Box 1 contains 5 red spheres and 5 purple spheres, giving the following rate:

$$\text{Box 1: Rate} = k(5)(5)^2 = 125k$$

Box 2 contains 7 red spheres and 3 purple spheres:

$$\text{Box 2: Rate} = k(7)(3)^2 = 63k$$

Box 3 contains 3 red spheres and 7 purple spheres:

$$\text{Box 3: Rate} = k(3)(7)^2 = 147k$$

The slowest rate is $63k$ (box 2), and the highest is $147k$ (box 3). Thus, the rates vary in the order $2 < 1 < 3$.

Check: Each box contains 10 spheres. The rate law indicates that in this case [B] has a greater influence on rate than [A] because B has a higher reaction order. Hence, the mixture with the highest concentration of B (most purple spheres) should react fastest. This analysis confirms the order $2 < 1 < 3$.

■ PRACTICE EXERCISE

Assuming that rate = $k[A][B]$, rank the mixtures represented in this Sample Exercise in order of increasing rate.

Answer: $2 = 3 < 1$

Units of Rate Constants

The units of the rate constant depend on the overall reaction order of the rate law. In a reaction that is second order overall, for example, the units of the rate constant must satisfy the equation:

$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})^2$$

Hence, in our usual units of concentration and time

$$\text{Units of rate constant} = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{M/s}{M^2} = M^{-1} s^{-1}$$

■ SAMPLE EXERCISE 14.5 Determining Reaction Orders and Units for Rate Constants

(a) What are the overall reaction orders for the reactions described in Equations 14.9 and 14.10? (b) What are the units of the rate constant for the rate law in Equation 14.9?

SOLUTION

Analyze: We are given two rate laws and asked to express (a) the overall reaction order for each and (b) the units for the rate constant for the first reaction.

Plan: The overall reaction order is the sum of the exponents in the rate law. The units for the rate constant, k , are found by using the normal units for rate (M/s) and concentration (M) in the rate law and applying algebra to solve for k .

Solve: (a) The rate of the reaction in Equation 14.9 is first order in N_2O_5 and first order overall. The reaction in Equation 14.10 is first order in $CHCl_3$ and one-half order in Cl_2 . The overall reaction order is three halves.

(b) For the rate law for Equation 14.9, we have

$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})$$

So

$$\text{Units of rate constant} = \frac{\text{units of rate}}{\text{units of concentration}} = \frac{M/s}{M} = s^{-1}$$

Notice that the units of the rate constant change as the overall order of the reaction changes.

■ PRACTICE EXERCISE

(a) What is the reaction order of the reactant H_2 in Equation 14.11? (b) What are the units of the rate constant for Equation 14.11?

Answers: (a) 1, (b) $M^{-1} s^{-1}$

Using Initial Rates to Determine Rate Laws

The rate law for any chemical reaction must be determined experimentally; it cannot be predicted by merely looking at the chemical equation. We often determine the rate law for a reaction by the same method we applied to the data in Table 14.2: We observe the effect of changing the initial concentrations of the reactants on the initial rate of the reaction.

We have seen that the rate laws for most reactions have the general form

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \dots$$

Thus, the task of determining the rate law becomes one of determining the reaction orders, m and n . In most reactions the reaction orders are 0, 1, or 2. If a reaction is zero order in a particular reactant, changing its concentration will have no effect on rate (as long as some of the reactant is present) because any concentration raised to the zero power equals 1. On the other hand, we have seen that when a reaction is first order in a reactant, changes in the concentration of that reactant will produce proportional changes in the rate. Thus, doubling the concentration will double the rate, and so forth. Finally, when the rate law is second order in a particular reactant, doubling its concentration increases the rate by a factor of $2^2 = 4$, tripling its concentration causes the rate to increase by a factor of $3^2 = 9$, and so forth.

In working with rate laws, it is important to realize that the *rate* of a reaction depends on concentration, but the *rate constant* does not. As we will see later in this chapter, the rate constant (and hence the reaction rate) is affected by temperature and by the presence of a catalyst.

SAMPLE EXERCISE 14.6 | Determining a Rate Law from Initial Rate Data

The initial rate of a reaction $A + B \longrightarrow C$ was measured for several different starting concentrations of A and B, and the results are as follows:

Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

Using these data, determine (a) the rate law for the reaction, (b) the rate constant, (c) the rate of the reaction when $[A] = 0.050 M$ and $[B] = 0.100 M$.

SOLUTION

Analyze: We are given a table of data that relates concentrations of reactants with initial rates of reaction and asked to determine (a) the rate law, (b) the rate constant, and (c) the rate of reaction for a set of concentrations not listed in the table.

Plan: (a) We assume that the rate law has the following form: $\text{Rate} = k[A]^m[B]^n$ so we must use the given data to deduce the reaction orders m and n . We do so by determining how changes in the concentration change the rate. (b) Once we know m and n , we can use the rate law and one of the sets of data to determine the rate constant k . (c) Now that we know both the rate constant and the reaction orders, we can use the rate law with the given concentrations to calculate rate.

Solve: (a) As we move from experiment 1 to experiment 2, $[A]$ is held constant and $[B]$ is doubled. Thus, this pair of experiments shows how $[B]$ affects the rate, allowing us to deduce the order of the rate law with respect to B. Because the rate remains the same when $[B]$ is doubled, the concentration of B has no effect on the reaction rate. The rate law is therefore zero order in B (that is, $n = 0$).

In experiments 1 and 3, $[B]$ is held constant so these data show how $[A]$ affects rate. Holding $[B]$ constant while doubling $[A]$ increases the rate fourfold. This result indicates that rate is proportional to $[A]^2$ (that is, the reaction is second order in A). Hence, the rate law is

$$\text{Rate} = k[A]^2[B]^0 = k[A]^2$$

This rate law could be reached in a more formal way by taking the ratio of the rates from two experiments:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{4.0 \times 10^{-5} \text{ M/s}}{4.0 \times 10^{-5} \text{ M/s}} = 1$$

Using the rate law, we have

$$1 = \frac{\text{rate 2}}{\text{rate 1}} = \frac{k[0.100 \text{ M}]^m [0.200 \text{ M}]^n}{k[0.100 \text{ M}]^m [0.100 \text{ M}]^n} = \frac{[0.200]^n}{[0.100]^n} = 2^n$$

2^n equals 1 under only one condition:

$$n = 0$$

We can deduce the value of m in a similar fashion:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{16.0 \times 10^{-5} \text{ M/s}}{4.0 \times 10^{-5} \text{ M/s}} = 4$$

Using the rate law gives

$$4 = \frac{\text{rate 3}}{\text{rate 1}} = \frac{k[0.200 \text{ M}]^m [0.100 \text{ M}]^n}{k[0.100 \text{ M}]^m [0.100 \text{ M}]^n} = \frac{[0.200]^m}{[0.100]^m} = 2^m$$

Because $2^m = 4$, we conclude that

$$m = 2$$

(b) Using the rate law and the data from experiment 1, we have

$$k = \frac{\text{rate}}{[A]^2} = \frac{4.0 \times 10^{-5} \text{ M/s}}{(0.100 \text{ M})^2} = 4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

(c) Using the rate law from part (a) and the rate constant from part (b), we have

$$\text{Rate} = k[A]^2 = (4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1})(0.050 \text{ M})^2 = 1.0 \times 10^{-5} \text{ M/s}$$

Because [B] is not part of the rate law, it is irrelevant to the rate, if there is at least some B present to react with A.

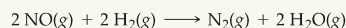
Check: A good way to check our rate law is to use the concentrations in experiment 2 or 3 and see if we can correctly calculate the rate. Using data from experiment 3, we have

$$\text{Rate} = k[A]^2 = (4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1})(0.200 \text{ M})^2 = 1.6 \times 10^{-4} \text{ M/s}$$

Thus, the rate law correctly reproduces the data, giving both the correct number and the correct units for the rate.

PRACTICE EXERCISE

The following data were measured for the reaction of nitric oxide with hydrogen:



Experiment Number	[NO] (M)	[H ₂] (M)	Initial Rate (M/s)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

(a) Determine the rate law for this reaction. (b) Calculate the rate constant. (c) Calculate the rate when [NO] = 0.050 M and [H₂] = 0.150 M

Answers: (a) rate = $k[\text{NO}]^2[\text{H}_2]$; (b) $k = 1.2 \text{ M}^{-2} \text{ s}^{-1}$; (c) rate = $4.5 \times 10^{-4} \text{ M/s}$

14.4 THE CHANGE OF CONCENTRATION WITH TIME

The rate laws that we have examined so far enable us to calculate the rate of a reaction from the rate constant and reactant concentrations. These rate laws can also be converted into equations that show the relationship between the concentrations of the reactants or products and time. The mathematics required to accomplish this conversion involves calculus. We do not expect you to be able to perform the calculus operations; however, you should be able to use the resulting equations. We will apply this conversion to two of the simplest rate laws: those that are first order overall and those that are second order overall.

First-Order Reactions

A **first-order reaction** is one whose rate depends on the concentration of a single reactant raised to the first power. For a reaction of the type $A \longrightarrow \text{products}$ the rate law may be first order:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

This form of a rate law, which expresses how rate depends on concentration, is called the *differential rate law*. Using an operation from calculus called integration, this relationship can be transformed into an equation that relates the concentration of A at the start of the reaction, $[A]_0$, to its concentration at any other time t , $[A]_t$:

$$\ln[A]_t - \ln[A]_0 = -kt \quad \text{or} \quad \ln \frac{[A]_t}{[A]_0} = -kt \quad [14.12]$$

This form of the rate law is called the *integrated rate law*. The function “ln” in Equation 14.12 is the natural logarithm (Appendix A.2). Equation 14.12 can also be rearranged and written as follows:

$$\ln[A]_t = -kt + \ln[A]_0 \quad [14.13]$$

Equations 14.12 and 14.13 can be used with any concentration units, as long as the units are the same for both $[A]_t$ and $[A]_0$.

For a first-order reaction, Equation 14.12 or 14.13 can be used in several ways. Given any three of the following quantities, we can solve for the fourth: k , t , $[A]_0$, and $[A]_t$. Thus, you can use these equations, for example, to determine (1) the concentration of a reactant remaining at any time after the reaction has started, (2) the time required for a given fraction of a sample to react, or (3) the time required for a reactant concentration to fall to a certain level.

SAMPLE EXERCISE 14.7 | Using the Integrated First-Order Rate Law

The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of 1.45 yr^{-1} at 12°C . A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of $5.0 \times 10^{-7} \text{ g/cm}^3$. Assume that the average temperature of the lake is 12°C . (a) What is the concentration of the insecticide on June 1 of the following year? (b) How long will it take for the concentration of the insecticide to decrease to $3.0 \times 10^{-7} \text{ g/cm}^3$?

SOLUTION

Analyze: We are given the rate constant for a reaction that obeys first-order kinetics, as well as information about concentrations and times, and asked to calculate how much reactant (insecticide) remains after one year. We must also determine the time interval needed to reach a particular insecticide concentration. Because the exercise gives time in (a) and asks for time in (b), we know that the integrated rate law, Equation 14.13, is required.

Plan: (a) We are given $k = 1.45 \text{ yr}^{-1}$, $t = 1.00 \text{ yr}$ and $[\text{insecticide}]_0 = 5.0 \times 10^{-7} \text{ g/cm}^3$, and so Equation 14.13 can be solved for $[\text{insecticide}]_t$. (b) We have $k = 1.45 \text{ yr}^{-1}$, $[\text{insecticide}]_0 = 5.0 \times 10^{-7} \text{ g/cm}^3$, and $[\text{insecticide}]_t = 3.0 \times 10^{-7} \text{ g/cm}^3$, and so we can solve Equation 14.13 for time, t .

Solve: (a) Substituting the known quantities into Equation 14.13, we have

$$\ln[\text{insecticide}]_{t=1 \text{ yr}} = -(1.45 \text{ yr}^{-1})(1.00 \text{ yr}) + \ln(5.0 \times 10^{-7})$$

We use the ln function on a calculator to evaluate the second term on the right, giving

$$\ln[\text{insecticide}]_{t=1 \text{ yr}} = -1.45 + (-14.51) = -15.96$$

To obtain $[\text{insecticide}]_{t=1 \text{ yr}}$, we use the inverse natural logarithm, or e^x , function on the calculator:

$$[\text{insecticide}]_{t=1 \text{ yr}} = e^{-15.96} = 1.2 \times 10^{-7} \text{ g/cm}^3$$

Note that the concentration units for $[A]_t$ and $[A]_0$ must be the same.

(b) Again substituting into Equation 14.13, with $[\text{insecticide}]_t = 3.0 \times 10^{-7} \text{ g/cm}^3$, gives

$$\ln(3.0 \times 10^{-7}) = -(1.45 \text{ yr}^{-1})(t) + \ln(5.0 \times 10^{-7})$$

Solving for t gives

$$\begin{aligned} t &= -[\ln(3.0 \times 10^{-7}) - \ln(5.0 \times 10^{-7})]/1.45 \text{ yr}^{-1} \\ &= -(-15.02 + 14.51)/1.45 \text{ yr}^{-1} = 0.35 \text{ yr} \end{aligned}$$

Check: In part (a) the concentration remaining after 1.00 yr (that is, $1.2 \times 10^{-7} \text{ g/cm}^3$) is less than the original concentration ($5.0 \times 10^{-7} \text{ g/cm}^3$), as it should be. In (b) the given concentration ($3.0 \times 10^{-7} \text{ g/cm}^3$) is greater than that remaining after 1.00 yr, indicating that the time must be less than a year. Thus, $t = 0.35 \text{ yr}$ is a reasonable answer.

PRACTICE EXERCISE

The decomposition of dimethyl ether, $(\text{CH}_3)_2\text{O}$, at 510°C is a first-order process with a rate constant of $6.8 \times 10^{-4} \text{ s}^{-1}$:



If the initial pressure of $(\text{CH}_3)_2\text{O}$ is 135 torr, what is its pressure after 1420 s?

Answer: 51 torr

Equation 14.13 can be used to verify whether a reaction is first order and to determine its rate constant. This equation has the form of the general equation for a straight line, $y = mx + b$, in which m is the slope and b is the y -intercept of the line (Appendix A.4):

$$\ln[A]_t = -k \cdot t + \ln[A]_0$$

$$y = m \cdot x + b$$

For a first-order reaction, therefore, a graph of $\ln[A]_t$ versus time gives a straight line with a slope of $-k$ and a y -intercept of $\ln[A]_0$. A reaction that is not first order will not yield a straight line.

As an example, consider the conversion of methyl isonitrile (CH_3NC) to acetonitrile (CH_3CN) (Figure 14.6). Because experiments show that the reaction is first order, we can write the rate equation:

$$\ln[\text{CH}_3\text{NC}]_t = -kt + \ln[\text{CH}_3\text{NC}]_0$$

Figure 14.7(a) shows how the pressure of methyl isonitrile varies with time as it rearranges in the gas phase at 198.9°C . We can use pressure as a unit of concentration for a gas because from the ideal-gas law the pressure is directly proportional to the number of moles per unit volume. Figure 14.7(b) shows a plot of the natural logarithm of the pressure versus time, a plot that yields a straight line. The slope of this line is $-5.1 \times 10^{-5} \text{ s}^{-1}$. (You should verify this for yourself, remembering that your result may vary slightly from ours because of inaccuracies associated with reading the graph.) Because the slope of the line equals $-k$, the rate constant for this reaction equals $5.1 \times 10^{-5} \text{ s}^{-1}$.

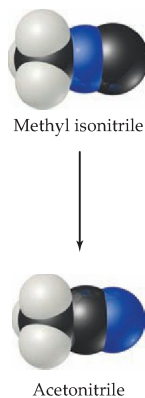


Figure 14.6 A first-order reaction.

The transformation of methyl isonitrile (CH_3NC) to acetonitrile (CH_3CN) is a first-order process. Methyl isonitrile and acetonitrile are isomers, molecules that have the same atoms arranged differently. This reaction is called an isomerization reaction.

GIVE IT SOME THOUGHT

What do the y -intercepts in Figure 14.7(a) and (b) represent?

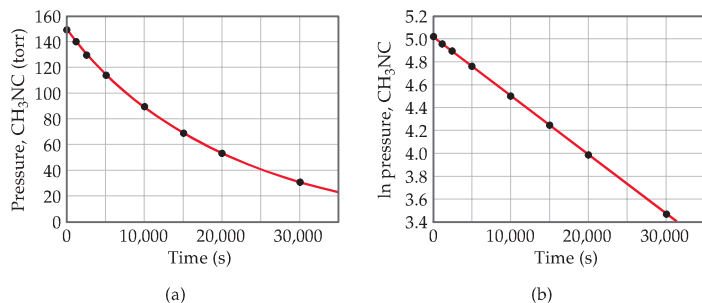


Figure 14.7 Kinetic data for conversion of methyl isonitrile.

(a) Variation in the partial pressure of methyl isonitrile (CH_3NC) with time during the reaction $\text{CH}_3\text{NC} \longrightarrow \text{CH}_3\text{CN}$ at 198.9°C . (b) A plot of the natural logarithm of the CH_3NC pressure as a function of time. The fact that a straight line fits the data confirms that the rate law is first order.

Second-Order Reactions

A **second-order reaction** is one whose rate depends on the reactant concentration raised to the second power or on the concentrations of two different reactants, each raised to the first power. For simplicity, let's consider reactions of the type $A \longrightarrow \text{products}$ or $A + B \longrightarrow \text{products}$ that are second order in just one reactant, A:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

With the use of calculus, this differential rate law can be used to derive the following integrated rate law:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad [14.14]$$

This equation, like Equation 14.13, has four variables, k , t , $[A]_0$, and $[A]_t$, and any one of these can be calculated knowing the other three. Equation 14.14 also has the form of a straight line ($y = mx + b$). If the reaction is second order, a plot of $1/[A]_t$ versus t will yield a straight line with a slope equal to k and a y -intercept equal to $1/[A]_0$. One way to distinguish between first- and second-order rate laws is to graph both $\ln[A]_t$ and $1/[A]_t$ against t . If the $\ln[A]_t$ plot is linear, the reaction is first order; if the $1/[A]_t$ plot is linear, the reaction is second order.

SAMPLE EXERCISE 14.8 | Determining Reaction Order from the Integrated Rate Law

The following data were obtained for the gas-phase decomposition of nitrogen dioxide at 300 °C, $\text{NO}_2(\text{g}) \longrightarrow \text{NO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$:

Time (s)	$[\text{NO}_2]$ (M)
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Is the reaction first or second order in NO_2 ?

SOLUTION

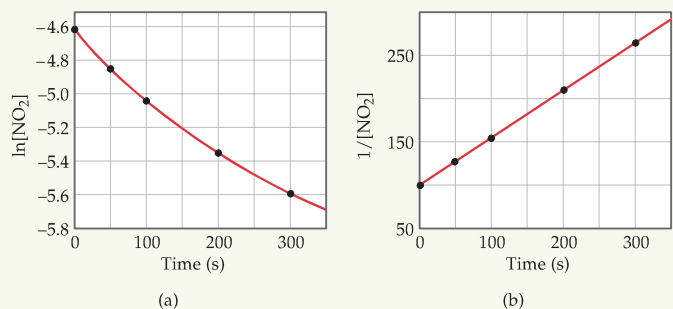
Analyze: We are given the concentrations of a reactant at various times during a reaction and asked to determine whether the reaction is first or second order.

Plan: We can plot $\ln[\text{NO}_2]$ and $1/[\text{NO}_2]$ against time. One or the other will be linear, indicating whether the reaction is first or second order.

