Chemical Kinetics

The rates of chemical reactions vary greatly. The conversion of graphite to diamond in Earth's crust may take millions of years to complete. Explosive reactions such as those of dynamite and TNT, on the other hand, are over in a fraction of a second.

Chapter Outline

A Look Ahead

- We begin by studying the rate of a reaction expressed in terms of the concentrations of reactants and products and how the rate is related to the stoichiometry of a reaction. (13.1)

- We then see how the rate law of a reaction is defined in terms of the rate constant and reaction order. (13.2)

- Next, we examine the relationship between reactant concentration and time for three types of reactions: zero order, first order, and second order. The half-life, which is the time required for the concentration of a reactant to decrease to half of its initial value, is useful for distinguishing between reactions of different orders. (13.3)

- We see that the rate of a reaction usually increases with temperature. Activation energy, which is the minimum amount of energy required to initiate a chemical reaction, also influences the rate. (13.4)

- We examine the mechanism of a reaction in terms of the elementary steps and see that we can determine the rate law from the slowest or rate-determining step. We learn how chemists verify mechanisms by experiments. (13.5)

- Finally, we study the effect of catalyst on the rate of a reaction. We learn the characteristics of heterogeneous catalysis, homogeneous catalysis, and enzyme catalysis. (13.6)

In previous chapters, we studied basic definitions in chemistry, and we examined the properties of gases, liquids, solids, and solutions. We have discussed molecular properties and looked at several types of reactions in some detail. In this chapter and in subsequent chapters, we will look more closely at the relationships and the laws that govern chemical reactions.

How can we predict whether or not a reaction will take place? Once started, how fast does the reaction proceed? How far will the reaction go before it stops? The laws of thermodynamics (to be discussed in Chapter 17) help us answer the first question. Chemical kinetics, the subject of this chapter, provides answers to the question about the speed of a reaction. The last question is one of many answered by the study of chemical equilibrium, which we will consider in Chapters 14, 15, and 16.

13.1 The Rate of a Reaction

Chemical kinetics is *the area of chemistry concerned with the speeds, or rates, at which a chemical reaction occurs*. The word "kinetic" suggests movement or change; in Chapter 5 we defined kinetic energy as the energy available because of the motion of an object. Here kinetics refers to the rate of a reaction, or the **reaction rate,** which is *the change in the concentration of a reactant or a product with time (M/s)*.

There are many reasons for studying the rate of a reaction. To begin with, there is intrinsic curiosity about why reactions have such vastly different rates. Some processes, such as the initial steps in vision and photosynthesis and nuclear chain reactions, take place on a time scale as short as 10^{-12} s to 10^{-6} s. Others, like the curing of cement and the conversion of graphite to diamond, take years or millions of years to complete. On a practical level, a knowledge of reaction rates is useful in drug design, in pollution control, and in food processing. Industrial chemists often place more emphasis on speeding up the rate of a reaction rather than on maximizing its yield.

We know that any reaction can be represented by the general equation

$$\text{reactants} \longrightarrow \text{products}$$

This equation tells us that during the course of a reaction, reactants are consumed while products are formed. As a result, we can follow the progress of a reaction by monitoring either the decrease in concentration of the reactants or the increase in concentration of the products.

Figure 13.1 shows the progress of a simple reaction in which A molecules are converted to B molecules:

$$A \longrightarrow B$$

The decrease in the number of A molecules and the increase in the number of B molecules with time are shown in Figure 13.2. In general, it is more convenient to
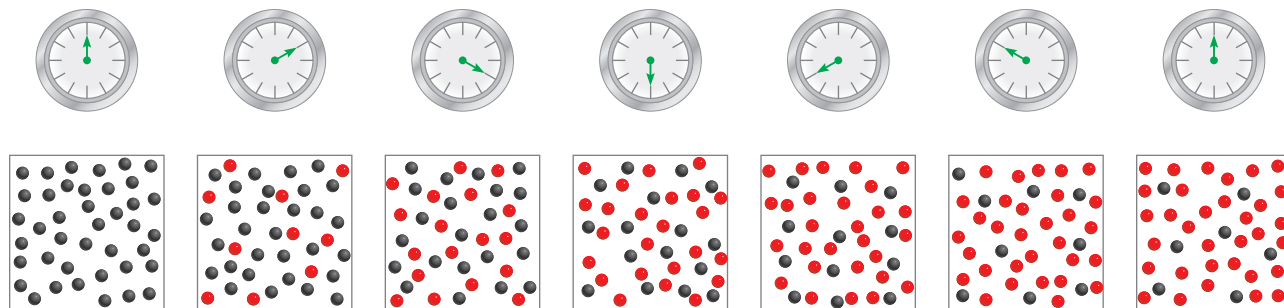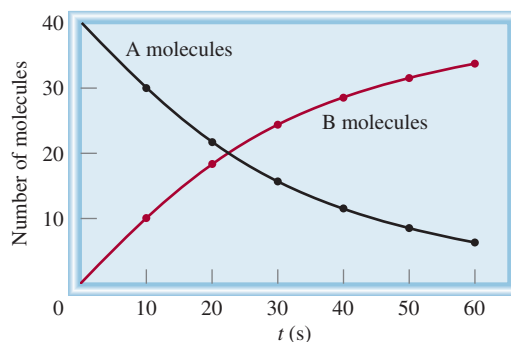

Figure 13.1 *The progress of reaction A $\longrightarrow$ B at 10-s intervals over a period of 60 s. Initially, only A molecules (gray spheres) are present. As time progresses, B molecules (red spheres) are formed.*

Figure 13.2 *The rate of reaction A ⟶ B, represented as the decrease of A molecules with time and as the increase of B molecules with time.*

express the reaction rate in terms of the change in concentration with time. Thus, for the reaction A ⟶ B we can express the rate as

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

Recall that Δ denotes the difference between the final and initial states.

where $\Delta[A]$ and $\Delta[B]$ are the changes in concentration (molarity) over a time period Δt. Because the concentration of A *decreases* during the time interval, $\Delta[A]$ is a negative quantity. The rate of a reaction is a positive quantity, so a minus sign is needed in the rate expression to make the rate positive. On the other hand, the rate of product formation does not require a minus sign because $\Delta[B]$ is a positive quantity (the concentration of B *increases* with time). These rates are *average rates* because they are averaged over a certain time period Δt.

Our next step is to see how the rate of a reaction is obtained experimentally. By definition, we know that to determine the rate of a reaction we have to monitor the concentration of the reactant (or product) as a function of time. For reactions in solution, the concentration of a species can often be measured by spectroscopic means. If ions are involved, the change in concentration can also be detected by an electrical conductance measurement. Reactions involving gases are most conveniently followed by pressure measurements. We will consider two specific reactions for which different methods are used to measure the reaction rates.

Reaction of Molecular Bromine and Formic Acid

In aqueous solutions, molecular bromine reacts with formic acid (HCOOH) as follows:

$$Br_2(aq) + HCOOH(aq) \longrightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

Molecular bromine is reddish-brown in color. All the other species in the reaction are colorless. As the reaction progresses, the concentration of Br_2 steadily decreases and its color fades (Figure 13.3). This loss of color and hence concentration can be monitored easily with a spectrometer, which registers the amount of visible light absorbed by bromine (Figure 13.4).

Measuring the change (decrease) in bromine concentration at some initial time and then at some final time enables us to determine the average rate of the reaction during that interval:

$$\text{average rate} = -\frac{\Delta[Br_2]}{\Delta t}$$
$$= -\frac{[Br_2]_{\text{final}} - [Br_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

Figure 13.3 *From left to right: The decrease in bromine concentration as time elapses shows up as a loss of color (from left to right).*
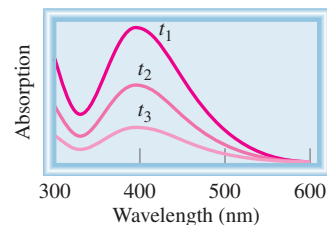

Figure 13.4 *Plot of absorption of bromine versus wavelength. The maximum absorption of visible light by bromine occurs at 393 nm. As the reaction progresses (t_1 to t_3), the absorption, which is proportional to [Br$_2$], decreases.*

Using the data provided in Table 13.1 we can calculate the average rate over the first 50-s time interval as follows:

$$\text{average rate} = -\frac{(0.0101 - 0.0120)\ M}{50.0\ \text{s}} = 3.80 \times 10^{-5}\ M/\text{s}$$

If we had chosen the first 100 s as our time interval, the average rate would then be given by:

$$\text{average rate} = -\frac{(0.00846 - 0.0120)\ M}{100.0\ \text{s}} = 3.54 \times 10^{-5}\ M/\text{s}$$

These calculations demonstrate that the average rate of the reaction depends on the time interval we choose.

By calculating the average reaction rate over shorter and shorter intervals, we can obtain the rate for a specific instant in time, which gives us the *instantaneous rate* of the reaction at that time. Figure 13.5 shows the plot of [Br$_2$] versus time, based on the data shown in Table 13.1. Graphically, the instantaneous rate at 100 s after the

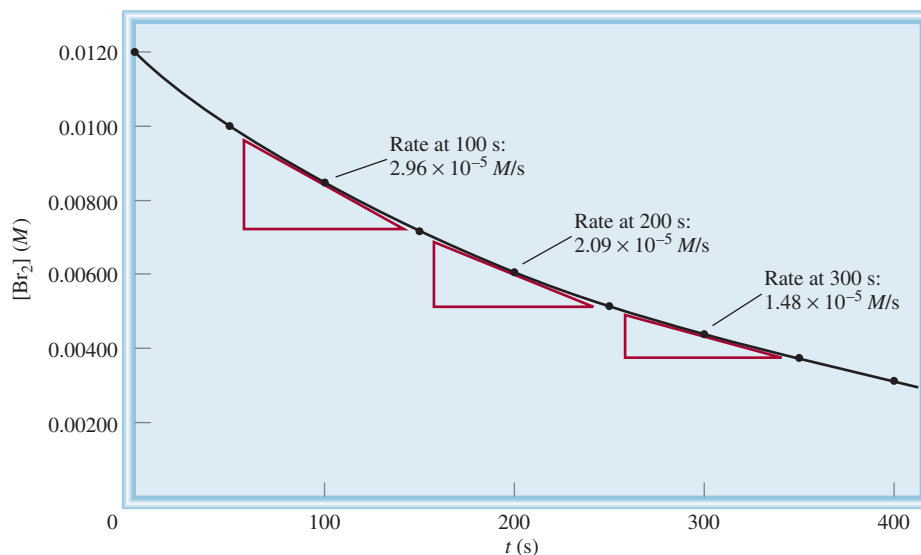| Table 13.1	Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C		
Time (s)	[Br$_2$] (*M*)	Rate (*M*/s)	$k = \dfrac{\text{rate}}{[\text{Br}_2]}\ (\text{s}^{-1})$
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500	1.75×10^{-5}	3.50×10^{-3}
300.0	0.00420	1.48×10^{-5}	3.52×10^{-3}
350.0	0.00353	1.23×10^{-5}	3.48×10^{-3}
400.0	0.00296	1.04×10^{-5}	3.51×10^{-3}

Figure 13.5 *The instantaneous rates of the reaction between molecular bromine and formic acid at t = 100 s, 200 s, and 300 s are given by the slopes of the tangents at these times.*

start of the reaction, say, is given by the slope of the tangent to the curve at that instant. The instantaneous rate at any other time can be determined in a similar manner. Note that the instantaneous rate determined in this way will always have the same value for the same concentrations of reactants, as long as the temperature is kept constant. We do not need to be concerned with what time interval to use. Unless otherwise stated, we will refer to the instantaneous rate at a specific time merely as "the rate" at that time.

The following travel analogy helps to distinguish between average rate and instantaneous rate. The distance by car from San Francisco to Los Angeles is 512 mi along a certain route. If it takes a person 11.4 h to go from one city to the other, the average speed is 512 mi/11.4 h or 44.9 mph. But if the car is traveling at 55.3 mph 3 h and 26 min after departure, then the instantaneous speed of the car is 55.3 mph at that time. In other words, instantaneous speed is the speed that you would read from the speedometer. Note that the speed of the car in our example can increase or decrease during the trip, but the instantaneous rate of a reaction always decreases with time.

The rate of the bromine-formic acid reaction also depends on the concentration of formic acid. However, by adding a large excess of formic acid to the reaction mixture we can ensure that the concentration of formic acid remains virtually constant throughout the course of the reaction. Under this condition the change in the amount of formic acid present in solution has no effect on the measured rate.

Let's consider the effect that the bromine concentration has on the rate of reaction. Look at the data in Table 13.1. Compare the concentration of Br_2 and the reaction rate at $t = 50$ s and $t = 250$ s. At $t = 50$ s, the bromine concentration is 0.0101 *M* and the rate of reaction is 3.52×10^{-5} *M*/s. At $t = 250$ s, the bromine concentration is 0.00500 *M* and the rate of reaction is 1.75×10^{-5} *M*/s. The concentration at $t = 50$ s is double the concentration at $t = 250$ s (0.0101 *M* versus 0.00500 *M*), and the rate of reaction at $t = 50$ s is double the rate at $t = 250$ s (3.52×10^{-5} *M*/s
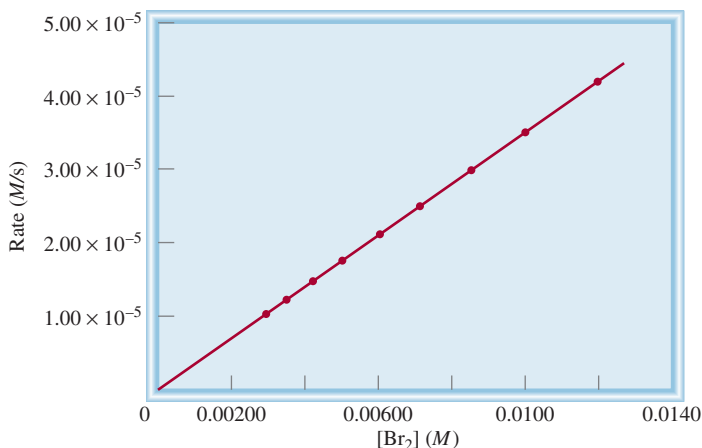
Figure 13.6 *Plot of rate versus molecular bromine concentration for the reaction between molecular bromine and formic acid. The straight-line relationship shows that the rate of reaction is directly proportional to the molecular bromine concentration.*

versus 1.75×10^{-5} M/s). We see that as the concentration of bromine is doubled, the rate of reaction also doubles. Thus, the rate is directly proportional to the Br_2 concentration, that is

$$\text{rate} \propto [Br_2]$$
$$= k[Br_2]$$

where the term k is known as the **rate constant,** *a constant of proportionality between the reaction rate and the concentration of reactant*. This direct proportionality between Br_2 concentration and rate is also supported by plotting the data.

Figure 13.6 is a plot of the rate versus Br_2 concentration. The fact that this graph is a straight line shows that the rate is directly proportional to the concentration; the higher the concentration, the higher the rate. Rearranging the last equation gives

$$k = \frac{\text{rate}}{[Br_2]}$$

Because reaction rate has the units M/s, and $[Br_2]$ is in M, the unit of k is 1/s, or s^{-1} in this case. It is important to understand that k is *not* affected by the concentration of Br_2. To be sure, the rate is greater at a higher concentration and smaller at a lower concentration of Br_2, but the *ratio* of rate/$[Br_2]$ remains the same provided the temperature does not change.

From Table 13.1 we can calculate the rate constant for the reaction. Taking the data for $t = 50$ s, we write

$$k = \frac{\text{rate}}{[Br_2]}$$
$$= \frac{3.52 \times 10^{-5}\ M/s}{0.0101\ M} = 3.49 \times 10^{-3}\ s^{-1}$$

We can use the data for any t to calculate k. The slight variations in the values of k listed in Table 13.1 are due to experimental deviations in rate measurements.

As we will see, for a given reaction, k is affected only by a change in temperature.
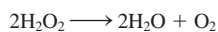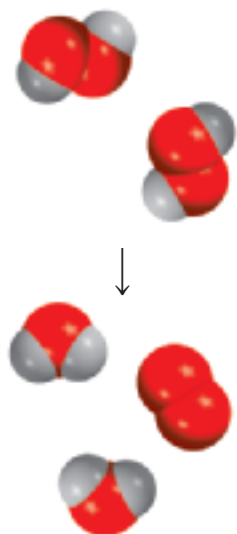
Decomposition of Hydrogen Peroxide

If one of the products or reactants is a gas, we can use a manometer to find the reaction rate. Consider the decomposition of hydrogen peroxide at 20°C:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$
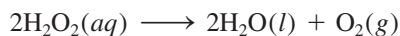
In this case, the rate of decomposition can be determined by monitoring the rate of oxygen evolution with a manometer (Figure 13.7). The oxygen pressure can be readily converted to concentration by using the ideal gas equation:

$$PV = nRT$$

or

$$P = \frac{n}{V}RT = [O_2]RT$$

where n/V gives the molarity of oxygen gas. Rearranging the equation, we get

$$[O_2] = \frac{1}{RT}P$$

The reaction rate, which is given by the rate of oxygen production, can now be written as

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{1}{RT}\frac{\Delta P}{\Delta t}$$

Figure 13.8 shows the increase in oxygen pressure with time and the determination of an instantaneous rate at 400 min. To express the rate in the normal units of M/s,
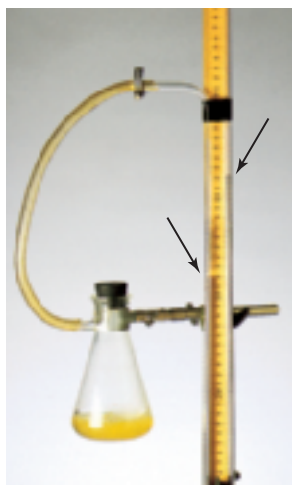
$2H_2O_2 \longrightarrow 2H_2O + O_2$

Figure 13.7 *The rate of hydrogen peroxide decomposition can be measured with a manometer, which shows the increase in the oxygen gas pressure with time. The arrows show the mercury levels in the U tube.*
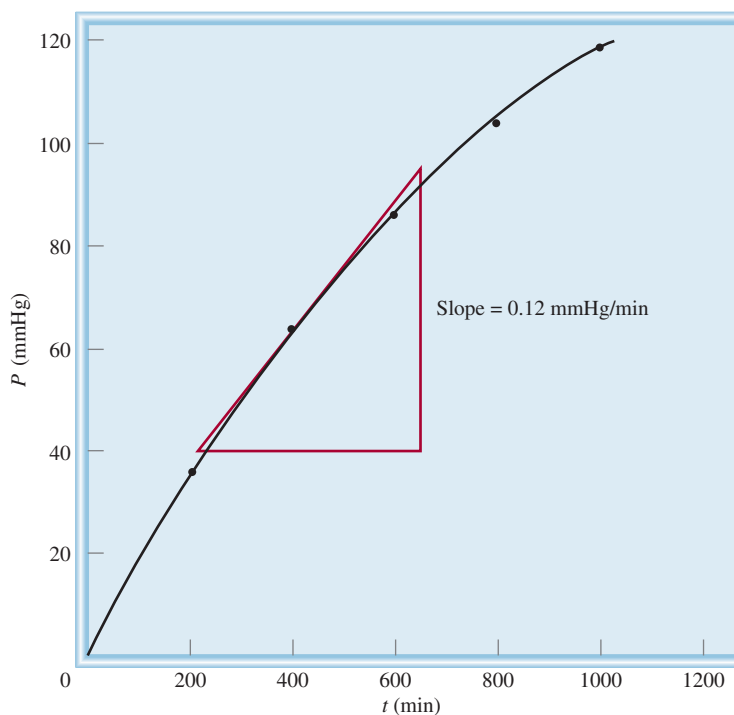
Slope = 0.12 mmHg/min

Figure 13.8 *The instantaneous rate for the decomposition of hydrogen peroxide at 400 min is given by the slope of the tangent multiplied by 1/RT.*

we convert mmHg/min to atm/s, then multiply the slope of the tangent ($\Delta P/\Delta t$) by $1/RT$, as shown in the previous equation.

After conversion, the rate is 1.1×10^{-7} M/s.

Reaction Rates and Stoichiometry

We have seen that for stoichiometrically simple reactions of the type A $\longrightarrow$ B, the rate can be either expressed in terms of the decrease in reactant concentration with time, $-\Delta[A]/\Delta t$, or the increase in product concentration with time, $\Delta[B]/\Delta t$. For more complex reactions, we must be careful in writing the rate expressions. Consider, for example, the reaction

$$2A \longrightarrow B$$
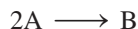
Two moles of A disappear for each mole of B that forms; that is, the rate at which B forms is one-half the rate at which A disappears. Thus, the rate can be expressed as

$$\text{rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} \qquad \text{or} \qquad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

In general, for the reaction

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

the rate is given by

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

Examples 13.1 and 13.2 show writing the reaction rate expressions and calculating rates of product formation and reactant disappearance.

Example 13.1

Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:

(a) $I^-(aq) + OCl^-(aq) \longrightarrow Cl^-(aq) + OI^-(aq)$

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

Strategy To express the rate of the reaction in terms of the change in concentration of a reactant or product with time, we need to use the proper sign (minus or plus) and the reciprocal of the stoichiometric coefficient.
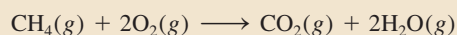
Solution (a) Because each of the stoichiometric coefficients equals 1,

$$\text{rate} = -\frac{\Delta[I^-]}{\Delta t} = -\frac{\Delta[OCl^-]}{\Delta t} = \frac{\Delta[Cl^-]}{\Delta t} = \frac{\Delta[OI^-]}{\Delta t}$$

(b) Here the coefficients are 4, 5, 4, and 6, so

$$\text{rate} = -\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$
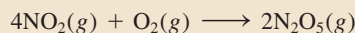
Similar problems: 13.5, 13.6.

Practice Exercise Write the rate expressions for the following reaction:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

Example 13.2

Consider the reaction

$$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g)$$

Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of 0.024 M/s. (a) At what rate is N_2O_5 being formed? (b) At what rate is NO_2 reacting?

Strategy To calculate the rate of formation of N_2O_5 and disappearance of NO_2, we need to express the rate of the reaction in terms of the stoichiometric coefficients as in Example 13.1:

$$\text{rate} = -\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$$

We are given

$$\frac{\Delta[O_2]}{\Delta t} = -0.024 \; M/s$$

where the minus sign shows that the concentration of O_2 is decreasing with time.

Solution (a) From the preceding rate expression we have

$$-\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$$

Therefore,

$$\frac{\Delta[N_2O_5]}{\Delta t} = -2(-0.024 \; M/s) = 0.048 \; M/s$$

(b) Here we have
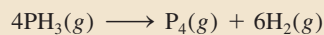
$$-\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t}$$

so

$$\frac{\Delta[NO_2]}{\Delta t} = 4(-0.024 \; M/s) = -0.096 \; M/s$$

Practice Exercise Consider the reaction

$$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$

Suppose that, at a particular moment during the reaction, molecular hydrogen is being formed at the rate of 0.078 M/s. (a) At what rate is P_4 being formed? (b) At what rate is PH_3 reacting?