Solve: To graph $\ln[\text{NO}_2]$ and $1/[\text{NO}_2]$ against time, we will first prepare the following table from the data given:

Time (s)	$[\text{NO}_2]$ (M)	$\ln[\text{NO}_2]$	$1/[\text{NO}_2]$
0.0	0.01000	-4.605	100
50.0	0.00787	-4.845	127
100.0	0.00649	-5.037	154
200.0	0.00481	-5.337	208
300.0	0.00380	-5.573	263

As Figure 14.8 shows, only the plot of $1/[\text{NO}_2]$ versus time is linear. Thus, the reaction obeys a second-order rate law: $\text{Rate} = k[\text{NO}_2]^2$. From the slope of this straight-line graph, we determine that $k = 0.543 \text{ M}^{-1} \text{ s}^{-1}$ for the disappearance of NO_2 .



▲ **Figure 14.8 Kinetic data for decomposition of NO₂.** The reaction is $\text{NO}_2(g) \longrightarrow \text{NO}(g) + \frac{1}{2} \text{O}_2(g)$, and the data were collected at 300 °C. (a) A plot of $\ln[\text{NO}_2]$ versus time is not linear, indicating that the reaction is not first order in NO₂. (b) A plot of $1/[\text{NO}_2]$ versus time is linear, indicating that the reaction is second order in NO₂.

■ PRACTICE EXERCISE

Consider again the decomposition of NO₂ discussed in the Sample Exercise. The reaction is second order in NO₂ with $k = 0.543 \text{ M}^{-1} \text{ s}^{-1}$. If the initial concentration of NO₂ in a closed vessel is 0.0500 M, what is the remaining concentration after 0.500 h? **Answer:** Using Equation 14.14, we find $[\text{NO}_2] = 1.00 \times 10^{-3} \text{ M}$

Half-life

The **half-life** of a reaction, $t_{1/2}$, is the time required for the concentration of a reactant to reach one-half of its initial value, $[\text{A}]_{t_{1/2}} = \frac{1}{2}[\text{A}]_0$. The half-life is a convenient way to describe how fast a reaction occurs, especially if it is a first-order process. A fast reaction will have a short half-life.

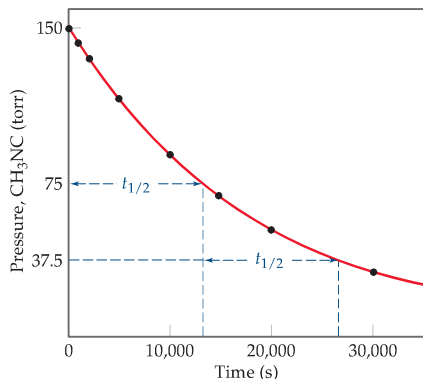
We can determine the half-life of a first-order reaction by substituting $[\text{A}]_{t_{1/2}}$ into Equation 14.12:

$$\begin{aligned} \ln \frac{\frac{1}{2}[\text{A}]_0}{[\text{A}]_0} &= -kt_{1/2} \\ \ln \frac{1}{2} &= -kt_{1/2} \\ t_{1/2} &= -\frac{\ln \frac{1}{2}}{k} = \frac{0.693}{k} \end{aligned} \quad [14.15]$$

From Equation 14.15, we see that $t_{1/2}$ for a first-order rate law does not depend on the starting concentration. Consequently, the half-life remains constant throughout the reaction. If, for example, the concentration of the reactant is 0.120 M at some moment in the reaction, it will be $\frac{1}{2}(0.120 \text{ M}) = 0.060 \text{ M}$ after one half-life. After one more half-life passes, the concentration will drop to 0.030 M, and so on. Equation 14.15 also indicates that we can calculate $t_{1/2}$ for a first-order reaction if k is known, or k if $t_{1/2}$ is known.

The change in concentration over time for the first-order rearrangement of methyl isonitrile at 198.9 °C is graphed in Figure 14.9. The first half-life is shown at 13,600 s (that is, 3.78 h). At a time 13,600 s later, the isonitrile concentration has decreased to one-half of one-half, or one-fourth the original concentration. In a first-order reaction, the concentration of the reactant decreases by $\frac{1}{2}$ in each of a series of regularly spaced time intervals, namely, $t_{1/2}$. The concept of half-life is widely used in describing radioactive decay, a first-order process that we will discuss in detail in Section 21.4.

▼ **Figure 14.9 Half-life of a first-order reaction.** Pressure of methyl isonitrile as a function of time showing two successive half-lives of the isomerization reaction depicted in Figure 14.6.

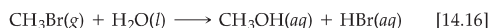


Several small molecules containing carbon–chlorine or carbon–bromine bonds, when present in the stratosphere, are capable of reacting with ozone (O_3) and thus contributing to the destruction of Earth's ozone layer. Whether a halogen-containing molecule contributes significantly to destruction of the ozone layer depends in part on the molecule's average lifetime in the atmosphere. It takes quite a long time for molecules formed at Earth's surface to diffuse through the lower atmosphere (called the troposphere) and move into the stratosphere, where the ozone layer is located (Figure 14.10 ▶). Decomposition in the lower atmosphere competes with diffusion into the stratosphere.

The much-discussed chlorofluorocarbons, or CFCs, contribute to the destruction of the ozone layer because they have long lifetimes in the troposphere. Thus, they persist long enough for a substantial fraction of the molecules to find their way to the stratosphere.

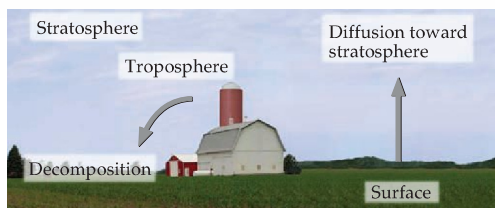
Another simple molecule that has the potential to destroy the stratospheric ozone layer is methyl bromide (CH_3Br). This substance has a wide range of uses, including antifungal treatment of plant seeds, and has therefore been produced in large quantities in the past (about 150 million pounds per year worldwide in 1997). In the stratosphere, the C–Br bond is broken through absorption of short-wavelength radiation. The resultant Br atoms then catalyze decomposition of O_3 .

Methyl bromide is removed from the lower atmosphere by a variety of mechanisms, including a slow reaction with ocean water:



To determine the potential importance of CH_3Br in destruction of the ozone layer, it is important to know how rapidly the reaction in Equation 14.16 and all other reactions together remove CH_3Br from the atmosphere before it can diffuse into the stratosphere.

Scientists have carried out research to estimate the average lifetime of CH_3Br in Earth's atmosphere. Such an estimate is difficult to make. It cannot be done in laboratory-based experiments because the conditions that exist in the atmosphere above the planet are too complex to be simulated in the laboratory. Instead, scientists gathered nearly 4000 samples of the



▲ **Figure 14.10 Distribution and fate of methyl bromide in the atmosphere.** Some CH_3Br is removed from the atmosphere by decomposition, and some diffuses upward into the stratosphere, where it contributes to destruction of the ozone layer. The relative rates of decomposition and diffusion determine how extensively methyl bromide is involved in destruction of the ozone layer.

atmosphere during aircraft flights all over the Pacific Ocean and analyzed them for the presence of several trace organic substances, including methyl bromide. From a detailed analysis of the concentrations, it was possible to estimate the *atmospheric residence time* for CH_3Br .

The atmospheric residence time is related to the half-life for CH_3Br in the lower atmosphere, assuming that it decomposes by a first-order process. From the experimental data, the half-life for methyl bromide in the lower atmosphere is estimated to be 0.8 ± 0.1 yr. That is, a collection of CH_3Br molecules present at any given time will, on average, be 50% decomposed after 0.8 years, 75% decomposed after 1.6 years, and so on. A half-life of 0.8 years, while comparatively short, is still sufficiently long so that CH_3Br contributes significantly to the destruction of the ozone layer. In 1997 an international agreement was reached to phase out use of methyl bromide in developed countries by 2005. However, in recent years exemptions for critical agricultural use have been requested and granted. Nevertheless, worldwide production was down to 30 million pounds worldwide in 2005, two-thirds of which is used in the United States.

Related Exercise: 14.111

GIVE IT SOME THOUGHT

If a solution containing 10.0 g of a substance reacts by first-order kinetics, how many grams remain after 3 half-lives?

SAMPLE EXERCISE 14.9 | Determining the Half-life of a First-Order Reaction

The reaction of C_4H_9Cl with water is a first-order reaction. Figure 14.4 shows how the concentration of C_4H_9Cl changes with time at a particular temperature. (a) From that graph, estimate the half-life for this reaction. (b) Use the half-life from (a) to calculate the rate constant.

SOLUTION

Analyze: We are asked to estimate the half-life of a reaction from a graph of concentration versus time and then to use the half-life to calculate the rate constant for the reaction.

Plan: (a) To estimate a half-life, we can select a concentration and then determine the time required for the concentration to decrease to half of that value. (b) Equation 14.15 is used to calculate the rate constant from the half-life.

Solve: (a) From the graph, we see that the initial value of $[\text{C}_4\text{H}_9\text{Cl}]$ is 0.100 M. The half-life for this first-order reaction is the time required for $[\text{C}_4\text{H}_9\text{Cl}]$ to decrease to 0.050 M, which we can read off the graph. This point occurs at approximately 340 s.

(b) Solving Equation 14.15 for k , we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{340 \text{ s}} = 2.0 \times 10^{-3} \text{ s}^{-1}$$

Check: At the end of the second half-life, which should occur at 680 s, the concentration should have decreased by yet another factor of 2, to 0.025 M. Inspection of the graph shows that this is indeed the case.

PRACTICE EXERCISE

(a) Using Equation 14.15, calculate $t_{1/2}$ for the decomposition of the insecticide described in Sample Exercise 14.7. (b) How long does it take for the concentration of the insecticide to reach one-quarter of the initial value?

Answers: (a) 0.478 yr = 1.51×10^7 s; (b) it takes two half-lives, $2(0.478 \text{ yr}) = 0.956 \text{ yr}$

In contrast to the behavior of first-order reactions, the half-life for second-order and other reactions depends on reactant concentrations and therefore changes as the reaction progresses. Using Equation 14.14, we find that the half-life of a second-order reaction is

$$t_{1/2} = \frac{1}{k[\text{A}]_0} \quad [14.17]$$

In this case the half-life depends on the initial concentration of reactant—the lower the initial concentration, the greater the half-life.

GIVE IT SOME THOUGHT

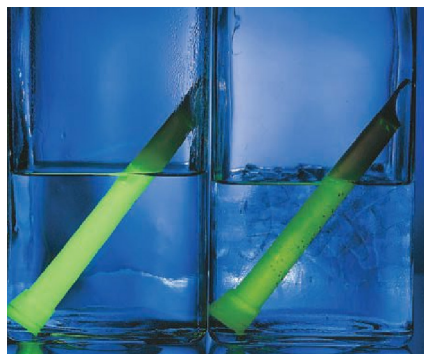
How does the half-life of a second-order reaction change as the reaction proceeds?

14.5 TEMPERATURE AND RATE

The rates of most chemical reactions increase as the temperature rises. For example, dough rises faster at room temperature than when refrigerated, and plants grow more rapidly in warm weather than in cold. We can literally see the effect of temperature on reaction rate by observing a chemiluminescence reaction (one that produces light). The characteristic glow of fireflies is a familiar example of chemiluminescence. Another is the light produced by Cyalume® light sticks, which contain chemicals that produce chemiluminescence when mixed. As seen in Figure 14.11, these light sticks produce a brighter light at higher temperature. The amount of light produced is greater because the rate of the reaction is faster at the higher temperature. Although the light stick glows more brightly initially, its luminescence also dies out more rapidly.

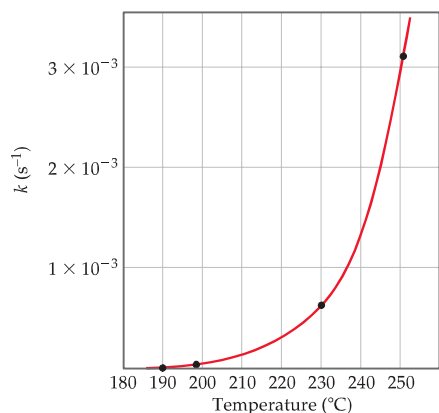
How is this experimentally observed temperature effect reflected in the rate expression? The faster rate at higher temperature is due to an increase in the rate constant with increasing temperature. For example, let's reconsider the first-order reaction $\text{CH}_3\text{NC} \longrightarrow \text{CH}_3\text{CN}$

▼ **Figure 14.11 Temperature affects the rate of the chemiluminescence reaction in Cyalume® light sticks.** The light stick in hot water (left) glows more brightly than the one in cold water (right); at the higher temperature, the reaction is initially faster and produces a brighter light.



Higher temperature

Lower temperature



▲ **Figure 14.12 Dependence of rate constant on temperature.** The data show the variation in the first-order rate constant for the rearrangement of methyl isonitrile as a function of temperature. The four points indicated are used in connection with Sample Exercise 14.11.

(Figure 14.6). Figure 14.12 ◀ shows the rate constant for this reaction as a function of temperature. The rate constant, and hence the rate of the reaction, increases rapidly with temperature, approximately doubling for each 10 °C rise.

The Collision Model

We have seen that reaction rates are affected both by the concentrations of reactants and by temperature. The **collision model**, which is based on the kinetic-molecular theory (Section 10.7), accounts for both of these effects at the molecular level. The central idea of the collision model is that molecules must collide to react. The greater the number of collisions occurring per second, the greater is the reaction rate. As the concentration of reactant molecules increases, therefore, the number of collisions increases, leading to an increase in reaction rate. According to the kinetic-molecular theory of gases, increasing the temperature increases molecular speeds. As molecules move faster, they collide more forcefully (with more energy) and more frequently, increasing reaction rates.

For a reaction to occur, though, more is required than simply a collision. For most reactions, only a tiny fraction of the collisions leads to a reaction. For example, in a mixture of H_2 and I_2 at ordinary temperatures and pressures, each molecule undergoes about 10^{10} collisions per second. If every collision between H_2 and I_2 resulted in the formation of HI , the reaction would be over in much less than a second. Instead, at room temperature the reaction proceeds very slowly. Only about one in every 10^{13} collisions produces a reaction. What keeps the reaction from occurring more rapidly?

GIVE IT SOME THOUGHT

What is the central idea of the collision model?

The Orientation Factor

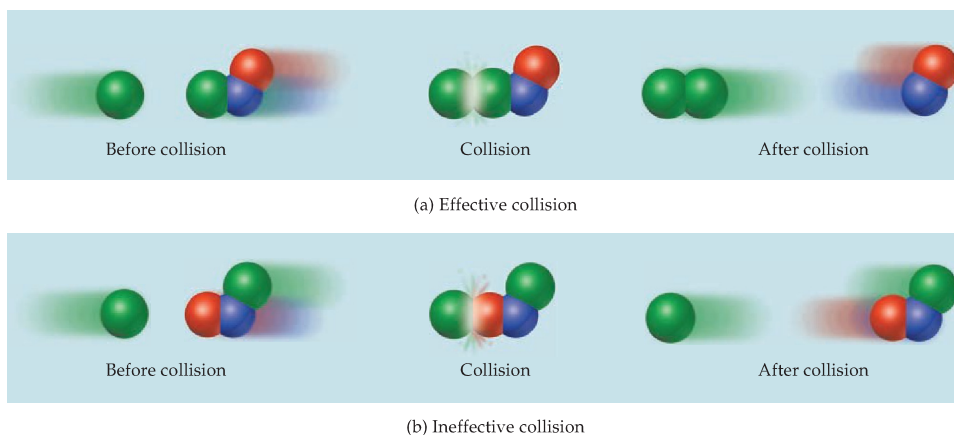
In most reactions, molecules must be oriented in a certain way during collisions for a reaction to occur. The relative orientations of the molecules during their collisions determine whether the atoms are suitably positioned to form new bonds. For example, consider the reaction of Cl atoms with $NOCl$:



The reaction will take place if the collision brings Cl atoms together to form Cl_2 as shown in Figure 14.13(a) ▶. In contrast, the collision shown in Figure 14.13(b) will be ineffective and will not yield products. Indeed, a great many collisions do not lead to reaction, merely because the molecules are not suitably oriented. Another factor, however, is usually even more important in determining whether particular collisions result in reaction.

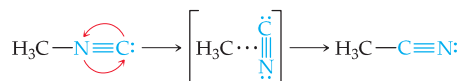
Activation Energy

In 1888 the Swedish chemist Svante Arrhenius suggested that molecules must possess a certain minimum amount of energy to react. According to the collision model, this energy comes from the kinetic energies of the colliding molecules. Upon collision, the kinetic energy of the molecules can be used to stretch, bend, and ultimately break bonds, leading to chemical reactions. That is, the kinetic energy is used to change the potential energy of the molecule. If molecules are moving too slowly, with too little kinetic energy, they merely bounce off one another without changing. To react, colliding molecules must have a total kinetic energy equal to or greater than some minimum value. The minimum energy required to initiate a chemical reaction is called the **activation energy**, E_a . The value of E_a varies from reaction to reaction.



▲ **Figure 14.13 Molecular collisions and chemical reactions.** Two possible ways that Cl atoms and NOCl molecules can collide are shown. (a) If molecules are oriented properly, a sufficiently energetic collision will lead to reaction. (b) If the orientation of the colliding molecules is wrong, no reaction occurs.

The situation during reactions is rather like that shown in Figure 14.14. The player on the putting green needs to move her ball over the hill to the vicinity of the cup. To do this, she must impart enough kinetic energy with the putter to move the ball to the top of the hill. If she does not impart enough energy, the ball will roll partway up the hill and then back down. In the same way, molecules may require a certain minimum energy to break existing bonds during a chemical reaction. In the rearrangement of methyl isonitrile to acetonitrile, for example, we might imagine the reaction passing through an intermediate state in which the $\text{N}\equiv\text{C}$ portion of the molecule is sitting sideways:



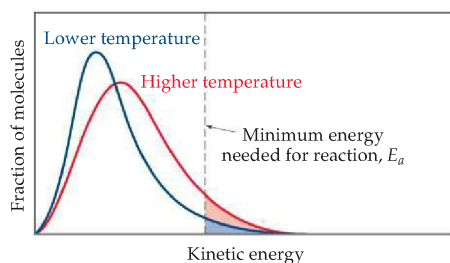
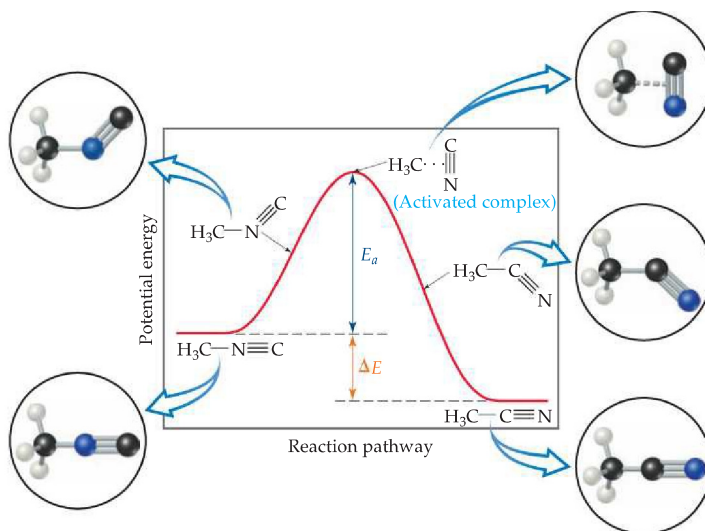
The change in the potential energy of the molecule during the reaction is shown in Figure 14.15. The diagram shows that energy must be supplied to stretch the bond between the H_3C group and the $\text{N}\equiv\text{C}$ group to allow the $\text{N}\equiv\text{C}$ group to rotate. After the $\text{N}\equiv\text{C}$ group has twisted sufficiently, the $\text{C}-\text{C}$ bond begins to form, and the energy of the molecule drops. Thus, the barrier represents the energy necessary to force the molecule through the relatively unstable intermediate state to the final product. The energy difference between that of the starting molecule and the highest energy along the reaction pathway is the activation energy, E_a . The particular arrangement of atoms at the top of the barrier is called the **activated complex**, or **transition state**.