Review of Concepts

Write a balanced equation for a gas-phase reaction whose rate is given by

$$\text{rate} = -\frac{1}{2}\frac{\Delta[NOCl]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO]}{\Delta t} = \frac{\Delta[Cl_2]}{\Delta t}$$

13.2 The Rate Law

So far we have learned that the rate of a reaction is proportional to the concentration of reactants and that the proportionality constant k is called the rate constant. The **rate law** *expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers*. For the general reaction

$$aA + bB \longrightarrow cC + dD$$

the rate law takes the form

$$\text{rate} = k[A]^x[B]^y \tag{13.1}$$

where x and y are numbers that must be determined experimentally. Note that, in general, x and y are *not* equal to the stoichiometric coefficients a and b. When we know the values of x, y, and k, we can use Equation (13.1) to calculate the rate of the reaction, given the concentrations of A and B.

The exponents x and y specify the relationships between the concentrations of reactants A and B and the reaction rate. Added together, they give us the overall **reaction order,** defined as *the sum of the powers to which all reactant concentrations appearing in the rate law are raised*. For Equation (13.1) the overall reaction order is $x + y$. Alternatively, we can say that the reaction is xth order in A, yth order in B, and $(x + y)$th order overall.

To see how to determine the rate law of a reaction, let us consider the reaction between fluorine and chlorine dioxide:

$$F_2(g) + 2ClO_2(g) \longrightarrow 2FClO_2(g)$$
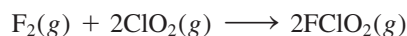
One way to study the effect of reactant concentration on reaction rate is to determine how the *initial rate* depends on the starting concentrations. It is preferable to measure the initial rates because as the reaction proceeds, the concentrations of the reactants decrease and it may become difficult to measure the changes accurately. Also, there may be a reverse reaction of the type

$$\text{products} \longrightarrow \text{reactants}$$

which would introduce error into the rate measurement. Both of these complications are virtually absent during the early stages of the reaction.

Table 13.2 shows three rate measurements for the formation of $FClO_2$. Looking at entries 1 and 3, we see that as we double $[F_2]$ while holding $[ClO_2]$ constant, the reaction rate doubles. Thus, the rate is directly proportional to $[F_2]$. Similarly, the data in entries 1 and 2 show that as we quadruple $[ClO_2]$ at constant $[F_2]$, the rate increases by
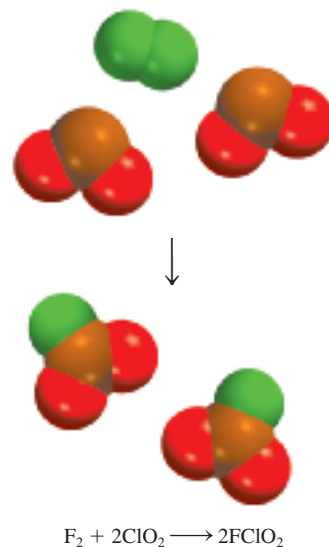

$F_2 + 2ClO_2 \longrightarrow 2FClO_2$

Table 13.2	Rate Data for the Reaction Between F_2 and ClO_2	
$[F_2]$ (M)	**$[ClO_2]$ (M)**	**Initial Rate (M/s)**
1. 0.10	0.010	1.2×10^{-3}
2. 0.10	0.040	4.8×10^{-3}
3. 0.20	0.010	2.4×10^{-3}

four times, so that the rate is also directly proportional to $[ClO_2]$. We can summarize our observations by writing the rate law as

$$\text{rate} = k[F_2][ClO_2]$$

Because both $[F_2]$ and $[ClO_2]$ are raised to the first power, the reaction is first order in F_2, first order in ClO_2, and $(1 + 1)$ or second order overall. Note that $[ClO_2]$ is raised to the power of 1 whereas its stoichiometric coefficient in the overall equation is 2. The equality of reaction order (first) and stoichiometric coefficient (1) for F_2 is coincidental in this case.

From the reactant concentrations and the initial rate, we can also calculate the rate constant. Using the first entry of data in Table 13.2, we can write

$$
\begin{aligned}
k &= \frac{\text{rate}}{[F_2][ClO_2]} \\
&= \frac{1.2 \times 10^{-3}\ M/s}{(0.10\ M)(0.010\ M)} \\
&= 1.2/M \cdot s
\end{aligned}
$$

Reaction order enables us to understand how the reaction depends on reactant concentrations. Suppose, for example, that for the general reaction $aA + bB \longrightarrow cC + dD$ we have $x = 1$ and $y = 2$. The rate law for the reaction is [see Equation (13.1)]

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

This reaction is first order in A, second order in B, and third order overall $(1 + 2 = 3)$. Let us assume that initially $[A] = 1.0\ M$ and $[B] = 1.0\ M$. The rate law tells us that if we double the concentration of A from $1.0\ M$ to $2.0\ M$ at constant $[B]$, we also double the reaction rate:

for $[A] = 1.0\ M$ 　　　　　 $\begin{aligned}\text{rate}_1 &= k(1.0\ M)(1.0\ M)^2 \\ &= k(1.0\ M^3)\end{aligned}$

for $[A] = 2.0\ M$ 　　　　　 $\begin{aligned}\text{rate}_2 &= k(2.0\ M)(1.0\ M)^2 \\ &= k(2.0\ M^3)\end{aligned}$

Hence, 　　　　　　　　　 $\text{rate}_2 = 2(\text{rate}_1)$

On the other hand, if we double the concentration of B from $1.0\ M$ to $2.0\ M$ at constant $[A] = 1\ M$, the rate will increase by a factor of 4 because of the power 2 in the exponent:

for $[B] = 1.0\ M$ 　　　　　 $\begin{aligned}\text{rate}_1 &= k(1.0\ M)(1.0\ M)^2 \\ &= k(1.0\ M^3)\end{aligned}$

for $[B] = 2.0\ M$ 　　　　　 $\begin{aligned}\text{rate}_2 &= k(1.0\ M)(2.0\ M)^2 \\ &= k(4.0\ M^3)\end{aligned}$

Hence, 　　　　　　　　　 $\text{rate}_2 = 4(\text{rate}_1)$

If, for a certain reaction, $x = 0$ and $y = 1$, then the rate law is

$$
\begin{aligned}
\text{rate} &= k[A]^0[B] \\
&= k[B]
\end{aligned}
$$

This reaction is zero order in A, first order in B, and first order overall. The exponent zero tells us that the rate of this reaction is *independent* of the concentration of A. Note that reaction order can also be a fraction.

The following points summarize our discussion of the rate law:

1. Rate laws are always determined experimentally. From the concentrations of reactants and the initial reaction rates we can determine the reaction order and then the rate constant of the reaction.

2. Reaction order is always defined in terms of reactant (not product) concentrations.

3. The order of a reactant is not related to the stoichiometric coefficient of the reactant in the overall balanced equation.

Example 13.3 illustrates the procedure for determining the rate law of a reaction.

Example 13.3

The reaction of nitric oxide with hydrogen at 1280°C is

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

From the following data collected at this temperature, determine (a) the rate law, (b) the rate constant, and (c) the rate of the reaction when $[NO] = 12.0 \times 10^{-3} M$ and $[H_2] = 6.0 \times 10^{-3} M$.

Experiment	[NO] (*M*)	[H$_2$] (*M*)	Initial Rate (*M*/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

Strategy We are given a set of concentration and reaction rate data and asked to determine the rate law and the rate constant. We assume that the rate law takes the form

$$\text{rate} = k[NO]^x[H_2]^y$$

How do we use the data to determine x and y? Once the orders of the reactants are known, we can calculate k from any set of rate and concentrations. Finally, the rate law enables us to calculate the rate at any concentrations of NO and H$_2$.

Solution (a) Experiments 1 and 2 show that when we double the concentration of NO at constant concentration of H$_2$, the rate quadruples. Taking the ratio of the rates from these two experiments

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{5.0 \times 10^{-5} \, M/s}{1.3 \times 10^{-5} \, M/s} \approx 4 = \frac{k(10.0 \times 10^{-3} M)^x(2.0 \times 10^{-3} M)^y}{k(5.0 \times 10^{-3}M)^x(2.0 \times 10^{-3}M)^y}$$
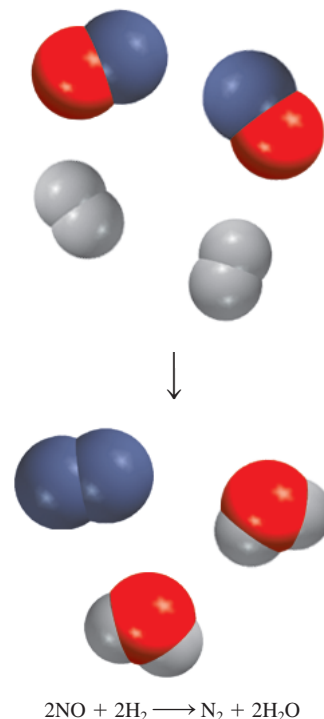
Therefore,

$$\frac{(10.0 \times 10^{-3}M)^x}{(5.0 \times 10^{-3}M)^x} = 2^x = 4$$

or $x = 2$; that is, the reaction is second order in NO. Experiments 2 and 3 indicate that doubling [H$_2$] at constant [NO] doubles the rate. Here we write the ratio as

$$\frac{\text{rate}_3}{\text{rate}_2} = \frac{10.0 \times 10^{-5}M/s}{5.0 \times 10^{-5}M/s} = 2 = \frac{k(10.0 \times 10^{-3} M)^x(4.0 \times 10^{-3}M)^y}{k(10.0 \times 10^{-3}M)^x(2.0 \times 10^{-3} M)^y}$$

(Continued)

$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$

Therefore,

$$\frac{(4.0 \times 10^{-3} M)^y}{(2.0 \times 10^{-3} M)^y} = 2^y = 2$$

or $y = 1$; that is, the reaction is first order in H_2. Hence the rate law is given by

$$\text{rate} = k[NO]^2[H_2]$$

which shows that it is a $(2 + 1)$ or third-order reaction overall.

(b) The rate constant k can be calculated using the data from any one of the experiments. Rearranging the rate law, we get

$$k = \frac{\text{rate}}{[NO]^2[H_2]}$$

The data from experiment 2 give us

$$k = \frac{5.0 \times 10^{-5} \, M/s}{(10.0 \times 10^{-3} \, M)^2 (2.0 \times 10^{-3} \, M)}$$
$$= 2.5 \times 10^2 / M^2 \cdot s$$

(c) Using the known rate constant and concentrations of NO and H_2, we write

$$\text{rate} = (2.5 \times 10^2 / M^2 \cdot s)(12.0 \times 10^{-3} \, M)^2 (6.0 \times 10^{-3} \, M)$$
$$= 2.2 \times 10^{-4} \, M/s$$

Comment Note that the reaction is first order in H_2, whereas the stoichiometric coefficient for H_2 in the balanced equation is 2. The order of a reactant is not related to the stoichiometric coefficient of the reactant in the overall balanced equation.

Practice Exercise The reaction of peroxydisulfate ion ($S_2O_8^{2-}$) with iodide ion (I^-) is

$$S_2O_8^{2-}(aq) + 3I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_3^-(aq)$$
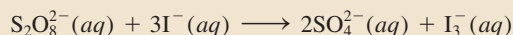
From the following data collected at a certain temperature, determine the rate law and calculate the rate constant.

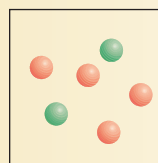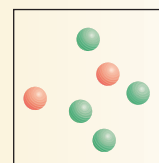| Experiment	$[S_2O_8^{2-}]$ (M)	$[I^-]$ (M)	Initial Rate (M/s)
1	0.080	0.034	2.2×10^{-4}
2	0.080	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

Review of Concepts

The relative rates of the reaction $2A + B \longrightarrow$ products shown in the diagrams (a)–(c) are 1:2:4. The red spheres represent A molecules and the green spheres represent B molecules. Write a rate law for this reaction.
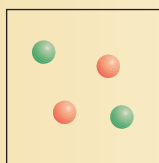

(a)   (b)   (c)

13.3 The Relation Between Reactant Concentration and Time

Rate law expressions enable us to calculate the rate of a reaction from the rate constant and reactant concentrations. The rate laws can also be used to determine the concentrations of reactants at any time during the course of a reaction. We will illustrate this application by first considering two of the most common rate laws—those applying to reactions that are first order overall and those applying to reactions that are second order overall.

First-Order Reactions

A ***first-order reaction*** is *a reaction whose rate depends on the reactant concentration raised to the first power*. In a first-order reaction of the type

$$A \longrightarrow product$$
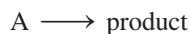
the rate is

$$rate = -\frac{\Delta[A]}{\Delta t}$$

From the rate law we also know that

$$rate = k[A]$$

To obtain the units of k for this rate law, we write

$$k = \frac{rate}{[A]} = \frac{M/s}{M} = 1/s \text{ or s}^{-1}$$

Combining the first two equations for the rate we get

$$-\frac{\Delta[A]}{\Delta t} = k[A] \tag{13.2}$$

Using calculus, we can show from Equation (13.2) that

$$\ln\frac{[A]_t}{[A]_0} = -kt \tag{13.3}$$

where ln is the natural logarithm, and $[A]_0$ and $[A]_t$ are the concentrations of A at times $t = 0$ and $t = t$, respectively. It should be understood that $t = 0$ need not correspond to the beginning of the experiment; it can be any time when we choose to start monitoring the change in the concentration of A.

Equation (13.3) can be rearranged as follows:

$$\ln [A]_t = -kt + \ln [A]_0 \tag{13.4}$$

Equation (13.4) has the form of the linear equation $y = mx + b$, in which m is the slope of the line that is the graph of the equation:

$$\ln [A]_t = (-k)(t) + \ln [A]_0$$
$$y \quad = \quad m \quad x \quad + \quad b$$

In differential form, Equation (13.2) becomes

$$-\frac{d[A]}{dt} = k[A]$$
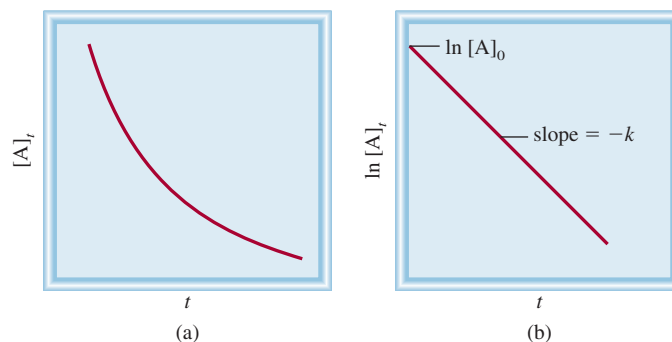
Rearranging, we get

$$-\frac{d[A]}{[A]} = -kdt$$

Integrating between $t = 0$ and $t = t$ gives

$$\int_{[A]_0}^{[A]_t}\frac{d[A]}{[A]} = -k\int_0^t dt$$

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

or

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

Figure 13.9 *First-order reaction characteristics: (a) the exponential decrease of reactant concentration with time; (b) a plot of ln $[A]_t$ versus t. The slope of the line is equal to $-k$.*


Consider Figure 13.9. As we would expect during the course of a reaction, the concentration of the reactant A decreases with time [Figure 13.9(a)]. For a first-order reaction, if we plot ln $[A]_t$ versus time (y versus x), we obtain a straight line with a slope equal to $-k$ and a y intercept equal to ln $[A]_0$ [Figure 13.9(b)]. Thus, we can calculate the rate constant from the slope of this plot.
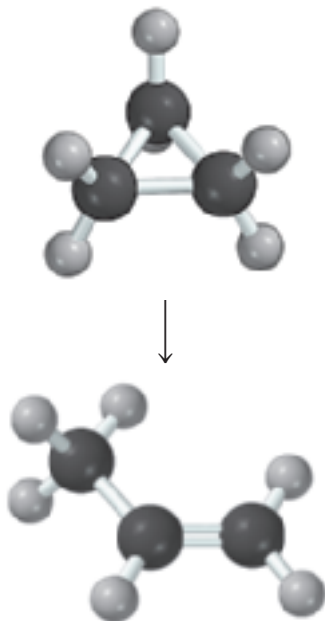
There are many first-order reactions. An example is the decomposition of ethane (C_2H_6) into highly reactive fragments called methyl radicals (CH_3):

$$C_2H_6 \longrightarrow 2CH_3$$

The decomposition of N_2O_5 is also a first-order reaction
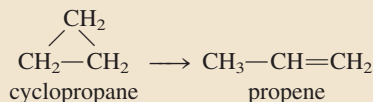
$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$
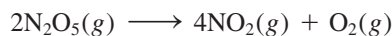
In Example 13.4 we apply Equation (13.3) to an organic reaction.

Example 13.4

The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of 6.7×10^{-4} s^{-1} at 500°C.

$$\underset{\text{cyclopropane}}{\overset{\displaystyle CH_2}{\overset{\diagup\diagdown}{CH_2-CH_2}}} \longrightarrow \underset{\text{propene}}{CH_3-CH=CH_2}$$

(a) If the initial concentration of cyclopropane was 0.25 M, what is the concentration after 8.8 min? (b) How long (in minutes) will it take for the concentration of cyclopropane to decrease from 0.25 M to 0.15 M? (c) How long (in minutes) will it take to convert 74 percent of the starting material?

Strategy The relationship between the concentrations of a reactant at different times in a first-order reaction is given by Equation (13.3) or (13.4). In (a) we are given $[A]_0 = 0.25$ M and asked for $[A]_t$ after 8.8 min. In (b) we are asked to calculate the time it takes for cyclopropane to decrease in concentration from 0.25 M to 0.15 M. No concentration values are given for (c). However, if initially we have 100 percent of the compound and 74 percent has reacted, then what is left must be (100% − 74%), or 26%. Thus, the ratio of the percentages will be equal to the ratio of the actual concentrations; that is, $[A]_t/[A]_0 = 26\%/100\%$, or 0.26/1.00.

(Continued)

Solution (a) In applying Equation (13.4), we note that because k is given in units of s^{-1}, we must first convert 8.8 min to seconds:

$$8.8 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} = 528 \text{ s}$$

We write

$$\ln [A]_t = -kt + \ln [A]_0$$
$$= -(6.7 \times 10^{-4} \text{ s}^{-1})(528 \text{ s}) + \ln (0.25)$$
$$= -1.74$$

Hence, $\qquad [A]_t = e^{-1.74} = \boxed{0.18 \text{ M}}$

Note that in the $\ln [A]_0$ term, $[A]_0$ is expressed as a dimensionless quantity (0.25) because we cannot take the logarithm of units.
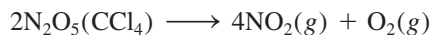
(b) Using Equation (13.3),

$$\ln \frac{0.15 \text{ M}}{0.25 \text{ M}} = -(6.7 \times 10^{-4} \text{ s}^{-1})t$$

$$t = 7.6 \times 10^2 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}}$$

$$= \boxed{13 \text{ min}}$$

(c) From Equation (13.3),

$$\ln \frac{0.26}{1.00} = -(6.7 \times 10^{-4} \text{ s}^{-1})t$$

$$t = 2.0 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = \boxed{33 \text{ min}}$$

Practice Exercise The reaction $2A \longrightarrow B$ is first order in A with a rate constant of $2.8 \times 10^{-2} \text{ s}^{-1}$ at 80°C. How long (in seconds) will it take for A to decrease from 0.88 M to 0.14 M?

N_2O_5

Now let us determine graphically the order and rate constant of the decomposition of dinitrogen pentoxide in carbon tetrachloride (CCl_4) solvent at 45°C:
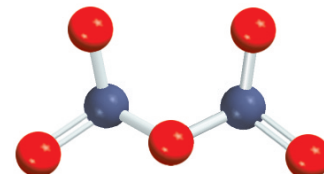
$$2N_2O_5(CCl_4) \longrightarrow 4NO_2(g) + O_2(g)$$

The following table shows the variation of N_2O_5 concentration with time, and the corresponding $\ln [N_2O_5]$ values.

t (s)	$[N_2O_5]$ (M)	$\ln [N_2O_5]$
0	0.91	−0.094
300	0.75	−0.29
600	0.64	−0.45
1200	0.44	−0.82
3000	0.16	−1.83

N_2O_5 decomposes to give NO_2 (brown color).

Applying Equation (13.4) we plot $\ln [N_2O_5]$ versus t, as shown in Figure 13.10. The fact that the points lie on a straight line shows that the rate law is first order. Next,

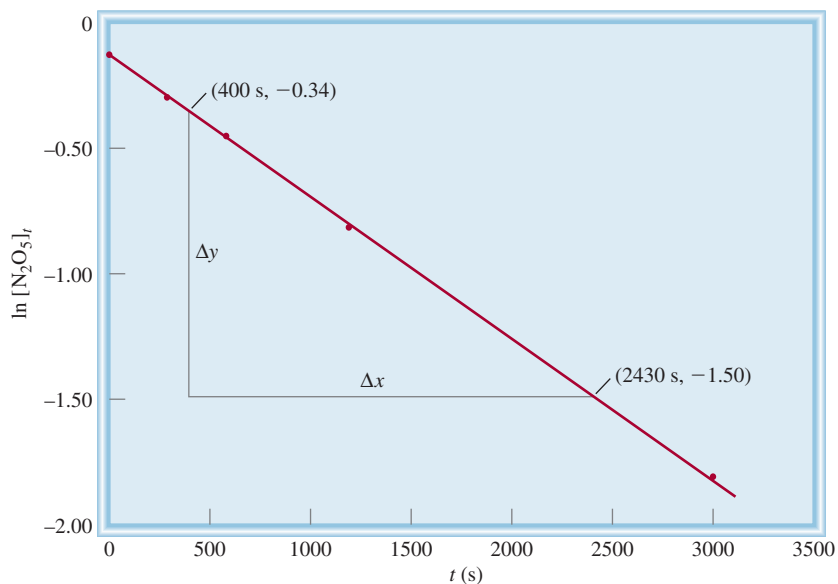**Figure 13.10** *Plot of ln* $[N_2O_5]_t$ *versus time. The rate constant can be determined from the slope of the straight line.*
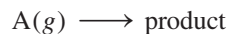

we determine the rate constant from the slope. We select two points far apart on the line and subtract their y and x values as follows:

$$\text{slope } (m) = \frac{\Delta y}{\Delta x}$$

$$= \frac{-1.50 - (-0.34)}{(2430 - 400) \text{ s}}$$

$$= -5.7 \times 10^{-4} \text{ s}^{-1}$$

Because $m = -k$, we get $k = 5.7 \times 10^{-4} \text{ s}^{-1}$.

For gas-phase reactions we can replace the concentration terms in Equation (13.3) with the pressures of the gaseous reactant. Consider the first-order reaction

$$A(g) \longrightarrow \text{product}$$

Using the ideal gas equation we write

$$PV = n_A RT$$

or

$$\frac{n_A}{V} = [A] = \frac{P}{RT}$$

Substituting $[A] = P/RT$ in Equation (13.3), we get

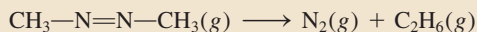$$\ln \frac{[A]_t}{[A]_0} = \ln \frac{P_t/RT}{P_0/RT} = \ln \frac{P_t}{P_0} = -kt$$

The equation corresponding to Equation (13.4) now becomes

$$\ln P_t = -kt + \ln P_0 \tag{13.5}$$

Example 13.5 shows the use of pressure measurements to study the kinetics of a first-order reaction.

Example 13.5

The rate of decomposition of azomethane ($C_2H_6N_2$) is studied by monitoring the partial pressure of the reactant as a function of time:

$$CH_3-N{=}N-CH_3(g) \longrightarrow N_2(g) + C_2H_6(g)$$

The data obtained at 300°C are shown in the following table:

Time (s)	Partial Pressure of Azomethane (mmHg)
0	284
100	220
150	193
200	170
250	150
300	132

Are these values consistent with first-order kinetics? If so, determine the rate constant.

Strategy To test for first-order kinetics, we consider the integrated first-order rate law that has a linear form, which is Equation (13.4)

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

If the reaction is first order, then a plot of $\ln [A]_t$ versus t (y versus x) will produce a straight line with a slope equal to $-k$. Note that the partial pressure of azomethane at any time is directly proportional to its concentration in moles per liter ($PV = nRT$, so $P \propto n/V$). Therefore, we substitute partial pressure for concentration [Equation (13.5)]:

$$\ln P_t = -kt + \ln P_0$$

where P_0 and P_t are the partial pressures of azomethane at $t = 0$ and $t = t$, respectively.

Solution First we construct the following table of t versus $\ln P_t$.

t (s)	$\ln P_t$
0	5.649
100	5.394
150	5.263
200	5.136
250	5.011
300	4.883

Figure 13.11, which is based on the data given in the table, shows that a plot of $\ln P_t$ versus t yields a straight line, so the reaction is indeed first order. The slope of the line is given by

$$\text{slope} = \frac{5.05 - 5.56}{(233 - 33)\,\text{s}} = -2.55 \times 10^{-3}\,\text{s}^{-1}$$

According to Equation (13.4), the slope is equal to $-k$, so $k = 2.55 \times 10^{-3}\,\text{s}^{-1}$.

$C_2H_6N_2 \longrightarrow N_2 + C_2H_6$
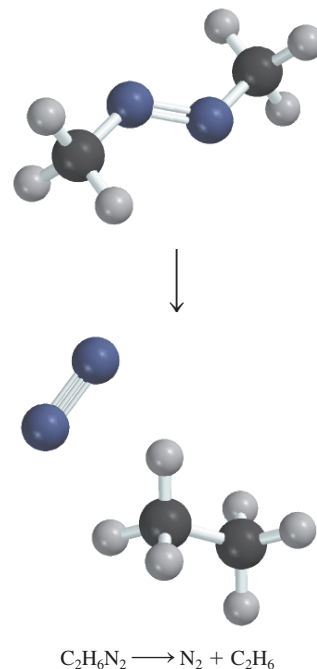
Similar problems: 13.19, 13.20.

(Continued)

Figure 13.11 *Plot of ln P_t versus time for the decomposition of azomethane.*

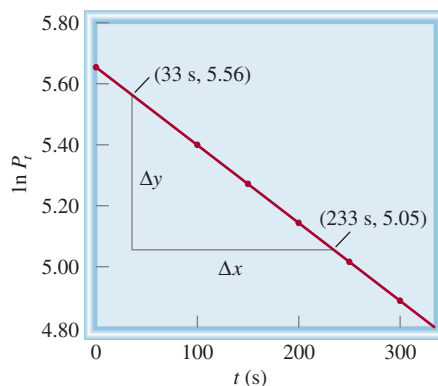*Practice Exercise* Ethyl iodide (C_2H_5I) decomposes at a certain temperature in the gas phase as follows:

$$C_2H_5I(g) \longrightarrow C_2H_4(g) + HI(g)$$

From the following data determine the order of the reaction and the rate constant.

Time (min)	$[C_2H_5I]$ (*M*)
0	0.36
15	0.30
30	0.25
48	0.19
75	0.13

Reaction Half-life

As a reaction proceeds, the concentration of the reactant(s) decreases. Another measure of the rate of a reaction, relating concentration to time, is the **half-life**, $t_{\frac{1}{2}}$, which is *the time required for the concentration of a reactant to decrease to half of its initial concentration*. We can obtain an expression for $t_{\frac{1}{2}}$ for a first-order reaction as follows. Equation (13.3) can be rearranged to give

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

By the definition of half-life, when $t = t_{\frac{1}{2}}$, $[A]_t = [A]_0/2$, so

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

or

$$t_{\frac{1}{2}} = \frac{1}{k} \ln 2 = \frac{0.693}{k} \tag{13.6}$$

Equation (13.6) tells us that the half-life of a first-order reaction is *independent* of the initial concentration of the reactant. Thus, it takes the same time for the concentration of the reactant to decrease from 1.0 *M* to 0.50 *M*, say, as it does for a
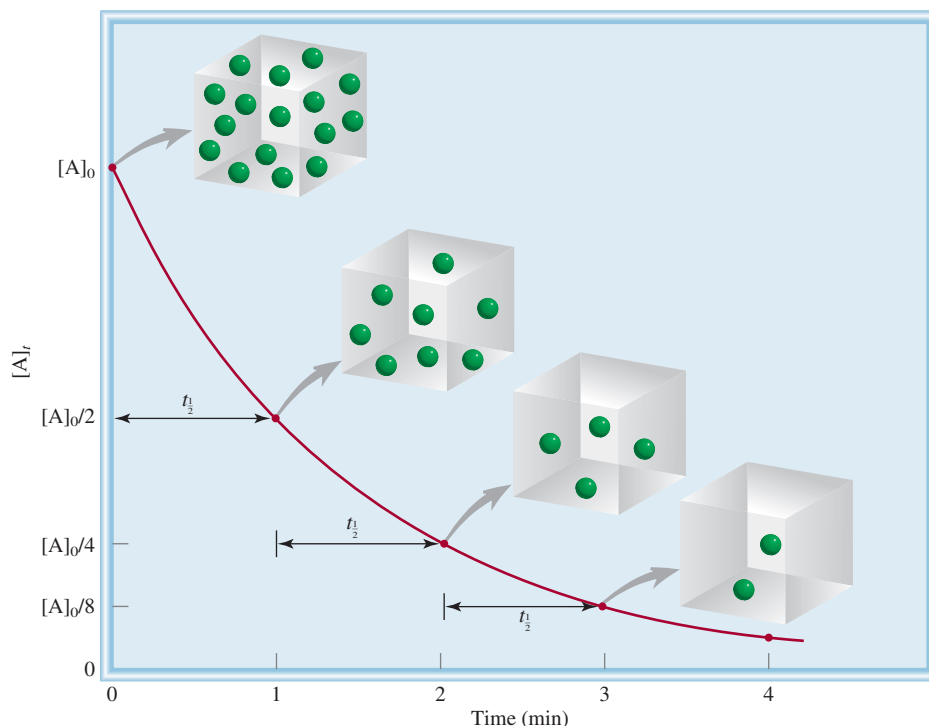
Figure 13.12 *A plot of [A]$_t$ versus time for the first-order reaction A ⟶ products. The half-life of the reaction is 1 min. After the elapse of each half-life, the concentration of A is halved.*

decrease in concentration from 0.10 *M* to 0.050 *M* (Figure 13.12). Measuring the half-life of a reaction is one way to determine the rate constant of a first-order reaction.

The following analogy may be helpful for understanding Equation (13.6). If a college student takes 4 yr to graduate, the half-life of his or her stay at the college is 2 yr. Thus, half-life is not affected by how many other students are present. Similarly, the half-life of a first-order reaction is concentration independent.

The usefulness of $t_{\frac{1}{2}}$ is that it gives us a measure of the magnitude of the rate constant—the shorter the half-life, the larger the *k*. Consider, for example, two radio-active isotopes used in nuclear medicine: ^{24}Na ($t_{\frac{1}{2}} = 14.7$ h) and ^{60}Co ($t_{\frac{1}{2}} = 5.3$ yr). It is obvious that the ^{24}Na isotope decays faster because it has a shorter half-life. If we started with 1 mole each of the isotopes, most of the ^{24}Na would be gone in a week while the ^{60}Co sample would be mostly intact.

In Example 13.6 we calculate the half-life of a first-order reaction.

Example 13.6

The decomposition of ethane (C_2H_6) to methyl radicals is a first-order reaction with a rate constant of 5.36×10^{-4} s^{-1} at 700°C:

$$C_2H_6(g) \longrightarrow 2CH_3(g)$$

Calculate the half-life of the reaction in minutes.

Strategy To calculate the half-life of a first-order reaction, we use Equation (13.6). A conversion is needed to express the half-life in minutes.

(Continued)

$C_2H_6 \longrightarrow 2CH_3$
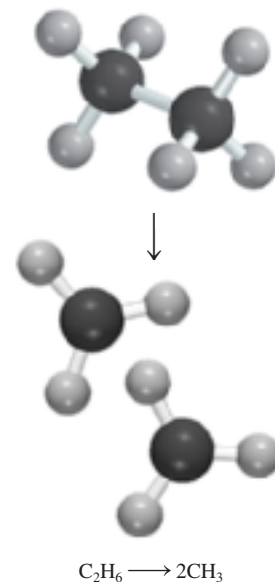
Solution For a first-order reaction, we only need the rate constant to calculate the half-life of the reaction. From Equation (13.6)

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

$$= \frac{0.693}{5.36 \times 10^{-4} \text{ s}^{-1}}$$

$$= 1.29 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}}$$
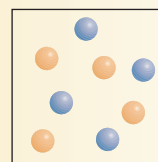
$$= 21.5 \text{ min}$$

Practice Exercise Calculate the half-life of the decomposition of N_2O_5, discussed on p. 579.

Review of Concepts

Consider the first-order reaction A ⟶ B in which A molecules (blue spheres) are converted to B molecules (orange spheres). (a) What are the half-life and rate constant for the reaction? (b) How many molecules of A and B are present at $t = 20$ s and $t = 30$ s?
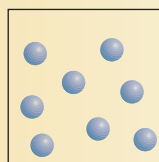
$t = 0$ s $t = 10$ s

Second-Order Reactions

A *second-order reaction* is *a reaction whose rate depends on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power*. The simpler type involves only one kind of reactant molecule:

$$A \longrightarrow \text{product}$$
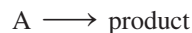
where

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

From the rate law,

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

As before, we can determine the units of k by writing

$$k = \frac{\text{rate}}{[A]^2} = \frac{M/\text{s}}{M^2} = 1/M \cdot \text{s}$$

Another type of second-order reaction is

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

and the rate law is given by

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

The reaction is first order in A and first order in B, so it has an overall reaction order of 2.

Using calculus, we can obtain the following expressions for "A $\longrightarrow$ product" second-order reactions:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \tag{13.7}$$

Equation (13.7) is the result of

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

Equation (13.7) has the form of a linear equation. As Figure 13.13 shows, a plot of $1/[A]_t$ versus t gives a straight line with slope $= k$ and y intercept $= 1/[A]_0$.

Pseudo-First-Order Reactions

The other type of second-order reaction

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

and the corresponding rate law

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

is actually more common than the $k[A]^2$ second-order kinetics already shown. However, it is considerably more difficult to treat mathematically. While it is possible to solve the integrated form of the rate law, a common approach is to measure the second-order reaction rates under *pseudo-first-order kinetics* conditions.

If the above reaction is carried out under the conditions where one of the reactants is in large excess over the other, then the concentration of the excess reactant will not change appreciably over the course of the reaction. For example, if $[B] \gg [A]$, then $[B]$ will be essentially constant and we have

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

Note that the rate law now has the appearance of a first-order reaction. The rate constant k_{obs}, called the pseudo-first-order rate constant, is given by $k_{obs} = k[B]$, where the subscript "obs" denotes observed and k is the second-order rate constant. If we measure k_{obs} for many different initial concentrations of B, then a plot of k_{obs} versus $[B]$ will yield a straight line with a slope equal to k.

Previously, we saw that the reaction between bromine and formic acid can be treated as a first-order reaction because formic acid is present in excess (see p. 566). Another well-studied example is the hydrolysis (meaning reaction with water) of ethyl acetate to yield acetic acid and ethanol:

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

Because the concentration of water, the solvent, is about 55.5 $M^{\dagger}$ compared to 1 M or less for ethyl acetate, $[H_2O]$ can be treated as a constant so the rate is given by

$$\text{rate} = k[CH_3COOC_2H_5][H_2O] = k_{obs}[CH_3COOC_2H_5]$$

where $k_{obs} = k[H_2O]$.

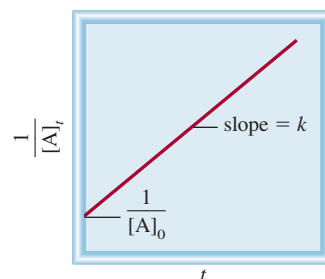**Figure 13.13** *A plot of $1/[A]_t$ versus t for the second-order reaction A $\longrightarrow$ products. The slope of the line is equal to k.*

$\dagger$In 1 L of a relatively dilute solution, the mass of water is approximately 1000 g so there are 1000 g/(18.02 g/mol) or 55.5 mole of water. Thus, the concentration of water is 55.5 M.

Reaction Half-life

We can obtain an equation for the half-life of a second-order reaction of the type A $\longrightarrow$ product by setting $[A]_t = [A]_0/2$ in Equation (13.7)

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

Solving for $t_{\frac{1}{2}}$ we obtain

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0} \tag{13.8}$$

Note that the half-life of a second-order reaction is inversely proportional to the initial reactant concentration. This result makes sense because the half-life should be shorter in the early stage of the reaction when more reactant molecules are present to collide with each other. Measuring the half-lives at different initial concentrations is one way to distinguish between a first-order and a second-order reaction.

The kinetic analysis of a second-order reaction is shown in Example 13.7.

I + I $\longrightarrow$ I$_2$
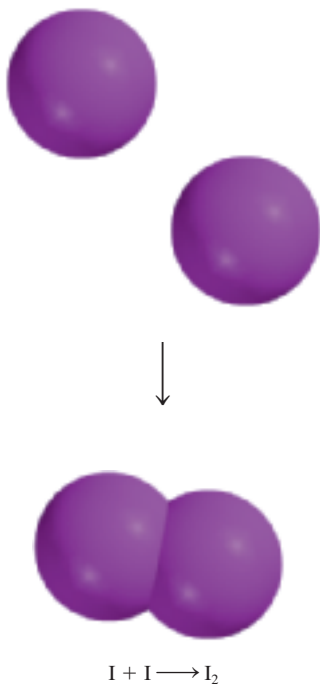
Example 13.7

Iodine atoms combine to form molecular iodine in the gas phase

$$I(g) + I(g) \longrightarrow I_2(g)$$
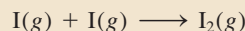
This reaction follows second-order kinetics and has the high rate constant $7.0 \times 10^9/M \cdot s$ at 23°C. (a) If the initial concentration of I was 0.086 M, calculate the concentration after 2.0 min. (b) Calculate the half-life of the reaction if the initial concentration of I is 0.60 M and if it is 0.42 M.

Strategy (a) The relationship between the concentrations of a reactant at different times is given by the integrated rate law. Because this is a second-order reaction, we use Equation (13.7). (b) We are asked to calculate the half-life. The half-life for a second-order reaction is given by Equation (13.8).

Solution (a) To calculate the concentration of a species at a later time of a second-order reaction, we need the initial concentration and the rate constant. Applying Equation (13.7)

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

$$\frac{1}{[A]_t} = (7.0 \times 10^9/M \cdot s)\left(2.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}}\right) + \frac{1}{0.086 \ M}$$

where $[A]_t$ is the concentration at $t = 2.0$ min. Solving the equation, we get

$$[A]_t = 1.2 \times 10^{-12} \ M$$

This is such a low concentration that it is virtually undetectable. The very large rate constant for the reaction means that practically all the I atoms combine after only 2.0 min of reaction time.

(Continued)

(b) We need Equation (13.8) for this part.

For $[I]_0 = 0.60\ M$

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

$$= \frac{1}{(7.0 \times 10^9/M \cdot s)(0.60\ M)}$$

$$= 2.4 \times 10^{-10}\ s$$

For $[I]_0 = 0.42\ M$

$$t_{\frac{1}{2}} = \frac{1}{(7.0 \times 10^9/M \cdot s)(0.42\ M)}$$

$$= 3.4 \times 10^{-10}\ s$$

Check These results confirm that the half-life of a second-order reaction, unlike that of a first-order reaction, is not a constant but depends on the initial concentration of the reactant(s). Does it make sense that a larger initial concentration should have a shorter half-life?

Practice Exercise The reaction 2A ⟶ B is second order with a rate constant of $51/M \cdot min$ at 24°C. (a) Starting with $[A]_0 = 0.0092\ M$, how long will it take for $[A]_t = 3.7 \times 10^{-3}\ M$? (b) Calculate the half-life of the reaction.
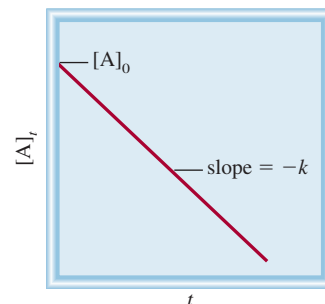

Figure 13.14 *A plot of $[A]_t$ versus t for a zero-order reaction. The slope of the line is equal to $-k$.*
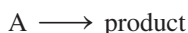
Similar problems: 13.27, 13.28.

Review of Concepts

Consider the reaction A ⟶ products. The half-life of the reaction depends on the initial concentration of A. Which of the following statements is inconsistent with the given information? (a) The half-life of the reaction decreases as the initial concentration increases. (b) A plot of ln $[A]_t$ versus t yields a straight line. (c) Doubling the concentration of A quadruples the rate.

Zero-Order Reactions

First- and second-order reactions are the most common reaction types. Reactions whose order is zero are rare. For a zero-order reaction

$$A \longrightarrow product$$

the rate law is given by

$$rate = k[A]^0$$
$$= k$$

Recall that any number raised to the power zero is equal to one.

Thus, the rate of a zero-order reaction is a *constant,* independent of reactant concentration. Using calculus, we can show that

$$[A]_t = -kt + [A]_0 \tag{13.9}$$

Equation (13.9) is the result of

$$\int_{[A]_0}^{[A]_t} d[A] = -k \int_0^t dt$$

Equation (13.9) has the form of a linear equation. As Figure 13.14 shows, a plot of $[A]_t$ versus t gives a straight line with slope $= -k$ and y intercept $= [A]_0$. To calculate the half-life of a zero-order reaction, we set $[A]_t = [A]_0/2$ in Equation (13.9) and obtain

$$t_{\frac{1}{2}} = \frac{[A]_0}{2k} \tag{13.10}$$

Radiocarbon Dating

How do scientists determine the ages of artifacts from archaeological excavations? If someone tried to sell you a manuscript supposedly dating from 1000 B.C., how could you be certain of its authenticity? Is a mummy found in an Egyptian pyramid *really* 3000 years old? Is the so-called Shroud of Turin truly the burial cloth of Jesus Christ? The answers to these and other similar questions can usually be found by applying chemical kinetics and the *radiocarbon dating technique*.

Earth's atmosphere is constantly being bombarded by cosmic rays of extremely high penetrating power. These rays, which originate in outer space, consist of electrons, neutrons, and atomic nuclei. One of the important reactions between the atmosphere and cosmic rays is the capture of neutrons by atmospheric nitrogen (nitrogen-14 isotope) to produce the radioactive carbon-14 isotope and hydrogen. The unstable carbon atoms eventually form $^{14}CO_2$, which mixes with the ordinary carbon dioxide ($^{12}CO_2$) in the air. As the carbon-14 isotope decays, it emits β particles (electrons). The rate of decay (as measured by the number of electrons emitted per second) obeys first-order kinetics. It is customary in the study of radioactive decay to write the rate law as

$$\text{rate} = kN$$

where k is the first-order rate constant and N the number of ^{14}C nuclei present. The half-life of the decay, $t_{\frac{1}{2}}$, is 5.73×10^3 yr, so that from Equation (13.6) we write

$$k = \frac{0.693}{5.73 \times 10^3 \text{ yr}} = 1.21 \times 10^{-4} \text{ yr}^{-1}$$

The Shroud of Turin. For generations there has been controversy about whether the Shroud, a piece of linen bearing the image of a man, was the burial cloth of Jesus Christ.

Many of the known zero-order reactions take place on a metal surface. An example is the decomposition of nitrous oxide (N_2O) to nitrogen and oxygen in the presence of platinum (Pt):

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$$
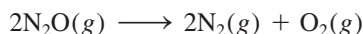
When all the binding sites on Pt are occupied, the rate becomes constant regardless of the amount of N_2O present in the gas phase. As we will see in Section 13.6, another well-studied zero-order reaction occurs in enzyme catalysis.

Third-order and higher order reactions are quite complex; they are not presented in this book. Table 13.3 summarizes the kinetics of zero-order, first-order, and second-order reactions. The above Chemistry in Action essay describes the application of chemical kinetics to estimating the ages of objects.

The carbon-14 isotopes enter the biosphere when carbon dioxide is taken up in plant photosynthesis. Plants are eaten by animals, which exhale carbon-14 in CO_2. Eventually, carbon-14 participates in many aspects of the carbon cycle. The ^{14}C lost by radioactive decay is constantly replenished by the production of new isotopes in the atmosphere. In this decay-replenishment process, a dynamic equilibrium is established whereby the ratio of ^{14}C to ^{12}C remains constant in living matter. But when an individual plant or an animal dies, the carbon-14 isotope in it is no longer replenished, so the ratio decreases as ^{14}C decays. This same change occurs when carbon atoms are trapped in coal, petroleum, or wood preserved underground, and, of course, in Egyptian mummies. After a number of years, there are proportionately fewer ^{14}C nuclei in, say, a mummy than in a living person.