The conversion of $\text{H}_3\text{C}-\text{N}\equiv\text{C}$ to $\text{H}_3\text{C}-\text{C}\equiv\text{N}$ is exothermic. Figure 14.15 therefore shows the product as having a lower energy than the reactant. The energy change for the reaction, ΔE , has no effect on the rate of the reaction. *The rate depends on the magnitude of E_a ; generally, the lower E_a is, the faster the reaction.* Notice that the reverse reaction is endothermic. The activation barrier for the reverse reaction is equal to the sum of ΔE and E_a for the forward reaction.



▲ **Figure 14.14 An energy barrier.** To move the golf ball to the vicinity of the cup, the player must impart enough kinetic energy to the ball to enable it to surmount the barrier represented by the hill. This situation is analogous to a chemical reaction, in which molecules must gain enough energy through collisions to enable them to overcome the barrier to chemical reaction.

► **Figure 14.15 Energy profile for methyl isonitrile isomerization.** The methyl isonitrile molecule must surmount the activation-energy barrier before it can form the product, acetonitrile. The horizontal axis is variously labeled “reaction pathway,” as here, or “progress of reaction.”



▲ **Figure 14.16 The effect of temperature on the distribution of kinetic energies.** At the higher temperature, a larger number of molecules have higher kinetic energies. Thus, a larger fraction at any one instant will have more than the minimum energy required for reaction.

How does any particular methyl isonitrile molecule acquire sufficient energy to overcome the activation barrier? It does so through collisions with other molecules. Recall from the kinetic-molecular theory of gases that, at any given instant, gas molecules are distributed in energy over a wide range. ∞ (Section 10.7) Figure 14.16 ◀ shows the distribution of kinetic energies for two different temperatures, comparing them with the minimum energy needed for reaction, E_a . At the higher temperature a much greater fraction of the molecules has kinetic energy greater than E_a , which leads to a much greater rate of reaction.

The fraction of molecules that has an energy equal to or greater than E_a is given by the expression

$$f = e^{-E_a/RT} \quad [14.18]$$

In this equation R is the gas constant (8.314 J/mol-K) and T is absolute temperature. To get an idea of the magnitude of f , let's suppose that E_a is 100 kJ/mol, a value typical of many reactions, and that T is 300 K, around room temperature. The calculated value of f is 3.9×10^{-18} , an extremely small number! At 310 K the fraction is $f = 1.4 \times 10^{-17}$. Thus, a 10-degree increase in temperature produces a 3.6-fold increase in the fraction of molecules possessing at least 100 kJ/mol of energy.

GIVE IT SOME THOUGHT

Why isn't collision frequency the only factor affecting a reaction rate?

The Arrhenius Equation

Arrhenius noted that for most reactions the increase in rate with increasing temperature is nonlinear, as shown in Figure 14.12. He found that most reaction-rate data obeyed an equation based on three factors: (a) the fraction of molecules possessing an energy of E_a or greater, (b) the number of collisions

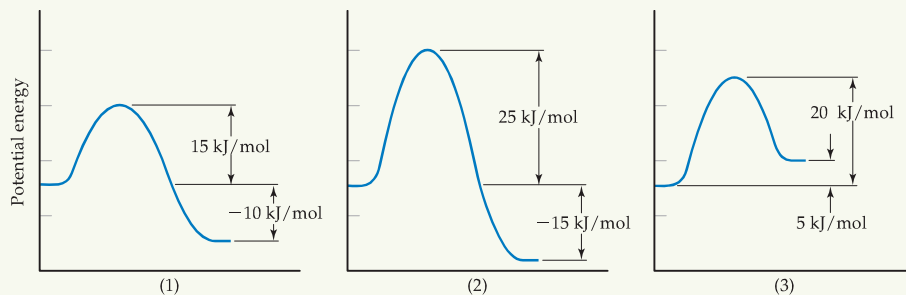
occurring per second, and (c) the fraction of collisions that have the appropriate orientation. These three factors are incorporated into the **Arrhenius equation**:

$$k = Ae^{-E_a/RT} \quad [14.19]$$

In this equation k is the rate constant, E_a is the activation energy, R is the gas constant (8.314 J/mol-K), and T is the absolute temperature. The **frequency factor**, A , is constant, or nearly so, as temperature is varied. This factor is related to the frequency of collisions and the probability that the collisions are favorably oriented for reaction.* As the magnitude of E_a increases, k decreases because the fraction of molecules that possess the required energy is smaller. Thus, *reaction rates decrease as E_a increases*.

SAMPLE EXERCISE 14.10 | Relating Energy Profiles to Activation Energies and Speeds of Reaction

Consider a series of reactions having the following energy profiles:



Rank the reactions from slowest to fastest assuming that they have nearly the same frequency factors.

SOLUTION

The lower the activation energy, the faster the reaction. The value of ΔE does not affect the rate. Hence the order is (2) < (3) < (1).

PRACTICE EXERCISE

Imagine that these reactions are reversed. Rank these reverse reactions from slowest to fastest.

Answer: (2) < (1) < (3) because E_a values are 40, 25, and 15 kJ/mol, respectively

Determining the Activation Energy

Taking the natural log of both sides of Equation 14.19, we have

$$\ln k = -\frac{E_a}{RT} + \ln A \quad [14.20]$$

$$\begin{array}{ccc} \updownarrow & \updownarrow & \updownarrow \\ y & = & mx + b \end{array}$$

As shown, Equation 14.20 has the form of the equation for a straight line. A graph of $\ln k$ versus $1/T$ will be a line with a slope equal to $-E_a/R$ and a y -intercept equal to $\ln A$. Thus, the activation energy can be determined by measuring k at a series of temperatures, graphing $\ln k$ versus $1/T$, and then calculating E_a from the slope of the resultant line.

We can also use Equation 14.20 to evaluate E_a in a nongraphical way if we know the rate constant of a reaction at two or more temperatures. For example,

*Because the frequency of collisions increases with temperature, A also has some temperature dependence, but it is small compared to the exponential term. Therefore, A is considered approximately constant.

suppose that at two different temperatures, T_1 and T_2 , a reaction has rate constants k_1 and k_2 . For each condition, we have

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \text{and} \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

Subtracting $\ln k_2$ from $\ln k_1$ gives

$$\ln k_1 - \ln k_2 = \left(-\frac{E_a}{RT_1} + \ln A\right) - \left(-\frac{E_a}{RT_2} + \ln A\right)$$

Simplifying this equation and rearranging it gives

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad [14.21]$$

Equation 14.21 provides a convenient way to calculate the rate constant, k_1 , at some temperature, T_1 , when we know the activation energy and the rate constant, k_2 , at some other temperature, T_2 .

SAMPLE EXERCISE 14.11 | Determining the Energy of Activation

The following table shows the rate constants for the rearrangement of methyl isonitrile at various temperatures (these are the data in Figure 14.12):

Temperature ($^{\circ}\text{C}$)	k (s^{-1})
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}

(a) From these data, calculate the activation energy for the reaction. (b) What is the value of the rate constant at 430.0 K?

SOLUTION

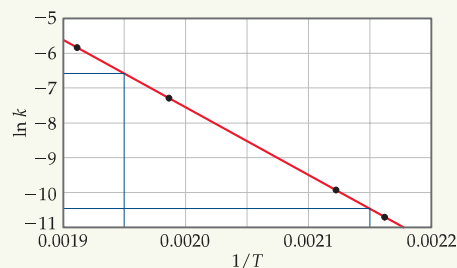
Analyze: We are given rate constants, k , measured at several temperatures and asked to determine the activation energy, E_a , and the rate constant, k , at a particular temperature.

Plan: We can obtain E_a from the slope of a graph of $\ln k$ versus $1/T$. Once we know E_a , we can use Equation 14.21 together with the given rate data to calculate the rate constant at 430.0 K.

Solve: (a) We must first convert the temperatures from degrees Celsius to kelvins. We then take the inverse of each temperature, $1/T$, and the natural log of each rate constant, $\ln k$. This gives us the table shown at the right:

T (K)	$1/T$ (K^{-1})	$\ln k$
462.9	2.160×10^{-3}	-10.589
472.1	2.118×10^{-3}	-9.855
503.5	1.986×10^{-3}	-7.370
524.4	1.907×10^{-3}	-5.757

A graph of $\ln k$ versus $1/T$ results in a straight line, as shown in Figure 14.17.



◀ **Figure 14.17 Graphical determination of activation energy.** The natural logarithm of the rate constant for the rearrangement of methyl isonitrile is plotted as a function of $1/T$. The linear relationship is predicted by the Arrhenius equation giving a slope equal to $-E_a/R$.

The slope of the line is obtained by choosing two well-separated points, as shown, and using the coordinates of each:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{-6.6 - (-10.4)}{0.00195 - 0.00215} = -1.9 \times 10^4$$

Because logarithms have no units, the numerator in this equation is dimensionless. The denominator has the units of $1/T$, namely, K^{-1} . Thus, the overall units for the slope are K . The slope equals $-E_a/R$. We use the value for the molar gas constant R in units of $\text{J/mol}\cdot\text{K}$ (Table 10.2). We thus obtain

$$\begin{aligned} \text{Slope} &= -\frac{E_a}{R} \\ E_a &= -(\text{slope})(R) = -(-1.9 \times 10^4 \text{ K}) \left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \\ &= 1.6 \times 10^2 \text{ kJ/mol} = 160 \text{ kJ/mol} \end{aligned}$$

We report the activation energy to only two significant figures because we are limited by the precision with which we can read the graph in Figure 14.17.

(b) To determine the rate constant, k_1 , at $T_1 = 430.0 \text{ K}$, we can use Equation 14.21 with $E_a = 160 \text{ kJ/mol}$, and one of the rate constants and temperatures from the given data, such as $k_2 = 2.52 \times 10^{-5} \text{ s}^{-1}$ and $T_2 = 462.9 \text{ K}$:

$$\ln \left(\frac{k_1}{2.52 \times 10^{-5} \text{ s}^{-1}} \right) = \left(\frac{160 \text{ kJ/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \right) \left(\frac{1}{462.9 \text{ K}} - \frac{1}{430.0 \text{ K}} \right) \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right) = -3.18$$

Thus,

$$\begin{aligned} \frac{k_1}{2.52 \times 10^{-5} \text{ s}^{-1}} &= e^{-3.18} = 4.15 \times 10^{-2} \\ k_1 &= (4.15 \times 10^{-2})(2.52 \times 10^{-5} \text{ s}^{-1}) = 1.0 \times 10^{-6} \text{ s}^{-1} \end{aligned}$$

Note that the units of k_1 are the same as those of k_2 .

■ PRACTICE EXERCISE

Using the data in Sample Exercise 14.11, calculate the rate constant for the rearrangement of methyl isonitrile at 280°C .

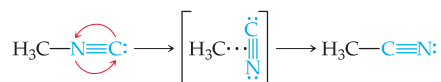
Answer: $2.2 \times 10^{-2} \text{ s}^{-1}$

14.6 REACTION MECHANISMS

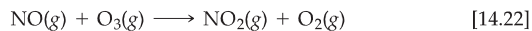
A balanced equation for a chemical reaction indicates the substances present at the start of the reaction and those produced as the reaction proceeds. It provides no information, however, about how the reaction occurs. The process by which a reaction occurs is called the **reaction mechanism**. At the most sophisticated level, a reaction mechanism will describe in great detail the order in which bonds are broken and formed and the changes in relative positions of the atoms in the course of the reaction. We will begin with more rudimentary descriptions of how reactions occur, considering further the nature of the collisions leading to reaction.

Elementary Reactions

We have seen that reactions take place because of collisions between reacting molecules. For example, the collisions between molecules of methyl isonitrile (CH_3NC) can provide the energy to allow the CH_3NC to rearrange:



Similarly, the reaction of NO and O₃ to form NO₂ and O₂ appears to occur as a result of a single collision involving suitably oriented and sufficiently energetic NO and O₃ molecules:



Both of these processes occur in a single event or step and are called **elementary reactions** (or elementary processes).

The number of molecules that participate as reactants in an elementary reaction defines its **molecularity**. If a single molecule is involved, the reaction is **unimolecular**. The rearrangement of methyl isonitrile is a unimolecular process. Elementary reactions involving the collision of two reactant molecules are **bimolecular**. The reaction between NO and O₃ (Equation 14.22) is bimolecular. Elementary reactions involving the simultaneous collision of three molecules are **termolecular**. Termolecular reactions are far less probable than unimolecular or bimolecular processes and are rarely encountered. The chance that four or more molecules will collide simultaneously with any regularity is even more remote; consequently, such collisions are never proposed as part of a reaction mechanism.



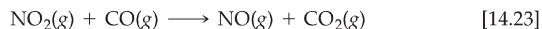
GIVE IT SOME THOUGHT

What is the molecularity of this elementary reaction?

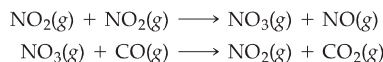


Multistep Mechanisms

The net change represented by a balanced chemical equation often occurs by a *multistep mechanism*, which consists of a sequence of elementary reactions. For example, consider the reaction of NO₂ and CO:



Below 225 °C, this reaction appears to proceed in two elementary reactions (or two *elementary steps*), each of which is bimolecular. First, two NO₂ molecules collide, and an oxygen atom is transferred from one to the other. The resultant NO₃ then collides with a CO molecule and transfers an oxygen atom to it:



Thus, we say that the reaction occurs by a two-step mechanism.

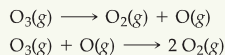
The chemical equations for the elementary reactions in a multistep mechanism must always add to give the chemical equation of the overall process. In the present example the sum of the two elementary reactions is



Simplifying this equation by eliminating substances that appear on both sides of the arrow gives Equation 14.23, the net equation for the process. Because NO₃ is neither a reactant nor a product in the overall reaction—it is formed in one elementary reaction and consumed in the next—it is called an **intermediate**. Multistep mechanisms involve one or more intermediates.

SAMPLE EXERCISE 14.12 | Determining Molecularity and Identifying Intermediates

It has been proposed that the conversion of ozone into O₂ proceeds by a two-step mechanism:



- (a) Describe the molecularity of each elementary reaction in this mechanism.
 (b) Write the equation for the overall reaction. (c) Identify the intermediate(s).

SOLUTION

Analyze: We are given a two-step mechanism and asked for (a) the molecularities of each of the two elementary reactions, (b) the equation for the overall process, and (c) the intermediate.

Plan: The molecularity of each elementary reaction depends on the number of reactant molecules in the equation for that reaction. The overall equation is the sum of the equations for the elementary reactions. The intermediate is a substance formed in one step of the mechanism and used in another and therefore not part of the equation for the overall reaction.

Solve: (a) The first elementary reaction involves a single reactant and is consequently unimolecular. The second reaction, which involves two reactant molecules, is bimolecular.

(b) Adding the two elementary reactions gives



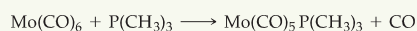
Because $\text{O}(\text{g})$ appears in equal amounts on both sides of the equation, it can be eliminated to give the net equation for the chemical process:



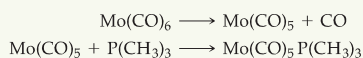
(c) The intermediate is $\text{O}(\text{g})$. It is neither an original reactant nor a final product but is formed in the first step of the mechanism and consumed in the second.

PRACTICE EXERCISE

For the reaction



the proposed mechanism is



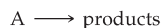
- (a) Is the proposed mechanism consistent with the equation for the overall reaction?
 (b) What is the molecularity of each step of the mechanism? (c) Identify the intermediate(s).

Answers: (a) Yes, the two equations add to yield the equation for the reaction. (b) The first elementary reaction is unimolecular, and the second one is bimolecular. (c) $\text{Mo}(\text{CO})_5$

Rate Laws for Elementary Reactions

In Section 14.3 we stressed that rate laws must be determined experimentally; they cannot be predicted from the coefficients of balanced chemical equations. We are now in a position to understand why this is so. Every reaction is made up of a series of one or more elementary steps, and the rate laws and relative speeds of these steps will dictate the overall rate law. Indeed, the rate law for a reaction can be determined from its mechanism, as we will see shortly. Thus, our next challenge in kinetics is to arrive at reaction mechanisms that lead to rate laws that are consistent with those observed experimentally. We will start by examining the rate laws of elementary reactions.

Elementary reactions are significant in a very important way: *If a reaction is an elementary reaction, then its rate law is based directly on its molecularity.* For example, consider a unimolecular process:



As the number of A molecules increases, the number that react in a given interval of time will increase proportionally. Thus, the rate of a unimolecular process will be first order:

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

TABLE 14.3 ■ Elementary Reactions and Their Rate Laws

Molecularity	Elementary Reaction	Rate Law
Unimolecular	$A \longrightarrow \text{products}$	Rate = $k[A]$
Bimolecular	$A + A \longrightarrow \text{products}$	Rate = $k[A]^2$
Bimolecular	$A + B \longrightarrow \text{products}$	Rate = $k[A][B]$
Termolecular	$A + A + A \longrightarrow \text{products}$	Rate = $k[A]^3$
Termolecular	$A + A + B \longrightarrow \text{products}$	Rate = $k[A]^2[B]$
Termolecular	$A + B + C \longrightarrow \text{products}$	Rate = $k[A][B][C]$

In the case of bimolecular elementary steps, the rate law is second order, as in the following example:

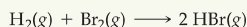


The second-order rate law follows directly from the collision theory. If we double the concentration of A, the number of collisions between molecules of A and B will double; likewise, if we double [B], the number of collisions will double. Therefore, the rate law will be first order in both [A] and [B], and second order overall.

The rate laws for all feasible elementary reactions are given in Table 14.3▲. Notice how the rate law for each kind of elementary reaction follows directly from the molecularity of that reaction. It is important to remember, however, that we cannot tell by merely looking at a balanced chemical equation whether the reaction involves one or several elementary steps.

■ SAMPLE EXERCISE 14.13 Predicting the Rate Law for an Elementary Reaction

If the following reaction occurs in a single elementary reaction, predict its rate law:



■ SOLUTION

Analyze: We are given the equation and asked for its rate law, assuming that it is an elementary process.

Plan: Because we are assuming that the reaction occurs as a single elementary reaction, we are able to write the rate law using the coefficients for the reactants in the equation as the reaction orders.

Solve: The reaction is bimolecular, involving one molecule of H_2 with one molecule of Br_2 . Thus, the rate law is first order in each reactant and second order overall:

$$\text{Rate} = k[\text{H}_2][\text{Br}_2]$$

Comment: Experimental studies of this reaction show that the reaction actually has a very different rate law:

$$\text{Rate} = k[\text{H}_2][\text{Br}_2]^{1/2}$$

Because the experimental rate law differs from the one obtained by assuming a single elementary reaction, we can conclude that the mechanism cannot occur by a single elementary step. It must, therefore, involve two or more elementary steps.

■ PRACTICE EXERCISE

Consider the following reaction: $2 \text{NO}(\text{g}) + \text{Br}_2(\text{g}) \longrightarrow 2 \text{NOBr}(\text{g})$. (a) Write the rate law for the reaction, assuming it involves a single elementary reaction. (b) Is a single-step mechanism likely for this reaction?

Answers: (a) Rate = $k[\text{NO}]^2[\text{Br}_2]$ (b) No, because termolecular reactions are very rare.

The Rate-Determining Step for a Multistep Mechanism

As with the reaction in Sample Exercise 14.13, most chemical reactions occur by mechanisms that involve two or more elementary reactions. Each of these steps of the mechanism has its own rate constant and activation energy. Often one of the steps is much slower than the others. The overall rate of a reaction cannot

exceed the rate of the slowest elementary step of its mechanism. Because the slow step limits the overall reaction rate, it is called the **rate-determining step** (or *rate-limiting step*).