In 1955, Willard F. Libby[†] suggested that this fact could be used to estimate the length of time the carbon-14 isotope in a particular specimen has been decaying without replenishment. Rearranging Equation (13.3), we can write

$$\ln \frac{N_0}{N_t} = kt$$

where N_0 and N_t are the number of ^{14}C nuclei present at $t = 0$ and $t = t$, respectively. Because the rate of decay is directly proportional to the number of ^{14}C nuclei present, the preceding equation can be rewritten as

---

[†]Willard Frank Libby (1908–1980). American chemist. Libby received the Nobel Prize in Chemistry in 1960 for his work on radiocarbon dating.

$$t = \frac{1}{k} \ln \frac{N_0}{N_t}$$

$$= \frac{1}{1.21 \times 10^{-4} \text{ yr}^{-1}} \ln \frac{\text{decay rate at } t = 0}{\text{decay rate at } t = t}$$

$$= \frac{1}{1.21 \times 10^{-4} \text{ yr}^{-1}} \ln \frac{\text{decay rate of fresh sample}}{\text{decay rate of old sample}}$$

Knowing k and the decay rates for the fresh sample and the old sample, we can calculate t, which is the age of the old sample. This ingenious technique is based on a remarkably simple idea. Its success depends on how accurately we can measure the rate of decay. In fresh samples, the ratio $^{14}C/^{12}C$ is about $1/10^{12}$, so the equipment used to monitor the radioactive decay must be very sensitive. Precision is more difficult with older samples because they contain even fewer ^{14}C nuclei. Nevertheless, radiocarbon dating has become an extremely valuable tool for estimating the age of archaeological artifacts, paintings, and other objects dating back 1000 to 50,000 years.

A well-publicized application of radiocarbon dating was the determination of the age of the Shroud of Turin. In 1988 three laboratories in Europe and the United States, working on samples of less than 50 mg of the Shroud, showed by carbon-14 dating that the Shroud dates from between A.D. 1260 and A.D. 1390. These findings seem to indicate that the Shroud could not have been the burial cloth of Christ. However, recent research reported new evidence suggesting the finding was invalid because the dating analysis was based on contaminants introduced by repairs to the Shroud in later years. It seems the controversy will continue for some time and further testing on the Shroud is warranted.

	Table 13.3	Summary of the Kinetics of Zero-Order, First-Order, and Second-Order Reactions		

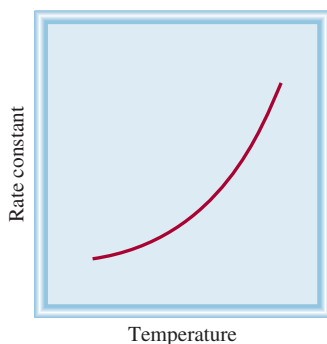| Order	Rate Law	Concentration-Time Equation	Half-Life
0	Rate = k	$[A]_t = -kt + [A]_0$	$\dfrac{[A]_0}{2k}$
1	Rate = $k[A]$	$\ln \dfrac{[A]_t}{[A]_0} = -kt$	$\dfrac{0.693}{k}$
2[†]	Rate = $k[A]^2$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$\dfrac{1}{k[A]_0}$

[†]A $\longrightarrow$ product.

Figure 13.15 *Dependence of rate constant on temperature. The rate constants of most reactions increase with increasing temperature.*

13.4 Activation Energy and Temperature Dependence of Rate Constants

With very few exceptions, reaction rates increase with increasing temperature. For example, the time required to hard-boil an egg in water is much shorter if the "reaction" is carried out at 100°C (about 10 min) than at 80°C (about 30 min). Conversely, an effective way to preserve foods is to store them at subzero temperatures, thereby slowing the rate of bacterial decay. Figure 13.15 shows a typical example of the relationship between the rate constant of a reaction and temperature. In order to explain this behavior, we must ask how reactions get started in the first place.

The Collision Theory of Chemical Kinetics

The kinetic molecular theory of gases (p. 202) postulates that gas molecules frequently collide with one another. Therefore, it seems logical to assume—and it is generally true—that chemical reactions occur as a result of collisions between reacting molecules. In terms of the *collision theory* of chemical kinetics, then, we expect the rate of a reaction to be directly proportional to the number of molecular collisions per second, or to the frequency of molecular collisions:

$$\text{rate} \, \propto \, \frac{\text{number of collisions}}{\text{s}}$$

(a)

(b)

(c)

Figure 13.16 *Dependence of number of collisions on concentration. We consider here only A-B collisions, which can lead to formation of products. (a) There are four possible collisions among two A and two B molecules. (b) Doubling the number of either type of molecule (but not both) increases the number of collisions to eight. (c) Doubling both the A and B molecules increases the number of collisions to sixteen. In each case, the collision between a red sphere and a gray sphere can only be counted once.*

This simple relationship explains the dependence of reaction rate on concentration.

Consider the reaction of A molecules with B molecules to form some product. Suppose that each product molecule is formed by the direct combination of an A molecule and a B molecule. If we doubled the concentration of A, then the number of A-B collisions would also double, because there would be twice as many A molecules that could collide with B molecules in any given volume (Figure 13.16). Consequently, the rate would increase by a factor of 2. Similarly, doubling the concentration of B molecules would increase the rate twofold. Thus, we can express the rate law as

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

The reaction is first order in both A and B and obeys second-order kinetics.

The collision theory is intuitively appealing, but the relationship between rate and molecular collisions is more complicated than you might expect. The implication of the collision theory is that a reaction always occurs when an A and a B molecule collide. However, not all collisions lead to reactions. Calculations based on the kinetic molecular theory show that, at ordinary pressures (say, 1 atm) and temperatures (say, 298 K), there are about 1×10^{27} binary collisions (collisions between two molecules) in 1 mL of volume every second in the gas phase. Even more collisions per second occur in liquids. If every binary collision led to a product, then most reactions would be complete almost instantaneously. In practice, we find that the rates of reactions differ greatly. This means that, in many cases, collisions alone do not guarantee that a reaction will take place.

Any molecule in motion possesses kinetic energy; the faster it moves, the greater the kinetic energy. But a fast-moving molecule will not break up into fragments on its own. To react, it must collide with another molecule. When molecules collide, part of their kinetic energy is converted to vibrational energy. If the initial kinetic energies are large, then the colliding molecules will vibrate so strongly as to break some of the chemical bonds. This bond fracture is the first step toward product formation. If the initial kinetic energies are small, the molecules will merely bounce off each other intact. Energetically speaking, there is some minimum collision energy below which
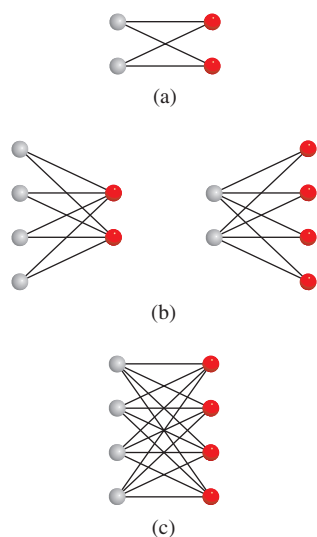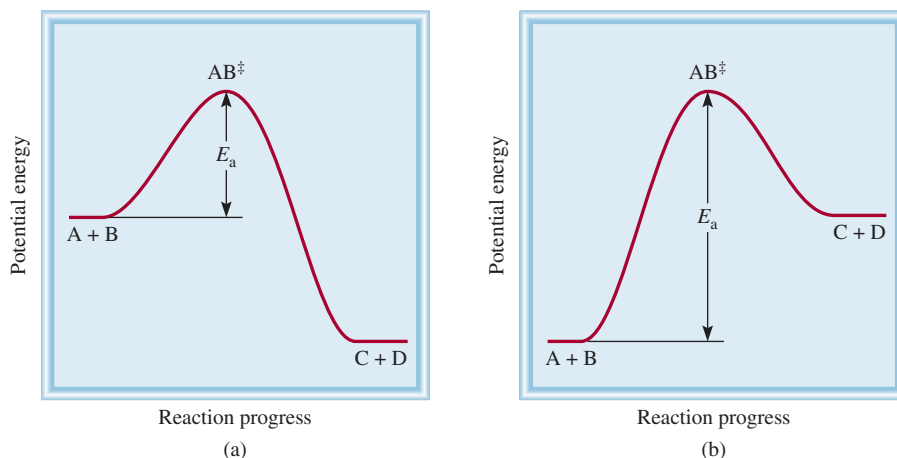
Figure 13.17 *Potential energy profiles for (a) exothermic and (b) endothermic reactions. These plots show the change in potential energy as reactants A and B are converted to products C and D. The activated complex (AB‡) is a highly unstable species with a high potential energy. The activation energy is defined for the forward reaction in both (a) and (b). Note that the products C and D are more stable than the reactants in (a) and less stable than those in (b).*

no reaction occurs. Lacking this energy, the molecules remain intact, and no change results from the collision.

We postulate that in order to react, the colliding molecules must have a total kinetic energy equal to or greater than the **activation energy (E_a),** which is *the minimum amount of energy required to initiate a chemical reaction*. When molecules collide they form an **activated complex** (also called the **transition state**), *a temporary species formed by the reactant molecules as a result of the collision before they form the product*.

Figure 13.17 shows two different potential energy profiles for the reaction

$$A + B \longrightarrow AB^‡ \longrightarrow C + D$$

where AB‡ denotes an activated complex formed by the collision between A and B. If the products are more stable than the reactants, then the reaction will be accompanied by a release of heat; that is, the reaction is exothermic [Figure 13.17(a)]. On the other hand, if the products are less stable than the reactants, then heat will be absorbed by the reacting mixture from the surroundings and we have an endothermic reaction [Figure 13.17(b)]. In both cases we plot the potential energy of the reacting system versus the progress of the reaction. Qualitatively, these plots show the potential energy changes as reactants are converted to products.

We can think of activation energy as a barrier that prevents less energetic molecules from reacting. Because the number of reactant molecules in an ordinary reaction is very large, the speeds, and hence also the kinetic energies of the molecules, vary greatly. Normally, only a small fraction of the colliding molecules—the fastest-moving ones— have enough kinetic energy to exceed the activation energy. These molecules can there-fore take part in the reaction. The increase in the rate (or the rate constant) with temperature can now be explained: The speeds of the molecules obey the Maxwell distributions shown in Figure 5.17. Compare the speed distributions at two different temperatures. Because more high-energy molecules are present at the higher tempera-ture, the rate of product formation is also greater at the higher temperature.

Animation
Activation Energy

The Arrhenius Equation

The dependence of the rate constant of a reaction on temperature can be expressed by the following equation, known as the *Arrhenius equation:*

$$k = Ae^{-E_a/RT} \tag{13.11}$$

where E_a is the activation energy of the reaction (in kJ/mol), R the gas constant (8.314 J/K · mol), T the absolute temperature, and e the base of the natural logarithm scale (see Appendix 4). The quantity A represents the collision frequency and is called the frequency factor. It can be treated as a constant for a given reacting system over a fairly wide temperature range. Equation (13.11) shows that the rate constant is directly proportional to A and, therefore, to the collision frequency. In addition, because of the minus sign associated with the exponent E_a/RT, the rate constant decreases with increasing activation energy and increases with increasing temperature. This equation can be expressed in a more useful form by taking the natural logarithm of both sides:

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

or

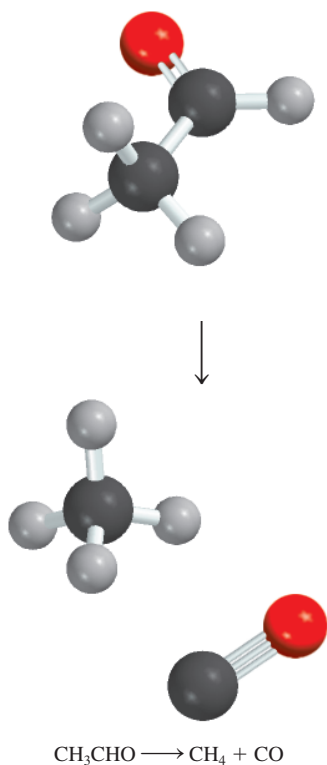$$\ln k = \ln A - \frac{E_a}{RT} \qquad (13.12)$$

Equation (13.12) can be rearranged to a linear equation:

$$\ln k = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \qquad (13.13)$$

$$\updownarrow \qquad \updownarrow \quad \updownarrow \qquad \updownarrow$$
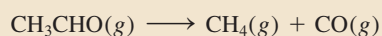$$y \;=\; m \quad x \;+\; b$$

Thus, a plot of $\ln k$ versus $1/T$ gives a straight line whose slope m is equal to $-E_a/R$ and whose intercept b with the y axis is $\ln A$.

Example 13.8 demonstrates a graphical method for determining the activation energy of a reaction.

Example 13.8

The rate constants for the decomposition of acetaldehyde

$$CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$$

were measured at five different temperatures. The data are shown in the table. Plot $\ln k$ versus $1/T$, and determine the activation energy (in kJ/mol) for the reaction. Note that the reaction is "$\frac{3}{2}$" order in CH_3CHO, so k has the units of $1/M^{\frac{1}{2}} \cdot$ s.

k ($1/M^{\frac{1}{2}} \cdot$ s)	T (K)
0.011	700
0.035	730
0.105	760
0.343	790
0.789	810

Strategy Consider the Arrhenius equation written as a linear equation

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

A plot of $\ln k$ versus $1/T$ (y versus x) will produce a straight line with a slope equal to $-E_a/R$. Thus, the activation energy can be determined from the slope of the plot.
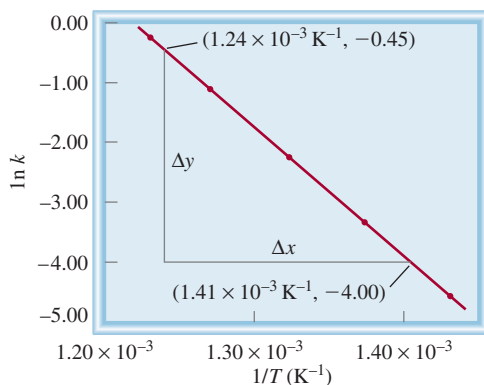
(Continued)

$CH_3CHO \longrightarrow CH_4 + CO$

Figure 13.18 *Plot of ln k versus 1/T. The slope of the line is equal to $-E_a/R$.*

Solution First we convert the data to the following table

ln k	1/T (K^{-1})
-4.51	1.43×10^{-3}
-3.35	1.37×10^{-3}
-2.254	1.32×10^{-3}
-1.070	1.27×10^{-3}
-0.237	1.23×10^{-3}

A plot of these data yields the graph in Figure 13.18. The slope of the line is calculated from two pairs of coordinates:

$$\text{slope} = \frac{-4.00 - (-0.45)}{(1.41 - 1.24) \times 10^{-3} \text{ K}^{-1}} = -2.09 \times 10^4 \text{ K}$$

From the linear form of Equation (13.13)

$$\text{slope} = -\frac{E_a}{R} = -2.09 \times 10^4 \text{ K}$$
$$E_a = (8.314 \text{ J/K} \cdot \text{mol})(2.09 \times 10^4 \text{ K})$$
$$= 1.74 \times 10^5 \text{ J/mol}$$
$$= \boxed{1.74 \times 10^2 \text{ kJ/mol}}$$

Check It is important to note that although the rate constant itself has the units $1/M^{\frac{1}{2}} \cdot$ s, the quantity ln k has no units (we cannot take the logarithm of a unit).

Practice Exercise The second-order rate constant for the decomposition of nitrous oxide (N_2O) into nitrogen molecule and oxygen atom has been measured at different temperatures:

k (1/M · s)	t (°C)
1.87×10^{-3}	600
0.0113	650
0.0569	700
0.244	750

Determine graphically the activation energy for the reaction.

An equation relating the rate constants k_1 and k_2 at temperatures T_1 and T_2 can be used to calculate the activation energy or to find the rate constant at another

temperature if the activation energy is known. To derive such an equation we start with Equation (13.12):

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

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

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

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

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right) \tag{13.14}$$

Example 13.9 illustrates the use of the equation we have just derived.

Example 13.9

The rate constant of a first-order reaction is 3.46×10^{-2} s^{-1} at 298 K. What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol?

Strategy A modified form of the Arrhenius equation relates two rate constants at two different temperatures [see Equation (13.14)]. Make sure the units of R and E_a are consistent.

Solution The data are

$$k_1 = 3.46 \times 10^{-2}\text{ s}^{-1} \quad k_2 = ?$$
$$T_1 = 298\text{ K} \quad\quad\quad T_2 = 350\text{ K}$$

Substituting in Equation (13.14),

$$\ln \frac{3.46 \times 10^{-2}\text{ s}^{-1}}{k_2} = \frac{50.2 \times 10^3\text{ J/mol}}{8.314\text{ J/K}\cdot\text{mol}}\left[\frac{298\text{ K} - 350\text{ K}}{(298\text{ K})(350\text{ K})}\right]$$

We convert E_a to units of J/mol to match the units of R. Solving the equation gives

$$\ln \frac{3.46 \times 10^{-2}\text{ s}^{-1}}{k_2} = -3.01$$

$$\frac{3.46 \times 10^{-2}\text{ s}^{-1}}{k_2} = e^{-3.01} = 0.0493$$

$$k_2 = 0.702\text{ s}^{-1}$$

Check The rate constant is expected to be greater at a higher temperature. Therefore, the answer is reasonable.

Practice Exercise The first-order rate constant for the reaction of methyl chloride (CH$_3$Cl) with water to produce methanol (CH$_3$OH) and hydrochloric acid (HCl) is 3.32×10^{-10} s^{-1} at 25°C. Calculate the rate constant at 40°C if the activation energy is 116 kJ/mol.

CO   NO₂   CO₂   NO
(a)

CO   NO₂   CO   NO₂
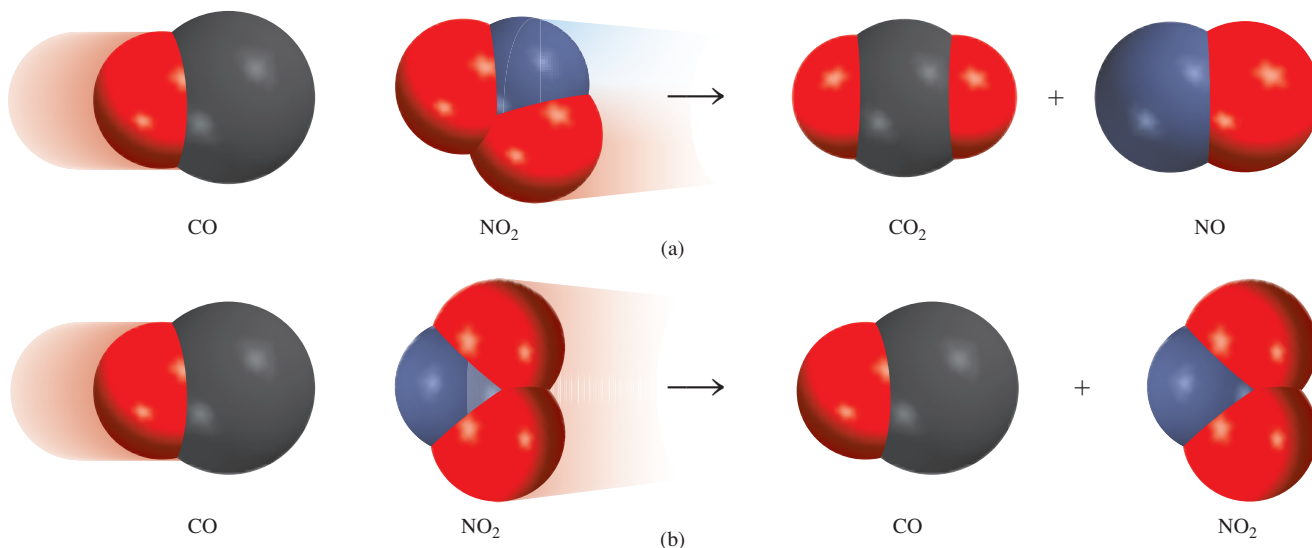(b)

Figure 13.19 *The orientations of the molecules shown in (a) are effective and will likely lead to formation of products. The orientations shown in (b) are ineffective and no products will be formed.*

For simple reactions (for example, reactions between atoms), we can equate the frequency factor (A) in the Arrhenius equation with the frequency of collision between the reacting species. For more complex reactions, we must also consider the "orientation factor," that is, how reacting molecules are oriented relative to each other. The reaction between carbon monoxide (CO) and nitrogen dioxide (NO_2) to form carbon dioxide (CO_2) and nitric oxide (NO) illustrates this point:

$$CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$$
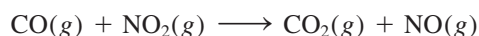
This reaction is most favorable when the reacting molecules approach each other according to that shown in Figure 13.19(a). Otherwise, few or no products are formed [Figure 13.19(b)]. The quantitative treatment of orientation factor is to modify Equation (13.11) as follows:

$$k = pAe^{-E_a/RT} \tag{13.15}$$

where p is the orientation factor. The orientation factor is a unitless quantity; its value ranges from 1 for reactions involving atoms such as $I + I \longrightarrow I_2$ to 10^{-6} or smaller for reactions involving molecules.

Animation
Orientation of Collision

Review of Concepts

(a) What can you deduce about the magnitude of the activation energy of a reaction if its rate constant changes appreciably with a small change in temperature?
(b) If a reaction occurs every time two reacting molecules collide, what can you say about the orientation factor and the activation energy of the reaction?

13.5 Reaction Mechanisms

As we mentioned earlier, an overall balanced chemical equation does not tell us much about how a reaction actually takes place. In many cases, it merely represents the sum of several *elementary steps,* or *elementary reactions, a series of simple reactions that represent the progress of the overall reaction at the molecular level*. The term for *the sequence of elementary steps that leads to product formation* is *reaction mechanism.* The reaction mechanism is comparable to the route of travel followed during a trip; the overall chemical equation specifies only the origin and destination.
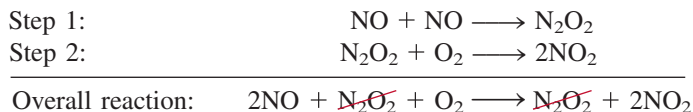
As an example of a reaction mechanism, let us consider the reaction between nitric oxide and oxygen:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
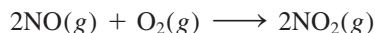
We know that the products are not formed directly from the collision of two NO molecules with an O_2 molecule because N_2O_2 is detected during the course of the reaction. Let us assume that the reaction actually takes place via two elementary steps as follows:

$$2NO(g) \longrightarrow N_2O_2(g)$$

$$N_2O_2(g) + O_2(g) \longrightarrow 2NO_2(g)$$
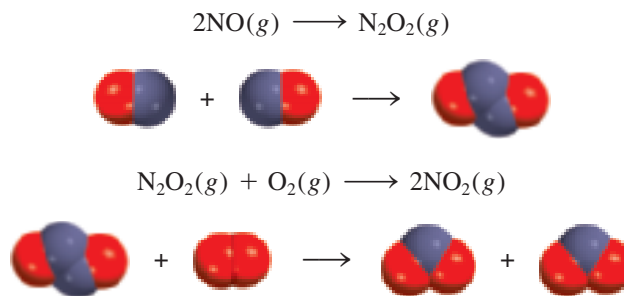
In the first elementary step, two NO molecules collide to form a N_2O_2 molecule. This event is followed by the reaction between N_2O_2 and O_2 to give two molecules of NO_2. The net chemical equation, which represents the overall change, is given by the sum of the elementary steps:


The sum of the elementary steps must give the overall balanced equation.

Step 1:	$NO + NO \longrightarrow N_2O_2$
Step 2:	$N_2O_2 + O_2 \longrightarrow 2NO_2$
Overall reaction:	$2NO + N_2O_2 + O_2 \longrightarrow N_2O_2 + 2NO_2$

Species such as N_2O_2 are called *intermediates* because they *appear in the mechanism of the reaction (that is, the elementary steps) but not in the overall balanced equation*. Keep in mind that an intermediate is always formed in an early elementary step and consumed in a later elementary step.

The *molecularity of a reaction* is *the number of molecules reacting in an elementary step*. These molecules may be of the same or different types. Each of the elementary steps discussed above is called a *bimolecular reaction,* an elementary step that *involves two molecules*. An example of a *unimolecular reaction,* an elementary step *in which only one reacting molecule participates*, is the conversion of cyclopropane to propene discussed in Example 13.4. Very few *termolecular reactions, reactions that involve the participation of three molecules in one elementary step,* are known, because the simultaneous encounter of three molecules is a far less likely event than a bimolecular collision.

Rate Laws and Elementary Steps

Knowing the elementary steps of a reaction enables us to deduce the rate law. Suppose we have the following elementary reaction:
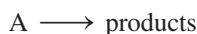
$$A \longrightarrow products$$

Because there is only one molecule present, this is a unimolecular reaction. It follows that the larger the number of A molecules present, the faster the rate of product formation. Thus, the rate of a unimolecular reaction is directly proportional to the concentration of A, or is first order in A:
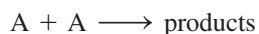
$$rate = k[A]$$

For a bimolecular elementary reaction involving A and B molecules
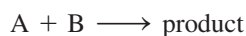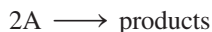
$$A + B \longrightarrow product$$

the rate of product formation depends on how frequently A and B collide, which in turn depends on the concentrations of A and B. Thus, we can express the rate as

$$rate = k[A][B]$$

Similarly, for a bimolecular elementary reaction of the type

$$A + A \longrightarrow products$$

or $$2A \longrightarrow products$$

the rate becomes

$$rate = k[A]^2$$

The preceding examples show that the reaction order for each reactant in an elementary reaction is equal to its stoichiometric coefficient in the chemical equation for that step. In general, we cannot tell by merely looking at the overall balanced equation whether the reaction occurs as shown or in a series of steps. This determination is made in the laboratory.

Note that the rate law can be written directly from the coefficients of an elementary step.

When we study a reaction that has more than one elementary step, the rate law for the overall process is given by the **rate-determining step,** which is *the slowest step in the sequence of steps leading to product formation.*

An analogy for the rate-determining step is the flow of traffic along a narrow road. Assuming the cars cannot pass one another on the road, the rate at which the cars travel is governed by the slowest-moving car.
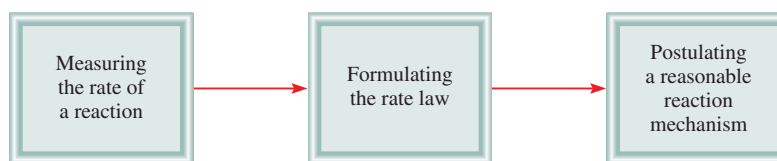
Experimental studies of reaction mechanisms begin with the collection of data (rate measurements). Next, we analyze the data to determine the rate constant and order of the reaction, and we write the rate law. Finally, we suggest a plausible mechanism for the reaction in terms of elementary steps (Figure 13.20). The elementary steps must satisfy two requirements:

- The sum of the elementary steps must give the overall balanced equation for the reaction.

- The rate-determining step should predict the same rate law as is determined experimentally.

Remember that for a proposed reaction scheme, we must be able to detect the presence of any intermediate(s) formed in one or more elementary steps.

Figure 13.20 *Sequence of steps in the study of a reaction mechanism.*

Measuring the rate of a reaction → Formulating the rate law → Postulating a reasonable reaction mechanism

The decomposition of hydrogen peroxide and the formation of hydrogen iodide from molecular hydrogen and molecular iodine illustrate the elucidation of reaction mechanisms by experimental studies.

Hydrogen Peroxide Decomposition

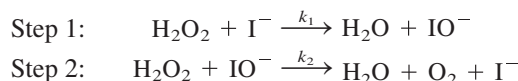The decomposition of hydrogen peroxide is facilitated by iodide ions (Figure 13.21). The overall reaction is

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$
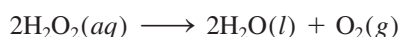
By experiment, the rate law is found to be

$$\text{rate} = k[H_2O_2][I^-]$$

Thus, the reaction is first order with respect to both H_2O_2 and I^-.

You can see that H_2O_2 decomposition does not occur in a single elementary step corresponding to the overall balanced equation. If it did, the reaction would be second order in H_2O_2 (as a result of the collision of two H_2O_2 molecules). What's more, the I^- ion, which is not even part of the overall equation, appears in the rate law expression. How can we reconcile these facts? First, we can account for the observed rate law by assuming that the reaction takes place in two separate elementary steps, each of which is bimolecular:

Figure 13.21 *The decomposition of hydrogen peroxide is catalyzed by the iodide ion. A few drops of liquid soap have been added to the solution to dramatize the evolution of oxygen gas. (Some of the iodide ions are oxidized to molecular iodine, which then reacts with iodide ions to form the brown triiodide I_3^- ion.)*

$$\text{Step 1:} \qquad H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^-$$
$$\text{Step 2:} \qquad H_2O_2 + IO^- \xrightarrow{k_2} H_2O + O_2 + I^-$$

If we further assume that step 1 is the rate-determining step, then the rate of the reaction can be determined from the first step alone:

$$\text{rate} = k_1[H_2O_2][I^-]$$

where $k_1 = k$. Note that the IO^- ion is an intermediate because it does not appear in the overall balanced equation. Although the I^- ion also does not appear in the overall equation, I^- differs from IO^- in that the former is present at the start of the reaction and at its completion. The function of I^- is to speed up the reaction—that is, it is a *catalyst*. We will discuss catalysis in Section 13.6. Figure 13.22 shows the potential energy profile for a reaction like the decomposition of H_2O_2. We see that the first step, which is rate determining, has a larger activation energy than the second step. The intermediate, although stable enough to be observed, reacts quickly to form the products.

Intermediate
E_a (Step 1)
R
E_a' (Step 2)
P
Potential energy
Reaction progress

Figure 13.22 *Potential energy profile for a two-step reaction in which the first step is rate-determining. R and P represent reactants and products, respectively.*

The Hydrogen Iodide Reaction

A common reaction mechanism is one that involves at least two elementary steps, the first of which is very rapid in both the forward and reverse directions compared with the second step. An example is the reaction between molecular hydrogen and molecular iodine to produce hydrogen iodide:
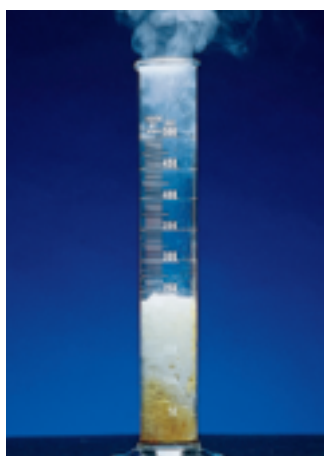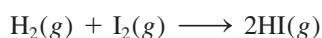
$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

Experimentally, the rate law is found to be

$$\text{rate} = k[H_2][I_2]$$

For many years it was thought that the reaction occurred just as written; that is, it is a bimolecular reaction involving a hydrogen molecule and an iodine molecule, as shown on p. 598. However, in the 1960s chemists found that the actual mechanism is more complicated. A two-step mechanism was proposed:

$$\text{Step 1:} \qquad I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I$$

$$\text{Step 2:} \qquad H_2 + 2I \xrightarrow{k_2} 2HI$$
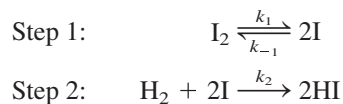
where k_1, k_{-1}, and k_2 are the rate constants for the reactions. The I atoms are the intermediate in this reaction.

When the reaction begins, there are very few I atoms present. But as I_2 dissociates, the concentration of I_2 decreases while that of I increases. Therefore, the forward rate of step 1 decreases and the reverse rate increases. Soon the two rates become equal, and a chemical equilibrium is established. Because the elementary reactions in step 1 are much faster than the one in step 2, equilibrium is reached before any significant reaction with hydrogen occurs, and it persists throughout the reaction.

In the equilibrium condition of step 1 the forward rate is equal to the reverse rate; that is,

$$k_1[I_2] = k_{-1}[I]^2$$

or

$$[I]^2 = \frac{k_1}{k_{-1}}[I_2]$$

The rate of the reaction is given by the slow, rate-determining step, which is step 2:

$$\text{rate} = k_2[H_2][I]^2$$

Substituting the expression for $[I]^2$ into this rate law, we obtain

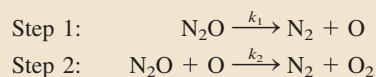$$\text{rate} = \frac{k_1 k_2}{k_{-1}}[H_2][I_2]$$
$$= k[H_2][I_2]$$

where $k = k_1 k_2/k_{-1}$. As you can see, this two-step mechanism also gives the correct rate law for the reaction. This agreement along with the observation of intermediate I atoms provides strong evidence that the mechanism is correct.

Finally, we note that not all reactions have a single rate-determining step. A reaction may have two or more comparably slow steps. The kinetic analysis of such reactions is generally more involved.

Example 13.10 concerns the mechanistic study of a relatively simple reaction.

$$H_2 + I_2 \longrightarrow 2HI$$

Chemical equilibrium will be discussed in Chapter 14.

Example 13.10

The gas-phase decomposition of nitrous oxide (N_2O) is believed to occur via two elementary steps:

$$\text{Step 1:} \qquad N_2O \xrightarrow{k_1} N_2 + O$$

$$\text{Step 2:} \qquad N_2O + O \xrightarrow{k_2} N_2 + O_2$$

(Continued)

$2N_2O \longrightarrow 2N_2 + O_2$
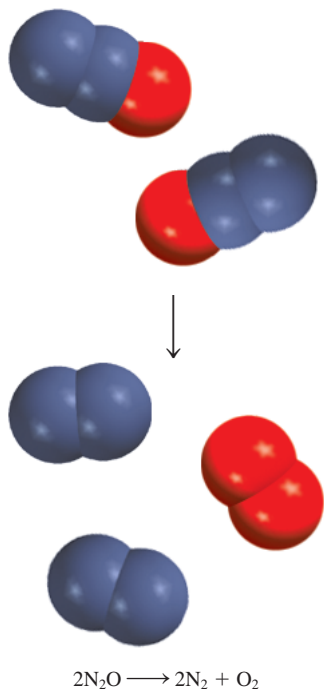
Experimentally the rate law is found to be rate = $k[N_2O]$. (a) Write the equation for the overall reaction. (b) Identify the intermediate. (c) What can you say about the relative rates of steps 1 and 2?

Strategy (a) Because the overall reaction can be broken down into elementary steps, knowing the elementary steps would enable us to write the overall reaction. (b) What are the characteristics of an intermediate? Does it appear in the overall reaction? (c) What determines which elementary step is rate determining? How does a knowledge of the rate-determining step help us write the rate law of a reaction?

Solution (a) Adding the equations for steps 1 and 2 gives the overall reaction

$$2N_2O \longrightarrow 2N_2 + O_2$$

(b) Because the O atom is produced in the first elementary step and it does not appear in the overall balanced equation, it is an intermediate.

(c) If we assume that step 1 is the rate-determining step, then the rate of the overall reaction is given by

$$\text{rate} = k_1[N_2O]$$

and $k = k_1$.

Check There are two criteria that must be met for a proposed reaction mechanism to be plausible. (1) The individual steps (elementary steps) must sum to the corrected overall reaction. (2) The rate-determining step (the slow step) must have the same rate law as the experimentally determined rate law.

Practice Exercise The reaction between NO_2 and CO to produce NO and CO_2 is believed to occur via two steps:

$$\text{Step 1:} \quad NO_2 + NO_2 \longrightarrow NO + NO_3$$
$$\text{Step 2:} \quad NO_3 + CO \longrightarrow NO_2 + CO_2$$
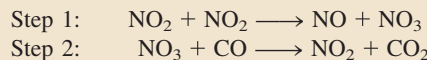
The experimental rate law is rate = $k[NO_2]^2$. (a) Write the equation for the overall reaction. (b) Identify the intermediate. (c) What can you say about the relative rates of steps 1 and 2?
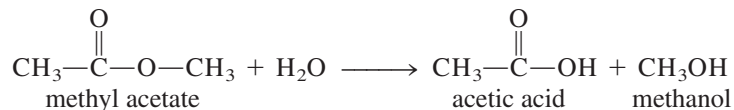
Similar problem: 13.55.

Review of Concepts
The rate law for the reaction $H_2 + 2IBr \longrightarrow I_2 + 2HBr$ is rate = $k[H_2][IBr]$. Given that HI is an intermediate, write a two-step mechanism for the reaction.
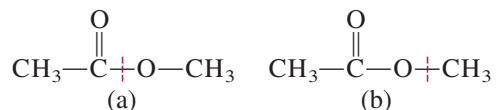
Experimental Support for Reaction Mechanisms

How can we find out whether the proposed mechanism for a particular reaction is correct? In the case of hydrogen peroxide decomposition we might try to detect the presence of the IO^- ions by spectroscopic means. Evidence of their presence would support the reaction scheme. Similarly, for the hydrogen iodide reaction, detection of iodine atoms would lend support to the two-step mechanism. For example, I_2 dissociates into atoms when it is irradiated with visible light. Thus, we might predict that the formation of HI from H_2 and I_2 would speed up as the intensity of light is increased because that should increase the concentration of I atoms. Indeed, this is just what is observed.

In another case, chemists wanted to know which C—O bond is broken in the reaction between methyl acetate and water in order to better understand the reaction mechanism

$$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3 + H_2O \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH + CH_3OH$$

methyl acetate   acetic acid   methanol

The two possibilities are

$$CH_3-\overset{\overset{O}{\|}}{C}\text{┼}O-CH_3 \qquad CH_3-\overset{\overset{O}{\|}}{C}-O\text{┼}CH_3$$

(a)   (b)

To distinguish between schemes (a) and (b), chemists used water containing the oxygen-18 isotope instead of ordinary water (which contains the oxygen-16 isotope). When the oxygen-18 water was used, only the acetic acid formed contained oxygen-18:

$$CH_3-\overset{\overset{O}{\|}}{C}-{}^{18}O-H$$
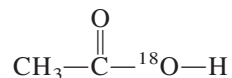
Thus, the reaction must have occurred via bond-breaking scheme (a), because the product formed via scheme (b) would retain both of its original oxygen atoms.

Another example is photosynthesis, the process by which green plants produce glucose from carbon dioxide and water

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

A question that arose early in studies of photosynthesis was whether the molecular oxygen was derived from water, from carbon dioxide, or from both. By using water containing the oxygen-18 isotope, it was demonstrated that the evolved oxygen came from water, and none came from carbon dioxide, because the O_2 contained only the ^{18}O isotopes. This result supported the mechanism in which water molecules are "split" by light:

$$2H_2O + hv \longrightarrow O_2 + 4H^+ + 4e^-$$
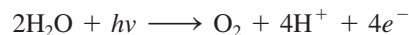
where hv represents the energy of a photon. The protons and electrons are used to drive energetically unfavorable reactions that are necessary for plant growth and function.

These examples give some idea of how inventive chemists must be in studying reaction mechanisms. For complex reactions, however, it is virtually impossible to prove the uniqueness of any particular mechanism.

13.6 Catalysis

For the decomposition of hydrogen peroxide we saw that the reaction rate depends on the concentration of iodide ions even though I^- does not appear in the overall equation. We noted that I^- acts as a catalyst for that reaction. A **catalyst** is *a substance that increases the rate of a reaction by lowering the activation energy*. It does so by providing an alternative reaction pathway. The catalyst may react to form an intermediate with the reactant, but it is regenerated in a subsequent step so it is not consumed in the reaction.

■■■ **Animation**
Catalysis

A rise in temperature also increases the rate of a reaction. However, at high temperatures, the products formed may undergo other reactions, thereby reducing the yield.

In the laboratory preparation of molecular oxygen, a sample of potassium chlorate is heated, as shown in Figure 4.13(b). The reaction is

$$2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$$
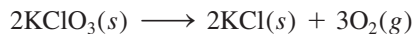
However, this thermal decomposition process is very slow in the absence of a catalyst. The rate of decomposition can be increased dramatically by adding a small amount of the catalyst manganese(IV) dioxide (MnO_2), a black powdery substance. All of the MnO_2 can be recovered at the end of the reaction, just as all the I^- ions remain following H_2O_2 decomposition.

A catalyst speeds up a reaction by providing a set of elementary steps with more favorable kinetics than those that exist in its absence. From Equation (13.11) we know that the rate constant k (and hence the rate) of a reaction depends on the frequency factor A and the activation energy E_a—the larger A or the smaller E_a, the greater the rate. In many cases, a catalyst increases the rate by lowering the activation energy for the reaction.

Let us assume that the following reaction has a certain rate constant k and an activation energy E_a.

$$A + B \xrightarrow{k} C + D$$
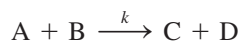
In the presence of a catalyst, however, the rate constant is k_c (called the *catalytic rate constant*):

$$A + B \xrightarrow{k_c} C + D$$
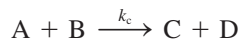
By the definition of a catalyst,

$$\text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}}$$

Figure 13.23 shows the potential energy profiles for both reactions. Note that the total energies of the reactants (A and B) and those of the products (C and D) are unaffected by the catalyst; the only difference between the two is a lowering of the activation energy from E_a to E_a'. Because the activation energy for the reverse reaction is also lowered, a catalyst enhances the rates of the reverse and forward reactions equally.

There are three general types of catalysis, depending on the nature of the rate-increasing substance: heterogeneous catalysis, homogeneous catalysis, and enzyme catalysis.

To extend the traffic analogy, adding a catalyst can be compared with building a tunnel through a mountain to connect two towns that were previously linked by a winding road over the mountain.

A catalyst lowers the activation energy for both the forward and reverse reactions.

Figure 13.23 *Comparison of the activation energy barriers of an uncatalyzed reaction and the same reaction with a catalyst. The catalyst lowers the energy barrier but does not affect the actual energies of the reactants or products. Although the reactants and products are the same in both cases, the reaction mechanisms and rate laws are different in (a) and (b).*
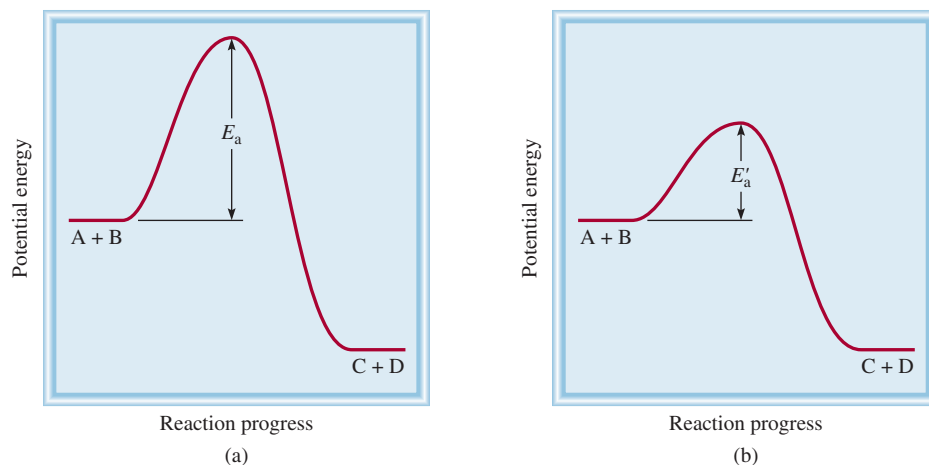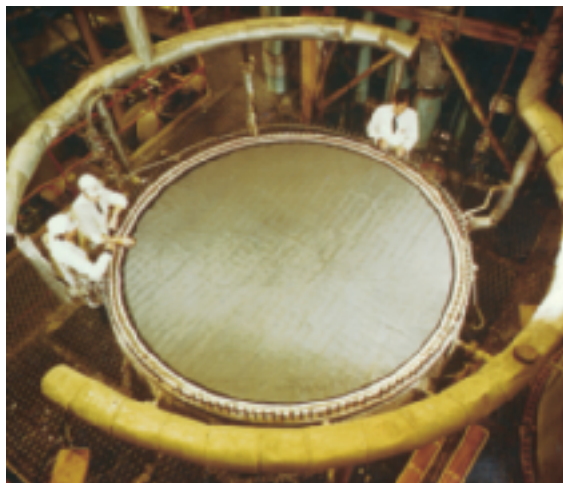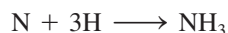
Heterogeneous Catalysis

In *heterogeneous catalysis,* the reactants and the catalyst are in different phases. Usually the catalyst is a solid and the reactants are either gases or liquids. Heterogeneous catalysis is by far the most important type of catalysis in industrial chemistry, especially in the synthesis of many key chemicals. Here we describe three specific examples of heterogeneous catalysis that account for millions of tons of chemicals produced annually on an industrial scale.

Metals and compounds of metals that are most frequently used in heterogeneous catalysis.

The Haber Synthesis of Ammonia

Ammonia is an extremely valuable inorganic substance used in the fertilizer industry, the manufacture of explosives, and many other applications. Around the turn of the twentieth century, many chemists strove to synthesize ammonia from nitrogen and hydrogen. The supply of atmospheric nitrogen is virtually inexhaustible, and hydrogen gas can be produced readily by passing steam over heated coal:

$$H_2O(g) + C(s) \longrightarrow CO(g) + H_2(g)$$

Hydrogen is also a by-product of petroleum refining.

The formation of NH_3 from N_2 and H_2 is exothermic:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H° = -92.6 \text{ kJ/mol}$$

But the reaction rate is extremely slow at room temperature. To be practical on a large scale, a reaction must occur at an appreciable rate *and* it must have a high yield of the desired product. Raising the temperature does accelerate the above reaction, but at the same time it promotes the decomposition of NH_3 molecules into N_2 and H_2, thus lowering the yield of NH_3.