To understand the concept of a rate-determining step, consider a toll road with two toll plazas (Figure 14.18). We will measure the rate at which cars pass through the second toll plaza. Cars enter the toll road at point 1 and pass through toll plaza A. They then pass an intermediate point 2 before passing through toll plaza B and arriving at point 3. We can therefore envision this trip along the toll road as occurring in two elementary steps:

Step 1: Point 1 \longrightarrow point 2 (through plaza A)

Step 2: Point 2 \longrightarrow point 3 (through plaza B)

Overall: Point 1 \longrightarrow point 3 (through plaza A and B)

Now suppose that several of the gates at toll plaza A are malfunctioning, so that traffic backs up behind it as depicted in Figure 14.18(a). The rate at which cars can get to point 3 is limited by the rate at which they can get through the traffic jam at plaza A. Thus, step 1 is the rate-determining step of the journey along the toll road. If, however, traffic flows quickly through plaza A but gets backed up at plaza B, as depicted in Figure 14.18(b), the number of cars builds up in the intermediate region between the plazas. In this case step 2 is rate determining: The rate at which cars can travel the toll road is limited by the rate at which they can pass through plaza B.

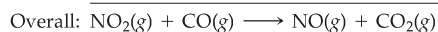
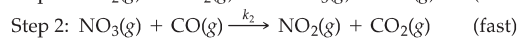
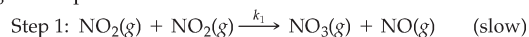
In the same way, *the slowest step in a multistep reaction limits the overall rate*. By analogy to Figure 14.18(a), the rate of a faster step following the rate-determining step does not speed up the overall rate. If the slow step is not the first one, as in Figure 14.18(b), the faster preceding steps produce intermediate products that accumulate before being consumed in the slow step. In either case *the rate-determining step governs the rate law for the overall reaction*.

GIVE IT SOME THOUGHT

Why can't the rate law for a reaction generally be deduced from the balanced equation for the reaction?

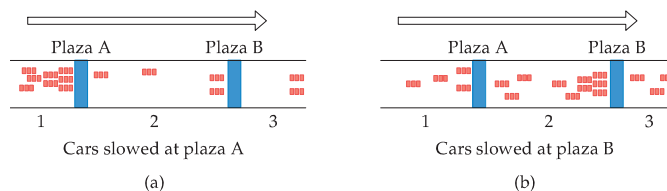
Mechanisms with a Slow Initial Step

We can most easily see the relationship between the slow step in a mechanism and the rate law for the overall reaction by considering an example in which the first step in a multistep mechanism is the slow, rate-determining step. As an example, consider the reaction of NO_2 and CO to produce NO and CO_2 (Equation 14.23). Below 225°C , it is found experimentally that the rate law for this reaction is second order in NO_2 and zero order in CO : $\text{Rate} = k[\text{NO}_2]^2$. Can we propose a reaction mechanism that is consistent with this rate law? Consider the following two-step mechanism:*



Step 2 is much faster than step 1; that is, $k_2 \gg k_1$. The intermediate $\text{NO}_3(\text{g})$ is slowly produced in step 1 and is immediately consumed in step 2.

*The subscript on the rate constant identifies the elementary step involved. Thus, k_1 is the rate constant for step 1, k_2 is the rate constant for step 2, and so forth. A negative subscript refers to the rate constant for the reverse of an elementary step. For example, k_{-1} is the rate constant for the reverse of the first step.



▲ **Figure 14.18 Rate-determining step.** The flow of traffic on a toll road illustrates how a rate-determining step controls reaction rate. The flow is limited by the flow of traffic through the slower toll plaza. In (a) the rate at which cars can reach point 3 is limited by how quickly they can get through plaza A. In this case, getting from point 1 to point 2 is the rate-determining step. In (b), getting from point 2 to point 3 is the rate-determining step.

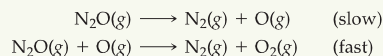
Because step 1 is slow and step 2 is fast, step 1 is rate determining. Thus, the rate of the overall reaction depends on the rate of step 1, and the rate law of the overall reaction equals the rate law of step 1. Step 1 is a bimolecular process that has the rate law

$$\text{Rate} = k_1[\text{NO}_2]^2$$

Thus, the rate law predicted by this mechanism agrees with the one observed experimentally. CO is absent from the rate law because it reacts in a step that follows the rate-determining step.

SAMPLE EXERCISE 14.14 Determining the Rate Law for a Multistep Mechanism

The decomposition of nitrous oxide, N_2O , is believed to occur by a two-step mechanism:



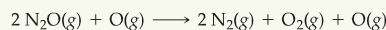
(a) Write the equation for the overall reaction. (b) Write the rate law for the overall reaction.

SOLUTION

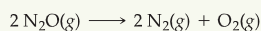
Analyze: Given a multistep mechanism with the relative speeds of the steps, we are asked to write the overall reaction and the rate law for that overall reaction.

Plan: (a) Find the overall reaction by adding the elementary steps and eliminating the intermediates. (b) The rate law for the overall reaction will be that of the slow, rate-determining step.

Solve: (a) Adding the two elementary reactions gives



Omitting the intermediate, $\text{O}(\text{g})$, which occurs on both sides of the equation, gives the overall reaction:

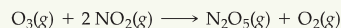


(b) The rate law for the overall reaction is just the rate law for the slow, rate-determining elementary reaction. Because that slow step is a unimolecular elementary reaction, the rate law is first order:

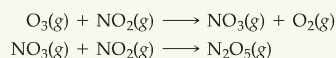
$$\text{Rate} = k[\text{N}_2\text{O}]$$

PRACTICE EXERCISE

Ozone reacts with nitrogen dioxide to produce dinitrogen pentoxide and oxygen:



The reaction is believed to occur in two steps:



The experimental rate law is $\text{rate} = k[\text{O}_3][\text{NO}_2]$. What can you say about the relative rates of the two steps of the mechanism?

Answer: Because the rate law conforms to the molecularity of the first step, that must be the rate-determining step. The second step must be much faster than the first one.

Mechanisms with a Fast Initial Step

It is less straightforward to derive the rate law for a mechanism in which an intermediate is a reactant in the rate-determining step. This situation arises in multistep mechanisms when the first step is fast and therefore *not* the rate-determining one.

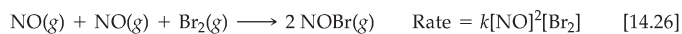
Let's consider one example: the gas-phase reaction of nitric oxide (NO) with bromine (Br_2).



The experimentally determined rate law for this reaction is second order in NO and first order in Br_2 :

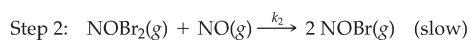
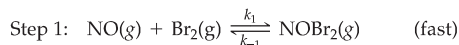
$$\text{Rate} = k[\text{NO}]^2[\text{Br}_2] \quad [14.25]$$

We seek a reaction mechanism that is consistent with this rate law. One possibility is that the reaction occurs in a single termolecular step:



As noted in Practice Exercise 14.13, this does not seem likely because termolecular processes are so rare.

Let's consider an alternative mechanism that does not invoke a termolecular step:



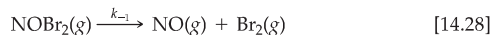
In this mechanism, step 1 actually involves two processes: a forward reaction and its reverse.

Because step 2 is the slow, rate-determining step, the rate law for that step governs the rate of the overall reaction:

$$\text{Rate} = k[\text{NOBr}_2][\text{NO}] \quad [14.27]$$

However, NOBr_2 is an intermediate generated in step 1. Intermediates are usually unstable molecules that have a low, unknown concentration. Thus, our rate law depends on the unknown concentration of an intermediate.

Fortunately, with the aid of some assumptions, we can express the concentration of the intermediate (NOBr_2) in terms of the concentrations of the starting reactants (NO and Br_2). We first assume that NOBr_2 is intrinsically unstable and that it does not accumulate to a significant extent in the reaction mixture. There are two ways for NOBr_2 to be consumed once it is formed: It can either react with NO to form NOBr or reform NO and Br_2 . The first of these possibilities is step 2, a slow process. The second is the reverse of step 1, a unimolecular process:



Because step 2 is slow, we assume that most of the NOBr_2 falls apart according to Equation 14.28. Thus, we have both the forward and reverse reactions of step 1 occurring much faster than step 2. Because the forward and reverse processes of step 1 occur rapidly with respect to the reaction in step 2, they establish an equilibrium. We have seen examples of dynamic equilibrium before, in the equilibrium between a liquid and its vapor \rightleftharpoons (Section 11.5) and between a solid solute and its solution. \rightleftharpoons (Section 13.3) As in any dynamic equilibrium, the rates of the forward and reverse reactions are equal. Thus, we can equate the rate expression for the forward reaction in step 1 with the rate expression for the reverse reaction:

$$\begin{array}{ccc} k_1[\text{NO}][\text{Br}_2] & = & k_{-1}[\text{NOBr}_2] \\ \text{Rate of forward reaction} & & \text{Rate of reverse reaction} \end{array}$$

Solving for $[\text{NOBr}_2]$, we have

$$[\text{NOBr}_2] = \frac{k_1}{k_{-1}} [\text{NO}][\text{Br}_2]$$

Substituting this relationship into the rate law for the rate-determining step (Equation 14.27), we have

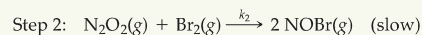
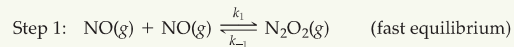
$$\text{Rate} = k_2 \frac{k_1}{k_{-1}} [\text{NO}][\text{Br}_2][\text{NO}] = k[\text{NO}]^2[\text{Br}_2]$$

This result is consistent with the experimental rate law (Equation 14.25). The experimental rate constant, k , equals k_2k_1/k_{-1} . This mechanism, which involves only unimolecular and bimolecular processes, is far more probable than the single termolecular step (Equation 14.26).

In general, *whenever a fast step precedes a slow one, we can solve for the concentration of an intermediate by assuming that an equilibrium is established in the fast step.*

■ SAMPLE EXERCISE 14.15 Deriving the Rate Law for a Mechanism with a Fast Initial Step

Show that the following mechanism for Equation 14.24 also produces a rate law consistent with the experimentally observed one:



SOLUTION

Analyze: We are given a mechanism with a fast initial step and asked to write the rate law for the overall reaction.

Plan: The rate law of the slow elementary step in a mechanism determines the rate law for the overall reaction. Thus, we first write the rate law based on the molecularity of the slow step. In this case the slow step involves the intermediate N_2O_2 as a reactant. Experimental rate laws, however, do not contain the concentrations of intermediates; instead they are expressed in terms of the concentrations of starting substances. Thus, we must relate the concentration of N_2O_2 to the concentration of NO by assuming that an equilibrium is established in the first step.

Solve: The second step is rate determining, so the overall rate is

$$\text{Rate} = k_2[\text{N}_2\text{O}_2][\text{Br}_2]$$

We solve for the concentration of the intermediate N_2O_2 by assuming that an equilibrium is established in step 1; thus, the rates of the forward and reverse reactions in step 1 are equal:

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$$

Solving for the concentration of the intermediate, N_2O_2 , gives

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

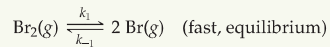
Substituting this expression into the rate expression gives

$$\text{Rate} = k_2 \frac{k_1}{k_{-1}} [\text{NO}]^2[\text{Br}_2] = k[\text{NO}]^2[\text{Br}_2]$$

Thus, this mechanism also yields a rate law consistent with the experimental one.

■ PRACTICE EXERCISE

The first step of a mechanism involving the reaction of bromine is



What is the expression relating the concentration of $\text{Br}(\text{g})$ to that of $\text{Br}_2(\text{g})$?

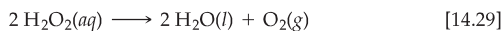
Answer: $[\text{Br}] = \left(\frac{k_1}{k_{-1}} [\text{Br}_2] \right)^{1/2}$

14.7 CATALYSIS

A **catalyst** is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself in the process. Catalysts are very common; most reactions in the body, the atmosphere, and the oceans occur with the help of catalysts. Much industrial chemical research is devoted to the search for new and more effective catalysts for reactions of commercial importance. Extensive research efforts also are devoted to finding means of inhibiting or removing certain catalysts that promote undesirable reactions, such as those that corrode metals, age our bodies, and cause tooth decay.

Homogeneous Catalysis

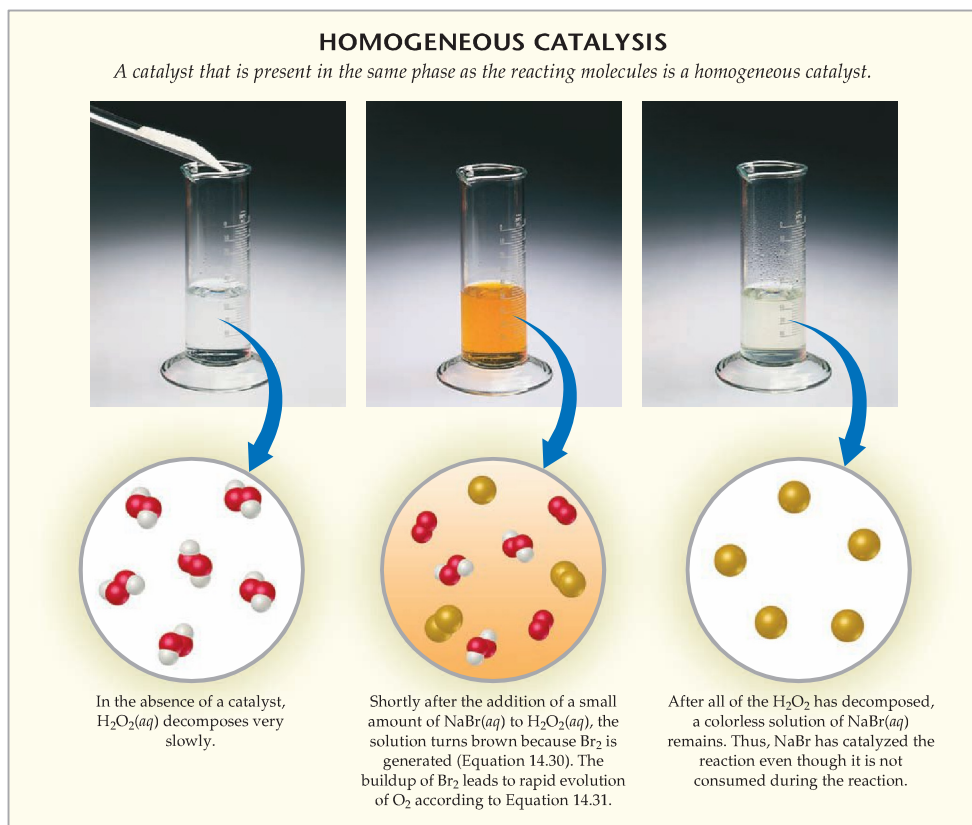
A catalyst that is present in the same phase as the reacting molecules is called a **homogeneous catalyst**. Examples abound both in solution and in the gas phase. Consider, for example, the decomposition of aqueous hydrogen peroxide, $\text{H}_2\text{O}_2(\text{aq})$, into water and oxygen:



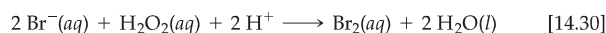
In the absence of a catalyst, this reaction occurs extremely slowly.

Many different substances are capable of catalyzing the reaction represented by Equation 14.29, including bromide ion, $\text{Br}^-(\text{aq})$, as shown in Figure 14.19 ▼.

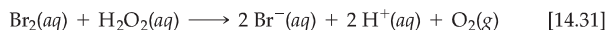
▼ **Figure 14.19 Effect of catalyst.** (H_2O molecules and Na^+ ions are omitted from the molecular art for clarity.)



The bromide ion reacts with hydrogen peroxide in acidic solution, forming aqueous bromine and water:

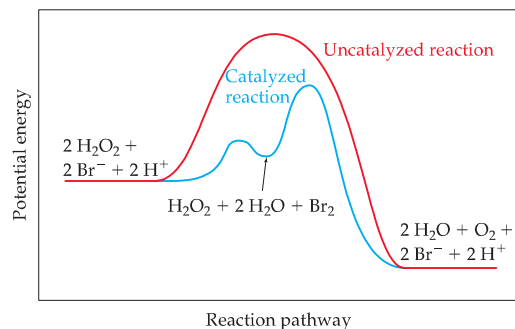
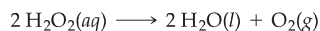


The brown color observed in the middle photograph of Figure 14.19 indicates the formation of $\text{Br}_2(aq)$. If this were the complete reaction, bromide ion would not be a catalyst, because it undergoes chemical change during the reaction. However, hydrogen peroxide also reacts with the $\text{Br}_2(aq)$ generated in Equation 14.30:



The bubbling evident in Figure 14.19(b) is due to the formation of $\text{O}_2(g)$.

The sum of Equations 14.30 and 14.31 is just Equation 14.29:



When H_2O_2 has been completely decomposed, we are left with a colorless solution of $\text{Br}^-(aq)$, as seen in the photograph on the right in Figure 14.19. Bromide ion, therefore, is indeed a catalyst of the reaction because it speeds the overall reaction without itself undergoing any net change. It is added at the start of the reaction, reacts, and then reforms at the end. In contrast, Br_2 is an intermediate because it is first formed (Equation 14.30) and then consumed (Equation 14.31). Neither the catalyst nor the intermediate appears in the chemical equation for the overall reaction. Notice, however, that *the catalyst is there at the start of the reaction, whereas the intermediate is formed during the course of the reaction.*

On the basis of the Arrhenius equation (Equation 14.19), the rate constant (k) is determined by the activation energy (E_a) and the frequency factor (A). A catalyst may affect the rate of reaction by altering the value of either E_a or A . The most dramatic catalytic effects come from lowering E_a . As a general rule, *a catalyst lowers the overall activation energy for a chemical reaction.*

A catalyst usually lowers the overall activation energy for a reaction by providing a different mechanism for the reaction. In the decomposition of hydrogen peroxide, for example, two successive reactions of H_2O_2 , with bromide and then with bromine, take place. Because these two reactions together serve as a catalytic pathway for hydrogen peroxide decomposition, *both* of them must have significantly lower activation energies than the uncatalyzed decomposition, as shown schematically in Figure 14.20 ◀.

GIVE IT SOME THOUGHT

How does a catalyst increase the rate of a reaction?

Heterogeneous Catalysis

A **heterogeneous catalyst** exists in a different phase from the reactant molecules, usually as a solid in contact with either gaseous reactants or with reactants in a liquid solution. Many industrially important reactions are catalyzed by the surfaces of solids. For example, hydrocarbon molecules are rearranged to form gasoline with the aid of what are called “cracking” catalysts (see the “Chemistry Put to Work” box in Section 25.3). Heterogeneous catalysts are often composed of metals or metal oxides. Because the catalyzed reaction occurs on the surface, special methods are often used to prepare catalysts so that they have very large surface areas.

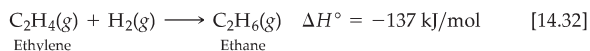
The initial step in heterogeneous catalysis is usually **adsorption** of reactants. *Adsorption* refers to the binding of molecules to a surface, whereas

▲ **Figure 14.20** Energy profiles for uncatalyzed and catalyzed reactions.