In 1905, after testing literally hundreds of compounds at various temperatures and pressures, Fritz Haber discovered that iron plus a few percent of oxides of potassium and aluminum catalyze the reaction of hydrogen with nitrogen to yield ammonia at about 500°C. This procedure is known as the *Haber process.*

In heterogeneous catalysis, the surface of the solid catalyst is usually the site of the reaction. The initial step in the Haber process involves the dissociation of N_2 and H_2 on the metal surface (Figure 13.24). Although the dissociated species are not truly free atoms because they are bonded to the metal surface, they are highly reactive. The two reactant molecules behave very differently on the catalyst surface. Studies show that H_2 dissociates into atomic hydrogen at temperatures as low as -196°C (the boiling point of liquid nitrogen). Nitrogen molecules, on the other hand, dissociate at

Figure 13.24 *The catalytic action in the synthesis of ammonia. First the H_2 and N_2 molecules bind to the surface of the catalyst. This interaction weakens the covalent bonds within the molecules and eventually causes the molecules to dissociate. The highly reactive H and N atoms combine to form NH_3 molecules, which then leave the surface.*

Figure 13.25 *Platinum-rhodium catalyst used in the Ostwald process.*

about 500°C. The highly reactive N and H atoms combine rapidly at high temperatures to produce the desired NH_3 molecules:

$$N + 3H \longrightarrow NH_3$$

The Manufacture of Nitric Acid

Nitric acid is one of the most important inorganic acids. It is used in the production of fertilizers, dyes, drugs, and explosives. The major industrial method of producing nitric acid is the *Ostwald*[†] *process*. The starting materials, ammonia and molecular oxygen, are heated in the presence of a platinum-rhodium catalyst (Figure 13.25) to about 800°C:

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

The nitric oxide readily oxidizes (without catalysis) to nitrogen dioxide:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
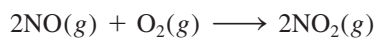
When dissolved in water, NO_2 forms both nitrous acid and nitric acid:

$$2NO_2(g) + H_2O(l) \longrightarrow HNO_2(aq) + HNO_3(aq)$$
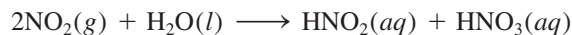
On heating, nitrous acid is converted to nitric acid as follows:

$$3HNO_2(aq) \longrightarrow HNO_3(aq) + H_2O(l) + 2NO(g)$$
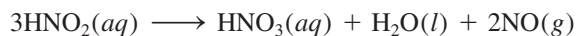
The NO generated can be recycled to produce NO_2 in the second step.

Catalytic Converters

At high temperatures inside a running car's engine, nitrogen and oxygen gases react to form nitric oxide:

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$
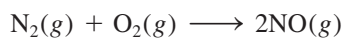
[†]Wilhelm Ostwald (1853–1932). German chemist. Ostwald made important contributions to chemical kinetics, thermodynamics, and electrochemistry. He developed the industrial process for preparing nitric acid that now bears his name. He received the Nobel Prize in Chemistry in 1909.
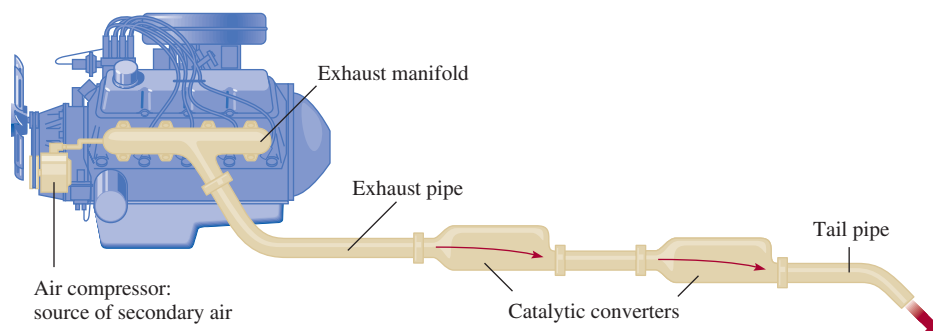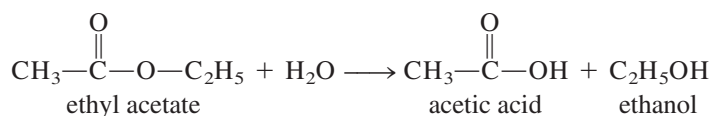
When released into the atmosphere, NO rapidly combines with O_2 to form NO_2. Nitrogen dioxide and other gases emitted by an automobile, such as carbon monoxide (CO) and various unburned hydrocarbons, make automobile exhaust a major source of air pollution.

Most new cars are equipped with catalytic converters (Figure 13.26). An efficient catalytic converter serves two purposes: It oxidizes CO and unburned hydrocarbons to CO_2 and H_2O, and it reduces NO and NO_2 to N_2 and O_2. Hot exhaust gases into which air has been injected are passed through the first chamber of one converter to accelerate the complete burning of hydrocarbons and to decrease CO emission. (A cross section of the catalytic converter is shown in Figure 13.27.) However, because high temperatures increase NO production, a second chamber containing a different catalyst (a transition metal or a transition metal oxide such as CuO or Cr_2O_3) and operating at a lower temperature are required to dissociate NO into N_2 and O_2 before the exhaust is discharged through the tailpipe.

Homogeneous Catalysis

In *homogeneous catalysis* the reactants and catalyst are dispersed in a single phase, usually liquid. Acid and base catalyses are the most important types of homogeneous catalysis in liquid solution. For example, the reaction of ethyl acetate with water to form acetic acid and ethanol normally occurs too slowly to be measured.

$$CH_3-\overset{\overset{O}{\|}}{C}-O-C_2H_5 + H_2O \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH + C_2H_5OH$$

$$\text{ethyl acetate} \qquad\qquad\qquad \text{acetic acid} \qquad \text{ethanol}$$

In the absence of the catalyst, the rate law is given by

$$\text{rate} = k[CH_3COOC_2H_5]$$

*This is a pseudo-first-order reaction discussed earlier.*

Figure 13.27 *A cross-sectional view of a catalytic converter. The beads contain platinum, palladium, and rhodium, which catalyze the conversion of CO and hydrocarbons to carbon dioxide and water.*

However, the reaction can be catalyzed by an acid. In the presence of hydrochloric acid, the rate is faster and the rate law is given by
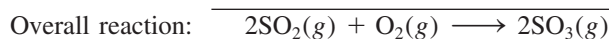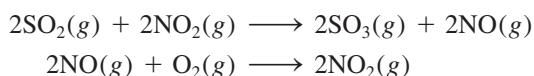
$$\text{rate} = k_c[CH_3COOC_2H_5][H^+]$$

Note that because $k_c > k$, the rate is determined solely by the catalyzed portion of the reaction.

Homogeneous catalysis can also take place in the gas phase. A well-known example of catalyzed gas-phase reactions is the lead chamber process, which for many years was the primary method of manufacturing sulfuric acid. Starting with sulfur, we would expect the production of sulfuric acid to occur in the following steps:

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$
$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$
$$H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq)$$
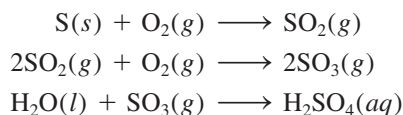
In reality, however, sulfur dioxide is not converted directly to sulfur trioxide; rather, the oxidation is more efficiently carried out in the presence of the catalyst nitrogen dioxide:

$$2SO_2(g) + 2NO_2(g) \longrightarrow 2SO_3(g) + 2NO(g)$$
$$\underline{2NO(g) + O_2(g) \longrightarrow 2NO_2(g)}$$

Overall reaction: $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

Note that there is no net loss of NO_2 in the overall reaction, so that NO_2 meets the criteria for a catalyst.

In recent years, chemists have devoted much effort to developing a class of transition metal compounds to serve as homogeneous catalysts. These compounds are soluble in various organic solvents and therefore can catalyze reactions in the same phase as the dissolved reactants. Many of the processes they catalyze are organic. For example, a red-violet compound of rhodium, $[(C_6H_5)_3P]_3RhCl$, catalyzes the conversion of a carbon-carbon double bond to a carbon-carbon single bond as follows:
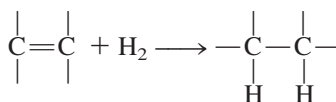
$$\underset{|}{\overset{|}{C}}=\underset{|}{\overset{|}{C}} + H_2 \longrightarrow -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}-$$

Homogeneous catalysis has several advantages over heterogeneous catalysis. For one thing, the reactions can often be carried out under atmospheric conditions, thus reducing production costs and minimizing the decomposition of products at high temperatures. In addition, homogeneous catalysts can be designed to function selectively for a particular type of reaction, and homogeneous catalysts cost less than the precious metals (for example, platinum and gold) used in heterogeneous catalysis.

Enzyme Catalysis

Of all the intricate processes that have evolved in living systems, none is more striking or more essential than enzyme catalysis. **Enzymes** are *biological catalysts*. The amazing fact about enzymes is that not only can they increase the rate of biochemical reactions by factors ranging from 10^6 to 10^{18}, but they are also highly specific. An enzyme acts only on certain molecules, called *substrates* (that is, reactants), while leaving the rest of the system unaffected. It has been estimated that an average living
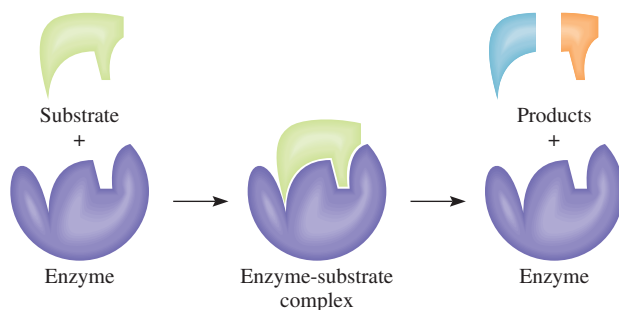
Figure 13.28 *The lock-and-key model of an enzyme's specificity for substrate molecules.*

cell may contain some 3000 different enzymes, each of them catalyzing a specific reaction in which a substrate is converted into the appropriate products. Enzyme catalysis is usually homogeneous because the substrate and enzyme are present in aqueous solution.

An enzyme is typically a large protein molecule that contains one or more *active sites* where interactions with substrates take place. These sites are structurally compatible with specific substrate molecules, in much the same way as a key fits a particular lock. In fact, the notion of a rigid enzyme structure that binds only to molecules whose shape exactly matches that of the active site was the basis of an early theory of enzyme catalysis, the so-called lock-and-key theory developed by the German chemist Emil Fischer[†] in 1894 (Figure 13.28). Fischer's hypothesis accounts for the specificity of enzymes, but it contradicts research evidence that a single enzyme binds to substrates of different sizes and shapes. Chemists now know that an enzyme molecule (or at least its active site) has a fair amount of structural flexibility and can modify its shape to accommodate more than one type of substrate. Figure 13.29 shows a molecular model of an enzyme in action.

[†]Emil Fischer (1852–1919). German chemist. Regarded by many as the greatest organic chemist of the nineteenth century, Fischer made many significant contributions in the synthesis of sugars and other important molecules. He was awarded the Nobel Prize in Chemistry in 1902.
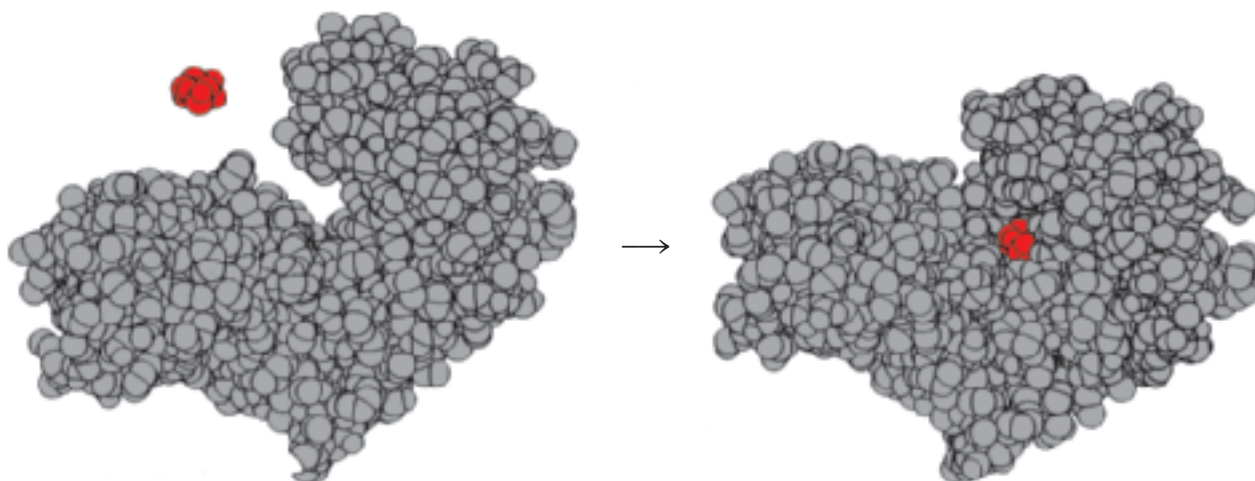

Figure 13.29 *Left to right: The binding of a glucose molecule (red) to hexokinase (an enzyme in the metabolic pathway). Note how the region at the active site closes around glucose after binding. Frequently, the geometries of both the substrate and the active site are altered to fit each other.*

Pharmacokinetics

Chemical kinetics is very important in understanding the absorption, distribution, metabolism, and excretion of drugs in the body. In this sense, pharmacokinetics is the study of what the body does to a drug (as opposed to pharmacodynamics, which is the study of what a drug does to the body). Knowledge of the rates of drug absorption and distribution in the body is essential to achieving and maintaining proper dosages as well as understanding the mechanisms of action.

Drug concentrations are typically measured in blood plasma or urine at various times to give a drug concentration versus time plot. As the drug is absorbed into the bloodstream, it is distributed to the various tissues and organs in the body and simultaneously eliminated by a combination of excretion and metabolism (biotransformation), all of which occur at different rates depending on the drug. The sum of all these processes is the mechanism of drug delivery and distribution. Because the drug must be distributed between different organs and cross between aqueous (blood and urine) and lipid (fat) tissue, and because many biological processes involve enzymes, kinetic behavior that is zero order in the drug is much more common in pharmacokinetics than it is in homogeneous solution reaction kinetics. For example, the decomposition of ethanol by the enzyme alcohol dehydrogenase is zero order in ethanol.
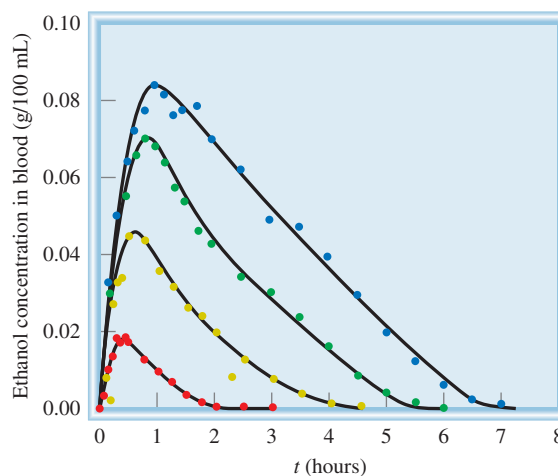
Concentration of ethanol in blood versus time after oral administration of various doses: red (14 g), yellow (28 g), green (42 g), blue (56 g).

Usually the absorption of a drug is more rapid than the elimination, giving a steeper rise in concentration compared to the more gradual decline. The *minimum effective concentration* (MEC) is the minimum concentration required for the drug to

The mathematical treatment of enzyme kinetics is quite complex, even when we know the basic steps involved in the reaction. A simplified scheme is given by the following elementary steps:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} E + P$$
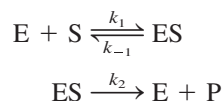
where E, S, and P represent enzyme, substrate, and product, and ES is the enzyme-substrate intermediate. It is often assumed that the formation of ES and its decomposition back to enzyme and substrate molecules occur rapidly and that the rate-determining step is the formation of product. (This is similar to the formation of HI discussed on p. 599.)

In general, the rate of such a reaction is given by the equation

$$\text{rate} = \frac{\Delta[P]}{\Delta t}$$

$$= k_2[ES]$$

provide the desired therapeutic effect. The *minimum toxic concentration* (MTC) is the drug concentration at which the drug becomes toxic or other undesired side effects outweigh the benefit of the drug. Taken together, the MEC and MTC define a *therapeutic index*, and one of the goals of pharmacokinetics is to determine a dosing regimen that keeps the drug concentration within the therapeutic index; that is, above the MEC but below the MTC. For example, most antibiotics such as amoxicillin have a fairly wide therapeutic index, but anticoagulant (blood thinner) medications such as Coumadin® have a narrow therapeutic index. Determination of the correct dosage is based on the kinetics of the drug's delivery as well as the rate of disappearance due to decomposition, biotransformation, and excretion. Often this dosage will depend on the body weight of the person, because blood volume will be roughly proportional to body weight and the drug concentration will depend on the volume of distribution (blood in this case) as well as the amount of drug administered. Doctors and nurses refer to dosage charts in references such as the *Physician's Desk Reference* (PDR), which are based on pharmacokinetic studies.

The *onset time* is the time required after the drug is administered for the concentration to reach the MEC and enter the therapeutic range. Sometimes a doctor will prescribe a higher first dose of the drug (*loading dose*) to reduce the onset time. After that, the drug must be administered at intervals to keep the concentration within the therapeutic index, giving a characteristic
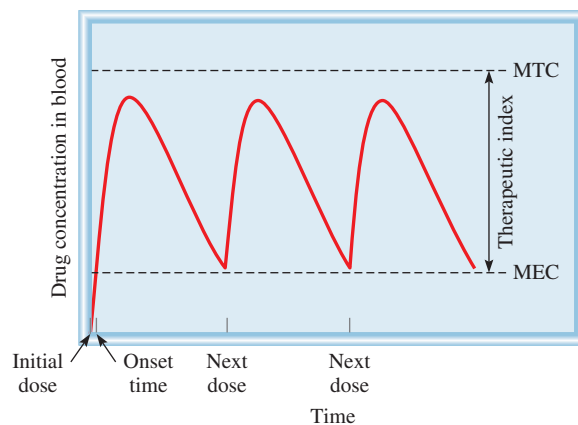
Drug concentration in blood as a function of time. The concentration of the drug increases after the drug is administered, and then decreases as the drug is metabolized and excreted. This process is repeated when the next dose is administered, giving the plot its characteristic "sawtooth" shape.

"sawtooth" profile of drug concentration versus time. The dosage is continued for as long as the drug is needed; however, physiological adaptations to the drug may require an adjustment in the regimen. For some drugs (for example, certain steroids), the drug dosage is tapered off rather than abruptly stopped in order to avoid shock to the system.

The concentration of the ES intermediate is itself proportional to the amount of the substrate present, and a plot of the rate versus the concentration of substrate typically yields a curve like that shown in Figure 13.30. Initially the rate rises rapidly with increasing substrate concentration. However, above a certain concentration all the active sites are occupied, and the reaction becomes zero order in the substrate. In other words, the rate remains the same even though the substrate concentration increases. At and beyond this point, the rate of formation of product depends only on how fast the ES intermediate breaks down, not on the number of substrate molecules present.
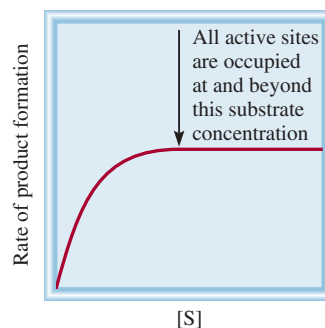

Figure 13.30 *Plot of the rate of product formation versus substrate concentration in an enzyme-catalyzed reaction.*

Review of Concepts

Which of the following is false regarding catalysis: (a) E_a is lower for a catalyzed reaction. (b) ΔH°_{rxn} is lower for a catalyzed reaction. (c) A catalyzed reaction has a different mechanism.

Key Equations

$\text{rate} = k[A]^x[B]^y$	(13.1)	Rate law expressions. The sum $(x + y)$ gives the overall order of the reaction.
$\ln \dfrac{[A]_t}{[A]_0} = -kt$	(13.3)	Relationship between concentration and time for a first-order reaction.
$\ln [A]_t = -kt + \ln [A]_0$	(13.4)	Equation for the graphical determination of k for a first-order reaction.
$t_{\frac{1}{2}} = \dfrac{0.693}{k}$	(13.6)	Half-life for a first-order reaction.
$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	(13.7)	Relationship between concentration and time for a second-order reaction.
$k = Ae^{-E_a/RT}$	(13.11)	The Arrhenius equation expressing the dependence of the rate constant on activation energy and temperature.
$\ln k = \left(-\dfrac{E_a}{R}\right)\left(\dfrac{1}{T}\right) + \ln A$	(13.13)	Equation for the graphical determination of activation energy.
$\ln \dfrac{k_1}{k_2} = \dfrac{E_a}{R}\left(\dfrac{T_1 - T_2}{T_1 T_2}\right)$	(13.14)	Relationships of rate constants at two different temperatures.

Summary of Facts & Concepts

1. The rate of a chemical reaction is the change in the concentration of reactants or products over time. The rate is not constant, but varies continuously as concentrations change.

2. The rate law expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to appropriate powers. The rate constant k for a given reaction changes only with temperature.

3. Reaction order is the power to which the concentration of a given reactant is raised in the rate law. Overall reaction order is the sum of the powers to which reactant concentrations are raised in the rate law. The rate law and the reaction order cannot be determined from the stoichiometry of the overall equation for a reaction; they must be determined by experiment. For a zero-order reaction, the reaction rate is equal to the rate constant.

4. The half-life of a reaction (the time it takes for the concentration of a reactant to decrease by one-half) can be used to determine the rate constant of a first-order reaction.

5. In terms of collision theory, a reaction occurs when molecules collide with sufficient energy, called the activation energy, to break the bonds and initiate the reaction. The rate constant and the activation energy are related by the Arrhenius equation.

6. The overall balanced equation for a reaction may be the sum of a series of simple reactions, called elementary steps. The complete series of elementary steps for a reaction is the reaction mechanism.

7. If one step in a reaction mechanism is much slower than all other steps, it is the rate-determining step.

8. A catalyst speeds up a reaction usually by lowering the value of E_a. A catalyst can be recovered unchanged at the end of a reaction.

9. In heterogeneous catalysis, which is of great industrial importance, the catalyst is a solid and the reactants are gases or liquids. In homogeneous catalysis, the catalyst and the reactants are in the same phase. Enzymes are catalysts in living systems.

Key Words

Activated complex, p. 591
Activation energy (E_a), p. 591
Bimolecular reaction, p. 596
Catalyst, p. 601
Chemical kinetics, p. 565
Elementary step, p. 596

Enzyme, p. 606
First-order reaction, p. 577
Half-life ($t_{\frac{1}{2}}$), p. 582
Intermediate, p. 596
Molecularity of a
    reaction, p. 596

Rate constant (k), p. 569
Rate-determining step, p. 597
Rate law, p. 573
Reaction mechanism, p. 596
Reaction order, p. 573
Reaction rate, p. 565

Second-order
    reaction, p. 584
Termolecular reaction, p. 596
Transition state, p. 591
Unimolecular
    reaction, p. 596

Questions & Problems

The Rate of a Reaction

Review Questions

13.1   What is meant by the rate of a chemical reaction? What are the units of the rate of a reaction?

13.2   Distinguish between average rate and instantaneous rate. Which of the two rates gives us an unambiguous measurement of reaction rate? Why?

13.3   What are the advantages of measuring the initial rate of a reaction?

13.4   Can you suggest two reactions that are very slow (take days or longer to complete) and two reactions that are very fast (reactions that are over in minutes or seconds)?