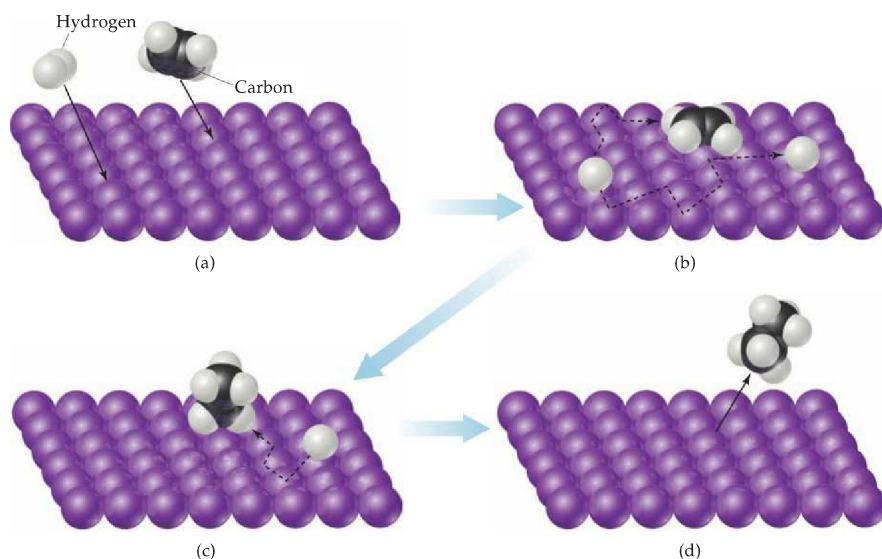
The energy profiles for the uncatalyzed decomposition of hydrogen peroxide and for the reaction as catalyzed by Br^- are compared. The catalyzed reaction involves two successive steps, each of which has a lower activation energy than the uncatalyzed reaction. Notice that the energies of reactants and products are unchanged by the catalyst.

absorption refers to the uptake of molecules into the interior of another substance. ∞ (Section 13.6) Adsorption occurs because the atoms or ions at the surface of a solid are extremely reactive. Unlike their counterparts in the interior of the substance, surface atoms and ions have unused bonding capacity. This unused bonding capability may be used to bond molecules from the gas or solution phase to the surface of the solid.

The reaction of hydrogen gas with ethylene gas to form ethane gas provides an example of heterogeneous catalysis:



Even though this reaction is exothermic, it occurs very slowly in the absence of a catalyst. In the presence of a finely powdered metal, however, such as nickel, palladium, or platinum, the reaction occurs rather easily at room temperature. The mechanism by which the reaction occurs is diagrammed in Figure 14.21 \blacktriangledown . Both ethylene and hydrogen are adsorbed on the metal surface [Figure 14.21(a)]. Upon adsorption the H—H bond of H_2 breaks, leaving two H atoms that are bonded to the metal surface, as shown in Figure 14.21(b). The hydrogen atoms are relatively free to move about the surface. When a hydrogen encounters an adsorbed ethylene molecule, it can form a σ bond to one of the carbon atoms, effectively destroying the C—C π bond and leaving an *ethyl group* (C_2H_5) bonded to the surface via a metal-to-carbon σ bond [Figure 14.21(c)]. This σ bond is relatively weak, so when the other carbon atom also encounters a hydrogen atom, a sixth C—H σ bond is readily formed and an ethane molecule is released from the metal surface [Figure 14.21(d)]. The site is ready to adsorb another ethylene molecule and thus begin the cycle again.

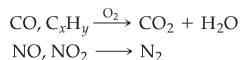


▲ Figure 14.21 Mechanism for reaction of ethylene with hydrogen on a catalytic surface. (a) The hydrogen and ethylene are adsorbed at the metal surface. (b) The H—H bond is broken to give adsorbed hydrogen atoms. (c) These migrate to the adsorbed ethylene and bond to the carbon atoms. (d) As C—H bonds are formed, the adsorption of the molecule to the metal surface is decreased and ethane is released.

Chemistry Put to Work CATALYTIC CONVERTERS

Heterogeneous catalysis plays a major role in the fight against urban air pollution. Two components of automobile exhausts that help form photochemical smog are nitrogen oxides and unburned hydrocarbons of various types (Section 18.4). In addition, automobile exhausts may contain considerable quantities of carbon monoxide. Even with the most careful attention to engine design, it is impossible under normal driving conditions to reduce the quantity of these pollutants to an acceptable level in the exhaust gases. It is therefore necessary to remove them from the exhaust before they are vented to the air. This removal is accomplished in the *catalytic converter*.

The catalytic converter, which is part of the exhaust system, must perform two distinct functions: (1) oxidation of CO and unburned hydrocarbons (C_xH_y) to carbon dioxide and water, and (2) reduction of nitrogen oxides to nitrogen gas:



These two functions require two distinctly different catalysts, so the development of a successful catalyst system is a difficult challenge. The catalysts must be effective over a wide range of operating temperatures. They must continue to be active despite the fact that various components of the exhaust can block the active sites of the catalyst. And the catalysts must be sufficiently rugged to withstand exhaust gas turbulence and the mechanical shocks of driving under various conditions for thousands of miles.

Catalysts that promote the combustion of CO and hydrocarbons are, in general, the transition-metal oxides and the noble metals, such as platinum. A mixture of two different metal oxides, CuO and Cr_2O_3 , might be used, for example. These materials are supported on a structure (Figure 14.22) that allows the best possible contact between the flowing exhaust gas and the catalyst surface. A honeycomb structure made from alumina (Al_2O_3) and impregnated with the catalyst is employed. Such catalysts operate by first adsorbing oxygen gas, also present in the exhaust gas. This adsorption weakens the O—O bond in O_2 , so that oxygen atoms are available for reaction with adsorbed CO to form CO_2 . Hydrocarbon oxidation probably proceeds somewhat similarly, with

the hydrocarbons first being adsorbed followed by rupture of a C—H bond.

The most effective catalysts for reduction of NO to yield N_2 and O_2 are transition-metal oxides and noble metals, the same kinds of materials that catalyze the oxidation of CO and hydrocarbons. The catalysts that are most effective in one reaction, however, are usually much less effective in the other. It is therefore necessary to have two different catalytic components.

Catalytic converters are remarkably efficient heterogeneous catalysts. The automotive exhaust gases are in contact with the catalyst for only 100 to 400 ms. In this very short time, 96% of the hydrocarbons and CO is converted to CO_2 and H_2O , and the emission of nitrogen oxides is reduced by 76%.

There are costs as well as benefits associated with the use of catalytic converters. Some of the metals used in the converters are very expensive. Catalytic converters currently account for about 35% of the platinum, 65% of the palladium, and 95% of the rhodium used annually. All of these metals, which come mainly from Russia and South Africa, are far more expensive than gold.

Related Exercises: 14.56, 14.75, and 14.76



▲ **Figure 14.22** Cross section of a catalytic converter. Automobiles are equipped with catalytic converters, which are part of their exhaust systems. The exhaust gases contain CO, NO, NO_2 , and unburned hydrocarbons that pass over surfaces impregnated with catalysts. The catalysts promote the conversion of the exhaust gases into CO_2 , H_2O , and N_2 .

GIVE IT SOME THOUGHT

How does a homogeneous catalyst compare with a heterogeneous one regarding the ease of recovery of the catalyst from the reaction mixture?

Enzymes

Many of the most interesting and important examples of catalysis involve reactions within living systems. The human body is characterized by an extremely complex system of interrelated chemical reactions. All these reactions must occur at carefully controlled rates to maintain life. A large number of

marvelously efficient biological catalysts known as **enzymes** are necessary for many of these reactions to occur at suitable rates. Most enzymes are large protein molecules with molecular weights ranging from about 10,000 to about 1 million amu. They are very selective in the reactions that they catalyze, and some are absolutely specific, operating for only one substance in only one reaction. The decomposition of hydrogen peroxide, for example, is an important biological process. Because hydrogen peroxide is strongly oxidizing, it can be physiologically harmful. For this reason, the blood and livers of mammals contain an enzyme, *catalase*, which catalyzes the decomposition of hydrogen peroxide into water and oxygen (Equation 14.29). Figure 14.23 shows the dramatic acceleration of this chemical reaction by the catalase in beef liver.

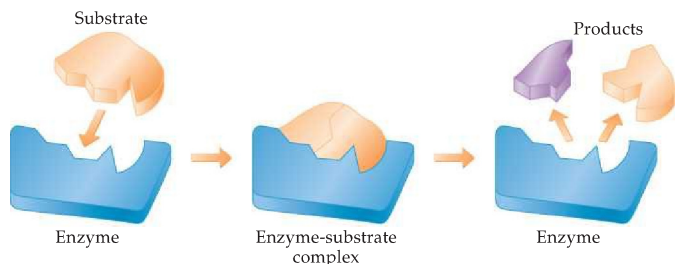


▲ **Figure 14.23 Effect of an enzyme.** Ground-up beef liver causes hydrogen peroxide to decompose rapidly into water and oxygen. The decomposition is catalyzed by the enzyme *catalase*. Grinding the liver breaks open the cells, so that the reaction takes place more rapidly. The frothing is due to escape of oxygen gas from the reaction mixture.

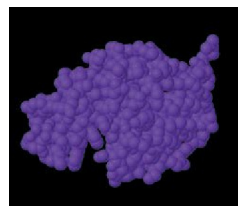
Although an enzyme is a large molecule, the reaction is catalyzed at a very specific location in the enzyme, called the **active site**. The substances that undergo reaction at this site are called **substrates**. The **lock-and-key model**, illustrated in Figure 14.24 ▼, provides a simple explanation for the specificity of an enzyme. The substrate is pictured as fitting neatly into a special place on the enzyme (the active site), much like a specific key fits into a lock. The active site is created by coiling and folding of the long protein molecule to form a space, something like a pocket, into which the substrate molecule fits. Figure 14.25 ► shows a model of the enzyme *lysozyme* with and without a bound substrate molecule.

The combination of the enzyme and the substrate is called the *enzyme-substrate complex*. Although Figure 14.24 shows both the active site and its complementary substrate as having rigid shapes, the active site is often fairly flexible. Thus, the active site may change shape as it binds the substrate. The binding between the substrate and the active site involves intermolecular forces such as dipole-dipole attractions, hydrogen bonds, and London dispersion forces. ∞ (Section 11.2)

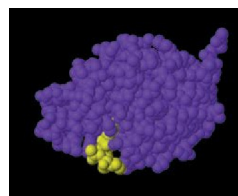
As the substrate molecules enter the active site, they are somehow activated, so that they are capable of extremely rapid reaction. This activation may result from the withdrawal or donation of electron density at a particular bond by the enzyme. In addition, in the process of fitting into the active site, the substrate molecule may be distorted and thus made more reactive. Once the reaction occurs, the products then depart, allowing another substrate molecule to enter.



▲ **Figure 14.24 The lock-and-key model for enzyme action.** The correct substrate is recognized by its ability to fit the active site of the enzyme, forming the enzyme-substrate complex. After the reaction of the substrate is complete, the products separate from the enzyme.



(a)



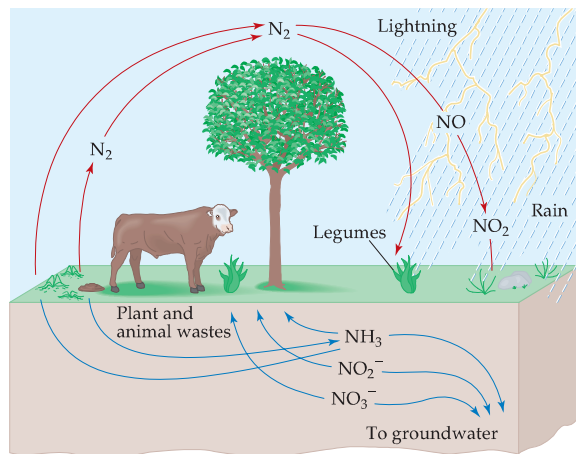
(b)

▲ **Figure 14.25 Molecular model of an enzyme.** (a) A molecular model of the enzyme *lysozyme*. Note the characteristic cleft, which is the location of the active site. (b) Lysozyme with a bound substrate molecule.

Nitrogen is one of the most essential elements in living organisms. It is found in many compounds that are vital to life, including proteins, nucleic acids, vitamins, and hormones. Plants use very simple nitrogen-containing compounds, especially NH_3 , NH_4^+ , and NO_3^- , as starting materials from which such complex, biologically necessary compounds are formed. Animals are unable to synthesize the complex nitrogen compounds they require from the simple substances used by plants. Instead, they rely on more complicated precursors present in vitamin- and protein-rich foods.

Nitrogen is continually cycling through this biological arena in various forms, as shown in the simplified nitrogen cycle in Figure 14.26. For example, certain microorganisms

convert the nitrogen in animal waste and dead plants and animals into molecular nitrogen, $\text{N}_2(\text{g})$, which returns to the atmosphere. For the food chain to be sustained, there must be a means of reincorporating this atmospheric N_2 in a form that plants can utilize. The process of converting N_2 into compounds that plants can use is called *nitrogen fixation*. Fixing nitrogen is difficult; N_2 is an exceptionally unreactive molecule, in large part because of its very strong $\text{N}\equiv\text{N}$ triple bond. ∞ (Section 8.3) Some fixed nitrogen results from the action of lightning on the atmosphere, and some is produced industrially using a process we will discuss in Chapter 15. About 60% of fixed nitrogen, however, is a consequence of the action of a remarkable and complex enzyme called *nitrogenase*. This enzyme



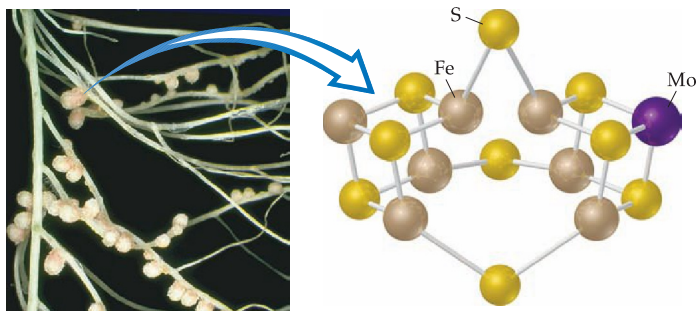
◀ **Figure 14.26 Simplified picture of the nitrogen cycle.** The compounds of nitrogen in the soil are water-soluble species, such as NH_3 , NO_2^- , and NO_3^- , which can be washed out of the soil by groundwater. These nitrogen compounds are converted into biomolecules by plants and are incorporated into animals that eat the plants. Certain bacteria that release N_2 to the atmosphere attack animal waste and dead plants and animals. Atmospheric N_2 is fixed in the soil predominantly by the action of certain plants that contain the enzyme nitrogenase, thereby completing the cycle.

The activity of an enzyme is destroyed if some molecule in the solution is able to bind strongly to the active site and block the entry of the substrate. Such substances are called *enzyme inhibitors*. Nerve poisons and certain toxic metal ions such as lead and mercury are believed to act in this way to inhibit enzyme activity. Some other poisons act by attaching elsewhere on the enzyme, thereby distorting the active site so that the substrate no longer fits.

Enzymes are enormously more efficient than ordinary nonbiochemical catalysts. The number of individual catalyzed reaction events occurring at a particular active site, called the *turnover number*, is generally in the range of 10^3 to 10^7 per second. Such large turnover numbers correspond to very low activation energies.

GIVE IT SOME THOUGHT

What names are given to the following aspects of enzymes and enzyme catalysis: (a) the place on the enzyme where catalysis occurs, (b) the substances that undergo catalysis?



▲ **Figure 14.27** The FeMo-cofactor of nitrogenase. Nitrogenase is found in nodules in the roots of certain plants, such as the white clover roots shown at the left. The cofactor, which is thought to be the active site of the enzyme, contains seven Fe atoms and one Mo atom, linked by sulfur atoms. The molecules on the outside of the cofactor connect it to the rest of the protein.

is *not* present in humans or other animals; rather, it is found in bacteria that live in the root nodules of certain plants such as the legumes clover and alfalfa.

Nitrogenase converts N_2 into NH_3 , a process that, in the absence of a catalyst, has a very large activation energy. This process is a *reduction* of nitrogen—during the reaction, its oxidation state is reduced from 0 in N_2 to -3 in NH_3 . The mechanism by which nitrogenase reduces N_2 is not fully understood. Like many other enzymes, including catalase, the active site of nitrogenase contains transition-metal atoms; such enzymes are called *metalloenzymes*. Because transition metals can readily change oxidation state, metalloenzymes are especially useful for effecting transformations in which substrates are either oxidized or reduced.

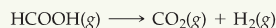
It has been known for nearly 20 years that a portion of nitrogenase contains iron and molybdenum atoms. This portion, called the *FeMo-cofactor*, is thought to serve as the active site of the enzyme. The FeMo-cofactor of nitrogenase is a striking cluster of seven Fe atoms and one Mo atom, all linked by sulfur atoms (Figure 14.27 ▲).

It is one of the wonders of life that simple bacteria can contain beautifully complex and vitally important enzymes such as nitrogenase. Because of this enzyme, nitrogen is continually cycled between its comparatively inert role in the atmosphere and its critical role in living organisms; without it, life as we know it could not exist on Earth.

Related Exercises: 14.79, 14.80, 14.102, 14.109

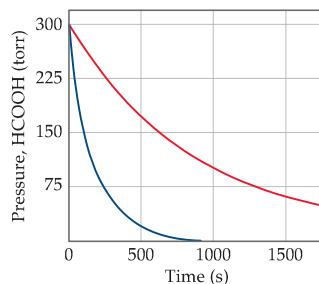
■ SAMPLE INTEGRATIVE EXERCISE | Putting Concepts Together

Formic acid (HCOOH) decomposes in the gas phase at elevated temperatures as follows:



The uncatalyzed decomposition reaction is determined to be first order. A graph of the partial pressure of HCOOH versus time for decomposition at 838 K is shown as the red curve in Figure 14.28 ►. When a small amount of solid ZnO is added to the reaction chamber, the partial pressure of acid versus time varies as shown by the blue curve in Figure 14.28.

- Estimate the half-life and first-order rate constant for formic acid decomposition.
- What can you conclude from the effect of added ZnO on the decomposition of formic acid?
- The progress of the reaction was followed by measuring the partial pressure of formic acid vapor at selected times. Suppose that, instead, we had plotted the concentration of formic acid in units of mol/L. What effect would this have had on the calculated value of k ?
- The pressure of formic acid vapor at the start of the reaction is 3.00×10^2 torr. Assuming constant temperature and ideal-gas behavior, what is the pressure in the



▲ **Figure 14.28** Variation in pressure of $\text{HCOOH}(g)$ as a function of time at 838 K. The red line corresponds to decomposition when only gaseous HCOOH is present. The blue line corresponds to decomposition in the presence of added $\text{ZnO}(s)$.

system at the end of the reaction? If the volume of the reaction chamber is 436 cm^3 , how many moles of gas occupy the reaction chamber at the end of the reaction?

(e) The standard heat of formation of formic acid vapor is $\Delta H_f^\circ = -378.6 \text{ kJ/mol}$. Calculate ΔH° for the overall reaction. If the activation energy (E_a) for the reaction is 184 kJ/mol , sketch an approximate energy profile for the reaction, and label E_a , ΔH° , and the transition state.

SOLUTION

(a) The initial pressure of HCOOH is $3.00 \times 10^2 \text{ torr}$. On the graph we move to the level at which the partial pressure of HCOOH is $1.50 \times 10^2 \text{ torr}$, half the initial value. This corresponds to a time of about $6.60 \times 10^2 \text{ s}$, which is therefore the half-life. The first-order rate constant is given by Equation 14.15: $k = 0.693/t_{1/2} = 0.693/660 \text{ s} = 1.05 \times 10^{-3} \text{ s}^{-1}$.

(b) The reaction proceeds much more rapidly in the presence of solid ZnO , so the surface of the oxide must be acting as a catalyst for the decomposition of the acid. This is an example of heterogeneous catalysis.

(c) If we had graphed the concentration of formic acid in units of moles per liter, we would still have determined that the half-life for decomposition is 660 seconds, and we would have computed the same value for k . Because the units for k are s^{-1} , the value for k is independent of the units used for concentration.

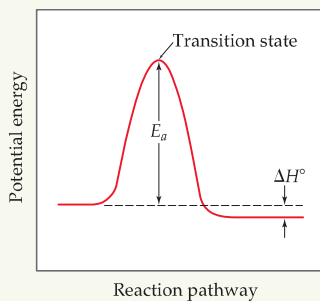
(d) According to the stoichiometry of the reaction, two moles of product are formed for each mole of reactant. When reaction is completed, therefore, the pressure will be 600 torr, just twice the initial pressure, assuming ideal-gas behavior. (Because we are working at quite high temperature and fairly low gas pressure, assuming ideal-gas behavior is reasonable.) The number of moles of gas present can be calculated using the ideal-gas equation (Section 10.4):

$$n = \frac{PV}{RT} = \frac{(600/760 \text{ atm})(0.436 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(838 \text{ K})} = 5.00 \times 10^{-3} \text{ moles}$$

(e) We first calculate the overall change in energy, ΔH° (Section 5.7 and Appendix C), as in

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ(\text{CO}_2(\text{g})) + \Delta H_f^\circ(\text{H}_2(\text{g})) - \Delta H_f^\circ(\text{HCOOH}(\text{g})) \\ &= -393.5 \text{ kJ/mol} + 0 - (-378.6 \text{ kJ/mol}) \\ &= -14.9 \text{ kJ/mol} \end{aligned}$$

From this and the given value for E_a , we can draw an approximate energy profile for the reaction, in analogy to Figure 14.15.



CHAPTER REVIEW

SUMMARY AND KEY TERMS

Introduction and Section 14.1 In this chapter we explored **chemical kinetics**, the area of chemistry that studies the rates of chemical reactions and the factors that affect them, namely, concentration, temperature, and catalysts.

Section 14.2 **Reaction rates** are usually expressed as changes in concentration per unit time: Typically, for reactions in solution, rates are given in units of molarity per second M/s . For most reactions, a plot of molarity versus time shows that the rate slows down as the reaction proceeds. The **instantaneous rate** is the slope of a line drawn tangent to the concentration-versus-time curve at a specific time. Rates can be written in terms of the appearance of products or the disappearance of reactants; the stoichiometry of the reaction dictates the relationship between rates of appearance and disappearance. Spectroscopy is one technique that can be used to monitor the course of a reaction. According to **Beer's law**, the absorption of electromagnetic radiation by a substance at a particular wavelength is directly proportional to its concentration.

Section 14.3 The quantitative relationship between rate and concentration is expressed by a **rate law**, which usually has the following form:

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \dots$$

The constant k in the rate law is called the **rate constant**; the exponents m , n , and so forth are called **reaction orders** for the reactants. The sum of the reaction orders gives the **overall reaction order**. Reaction orders must be determined experimentally. The units of the rate constant depend on the overall reaction order. For a reaction in which the overall reaction order is 1, k has units of s^{-1} ; for one in which the overall reaction order is 2, k has units of $M^{-1} s^{-1}$.

Section 14.4 Rate laws can be used to determine the concentrations of reactants or products at any time during a reaction. In a **first-order reaction** the rate is proportional to the concentration of a single reactant raised to the first power: $\text{Rate} = k[A]$. In such cases the integrated form of the rate law is $\ln[A]_t = -kt + \ln[A]_0$, where $[A]_t$ is the concentration of reactant A at time t , k is the rate constant, and $[A]_0$ is the initial concentration of A. Thus, for a first-order reaction, a graph of $\ln[A]$ versus time yields a straight line of slope $-k$.

A **second-order reaction** is one for which the overall reaction order is 2. If a second-order rate law depends on the concentration of only one reactant, then $\text{rate} = k[A]^2$, and the time dependence of $[A]$ is given by the integrated form of the rate law: $1/[A]_t = 1/[A]_0 + kt$. In this case a graph of $1/[A]_t$ versus time yields a straight line.

The **half-life** of a reaction, $t_{1/2}$, is the time required for the concentration of a reactant to drop to one-half of its original value. For a first-order reaction, the half-life depends only on the rate constant and not on the initial concentration: $t_{1/2} = 0.693/k$. The half-life of a second-order reaction depends on both the rate constant and the initial concentration of A: $t_{1/2} = 1/k[A]_0$.

Section 14.5 The **collision model**, which assumes that reactions occur as a result of collisions between molecules, helps explain why the magnitudes of rate constants increase with increasing temperature. The greater the kinetic energy of the colliding molecules, the greater is the energy of collision. The minimum energy required for a reaction to occur is called the **activation energy**, E_a . A collision with energy E_a or greater can cause the atoms of the colliding molecules to reach the **activated complex** (or **transition state**), which is the highest energy arrangement in the pathway from reactants to products. Even if a collision is energetic enough, it may not lead to reaction; the reactants must also be correctly oriented relative to one another in order for a collision to be effective.

Because the kinetic energy of molecules depends on temperature, the rate constant of a reaction is very dependent on temperature. The relationship between k and temperature is given by the **Arrhenius equation**: $k = Ae^{-E_a/RT}$. The term A is called the **frequency factor**; it relates to the number of collisions that are favorably oriented for reaction. The Arrhenius equation is often used in logarithmic form: $k = \ln A - E_a/RT$. Thus, a graph of $\ln k$ versus $1/T$ yields a straight line with slope $-E_a/R$.

Section 14.6 A **reaction mechanism** details the individual steps that occur in the course of a reaction. Each of these steps, called **elementary reactions**, has a well-defined rate law that depends on the number of molecules (the **molecularity**) of the step. Elementary reactions are defined as either **unimolecular**, **bimolecular**, or **termolecular**, depending on whether one, two, or three reactant molecules are involved, respectively. Termolecular elementary reactions are very rare. Unimolecular, bimolecular, and termolecular reactions follow rate laws that are first order overall, second order overall, and third order overall, respectively. Many reactions occur by a multistep mechanism, involving two or more elementary reactions, or steps. An **intermediate** is produced in one elementary step, is consumed in a later elementary step, and therefore does not appear in the overall equation for the reaction. When a mechanism has several elementary steps, the overall rate is limited by the slowest elementary step, called the **rate-determining step**. A fast elementary step that follows the rate-determining step will have no effect on the rate law of the reaction. A fast step

that precedes the rate-determining step often creates an equilibrium that involves an intermediate. For a mechanism to be valid, the rate law predicted by the mechanism must be the same as that observed experimentally.

Section 14.7 A **catalyst** is a substance that increases the rate of a reaction without undergoing a net chemical change itself. It does so by providing a different mechanism for the reaction, one that has a lower activation energy. A **homogeneous catalyst** is one that is in the same phase as the reactants. A **heterogeneous catalyst** has a different phase from the reactants. Finely divided metals are often used as heterogeneous catalysts for solution-

and gas-phase reactions. Reacting molecules can undergo binding, or **adsorption**, at the surface of the catalyst. The adsorption of a reactant at specific sites on the surface makes bond breaking easier, lowering the activation energy. Catalysis in living organisms is achieved by **enzymes**, large protein molecules that usually catalyze a very specific reaction. The specific reactant molecules involved in an enzymatic reaction are called **substrates**. The site of the enzyme where the catalysis occurs is called the **active site**. In the **lock-and-key model** for enzyme catalysis, substrate molecules bind very specifically to the active site of the enzyme, after which they can undergo reaction.

KEY SKILLS

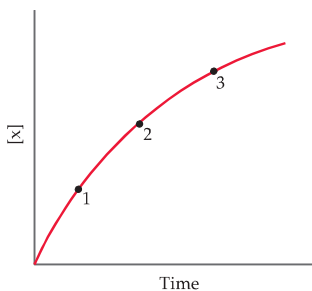
- Understand the factors that affect the rate of chemical reactions.
- Be able to determine the rate of a reaction given time and concentration.
- Be able to relate the rate of formation of products and the rate of disappearance of reactants given the balanced chemical equation for the reaction.
- Understand the form and meaning of a rate law including the ideas of reaction order and rate constant.
- Be able to determine the rate law and rate constant for a reaction from a series of experiments given the measured rates for various concentrations of reactants.
- Be able to use the integrated form of a rate law to determine the concentration of a reactant at a given time.
- Explain how the activation energy affects a rate and be able to use the Arrhenius Equation.
- Be able to predict a rate law for a reaction having a multistep mechanism given the individual steps in the mechanism.
- Explain how a catalyst works.

KEY EQUATIONS

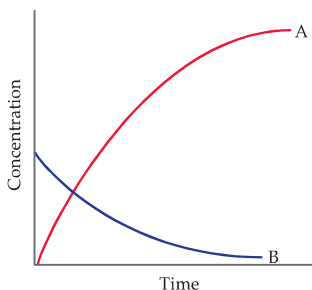
- $\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$ [14.4] Relating rates to the components of a balanced chemical equation
- $\text{Rate} = k[A]^m[B]^n$ [14.7] General form of a rate law
- $\ln[A]_t - \ln[A]_0 = -kt$ or $\ln \frac{[A]_t}{[A]_0} = -kt$ [14.12] The integrated form of a first-order rate law
- $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ [14.14] The integrated form of the second-order rate law
- $t_{1/2} = \frac{0.693}{k}$ [14.15] Relating the half-life and rate constant for a first-order reaction
- $k = Ae^{-E_a/RT}$ [14.19] The Arrhenius equation, which expresses how the rate constant depends on temperature
- $\ln k = -\frac{E_a}{RT} + \ln A$ [14.20] Linear form of the Arrhenius equation

VISUALIZING CONCEPTS

- 14.1 Consider the following graph of the concentration of a substance over time. (a) Is X a reactant or product of the reaction? (b) Why is the average rate of the reaction greater between points 1 and 2 than between points 2 and 3? [Section 14.2]

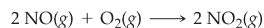


- 14.2 You study the rate of a reaction, measuring both the concentration of the reactant and the concentration of the product as a function of time, and obtain the following results:



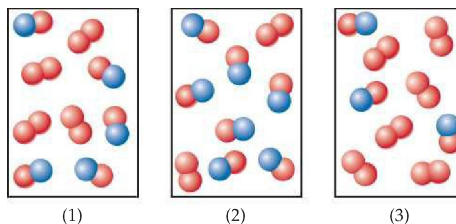
What chemical equation is consistent with this data:

- (a) $A \rightarrow B$, (b) $B \rightarrow A$, (c) $A \rightarrow 2B$,
 (d) $B \rightarrow 2A$. Explain your choice. [Section 14.2]
- 14.3 You perform a series of experiments for the reaction $A \rightarrow B + C$ and find that the rate law has the form $\text{rate} = k[A]^x$. Determine the value of x in each of the following cases: (a) There is no rate change when $[A]$ is tripled. (b) The rate increases by a factor of 9 when $[A]$ is tripled. (c) When $[A]$ is doubled, the rate increases by a factor of 8. [Section 14.3]
- 14.4 The following diagrams represent mixtures of $\text{NO}(g)$ and $\text{O}_2(g)$. These two substances react as follows:

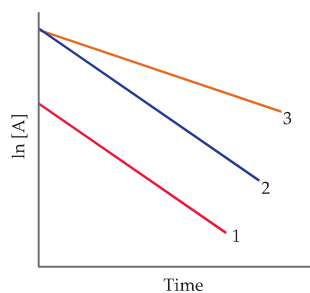


It has been determined experimentally that the rate is second order in NO and first order in O_2 . Based on this

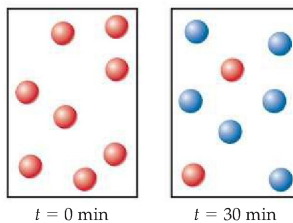
fact, which of the following mixtures will have the fastest initial rate? [Section 14.3]



- 14.5 A friend studies a first-order reaction and obtains the following three graphs for experiments done at two different temperatures. (a) Which two lines represent experiments done at the same temperature? What accounts for the difference in these two lines? In what way are they the same? (b) Which two lines represent experiments done with the same starting concentration but at different temperatures? Which line probably represents the lower temperature? How do you know? [Section 14.4]

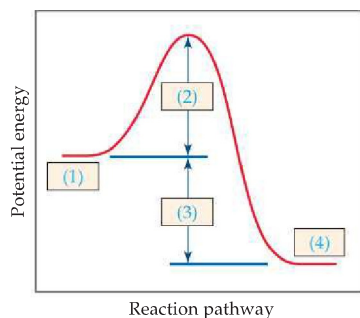


- 14.6 (a) Given the following diagrams at $t = 0$ and $t = 30$, what is the half-life of the reaction if it follows first-order kinetics?

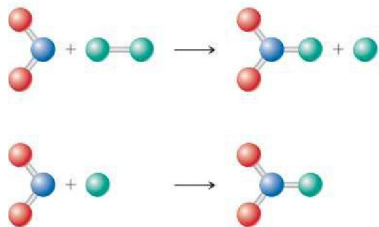


- (b) After four half-life periods for a first-order reaction, what fraction of reactant remains? [Section 14.4]

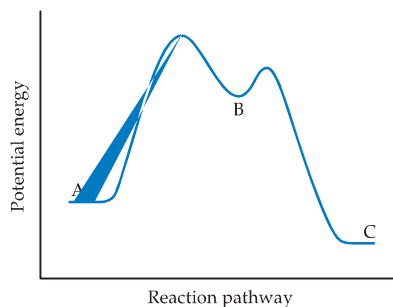
- 14.7 The following diagram shows the reaction profile of a reaction. Label the components indicated by the boxes. [Section 14.5]



- 14.8 You study the effect of temperature on the rate of two reactions and graph the natural logarithm of the rate constant for each reaction as a function of $1/T$. How do the two graphs compare (a) if the activation energy of the second reaction is higher than the activation energy of the first reaction but the two reactions have the same frequency factor, and (b) if the frequency factor of the second reaction is higher than the frequency factor of the first reaction but the two reactions have the same activation energy? [Section 14.5]
- 14.9 Consider the diagram below, which represents two steps in an overall reaction. The red spheres are oxygen, the blue ones nitrogen, and the green ones fluorine. (a) Write the chemical equation for each step in the reaction. (b) Write the equation for the overall reaction. (c) Identify the intermediate in the mechanism. (d) Write the rate law for the overall reaction if the first step is the slow, rate-determining step. [Section 14.6]



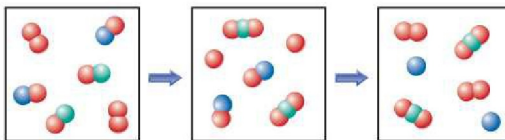
- 14.10 Based on the following reaction profile, how many intermediates are formed in the reaction $A \rightarrow C$? How many transition states are there? Which step is the fastest? Is the reaction $A \rightarrow C$ exothermic or endothermic? [Section 14.6]



- 14.11 Draw a possible transition state for the bimolecular reaction depicted below. (The blue spheres are nitrogen atoms, and the red ones are oxygen atoms.) Use dashed lines to represent the bonds that are in the process of being broken or made in the transition state. [Section 14.6]



- 14.12 The following diagram represents an imaginary two-step mechanism. Let the red spheres represent element A, the green ones element B, and the blue ones element C. (a) Write the equation for the net reaction that is occurring. (b) Identify the intermediate. (c) Identify the catalyst. [Sections 14.6 and 14.7]



EXERCISES

Reaction Rates

- 14.13 (a) What is meant by the term *reaction rate*? (b) Name three factors that can affect the rate of a chemical reaction. (c) What information is necessary to relate the rate of disappearance of reactants to the rate of appearance of products?
- 14.14 (a) What are the units usually used to express the rates of reactions occurring in solution? (b) From your everyday experience, give two examples of the effects of temperature on the rates of reactions. (c) What is the difference between average rate and instantaneous rate?

- 14.15 Consider the following hypothetical aqueous reaction: $A(aq) \rightarrow B(aq)$. A flask is charged with 0.065 mol of A in a total volume of 100.0 mL. The following data are collected:

Time (min)	0	10	20	30	40
Moles of A	0.065	0.051	0.042	0.036	0.031

(a) Calculate the number of moles of B at each time in the table, assuming that there are no molecules of B at time zero. (b) Calculate the average rate of disappearance of A for each 10-min interval, in units of M/s . (c) Between $t = 10$ min and $t = 30$ min, what is the average rate of appearance of B in units of M/s ? Assume that the volume of the solution is constant.

- 14.16 A flask is charged with 0.100 mol of A and allowed to react to form B according to the hypothetical gas-phase reaction $A(g) \longrightarrow B(g)$. The following data are collected:

Time (s)	0	40	80	120	160
Moles of A	0.100	0.067	0.045	0.030	0.020

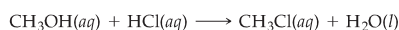
(a) Calculate the number of moles of B at each time in the table. (b) Calculate the average rate of disappearance of A for each 40-s interval, in units of mol/s . (c) What additional information would be needed to calculate the rate in units of concentration per time?

- 14.17 The isomerization of methyl isonitrile (CH_3NC) to acetonitrile (CH_3CN) was studied in the gas phase at 215 °C, and the following data were obtained:

Time (s)	$[CH_3NC] (M)$
0	0.0165
2,000	0.0110
5,000	0.00591
8,000	0.00314
12,000	0.00137
15,000	0.00074

(a) Calculate the average rate of reaction, in M/s , for the time interval between each measurement. (b) Graph $[CH_3NC]$ versus time, and determine the instantaneous rates in M/s at $t = 5000$ s and $t = 8000$ s.

- 14.18 The rate of disappearance of HCl was measured for the following reaction:

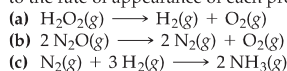


The following data were collected:

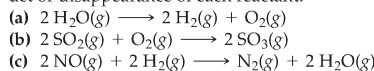
Time (min)	$[HCl] (M)$
0.0	1.85
54.0	1.58
107.0	1.36
215.0	1.02
430.0	0.580

- (a) Calculate the average rate of reaction, in M/s , for the time interval between each measurement. (b) Graph $[HCl]$ versus time, and determine the instantaneous rates in M/min and M/s at $t = 75.0$ min and $t = 250$ min.

- 14.19 For each of the following gas-phase reactions, indicate how the rate of disappearance of each reactant is related to the rate of appearance of each product:



- 14.20 For each of the following gas-phase reactions, write the rate expression in terms of the appearance of each product or disappearance of each reactant:



- 14.21 (a) Consider the combustion of $H_2(g)$: $2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(g)$. If hydrogen is burning at the rate of 0.85 mol/s, what is the rate of consumption of oxygen? What is the rate of formation of water vapor? (b) The reaction $2 NO(g) + Cl_2(g) \longrightarrow 2 NOCl(g)$ is carried out in a closed vessel. If the partial pressure of NO is decreasing at the rate of 23 torr/min, what is the rate of change of the total pressure of the vessel?

- 14.22 (a) Consider the combustion of ethylene, $C_2H_4(g) + 3 O_2(g) \longrightarrow 2 CO_2(g) + 2 H_2O(g)$. If the concentration of C_2H_4 is decreasing at the rate of 0.025 M/s , what are the rates of change in the concentrations of CO_2 and H_2O ? (b) The rate of decrease in N_2H_4 partial pressure in a closed reaction vessel from the reaction $N_2H_4(g) + H_2(g) \longrightarrow 2 NH_3(g)$ is 63 torr/h. What are the rates of change of NH_3 partial pressure and total pressure in the vessel?

Rate Laws

- 14.23 A reaction $A + B \longrightarrow C$ obeys the following rate law: $Rate = k[B]^2$. (a) If $[A]$ is doubled, how will the rate change? Will the rate constant change? Explain. (b) What are the reaction orders for A and B? What is the overall reaction order? (c) What are the units of the rate constant?
- 14.24 Consider a hypothetical reaction between A, B, and C that is first order in A, zero order in B, and second order in C. (a) Write the rate law for the reaction. (b) How does the rate change when $[A]$ is doubled and the other reactant concentrations are held constant? (c) How does the rate change when $[B]$ is tripled and the other reac-

tant concentrations are held constant? (d) How does the rate change when $[C]$ is tripled and the other reactant concentrations are held constant? (e) By what factor does the rate change when the concentrations of all three reactants are tripled?

- 14.25 The decomposition of N_2O_5 in carbon tetrachloride proceeds as follows: $2 N_2O_5 \longrightarrow 4 NO_2 + O_2$. The rate law is first order in N_2O_5 . At 64 °C the rate constant is $4.82 \times 10^{-3} s^{-1}$. (a) Write the rate law for the reaction. (b) What is the rate of reaction when $[N_2O_5] = 0.0240 M$? (c) What happens to the rate when the concentration of N_2O_5 is doubled to 0.0480 M ?