Problems

13.5   Write the reaction rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of products:
(a) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$
(b) $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow$
$ 3Br_2(aq) + 3H_2O(l)$

13.6   Write the reaction rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of products:
(a) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$
(b) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$
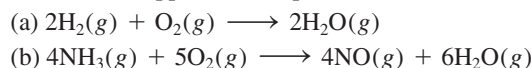
13.7   Consider the reaction

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
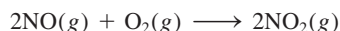
Suppose that at a particular moment during the reaction nitric oxide (NO) is reacting at the rate of 0.066 M/s. (a) At what rate is NO_2 being formed? (b) At what rate is molecular oxygen reacting?

13.8   Consider the reaction

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$
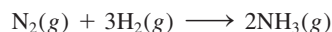
Suppose that at a particular moment during the reaction molecular hydrogen is reacting at the rate of

0.074 M/s. (a) At what rate is ammonia being formed? (b) At what rate is molecular nitrogen reacting?

The Rate Law

Review Questions

13.9   Explain what is meant by the rate law of a reaction.

13.10   What are the units for the rate constants of zero-order, first-order, and second-order reactions?

13.11   Consider the zero-order reaction: A $\longrightarrow$ product. (a) Write the rate law for the reaction. (b) What are the units for the rate constant? (c) Plot the rate of the reaction versus [A].

13.12   On which of the following properties does the rate constant of a reaction depend? (a) reactant concentrations, (b) nature of reactants, (c) temperature.

Problems

13.13   The rate law for the reaction

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$$
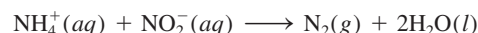
is given by rate = $k[NH_4^+][NO_2^-]$. At 25°C, the rate constant is $3.0 \times 10^{-4}/M \cdot$ s. Calculate the rate of the reaction at this temperature if $[NH_4^+] = 0.26$ M and $[NO_2^-] = 0.080$ M.

13.14   Use the data in Table 13.2 to calculate the rate of the reaction at the time when $[F_2] = 0.010$ M and $[ClO_2] = 0.020$ M.

13.15   Consider the reaction

$$A + B \longrightarrow products$$

From the following data obtained at a certain temperature, determine the order of the reaction and calculate the rate constant:

[A] (M)	[B] (M)	Rate (M/s)
1.50	1.50	3.20×10^{-1}
1.50	2.50	3.20×10^{-1}
3.00	1.50	6.40×10^{-1}

13.16 Consider the reaction

$$X + Y \longrightarrow Z$$

From the following data, obtained at 360 K, (a) determine the order of the reaction, and (b) determine the initial rate of disappearance of X when the concentration of X is 0.30 M and that of Y is 0.40 M.

Initial Rate of Disappearance of X (M/s)	[X] (M)	[Y] (M)
0.053	0.10	0.50
0.127	0.20	0.30
1.02	0.40	0.60
0.254	0.20	0.60
0.509	0.40	0.30

13.17 Determine the overall orders of the reactions to which the following rate laws apply: (a) rate = $k[NO_2]^2$, (b) rate = k, (c) rate = $k[H_2][Br_2]^{\frac{1}{2}}$, (d) rate = $k[NO]^2 [O_2]$.

13.18 Consider the reaction

$$A \longrightarrow B$$

The rate of the reaction is 1.6×10^{-2} M/s when the concentration of A is 0.35 M. Calculate the rate constant if the reaction is (a) first order in A and (b) second order in A.

13.19 Cyclobutane decomposes to ethylene according to the equation

$$C_4H_8(g) \longrightarrow 2C_2H_4(g)$$
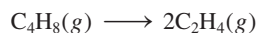
Determine the order of the reaction and the rate constant based on the following pressures, which were recorded when the reaction was carried out at 430°C in a constant-volume vessel.

Time (s)	$P_{C_4H_8}$ (mmHg)
0	400
2,000	316
4,000	248
6,000	196
8,000	155
10,000	122

13.20 The following gas-phase reaction was studied at 290°C by observing the change in pressure as a function of time in a constant-volume vessel:

$$ClCO_2CCl_3(g) \longrightarrow 2COCl_2(g)$$
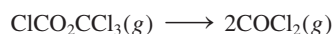
Determine the order of the reaction and the rate constant based on the following data:

Time (s)	P (mmHg)
0	15.76
181	18.88
513	22.79
1164	27.08

where P is the total pressure.

The Relation Between Reactant Concentration and Time
Review Questions

13.21 Write an equation relating the concentration of a reactant A at $t = 0$ to that at $t = t$ for a first-order reaction. Define all the terms and give their units. Do the same for a second-order reaction.

13.22 Define half-life. Write the equation relating the half-life of a first-order reaction to the rate constant.

13.23 Write the equations relating the half-life of a second-order reaction to the rate constant. How does it differ from the equation for a first-order reaction?

13.24 For a first-order reaction, how long will it take for the concentration of reactant to fall to one-eighth its original value? Express your answer in terms of the half-life ($t_{\frac{1}{2}}$) and in terms of the rate constant k.

Problems

13.25 What is the half-life of a compound if 75 percent of a given sample of the compound decomposes in 60 min? Assume first-order kinetics.

13.26 The thermal decomposition of phosphine (PH$_3$) into phosphorus and molecular hydrogen is a first-order reaction:

$$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$
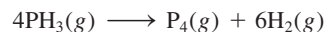
The half-life of the reaction is 35.0 s at 680°C. Calculate (a) the first-order rate constant for the reaction and (b) the time required for 95 percent of the phosphine to decompose.

13.27 The rate constant for the second-order reaction

$$2NOBr(g) \longrightarrow 2NO(g) + Br_2(g)$$
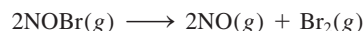
is 0.80/$M \cdot$ s at 10°C. (a) Starting with a concentration of 0.086 M, calculate the concentration of NOBr after 22 s. (b) Calculate the half-lives when [NOBr]$_0$ = 0.072 M and [NOBr]$_0$ = 0.054 M.

13.28 The rate constant for the second-order reaction

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

is 0.54/$M \cdot$ s at 300°C. How long (in seconds) would it take for the concentration of NO$_2$ to decrease from 0.62 M to 0.28 M?

13.29 Consider the first-order reaction A $\longrightarrow$ B shown here. (a) What is the rate constant of the reaction? (b) How many A (yellow) and B (blue) molecules are present at $t = 20$ s and 30 s?

t = 0 s   t = 10 s
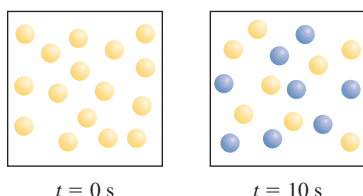
13.30 The reaction X $\longrightarrow$ Y shown here follows first-order kinetics. Initially different amounts of X molecules are placed in three equal-volume containers at the same temperature. (a) What are the relative rates of the reaction in these three containers? (b) How would the relative rates be affected if the volume of each container were doubled? (c) What are the relative half-lives of the reactions in (i) to (iii)?

(i)   (ii)   (iii)
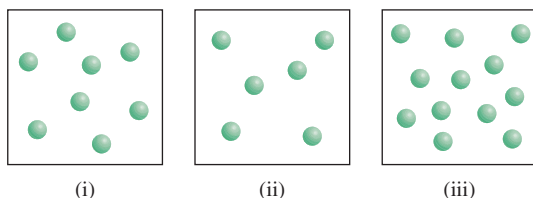
Activation Energy

Review Questions

13.31 Define activation energy. What role does activation energy play in chemical kinetics?

13.32 Write the Arrhenius equation and define all terms.

13.33 Use the Arrhenius equation to show why the rate constant of a reaction (a) decreases with increasing activation energy and (b) increases with increasing temperature.

13.34 The burning of methane in oxygen is a highly exothermic reaction. Yet a mixture of methane and oxygen gas can be kept indefinitely without any apparent change. Explain.

13.35 Sketch a potential energy versus reaction progress plot for the following reactions:
(a) $S(s) + O_2(g) \longrightarrow SO_2(g)$ $\Delta H° = -296$ kJ/mol
(b) $Cl_2(g) \longrightarrow Cl(g) + Cl(g)$ $\Delta H° = 243$ kJ/mol

13.36 The reaction H + H$_2$ $\longrightarrow$ H$_2$ + H has been studied for many years. Sketch a potential energy versus reaction progress diagram for this reaction.

Problems

13.37 (1) The diagram in (a) shows the plots of ln k versus $1/T$ for two first-order reactions, where k is the rate

constant and T is the absolute temperature. Which reaction has a greater activation energy? (2) The diagram in (b) shows the plots for a first-order reaction at two different temperatures. Which plot corresponds to a higher temperature?


(a)   (b)
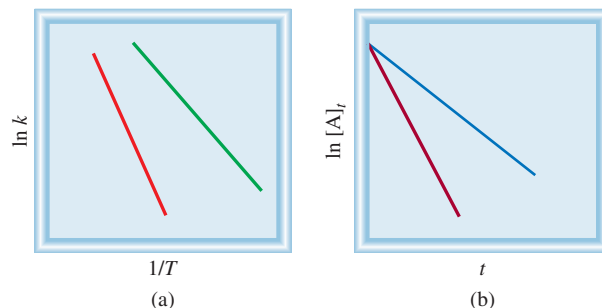
13.38 Given the same reactant concentrations, the reaction
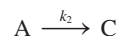
$$CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$$
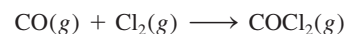
at 250°C is 1.50×10^3 times as fast as the same reaction at 150°C. Calculate the activation energy for this reaction. Assume that the frequency factor is constant.

13.39 Some reactions are described as parallel in that the reactant simultaneously forms different products with different rate constants. An example is
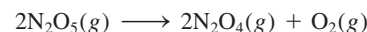
$$A \xrightarrow{k_1} B$$

and $$A \xrightarrow{k_2} C$$
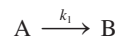
The activation energies are 45.3 kJ/mol for k_1 and 69.8 kJ/mol for k_2. If the rate constants are equal at 320 K, at what temperature will $k_1/k_2 = 2.00$?

13.40 Variation of the rate constant with temperature for the first-order reaction

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$

is given in the following table. Determine graphically the activation energy for the reaction.

T (K)	k (s^{-1})
298	1.74×10^{-5}
308	6.61×10^{-5}
318	2.51×10^{-4}
328	7.59×10^{-4}
338	2.40×10^{-3}

13.41 For the reaction

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

the frequency factor A is 8.7×10^{12} s^{-1} and the activation energy is 63 kJ/mol. What is the rate constant for the reaction at 75°C?

13.42 The rate constant of a first-order reaction is $4.60 \times 10^{-4}\,s^{-1}$ at 350°C. If the activation energy is 104 kJ/mol, calculate the temperature at which its rate constant is $8.80 \times 10^{-4}\,s^{-1}$.

13.43 The rate constants of some reactions double with every 10-degree rise in temperature. Assume that a reaction takes place at 295 K and 305 K. What must the activation energy be for the rate constant to double as described?

13.44 Consider the first-order reaction

$$CH_3NC(g) \longrightarrow CH_3CN(g)$$

Given that the frequency factor and activation energy for the reaction are $3.98 \times 10^{13}\,s^{-1}$ and 161 kJ/mol, respectively, calculate the rate constant at 600°C.

13.45 Consider the second-order reaction

$$NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$$
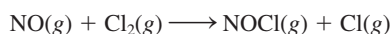
Given that the frequency factor and activation energy for the reaction are $4.0 \times 10^{9}/M \cdot s$ and 85 kJ/mol, respectively, calculate the rate constant at 500°C.

13.46 The rate at which tree crickets chirp is 2.0×10^2 per minute at 27°C but only 39.6 per minute at 5°C. From these data, calculate the "activation energy" for the chirping process. (*Hint:* The ratio of rates is equal to the ratio of rate constants.)

13.47 The diagram here describes the initial state of the reaction $A_2 + B_2 \longrightarrow 2AB$.
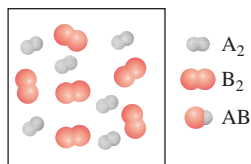
Suppose the reaction is carried out at two temperatures as shown below. Which picture represents the result at the higher temperature? (The reaction proceeds for the same amount of time at both temperatures.)
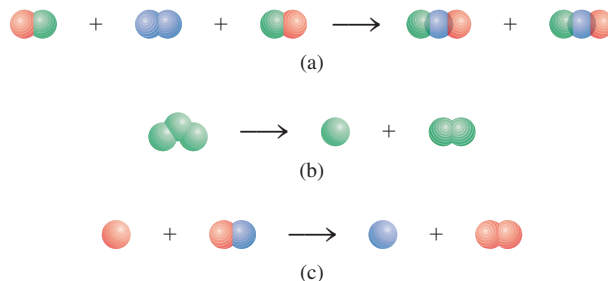

(a)　　　　　(b)
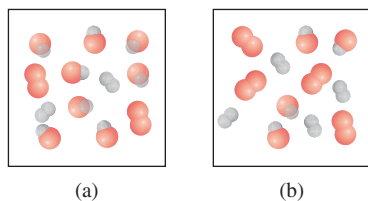
Reaction Mechanisms
Review Questions

13.48 What do we mean by the mechanism of a reaction? What is an elementary step? What is the molecularity of a reaction?

13.49 Classify each of the following elementary steps as unimolecular, bimolecular, or termolecular.

(a)

(b)

(c)

13.50 Reactions can be classified as unimolecular, bimolecular, and so on. Why are there no zero-molecular reactions? Explain why termolecular reactions are rare.

13.51 Determine the molecularity and write the rate law for each of the following elementary steps:
  (a) $X \longrightarrow$ products
  (b) $X + Y \longrightarrow$ products
  (c) $X + Y + Z \longrightarrow$ products
  (d) $X + X \longrightarrow$ products
  (e) $X + 2Y \longrightarrow$ products

13.52 What is the rate-determining step of a reaction? Give an everyday analogy to illustrate the meaning of "rate determining."

13.53 The equation for the combustion of ethane (C_2H_6) is

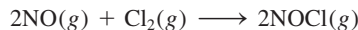$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$$

Explain why it is unlikely that this equation also represents the elementary step for the reaction.
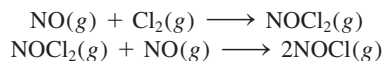
13.54 Specify which of the following species cannot be isolated in a reaction: activated complex, product, intermediate.

Problems

13.55 The rate law for the reaction

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

is given by rate $= k[NO][Cl_2]$. (a) What is the order of the reaction? (b) A mechanism involving the following steps has been proposed for the reaction:

$$NO(g) + Cl_2(g) \longrightarrow NOCl_2(g)$$
$$NOCl_2(g) + NO(g) \longrightarrow 2NOCl(g)$$

If this mechanism is correct, what does it imply about the relative rates of these two steps?

13.56 For the reaction $X_2 + Y + Z \longrightarrow XY + XZ$ it is found that doubling the concentration of X_2 doubles the reaction rate, tripling the concentration of Y triples the rate, and doubling the concentration of Z has no effect. (a) What is the rate law for this reaction?

(b) Why is it that the change in the concentration of Z has no effect on the rate? (c) Suggest a mechanism for the reaction that is consistent with the rate law.
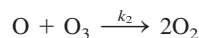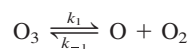
13.57 The rate law for the decomposition of ozone to molecular oxygen

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

is

$$\text{rate} = k\frac{[O_3]^2}{[O_2]}$$

The mechanism proposed for this process is

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O + O_2$$

$$O + O_3 \overset{k_2}{\longrightarrow} 2O_2$$

Derive the rate law from these elementary steps. Clearly state the assumptions you use in the derivation. Explain why the rate decreases with increasing O_2 concentration.

13.58 The rate law for the reaction

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

is rate $= k[H_2][NO]^2$. Which of the following mechanisms can be ruled out on the basis of the observed rate expression?

Mechanism I
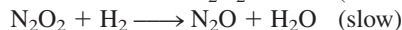|	
$H_2 + NO \longrightarrow H_2O + N$	(slow)
$N + NO \longrightarrow N_2 + O$	(fast)
$O + H_2 \longrightarrow H_2O$	(fast)

Mechanism II
$H_2 + 2NO \longrightarrow N_2O + H_2O$	(slow)
$N_2O + H_2 \longrightarrow N_2 + H_2O$	(fast)

Mechanism III
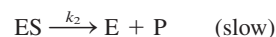|	
$2NO \rightleftharpoons N_2O_2$	(fast equilibrium)
$N_2O_2 + H_2 \longrightarrow N_2O + H_2O$	(slow)
$N_2O + H_2 \longrightarrow N_2 + H_2O$	(fast)
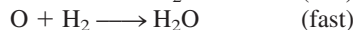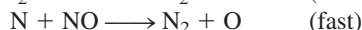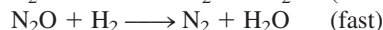
Catalysis
Review Questions

13.59 How does a catalyst increase the rate of a reaction?

13.60 What are the characteristics of a catalyst?

13.61 A certain reaction is known to proceed slowly at room temperature. Is it possible to make the reaction proceed at a faster rate without changing the temperature?

13.62 Distinguish between homogeneous catalysis and heterogeneous catalysis. Describe three important industrial processes that utilize heterogeneous catalysis.

13.63 Are enzyme-catalyzed reactions examples of homogeneous or heterogeneous catalysis? Explain.

13.64 The concentrations of enzymes in cells are usually quite small. What is the biological significance of this fact?

Problems

13.65 The diagram shown here represents a two-step mechanism. (a) Write the equation for each step and the overall reaction. (b) Identify the intermediate and catalyst. The color codes are A = green and B = red.
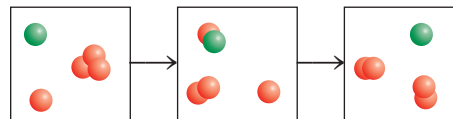

13.66 Consider the following mechanism for the enzyme-catalyzed reaction:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \qquad \text{(fast equilibrium)}$$

$$ES \overset{k_2}{\longrightarrow} E + P \qquad \text{(slow)}$$

Derive an expression for the rate law of the reaction in terms of the concentrations of E and S. (*Hint:* To solve for [ES], make use of the fact that, at equilibrium, the rate of forward reaction is equal to the rate of the reverse reaction.)

Additional Problems

13.67 The following diagrams represent the progress of the reaction A $\longrightarrow$ B, where the red spheres represent A molecules and the green spheres represent B molecules. Calculate the rate constant of the reaction.

$t = 0$ s	$t = 20$ s	$t = 40$ s
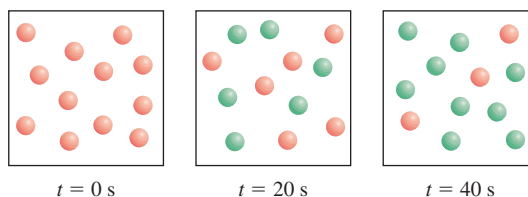
13.68 The following diagrams show the progress of the reaction 2A $\longrightarrow$ A$_2$. Determine whether the reaction is first order or second order and calculate the rate constant.

$t = 0$ min	$t = 15$ min	$t = 30$ min
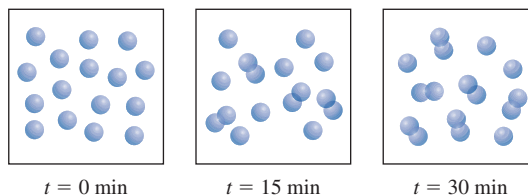
13.69 Suggest experimental means by which the rates of the following reactions could be followed:
(a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
(b) $Cl_2(g) + 2Br^-(aq) \longrightarrow Br_2(aq) + 2Cl^-(aq)$
(c) $C_2H_6(g) \longrightarrow C_2H_4(g) + H_2(g)$
(d) $C_2H_5I(g) + H_2O(l) \longrightarrow$
$\qquad\qquad C_2H_5OH(aq) + H^+(aq) + I^-(aq)$

13.70 List four factors that influence the rate of a reaction.

13.71 "The rate constant for the reaction

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

is $1.64 \times 10^{-6}/M \cdot s$." What is incomplete about this statement?

13.72 In a certain industrial process involving a hetero-geneous catalyst, the volume of the catalyst (in the shape of a sphere) is 10.0 cm^3. Calculate the sur-face area of the catalyst. If the sphere is broken down into eight spheres, each having a volume of 1.25 cm^3, what is the total surface area of the spheres? Which of the two geometric configura-tions of the catalyst is more effective? (The surface area of a sphere is $4\pi r^2$, where r is the radius of the sphere.) Based on your analysis here, explain why it is sometimes dangerous to work in grain elevators.

13.73 Use the data in Example 13.5 to determine graphi-cally the half-life of the reaction.

13.74 The following data were collected for the reaction between hydrogen and nitric oxide at 700°C:

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

| Experiment	[H$_2$]	[NO]	Initial Rate (M/s)
1	0.010	0.025	2.4×10^{-6}
2	0.0050	0.025	1.2×10^{-6}
3	0.010	0.0125	0.60×10^{-6}

(a) Determine the order of the reaction. (b) Calcu-late the rate constant. (c) Suggest a plausible mech-anism that is consistent with the rate law. (*Hint:* Assume that the oxygen atom is the intermediate.)

13.75 When methyl phosphate is heated in acid solution, it reacts with water:

$$CH_3OPO_3H_2 + H_2O \longrightarrow CH_3OH + H_3PO_4$$
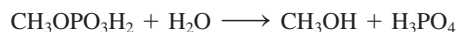
If the reaction is carried out in water enriched with ^{18}O, the oxygen-18 isotope is found in the phosphoric acid product but not in the methanol. What does this tell us about the mechanism of the reaction?

**13.76** The rate of the reaction

$$CH_3COOC_2H_5(aq) + H_2O(l) \longrightarrow$$
$$CH_3COOH(aq) + C_2H_5OH(aq)$$
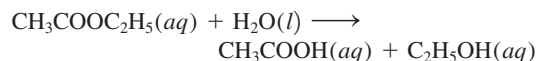
shows first-order characteristics—that is, rate = $k[CH_3COOC_2H_5]$—even though this is a second-order reaction (first order in $CH_3COOC_2H_5$ and first order in H_2O). Explain.

13.77 Which of the following equations best describes the diagram shown above: (a) A $\longrightarrow$ B, (b) A $\longrightarrow$ 3B, (c) 3A $\longrightarrow$ B?
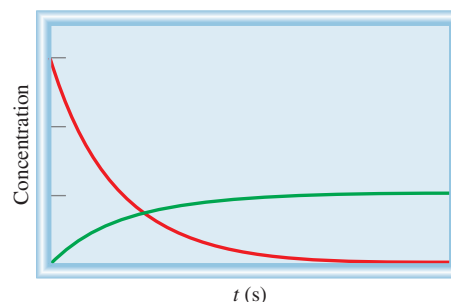
13.78 The reaction 2A + 3B $\longrightarrow$ C is first order with respect to A and B. When the initial concentrations are [A] = 1.6×10^{-2} M and [B] = 2.4×10^{-3} M, the rate is 4.1×10^{-4} M/s. Calculate the rate con-stant of the reaction.