14.26 Consider the following reaction:



(a) The rate law for this reaction is first order in H_2 and second order in NO . Write the rate law. (b) If the rate constant for this reaction at 1000 K is $6.0 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$, what is the reaction rate when $[\text{NO}] = 0.035 \text{ M}$ and $[\text{H}_2] = 0.015 \text{ M}$? (c) What is the reaction rate at 1000 K when the concentration of NO is increased to 0.10 M , while the concentration of H_2 is 0.010 M ?

14.27 Consider the following reaction:



The rate law for this reaction is first order in CH_3Br and first order in OH^- . When $[\text{CH}_3\text{Br}]$ is $5.0 \times 10^{-3} \text{ M}$ and $[\text{OH}^-]$ is 0.050 M , the reaction rate at 298 K is 0.0432 M/s . (a) What is the value of the rate constant? (b) What are the units of the rate constant? (c) What would happen to the rate if the concentration of OH^- were tripled?

14.28 The reaction between ethyl bromide ($\text{C}_2\text{H}_5\text{Br}$) and hydroxide ion in ethyl alcohol at 330 K, $\text{C}_2\text{H}_5\text{Br}(alc) + \text{OH}^-(alc) \longrightarrow \text{C}_2\text{H}_5\text{OH}(l) + \text{Br}^-(alc)$, is first order each in ethyl bromide and hydroxide ion. When $[\text{C}_2\text{H}_5\text{Br}]$ is 0.0477 M and $[\text{OH}^-]$ is 0.100 M , the rate of disappearance of ethyl bromide is $1.7 \times 10^{-7} \text{ M/s}$. (a) What is the value of the rate constant? (b) What are the units of the rate constant? (c) How would the rate of disappearance of ethyl bromide change if the solution were diluted by adding an equal volume of pure ethyl alcohol to the solution?

14.29 The iodide ion reacts with hypochlorite ion (the active ingredient in chlorine bleaches) in the following way: $\text{OCl}^- + \text{I}^- \longrightarrow \text{OI}^- + \text{Cl}^-$. This rapid reaction gives the following rate data:

$[\text{OCl}^-] \text{ (M)}$	$[\text{I}^-] \text{ (M)}$	Rate (M/s)
1.5×10^{-3}	1.5×10^{-3}	1.36×10^{-4}
3.0×10^{-3}	1.5×10^{-3}	2.72×10^{-4}
1.5×10^{-3}	3.0×10^{-3}	2.72×10^{-4}

(a) Write the rate law for this reaction. (b) Calculate the rate constant. (c) Calculate the rate when $[\text{OCl}^-] = 2.0 \times 10^{-3} \text{ M}$ and $[\text{I}^-] = 5.0 \times 10^{-4} \text{ M}$.

14.30 The reaction $2 \text{ClO}_2(aq) + 2 \text{OH}^-(aq) \longrightarrow \text{ClO}_3^-(aq) + \text{ClO}_2^-(aq) + \text{H}_2\text{O}(l)$ was studied with the following results:

Experiment	$[\text{ClO}_2] \text{ (M)}$	$[\text{OH}^-] \text{ (M)}$	Rate (M/s)
1	0.060	0.030	0.0248
2	0.020	0.030	0.00276
3	0.020	0.090	0.00828

(a) Determine the rate law for the reaction. (b) Calculate the rate constant. (c) Calculate the rate when $[\text{ClO}_2] = 0.100 \text{ M}$ and $[\text{OH}^-] = 0.050 \text{ M}$.

14.31 The following data were measured for the reaction $\text{BF}_3(g) + \text{NH}_3(g) \longrightarrow \text{F}_3\text{BNH}_3(g)$:

Experiment	$[\text{BF}_3] \text{ (M)}$	$[\text{NH}_3] \text{ (M)}$	Initial Rate (M/s)
1	0.250	0.250	0.2130
2	0.250	0.125	0.1065
3	0.200	0.100	0.0682
4	0.350	0.100	0.1193
5	0.175	0.100	0.0596

(a) What is the rate law for the reaction? (b) What is the overall order of the reaction? (c) What is the value of the rate constant for the reaction? (d) What is the rate when $[\text{BF}_3] = 0.100 \text{ M}$ and $[\text{NH}_3] = 0.500 \text{ M}$?

14.32 The following data were collected for the rate of disappearance of NO in the reaction $2 \text{NO}(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}_2(g)$:

Experiment	$[\text{NO}] \text{ (M)}$	$[\text{O}_2] \text{ (M)}$	Initial Rate (M/s)
1	0.0126	0.0125	1.41×10^{-2}
2	0.0252	0.0125	5.64×10^{-2}
3	0.0252	0.0250	1.13×10^{-1}

(a) What is the rate law for the reaction? (b) What are the units of the rate constant? (c) What is the average value of the rate constant calculated from the three data sets? (d) What is the rate of disappearance of NO when $[\text{NO}] = 0.0750 \text{ M}$ and $[\text{O}_2] = 0.0100 \text{ M}$? (e) What is the rate of disappearance of O_2 at the concentrations given in part (d)?

14.33 Consider the gas-phase reaction between nitric oxide and bromine at 273°C : $2 \text{NO}(g) + \text{Br}_2(g) \longrightarrow 2 \text{NOBr}(g)$. The following data for the initial rate of appearance of NOBr were obtained:

Experiment	$[\text{NO}] \text{ (M)}$	$[\text{Br}_2] \text{ (M)}$	Initial Rate (M/s)
1	0.10	0.20	24
2	0.25	0.20	150
3	0.10	0.50	60
4	0.35	0.50	735

(a) Determine the rate law. (b) Calculate the average value of the rate constant for the appearance of NOBr from the four data sets. (c) How is the rate of appearance of NOBr related to the rate of disappearance of Br_2 ? (d) What is the rate of disappearance of Br_2 when $[\text{NO}] = 0.075 \text{ M}$ and $[\text{Br}_2] = 0.25 \text{ M}$?

14.34 Consider the reaction of peroxydisulfate ion ($\text{S}_2\text{O}_8^{2-}$) with iodide ion (I^-) in aqueous solution:



At a particular temperature the rate of disappearance of $\text{S}_2\text{O}_8^{2-}$ varies with reactant concentrations in the following manner:

Experiment	$[\text{S}_2\text{O}_8^{2-}]$ (M)	$[\text{I}^-]$ (M)	Initial Rate (M/s)
1	0.018	0.036	2.6×10^{-6}
2	0.027	0.036	3.9×10^{-6}
3	0.036	0.054	7.8×10^{-6}
4	0.050	0.072	1.4×10^{-5}

Change of Concentration with Time

14.35 (a) Define the following symbols that are encountered in rate equations: $[A]_0$, $t_{1/2}$, $[A]$, k . (b) What quantity, when graphed versus time, will yield a straight line for a first-order reaction?

14.36 (a) For a second-order reaction, what quantity, when graphed versus time, will yield a straight line? (b) How do the half-lives of first-order and second-order reactions differ?

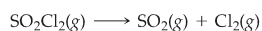
14.37 (a) The gas-phase decomposition of SO_2Cl_2 , $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$, is first order in SO_2Cl_2 . At 600 K the half-life for this process is 2.3×10^3 s. What is the rate constant at this temperature? (b) At 320 °C the rate constant is $2.2 \times 10^{-3} \text{ s}^{-1}$. What is the half-life at this temperature?

14.38 Molecular iodine, $\text{I}_2(\text{g})$, dissociates into iodine atoms at 625 K with a first-order rate constant of 0.271 s^{-1} . (a) What is the half-life for this reaction? (b) If you start with 0.050 M I_2 at this temperature, how much will remain after 5.12 s assuming that the iodine atoms do not recombine to form I_2 ?

14.39 As described in Exercise 14.37, the decomposition of sulfuric chloride (SO_2Cl_2) is a first-order process. The rate constant for the decomposition at 660 K is $4.5 \times 10^{-2} \text{ s}^{-1}$. (a) If we begin with an initial SO_2Cl_2 pressure of 375 torr, what is the pressure of this substance after 65 s? (b) At what time will the pressure of SO_2Cl_2 decline to one-tenth its initial value?

14.40 The first-order rate constant for the decomposition of N_2O_5 , $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$, at 70 °C is $6.82 \times 10^{-3} \text{ s}^{-1}$. Suppose we start with 0.0250 mol of N_2O_5 in a volume of 2.0 L. (a) How many moles of N_2O_5 will remain after 5.0 min? (b) How many minutes will it take for the quantity of N_2O_5 to drop to 0.010 mol? (c) What is the half-life of N_2O_5 at 70 °C?

14.41 The reaction



is first order in SO_2Cl_2 . Using the following kinetic data, determine the magnitude of the first-order rate constant:

(a) Determine the rate law for the reaction. (b) What is the average value of the rate constant for the disappearance of $\text{S}_2\text{O}_8^{2-}$ based on the four sets of data? (c) How is the rate of disappearance of $\text{S}_2\text{O}_8^{2-}$ related to the rate of disappearance of I^- ? (d) What is the rate of disappearance of I^- when $[\text{S}_2\text{O}_8^{2-}] = 0.025 \text{ M}$ and $[\text{I}^-] = 0.050 \text{ M}$?

Time (s)	Pressure SO_2Cl_2 (atm)
0	1.000
2,500	0.947
5,000	0.895
7,500	0.848
10,000	0.803

14.42 From the following data for the first-order gas-phase isomerization of CH_3NC at 215 °C, calculate the first-order rate constant and half-life for the reaction:

Time (s)	Pressure CH_3NC (torr)
0	502
2,000	335
5,000	180
8,000	95.5
12,000	41.7
15,000	22.4

14.43 Consider the data presented in Exercise 14.15. (a) By using appropriate graphs, determine whether the reaction is first order or second order. (b) What is the value of the rate constant for the reaction? (c) What is the half-life for the reaction?

14.44 Consider the data presented in Exercise 14.16. (a) Determine whether the reaction is first order or second order. (b) What is the value of the rate constant? (c) What is the half-life?

14.45 The gas-phase decomposition of NO_2 , $2 \text{NO}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$, is studied at 383 °C, giving the following data:

Time (s)	$[\text{NO}_2]$ (M)
0.0	0.100
5.0	0.017
10.0	0.0090
15.0	0.0062
20.0	0.0047

(a) Is the reaction first order or second order with respect to the concentration of NO_2 ? (b) What is the value of the rate constant?

- 14.46 Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), which is commonly known as table sugar, reacts in dilute acid solutions to form two simpler sugars, glucose and fructose, both of which have the formula $\text{C}_6\text{H}_{12}\text{O}_6$. At 23°C and in 0.5 M HCl , the following data were obtained for the disappearance of sucrose:

Time (min)	$[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$ (M)
0	0.316
39	0.274
80	0.238
140	0.190
210	0.146

(a) Is the reaction first order or second order with respect to $[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$? (b) What is the value of the rate constant?

Temperature and Rate

- 14.47 (a) What factors determine whether a collision between two molecules will lead to a chemical reaction? (b) According to the collision model, why does temperature affect the value of the rate constant?
- 14.48 (a) In which of the following reactions would you expect the orientation factor to be least important in leading to reaction? $\text{NO} + \text{O} \rightarrow \text{NO}_2$ or $\text{H} + \text{Cl} \rightarrow \text{HCl}$? (b) How does the kinetic-molecular theory help us understand the temperature dependence of chemical reactions?

- 14.49 Calculate the fraction of atoms in a sample of argon gas at 400 K that has an energy of 10.0 kJ or greater.

- 14.50 (a) The activation energy for the isomerization of methyl isonitrile (Figure 14.6) is 160 kJ/mol . Calculate the fraction of methyl isonitrile molecules that has an energy of 160.0 kJ or greater at 500 K . (b) Calculate this fraction for a temperature of 510 K . What is the ratio of the fraction at 510 K to that at 500 K ?

- 14.51 The gas-phase reaction $\text{Cl}(\text{g}) + \text{HBr}(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{Br}(\text{g})$ has an overall enthalpy change of -66 kJ . The activation energy for the reaction is 7 kJ . (a) Sketch the energy profile for the reaction, and label E_a and ΔE . (b) What is the activation energy for the reverse reaction?

- 14.52 For the elementary process $\text{N}_2\text{O}_5(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{NO}_3(\text{g})$ the activation energy (E_a) and overall ΔE are 154 kJ/mol , and 136 kJ/mol , respectively. (a) Sketch the energy profile for this reaction, and label E_a and ΔE . (b) What is the activation energy for the reverse reaction?

- 14.53 Based on their activation energies and energy changes and assuming that all collision factors are the same, which of the following reactions would be fastest and which would be slowest? Explain your answer.

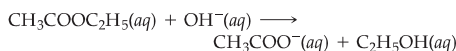
- (a) $E_a = 45\text{ kJ/mol}; \Delta E = -25\text{ kJ/mol}$
 (b) $E_a = 35\text{ kJ/mol}; \Delta E = -10\text{ kJ/mol}$
 (c) $E_a = 55\text{ kJ/mol}; \Delta E = 10\text{ kJ/mol}$

- 14.54 Which of the reactions in Exercise 14.53 will be fastest in the reverse direction? Which will be slowest? Explain.

- 14.55 A certain first-order reaction has a rate constant of $2.75 \times 10^{-2}\text{ s}^{-1}$ at 20°C . What is the value of k at 60°C if (a) $E_a = 75.5\text{ kJ/mol}$; (b) $E_a = 125\text{ kJ/mol}$?

- 14.56 Understanding the high-temperature behavior of nitrogen oxides is essential for controlling pollution generated in automobile engines. The decomposition of nitric oxide (NO) to N_2 and O_2 is second order with a rate constant of $0.0796\text{ M}^{-1}\text{ s}^{-1}$ at 737°C and $0.0815\text{ M}^{-1}\text{ s}^{-1}$ at 947°C . Calculate the activation energy for the reaction.

- 14.57 The rate of the reaction



was measured at several temperatures, and the following data were collected:

Temperature ($^\circ\text{C}$)	k ($\text{M}^{-1}\text{ s}^{-1}$)
15	0.0521
25	0.101
35	0.184
45	0.332

Using these data, graph $\ln k$ versus $1/T$. Using your graph, determine the value of E_a .

- 14.58 The temperature dependence of the rate constant for the reaction is tabulated as follows:

Temperature (K)	k ($\text{M}^{-1}\text{ s}^{-1}$)
600	0.028
650	0.22
700	1.3
750	6.0
800	23

Calculate E_a and A .

- [14.59] The activation energy of a certain reaction is 65.7 kJ/mol . How many times faster will the reaction occur at 50°C than at 0°C ?

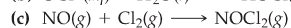
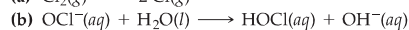
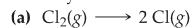
- [14.60] The following is a quote from an article in the August 18, 1998, issue of *The New York Times* about the breakdown of cellulose and starch: "A drop of 18 degrees Fahrenheit [from 77°F to 59°F] lowers the reaction rate six times; a 36-degree drop [from 77°F to 41°F] produces a fortyfold decrease in the rate." (a) Calculate activation energies for the breakdown process based on the two estimates of the effect of temperature on rate. Are the values consistent? (b) Assuming the value of E_a calculated from the 36-degree drop and that the rate of breakdown is first order with a half-life at 25°C of 2.7 years, calculate the half-life for breakdown at a temperature of -15°C .

Reaction Mechanisms

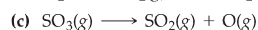
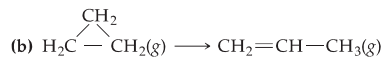
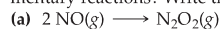
14.61 (a) What is meant by the term *elementary reaction*? (b) What is the difference between a *unimolecular* and a *bimolecular elementary reaction*? (c) What is a *reaction mechanism*?

14.62 (a) What is meant by the term *molecularity*? (b) Why are termolecular elementary reactions so rare? (c) What is an *intermediate* in a mechanism?

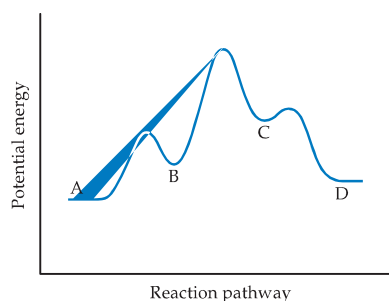
14.63 What is the molecularity of each of the following elementary reactions? Write the rate law for each.



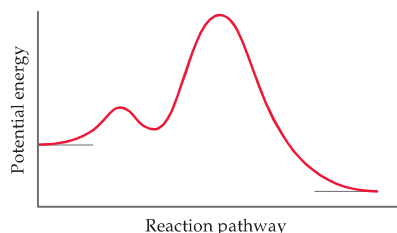
14.64 What is the molecularity of each of the following elementary reactions? Write the rate law for each.



14.65 (a) Based on the following reaction profile, how many intermediates are formed in the reaction $\text{A} \longrightarrow \text{D}$? (b) How many transition states are there? (c) Which step is the fastest? (d) Is the reaction $\text{A} \longrightarrow \text{D}$ exothermic or endothermic?

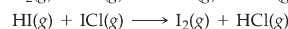
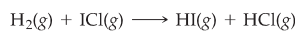


14.66 Consider the following energy profile.



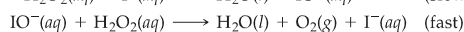
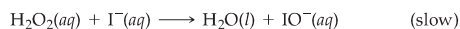
(a) How many elementary reactions are in the reaction mechanism? (b) How many intermediates are formed in the reaction? (c) Which step is rate limiting? (d) Is the overall reaction exothermic or endothermic?

14.67 The following mechanism has been proposed for the gas-phase reaction of H_2 with ICl :



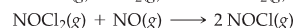
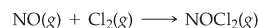
(a) Write the balanced equation for the overall reaction. (b) Identify any intermediates in the mechanism. (c) Write rate laws for each elementary reaction in the mechanism. (d) If the first step is slow and the second one is fast, what rate law do you expect to be observed for the overall reaction?

14.68 The decomposition of hydrogen peroxide is catalyzed by iodide ion. The catalyzed reaction is thought to proceed by a two-step mechanism:



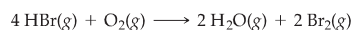
(a) Write the rate law for each of the elementary reactions of the mechanism. (b) Write the chemical equation for the overall process. (c) Identify the intermediate, if any, in the mechanism. (d) Assuming that the first step of the mechanism is rate determining, predict the rate law for the overall process.

14.69 The reaction $2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2 \text{NOCl}(\text{g})$ obeys the rate law, $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$. The following mechanism has been proposed for this reaction:

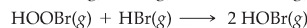
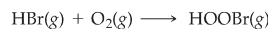


(a) What would the rate law be if the first step were rate determining? (b) Based on the observed rate law, what can we conclude about the relative rates of the two steps?

14.70 You have studied the gas-phase oxidation of HBr by O_2 :



You find the reaction to be first order with respect to HBr and first order with respect to O_2 . You propose the following mechanism:



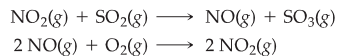
(a) Indicate how the elementary reactions add to give the overall reaction. (*Hint*: You will need to multiply the coefficients of one of the equations by 2.) (b) Based on the rate law, which step is rate determining? (c) What are the intermediates in this mechanism? (d) If you are unable to detect HOBr or HOOBr among the products, does this disprove your mechanism?

Catalysis

14.71 (a) What part of the energy profile of a reaction is affected by a catalyst? (b) What is the difference between a homogeneous and a heterogeneous catalyst?

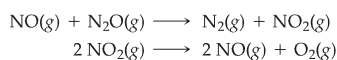
14.72 (a) Most heterogeneous catalysts of importance are extremely finely divided solid materials. Why is particle size important? (b) What role does adsorption play in the action of a heterogeneous catalyst?

14.73 The oxidation of SO_2 to SO_3 is catalyzed by NO_2 . The reaction proceeds as follows:



(a) Show that the two reactions can be summed to give the overall oxidation of SO_2 by O_2 to give SO_3 . (*Hint*: The top reaction must be multiplied by a factor so the NO and NO_2 cancel out.) (b) Why do we consider NO_2 a catalyst and not an intermediate in this reaction? (c) Is this an example of homogeneous catalysis or heterogeneous catalysis?

14.74 NO catalyzes the decomposition of N_2O , possibly by the following mechanism:



(a) What is the chemical equation for the overall reaction? Show how the two steps can be added to give the overall equation. (b) Why is NO considered a catalyst and not an intermediate? (c) If experiments show that during the decomposition of N_2O , NO_2 does not accumulate in measurable quantities, does this rule out the proposed mechanism? If you think not, suggest what might be going on.

14.75 Many metallic catalysts, particularly the precious-metal ones, are often deposited as very thin films on a substance of high surface area per unit mass, such as alumina (Al_2O_3) or silica (SiO_2). (a) Why is this an effective way of utilizing the catalyst material? (b) How does the surface area affect the rate of reaction?

14.76 (a) If you were going to build a system to check the effectiveness of automobile catalytic converters on cars, what substances would you want to look for in the car exhaust? (b) Automobile catalytic converters have to work at high temperatures, as hot exhaust gases stream through them. In what ways could this be an advantage? In what ways a disadvantage? (c) Why is the rate of flow of exhaust gases over a catalytic converter important?

14.77 When D_2 reacts with ethylene (C_2H_4) in the presence of a finely divided catalyst, ethane with two deuteriums, $\text{CH}_2\text{D}-\text{CH}_2\text{D}$, is formed. (Deuterium, D , is an isotope of hydrogen of mass 2.) Very little ethane forms in which two deuteriums are bound to one carbon (for example, CH_3-CHD_2). Use the sequence of steps involved in the reaction to explain why this is so.

14.78 Heterogeneous catalysts that perform hydrogenation reactions, as illustrated in Figure 14.21, are subject to poisoning, which shuts down their catalytic ability. Compounds of sulfur are often poisons. Suggest a mechanism by which such compounds might act as poisons.

14.79 (a) Explain the importance of enzymes in biological systems. (b) What chemical transformations are catalyzed (i) by the enzyme catalase, (ii) by nitrogenase?

14.80 There are literally thousands of enzymes at work in complex living systems such as human beings. What properties of the enzymes give rise to their ability to distinguish one substrate from another?

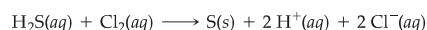
[14.81] The activation energy of an uncatalyzed reaction is 95 kJ/mol. The addition of a catalyst lowers the activation energy to 55 kJ/mol. Assuming that the collision factor remains the same, by what factor will the catalyst increase the rate of the reaction at (a) 25 °C, (b) 125 °C?

[14.82] Suppose that a certain biologically important reaction is quite slow at physiological temperature (37 °C) in the absence of a catalyst. Assuming that the collision factor remains the same, by how much must an enzyme lower the activation energy of the reaction in order to achieve a 1×10^5 -fold increase in the reaction rate?

ADDITIONAL EXERCISES

14.83 Explain why rate laws generally cannot be written from balanced equations. Under what circumstance is the rate law related directly to the balanced equation for a reaction?

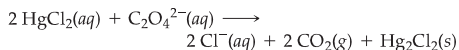
14.84 Hydrogen sulfide (H_2S) is a common and troublesome pollutant in industrial wastewaters. One way to remove H_2S is to treat the water with chlorine, in which case the following reaction occurs:



The rate of this reaction is first order in each reactant. The rate constant for the disappearance of H_2S at 28 °C is $3.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. If at a given time the concentration of H_2S is $2.0 \times 10^{-4} \text{ M}$ and that of Cl_2 is 0.025 M, what is the rate of formation of Cl^- ?

14.85 The reaction $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g})$ is second order in NO and first order in O_2 . When $[\text{NO}] = 0.040 \text{ M}$ and $[\text{O}_2] = 0.035 \text{ M}$, the observed rate of disappearance of NO is $9.3 \times 10^{-5} \text{ M/s}$. (a) What is the rate of disappearance of O_2 at this moment? (b) What is the value of the rate constant? (c) What are the units of the rate constant? (d) What would happen to the rate if the concentration of NO were increased by a factor of 1.8?

14.86 Consider the following reaction between mercury(II) chloride and oxalate ion:



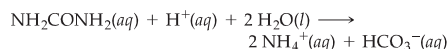
The initial rate of this reaction was determined for several concentrations of HgCl_2 and $\text{C}_2\text{O}_4^{2-}$, and the

following rate data were obtained for the rate of disappearance of $C_2O_4^{2-}$:

Experiment	$[HgCl_2] (M)$	$[C_2O_4^{2-}] (M)$	Rate (M/s)
1	0.164	0.15	3.2×10^{-5}
2	0.164	0.45	2.9×10^{-4}
3	0.082	0.45	1.4×10^{-4}
4	0.246	0.15	4.8×10^{-5}

(a) What is the rate law for this reaction? (b) What is the value of the rate constant? (c) What is the reaction rate when the concentration of $HgCl_2$ is 0.100 M and that of $(C_2O_4^{2-})$ is 0.25 M, if the temperature is the same as that used to obtain the data shown?

- 14.87 The reaction $2 NO_2 \rightarrow 2 NO + O_2$ has the rate constant $k = 0.63 M^{-1} s^{-1}$. Based on the units for k , is the reaction first or second order in NO_2 ? If the initial concentration of NO_2 is 0.100 M, how would you determine how long it would take for the concentration to decrease to 0.025 M?
- 14.88 Consider two reactions. Reaction (1) has a constant half-life, whereas reaction (2) has a half-life that gets longer as the reaction proceeds. What can you conclude about the rate laws of these reactions from these observations?
- 14.89 (a) The reaction $H_2O_2(aq) \rightarrow H_2O(l) + \frac{1}{2} O_2(g)$, is first order. Near room temperature, the rate constant equals $7.0 \times 10^{-4} s^{-1}$. Calculate the half-life at this temperature. (b) At 415 °C, $(CH_2)_2O$ decomposes in the gas phase, $(CH_2)_2O(g) \rightarrow CH_4(g) + CO(g)$. If the reaction is first order with a half-life of 56.3 min at this temperature, calculate the rate constant in s^{-1} .
- 14.90 Americium-241 is used in smoke detectors. It has a rate constant for radioactive decay of $k = 1.6 \times 10^{-3} yr^{-1}$. By contrast, iodine-125, which is used to test for thyroid functioning, has a rate constant for radioactive decay of $k = 0.011 day^{-1}$. (a) What are the half-lives of these two isotopes? (b) Which one decays at a faster rate? (c) How much of a 1.00-mg sample of either isotope remains after three half-lives?
- 14.91 Urea (NH_2CONH_2) is the end product in protein metabolism in animals. The decomposition of urea in 0.1 M HCl occurs according to the reaction



The reaction is first order in urea and first order overall. When $[NH_2CONH_2] = 0.200 M$, the rate at 61.05 °C is $8.56 \times 10^{-5} M/s$. (a) What is the value for the rate constant, k ? (b) What is the concentration of urea in this solution after $4.00 \times 10^3 s$ if the starting concentration is 0.500 M? (c) What is the half-life for this reaction at 61.05 °C?

- 14.92 The rate of a first-order reaction is followed by spectroscopy, monitoring the absorption of a colored reactant. The reaction occurs in a 1.00-cm sample cell, and the only colored species in the reaction has a molar absorptivity constant of $5.60 \times 10^3 cm^{-1} M^{-1}$. (a) Calculate the initial concentration of the colored reactant if the absorbance is 0.605 at the beginning of the reaction. (b) The absorbance falls to 0.250 within 30.0 min. Calculate the

rate constant in units of s^{-1} . (c) Calculate the half-life of the reaction. (d) How long does it take for the absorbance to fall to 0.100?

- 14.93 Cyclopentadiene (C_5H_6) reacts with itself to form dicyclopentadiene ($C_{10}H_{12}$). A 0.0400 M solution of C_5H_6 was monitored as a function of time as the reaction $2 C_5H_6 \rightarrow C_{10}H_{12}$ proceeded. The following data were collected:

Time (s)	$[C_5H_6] (M)$
0.0	0.0400
50.0	0.0300
100.0	0.0240
150.0	0.0200
200.0	0.0174

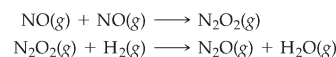
Plot $[C_5H_6]$ versus time, $\ln [C_5H_6]$ versus time, and $1/[C_5H_6]$ versus time. What is the order of the reaction? What is the value of the rate constant?

- 14.94 (a) Two reactions have identical values for E_a . Does this ensure that they will have the same rate constant if run at the same temperature? Explain. (b) Two similar reactions have the same rate constant at 25 °C, but at 35 °C one of the reactions has a higher rate constant than the other. Account for these observations.
- 14.95 The first-order rate constant for reaction of a particular organic compound with water varies with temperature as follows:

Temperature (K)	Rate Constant (s^{-1})
300	3.2×10^{-11}
320	1.0×10^{-9}
340	3.0×10^{-8}
355	2.4×10^{-7}

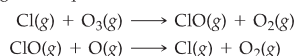
From these data, calculate the activation energy in units of kJ/mol.

- 14.96 The following mechanism has been proposed for the reaction of NO with H_2 to form N_2O and H_2O :



(a) Show that the elementary reactions of the proposed mechanism add to provide a balanced equation for the reaction. (b) Write a rate law for each elementary reaction in the mechanism. (c) Identify any intermediates in the mechanism. (d) The observed rate law is $rate = k[NO]^2[H_2]$. If the proposed mechanism is correct, what can we conclude about the relative speeds of the first and second reactions?

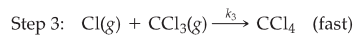
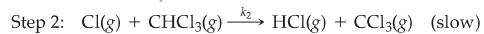
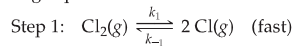
- 14.97 Ozone in the upper atmosphere can be destroyed by the following two-step mechanism:



(a) What is the overall equation for this process? (b) What is the catalyst in the reaction? How do you know? (c) What is the intermediate in the reaction? How do you distinguish it from the catalyst?

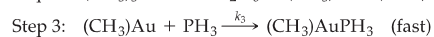
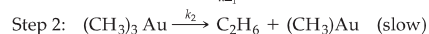
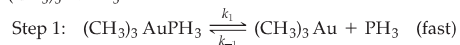
14.98 Using Figure 14.20 as your basis, draw the energy profile for the bromide ion-catalyzed decomposition of hydrogen peroxide. (a) Label the curve with the activation energies for reactions [14.30] and [14.31]. (b) Notice from Figure 14.19(b) that when $\text{Br}^-(aq)$ is added initially, Br_2 accumulates to some extent during the reaction. What does this tell us about the relative rates of reactions [14.30] and [14.31]?

[14.99] The following mechanism has been proposed for the gas-phase reaction of chloroform (CHCl_3) and chlorine:



(a) What is the overall reaction? (b) What are the intermediates in the mechanism? (c) What is the molecularity of each of the elementary reactions? (d) What is the rate-determining step? (e) What is the rate law predicted by this mechanism? (*Hint:* The overall reaction order is not an integer.)

[14.100] In a hydrocarbon solution, the gold compound $(\text{CH}_3)_3\text{AuPH}_3$ decomposes into ethane (C_2H_6) and a different gold compound, $(\text{CH}_3)\text{AuPH}_3$. The following mechanism has been proposed for the decomposition of $(\text{CH}_3)_3\text{AuPH}_3$:

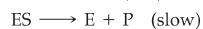
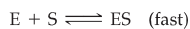


(a) What is the overall reaction? (b) What are the intermediates in the mechanism? (c) What is the molecularity

of each of the elementary steps? (d) What is the rate-determining step? (e) What is the rate law predicted by this mechanism? (f) What would be the effect on the reaction rate of adding PH_3 to the solution of $(\text{CH}_3)_3\text{AuPH}_3$?

14.101 One of the many remarkable enzymes in the human body is carbonic anhydrase, which catalyzes the interconversion of carbonic acid with carbon dioxide and water. If it were not for this enzyme, the body could not rid itself rapidly enough of the CO_2 accumulated by cell metabolism. The enzyme catalyzes the dehydration (release to air) of up to 10^7 CO_2 molecules per second. Which components of this description correspond to the terms *enzyme*, *substrate*, and *turnover number*?

14.102 Enzymes are often described as following the two-step mechanism:



Where E = enzyme, S = substrate, and P = product. If an enzyme follows this mechanism, what rate law is expected for the reaction?

14.103 The enzyme *invertase* catalyzes the conversion of sucrose, a disaccharide, to invert sugar, a mixture of glucose and fructose. When the concentration of invertase is $4.2 \times 10^{-7} \text{ M}$ and the concentration of sucrose is 0.0077 M , invert sugar is formed at the rate of $1.5 \times 10^{-4} \text{ M/s}$. When the sucrose concentration is doubled, the rate of formation of invert sugar is doubled also. (a) Assuming that the enzyme-substrate model is operative, is the fraction of enzyme tied up as a complex large or small? Explain. (b) Addition of inositol, another sugar, decreases the rate of formation of invert sugar. Suggest a mechanism by which this occurs.

INTEGRATIVE EXERCISES

14.104 Dinitrogen pentoxide (N_2O_5) decomposes in chloroform as a solvent to yield NO_2 and O_2 . The decomposition is first order with a rate constant at 45°C of $1.0 \times 10^{-5} \text{ s}^{-1}$. Calculate the partial pressure of O_2 produced from 1.00 L of $0.600 \text{ M N}_2\text{O}_5$ solution at 45°C over a period of 20.0 h if the gas is collected in a 10.0-L container. (Assume that the products do not dissolve in chloroform.)

[14.105] The reaction between ethyl iodide and hydroxide ion in ethanol ($\text{C}_2\text{H}_5\text{OH}$) solution, $\text{C}_2\text{H}_5\text{I}(alc) + \text{OH}^-(alc) \longrightarrow \text{C}_2\text{H}_5\text{OH}(l) + \text{I}^-(alc)$, has an activation energy of 86.8 kJ/mol and a frequency factor of $2.10 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. (a) Predict the rate constant for the reaction at 35°C . (b) A solution of KOH in ethanol is made up by dissolving 0.335 g KOH in ethanol to form 250.0 mL of solution. Similarly, $1.453 \text{ g of C}_2\text{H}_5\text{I}$ is dissolved in ethanol to form 250.0 mL of solution. Equal volumes of the two solutions are mixed. Assuming the reaction is first order in each reactant, what is the initial rate at 35°C ? (c) Which reagent in the reaction is limiting, assuming the reaction proceeds to completion?

14.106 Zinc metal dissolves in hydrochloric acid according to the reaction



Suppose you are asked to study the kinetics of this reaction by monitoring the rate of production of $\text{H}_2(g)$.

(a) By using a reaction flask, a manometer, and any other common laboratory equipment, design an experimental apparatus that would allow you to monitor the partial pressure of $\text{H}_2(g)$ produced as a function of time. (b) Explain how you would use the apparatus to determine the rate law of the reaction. (c) Explain how you would use the apparatus to determine the reaction order for $[\text{H}^+]$ for the reaction. (d) How could you use the apparatus to determine the activation energy of the reaction? (e) Explain how you would use the apparatus to determine the effects of changing the form of $\text{Zn}(s)$ from metal strips to granules.

14.107 The gas-phase reaction of NO with F_2 to form NOF and F has an activation energy of $E_a = 6.3 \text{ kJ/mol}$ and a

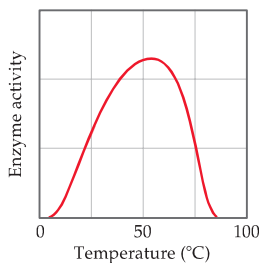
frequency factor of $A = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The reaction is believed to be bimolecular:



(a) Calculate the rate constant at 100 °C. (b) Draw the Lewis structures for the NO and the NOF molecules, given that the chemical formula for NOF is misleading because the nitrogen atom is actually the central atom in the molecule. (c) Predict the structure for the NOF molecule. (d) Draw a possible transition state for the formation of NOF, using dashed lines to indicate the weak bonds that are beginning to form. (e) Suggest a reason for the low activation energy for the reaction.

14.108 The mechanism for the oxidation of HBr by O_2 to form 2 H_2O and Br_2 is shown in Exercise 14.70. (a) Calculate the overall standard enthalpy change for the reaction process. (b) HBr does not react with O_2 at a measurable rate at room temperature under ordinary conditions. What can you infer from this about the magnitude of the activation energy for the rate-determining step? (c) Draw a plausible Lewis structure for the intermediate HOOBr . To what familiar compound of hydrogen and oxygen does it appear similar?

14.109 Enzymes, the catalysts of biological systems, are high molecular weight protein materials. The active site of the enzyme is formed by the three-dimensional arrangement of the protein in solution. When heated in solution, proteins undergo denaturation, a process in which the three-dimensional structure of the protein unravels or at least partly does so. The accompanying graph shows the variation with temperature of the activity of a typical enzyme. The activity increases with temperature to a point above the usual operating region for the enzyme, then declines rapidly with further temperature increases. What role does denaturation play in determining the shape of this curve? How does your explanation fit in with the lock-and-key model of enzyme action?



[14.110] Metals often form several cations with different charges. Cerium, for example, forms Ce^{3+} and Ce^{4+} ions, and thallium forms Tl^+ and Tl^{3+} ions. Cerium and thallium ions react as follows:



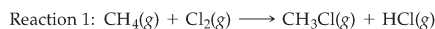
This reaction is very slow and is thought to occur in a single elementary step. The reaction is catalyzed by the

addition of $\text{Mn}^{2+}(\text{aq})$, according to the following mechanism:

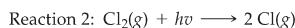


(a) Write the rate law for the uncatalyzed reaction. (b) What is unusual about the uncatalyzed reaction? Why might it be a slow reaction? (c) The rate for the catalyzed reaction is first order in $[\text{Ce}^{4+}]$ and first order in $[\text{Mn}^{2+}]$. Based on this rate law, which of the steps in the catalyzed mechanism is rate determining? (d) Use the available oxidation states of Mn to comment on its special suitability to catalyze this reaction.

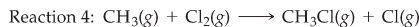
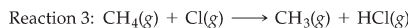
[14.111] The rates of many atmospheric reactions are accelerated by the absorption of light by one of the reactants. For example, consider the reaction between methane and chlorine to produce methyl chloride and hydrogen chloride:



This reaction is very slow in the absence of light. However, $\text{Cl}_2(\text{g})$ can absorb light to form Cl atoms:



Once the Cl atoms are generated, they can catalyze the reaction of CH_4 and Cl_2 , according to the following proposed mechanism:



The enthalpy changes and activation energies for these two reactions are tabulated as follows:

Reaction	$\Delta H_{\text{ran}}^\circ$ (kJ/mol)	E_a (kJ/mol)
3	+4	17
4	-109	4

(a) By using the bond enthalpy for Cl_2 (Table 8.4), determine the longest wavelength of light that is energetic enough to cause reaction 2 to occur. In which portion of the electromagnetic spectrum is this light found? (b) By using the data tabulated here, sketch a quantitative energy profile for the catalyzed reaction represented by reactions 3 and 4. (c) By using bond enthalpies, estimate where the reactants, $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g})$, should be placed on your diagram in part (b). Use this result to estimate the value of E_a for the reaction $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{CH}_3(\text{g}) + \text{HCl}(\text{g}) + \text{Cl}(\text{g})$. (d) The species $\text{Cl}(\text{g})$ and $\text{CH}_3(\text{g})$ in reactions 3 and 4 are radicals, that is, atoms or molecules with unpaired electrons. Draw a Lewis structure of CH_3 , and verify that it is a radical. (e) The sequence of reactions 3 and 4 comprise a radical chain mechanism. Why do you think this is called a "chain reaction"? Propose a reaction that will terminate the chain reaction.