13.79 The bromination of acetone is acid-catalyzed:
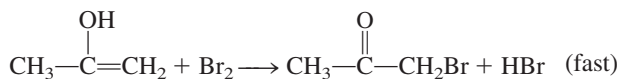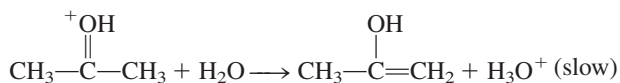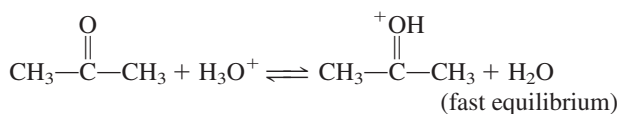
$$CH_3COCH_3 + Br_2 \xrightarrow[\text{catalyst}]{H^+} CH_3COCH_2Br + H^+ + Br^-$$
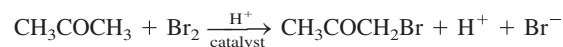
The rate of disappearance of bromine was measured for several different concentrations of acetone, bro-mine, and H$^+$ ions at a certain temperature:

	[CH$_3$COCH$_3$]	[Br$_2$]	[H$^+$]	Rate of Disappearance of Br$_2$ (M/s)
(1)	0.30	0.050	0.050	5.7×10^{-5}
(2)	0.30	0.10	0.050	5.7×10^{-5}
(3)	0.30	0.050	0.10	1.2×10^{-4}
(4)	0.40	0.050	0.20	3.1×10^{-4}
(5)	0.40	0.050	0.050	7.6×10^{-5}

(a) What is the rate law for the reaction? (b) Determine the rate constant. (c) The following mechanism has been proposed for the reaction:

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_3O^+ \rightleftharpoons CH_3-\overset{+OH}{\overset{\|}{C}}-CH_3 + H_2O$$
(fast equilibrium)

$$CH_3-\overset{+OH}{\overset{\|}{C}}-CH_3 + H_2O \longrightarrow CH_3-\overset{OH}{\overset{|}{C}}=CH_2 + H_3O^+ \text{ (slow)}$$

$$CH_3-\overset{OH}{\overset{|}{C}}=CH_2 + Br_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2Br + HBr \text{ (fast)}$$

Show that the rate law deduced from the mechanism is consistent with that shown in (a).

13.80 The decomposition of N$_2$O to N$_2$ and O$_2$ is a first-order reaction. At 730°C the half-life of the reaction is 3.58×10^3 min. If the initial pressure of N$_2$O is 2.10 atm at 730°C, calculate the total gas pressure after one half-life. Assume that the volume remains constant.

13.81 The reaction $S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$ proceeds slowly in aqueous solution, but it can be catalyzed by the Fe^{3+} ion. Given that Fe^{3+} can oxidize I^- and Fe^{2+} can reduce $S_2O_8^{2-}$, write a plausible two-step mechanism for this reaction. Explain why the uncatalyzed reaction is slow.

**13.82** What are the units of the rate constant for a third-order reaction?

13.83 The integrated rate law for the zero-order reaction $A \longrightarrow B$ is $[A]_t = [A]_0 - kt$. (a) Sketch the following plots: (i) rate versus $[A]_t$ and (ii) $[A]_t$ versus t. (b) Derive an expression for the half-life of the reaction. (c) Calculate the time in half-lives when the integrated rate law is no longer valid, that is, when $[A]_t = 0$.

13.84 A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 50.0 min for A and 18.0 min for B. If the concentrations of A and B are equal initially, how long will it take for the concentration of A to be four times that of B?

13.85 Shown here are plots of concentration of reactant versus time for two first-order reactions at the same temperature. In each case, determine which reaction has a greater rate constant.

(a)   (b)
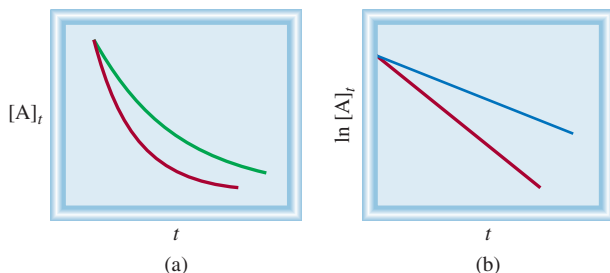
13.86 The diagrams here represent the reaction $A + B \longrightarrow C$ carried out under different initial concentrations of A and B. Determine the rate law of the reaction. (The color codes are A = red, B = green, C = blue.)

I

$t = 0$ s $t = 50$ s

II

$t = 0$ s $t = 50$ s

III

$t = 0$ s $t = 50$ s
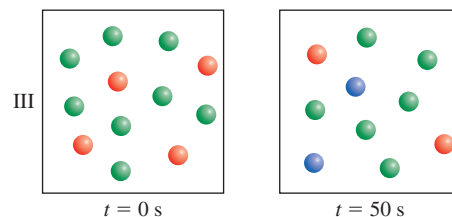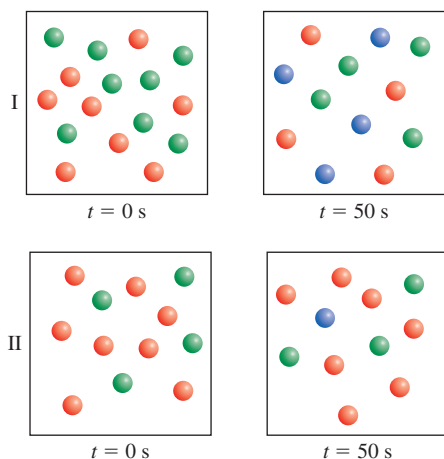
13.87 Referring to Example 13.5, explain how you would measure the partial pressure of azomethane experimentally as a function of time.

13.88 The rate law for the reaction $2NO_2(g) \longrightarrow N_2O_4(g)$ is rate $= k[NO_2]^2$. Which of the following changes will change the value of k? (a) The pressure of NO_2 is doubled. (b) The reaction is run in an organic solvent. (c) The volume of the container is doubled. (d) The temperature is decreased. (e) A catalyst is added to the container.

13.89 The reaction of G_2 with E_2 to form 2EG is exothermic, and the reaction of G_2 with X_2 to form 2XG is endothermic. The activation energy of the exothermic reaction is greater than that of the endothermic reaction. Sketch the potential energy profile diagrams for these two reactions on the same graph.

13.90 In the nuclear industry, workers use a rule of thumb that the radioactivity from any sample will be relatively harmless after 10 half-lives. Calculate the fraction of a radioactive sample that remains after this time period. (*Hint:* Radioactive decays obey first-order kinetics.)

13.91 Briefly comment on the effect of a catalyst on each of the following: (a) activation energy, (b) reaction mechanism, (c) enthalpy of reaction, (d) rate of forward step, (e) rate of reverse step.

13.92 When 6 g of granulated Zn is added to a solution of 2 M HCl in a beaker at room temperature, hydrogen gas is generated. For each of the following changes (at constant volume of the acid) state whether the rate of hydrogen gas evolution will be increased, decreased, or unchanged: (a) 6 g of powdered Zn is used; (b) 4 g of granulated Zn is used; (c) 2 M acetic acid is used instead of 2 M HCl; (d) temperature is raised to 40°C.

13.93 Strictly speaking, the rate law derived for the reaction in Problem 13.74 applies only to certain concentrations of H_2. The general rate law for the reaction takes the form

$$\text{rate} = \frac{k_1[NO]^2[H_2]}{1 + k_2[H_2]}$$

where k_1 and k_2 are constants. Derive rate law expressions under the conditions of very high and very low hydrogen concentrations. Does the result from Problem 13.74 agree with one of the rate expressions here?

13.94 A certain first-order reaction is 35.5 percent complete in 4.90 min at 25°C. What is its rate constant?

13.95 The decomposition of dinitrogen pentoxide has been studied in carbon tetrachloride solvent (CCl_4) at a certain temperature:

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$
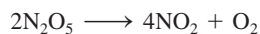
[N_2O_5]	Initial Rate (*M*/s)
0.92	0.95×10^{-5}
1.23	1.20×10^{-5}
1.79	1.93×10^{-5}
2.00	2.10×10^{-5}
2.21	2.26×10^{-5}

Determine graphically the rate law for the reaction and calculate the rate constant.

13.96 The thermal decomposition of N_2O_5 obeys first-order kinetics. At 45°C, a plot of ln [N_2O_5] versus t gives a slope of -6.18×10^{-4} min^{-1}. What is the half-life of the reaction?

13.97 When a mixture of methane and bromine is exposed to visible light, the following reaction occurs slowly:

$$CH_4(g) + Br_2(g) \longrightarrow CH_3Br(g) + HBr(g)$$
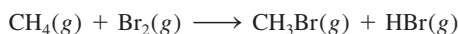
Suggest a reasonable mechanism for this reaction. (*Hint:* Bromine vapor is deep red; methane is colorless.)

13.98 The rate of the reaction between H_2 and I_2 to form HI (discussed on p. 598) increases with the intensity of visible light. (a) Explain why this fact supports the two-step mechanism given. (The color of I_2 vapor is shown on p. 504.) (b) Explain why the visible light has no effect on the formation of H atoms.

13.99 The carbon-14 decay rate of a sample obtained from a young tree is 0.260 disintegration per second per gram of the sample. Another wood sample prepared from an object recovered at an archaeological excavation gives a decay rate of 0.186 disintegration per second per gram of the sample. What is the age of the object? (*Hint:* See Chemistry in Action essay on p. 588.)

13.100 Consider the following elementary step:

$$X + 2Y \longrightarrow XY_2$$
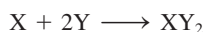
(a) Write a rate law for this reaction. (b) If the initial rate of formation of XY_2 is 3.8×10^{-3} *M*/s and the initial concentrations of X and Y are 0.26 *M* and 0.88 *M*, what is the rate constant of the reaction?

13.101 In recent years ozone in the stratosphere has been depleted at an alarmingly fast rate by chlorofluorocarbons (CFCs). A CFC molecule such as $CFCl_3$ is first decomposed by UV radiation:

$$CFCl_3 \longrightarrow CFCl_2 + Cl$$
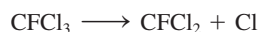
The chlorine radical then reacts with ozone as follows:

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$
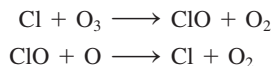
The O atom is from the photochemical decomposition of O_2 molecules.
(a) Write the overall reaction for the last two steps. (b) What are the roles of Cl and ClO? (c) Why is the fluorine radical not important in this mechanism? (d) One suggestion to reduce the concentration of chlorine radicals is to add hydrocarbons such as ethane (C_2H_6) to the stratosphere. How will this work? (e) Draw potential energy versus reaction progress diagrams for the uncatalyzed and catalyzed (by Cl) destruction of ozone: $O_3 + O \longrightarrow 2O_2$. Use the thermodynamic data in Appendix 3 to determine whether the reaction is exothermic or endothermic.

13.102 Chlorine oxide (ClO), which plays an important role in the depletion of ozone (see Problem 13.101), decays rapidly at room temperature according to the equation

$$2ClO(g) \longrightarrow Cl_2(g) + O_2(g)$$
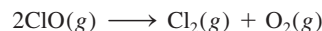
From the following data, determine the reaction order and calculate the rate constant of the reaction

Time (s)	[ClO] (*M*)
0.12×10^{-3}	8.49×10^{-6}
0.96×10^{-3}	7.10×10^{-6}
2.24×10^{-3}	5.79×10^{-6}
3.20×10^{-3}	5.20×10^{-6}
4.00×10^{-3}	4.77×10^{-6}

13.103 A compound X undergoes two *simultaneous* first-order reactions as follows: X $\longrightarrow$ Y with rate constant k_1 and X $\longrightarrow$ Z with rate constant k_2. The ratio of k_1/k_2 at 40°C is 8.0. What is the ratio at 300°C? Assume that the frequency factors of the two reactions are the same.

13.104 Consider a car fitted with a catalytic converter. The first 5 minutes or so after it is started are the most polluting. Why?

13.105 The following scheme in which A is converted to B, which is then converted to C is known as a consecutive reaction.
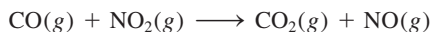
$$A \longrightarrow B \longrightarrow C$$

Assuming that both steps are first order, sketch on the same graph the variations of [A], [B], and [C] with time.

13.106 Hydrogen and iodine monochloride react as follows:

$$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$$

The rate law for the reaction is rate $= k[H_2][ICl]$. Suggest a possible mechanism for the reaction.

13.107 The rate law for the following reaction

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

is rate $= k[NO_2]^2$. Suggest a plausible mechanism for the reaction, given that the unstable species NO_3 is an intermediate.

13.108 Radioactive plutonium-239 ($t_{\frac{1}{2}} = 2.44 \times 10^5$ yr) is used in nuclear reactors and atomic bombs. If there are 5.0×10^2 g of the isotope in a small atomic bomb, how long will it take for the substance to decay to 1.0×10^2 g, too small an amount for an effective bomb?

13.109 Many reactions involving heterogeneous catalysts are zero order; that is, rate $= k$. An example is the decomposition of phosphine (PH_3) over tungsten (W):

$$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$
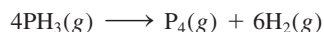
It is found that the reaction is independent of $[PH_3]$ as long as phosphine's pressure is sufficiently high (≥ 1 atm). Explain.

**13.110** Thallium(I) is oxidized by cerium(IV) as follows:

$$Tl^+ + 2Ce^{4+} \longrightarrow Tl^{3+} + 2Ce^{3+}$$

The elementary steps, in the presence of Mn(II), are as follows:

$$Ce^{4+} + Mn^{2+} \longrightarrow Ce^{3+} + Mn^{3+}$$
$$Ce^{4+} + Mn^{3+} \longrightarrow Ce^{3+} + Mn^{4+}$$
$$Tl^+ + Mn^{4+} \longrightarrow Tl^{3+} + Mn^{2+}$$

(a) Identify the catalyst, intermediates, and the rate-determining step if the rate law is rate $= k[Ce^{4+}][Mn^{2+}]$. (b) Explain why the reaction is slow without the catalyst. (c) Classify the type of catalysis (homogeneous or heterogeneous).

13.111 Sucrose ($C_{12}H_{22}O_{11}$), commonly called table sugar, undergoes hydrolysis (reaction with water) to produce fructose ($C_6H_{12}O_6$) and glucose ($C_6H_{12}O_6$):

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$
$$\text{fructose} \qquad \text{glucose}$$
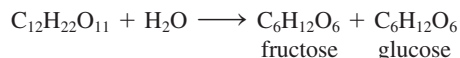
This reaction is of considerable importance in the candy industry. First, fructose is sweeter than sucrose. Second, a mixture of fructose and glucose, called *invert sugar,* does not crystallize, so the candy containing this sugar would be chewy rather than brittle as candy containing sucrose crystals would be. (a) From the following data determine the order of the reaction. (b) How long does it take to hydrolyze 95 percent of sucrose? (c) Explain why the rate law does not include [H_2O] even though water is a reactant.

Time (min)	[$C_{12}H_{22}O_{11}$]
0	0.500
60.0	0.400
96.4	0.350
157.5	0.280

13.112 The first-order rate constant for the decomposition of dimethyl ether

$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

is 3.2×10^{-4} s^{-1} at 450°C. The reaction is carried out in a constant-volume flask. Initially only dimethyl ether is present and the pressure is 0.350 atm. What is the pressure of the system after 8.0 min? Assume ideal behavior.

13.113 At 25°C, the rate constant for the ozone-depleting reaction $O(g) + O_3(g) \longrightarrow 2O_2(g)$ is 7.9×10^{-15} cm^3/molecule $\cdot$ s. Express the rate constant in units of $1/M \cdot$ s.

13.114 Consider the following elementary steps for a consecutive reaction:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
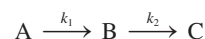
(a) Write an expression for the rate of change of B. (b) Derive an expression for the concentration of B under steady-state conditions; that is, when B is decomposing to C at the same rate as it is formed from A.

13.115 Ethanol is a toxic substance that, when consumed in excess, can impair respiratory and cardiac functions by interference with the neurotransmitters of the nervous system. In the human body, ethanol is metabolized by the enzyme alcohol dehydrogenase to acetaldehyde, which causes "hangovers." (a) Based on your knowledge of enzyme kinetics, explain why binge drinking (that is, consuming too much alcohol too fast) can prove fatal. (b) Methanol is even more toxic than ethanol. It is also metabolized by alcohol dehydrogenase, and the product, formaldehyde, can cause blindness or death. An antidote to methanol poisoning is ethanol. Explain how this procedure works.

13.116 Strontium-90, a radioactive isotope, is a major product of an atomic bomb explosion. It has a half-life of 28.1 yr. (a) Calculate the first-order rate constant for the nuclear decay. (b) Calculate the fraction of ^{90}Sr that remains after 10 half-lives. (c) Calculate the number of years required for 99.0 percent of ^{90}Sr to disappear.

13.117 Consider the potential energy profiles for the following three reactions (from left to right). (1) Rank the rates (slowest to fastest) of the reactions. (2) Calculate ΔH for each reaction and determine which reaction(s) are exothermic and which reaction(s) are endothermic. Assume the reactions have roughly the same frequency factors.


Reaction progress
(a)

Reaction progress
(b)

Reaction progress
(c)
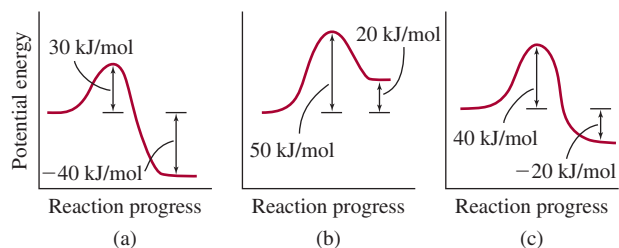
13.118 Consider the following potential energy profile for the A $\longrightarrow$ D reaction. (a) How many elementary steps are there? (b) How many intermediates are formed? (c) Which step is rate determining? (d) Is the overall reaction exothermic or endothermic?

Reaction progress
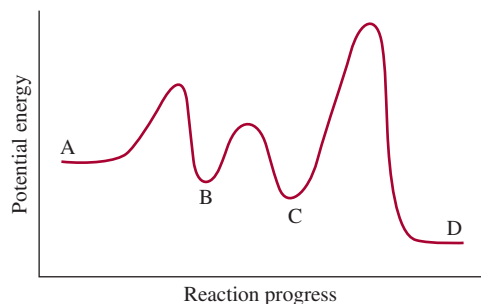
13.119 A factory that specializes in the refinement of transition metals such as titanium was on fire. The firefighters were advised not to douse the fire with water. Why?

13.120 The activation energy for the decomposition of hydrogen peroxide

$$2H_2O_2(aq) \longrightarrow 2H_2O_2(l) + O_2(g)$$
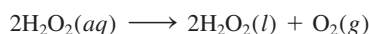
is 42 kJ/mol, whereas when the reaction is catalyzed by the enzyme catalase, it is 7.0 kJ/mol. Calculate the temperature that would cause the uncatalyzed reaction to proceed as rapidly as the enzyme-catalyzed decomposition at 20°C. Assume the frequency factor A to be the same in both cases.

13.121 The *activity* of a radioactive sample is the number of nuclear disintegrations per second, which is equal to the first-order rate constant times the number of radioactive nuclei present. The fundamental unit of radioactivity is the *curie* (Ci), where 1 Ci corresponds to exactly 3.70×10^{10} disintegrations per second. This decay rate is equivalent to that of 1 g of radium-226. Calculate the rate constant and half-life for the radium decay. Starting with 1.0 g of the radium sample, what is the activity after 500 yr? The molar mass of Ra-226 is 226.03 g/mol.

13.122 To carry out metabolism, oxygen is taken up by hemoglobin (Hb) to form oxyhemoglobin (HbO$_2$) according to the simplified equation

$$Hb(aq) + O_2(aq) \xrightarrow{k} HbO_2(aq)$$
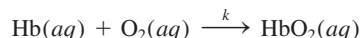
where the second-order rate constant is $2.1 \times 10^6/M \cdot s$ at 37°C. (The reaction is first order in Hb and O$_2$.) For an average adult, the concentrations of Hb and O$_2$ in the blood at the lungs are 8.0×10^{-6} M and 1.5×10^{-6} M, respectively. (a) Calculate the rate of formation of HbO$_2$. (b) Calculate the rate of consumption of O$_2$. (c) The rate of formation of HbO$_2$ increases to 1.4×10^{-4} M/s during exercise to meet the demand of increased metabolism rate. Assuming the Hb concentration to remain the same, what must be the oxygen concentration to sustain this rate of HbO$_2$ formation?

13.123 At a certain elevated temperature, ammonia decomposes on the surface of tungsten metal as follows:

$$2NH_3 \longrightarrow N_2 + 3H_2$$
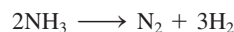
From the following plot of the rate of the reaction versus the pressure of NH$_3$, describe the mechanism of the reaction.
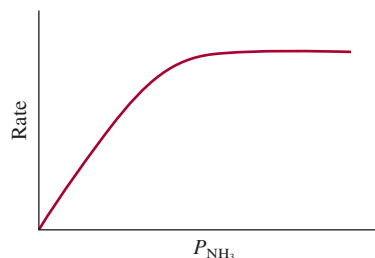
13.124 The following expression shows the dependence of the half-life of a reaction ($t_{\frac{1}{2}}$) on the initial reactant concentration [A]$_0$:

$$t_{\frac{1}{2}} \propto \frac{1}{[A]_0^{n-1}}$$

where n is the order of the reaction. Verify this dependence for zero-, first-, and second-order reactions.

13.125 Polyethylene is used in many items, including water pipes, bottles, electrical insulation, toys, and mailer envelopes. It is a *polymer,* a molecule with a very high molar mass made by joining many ethylene molecules together. (Ethylene is the basic unit, or monomer for polyethylene.) The initiation step is

$$R_2 \xrightarrow{k_1} 2R \cdot \qquad \text{initiation}$$

The R $\cdot$ species (called a radical) reacts with an ethylene molecule (M) to generate another radical

$$R \cdot + M \longrightarrow M_1 \cdot$$
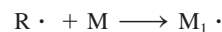
Reaction of M$_1$ $\cdot$ with another monomer leads to the growth or propagation of the polymer chain:

$$M_1 \cdot + M \xrightarrow{k_p} M_2 \cdot \qquad \text{propagation}$$

This step can be repeated with hundreds of monomer units. The propagation terminates when two radicals combine

$$M' \cdot + M'' \cdot \xrightarrow{k_t} M'-M'' \qquad \text{termination}$$

The initiator frequently used in the polymerization of ethylene is benzoyl peroxide [(C$_6$H$_5$COO)$_2$]:

$$[(C_6H_5COO)_2] \longrightarrow 2C_6H_5COO \cdot$$

This is a first-order reaction. The half-life of benzoyl peroxide at 100°C is 19.8 min. (a) Calculate the rate constant (in min^{-1}) of the reaction. (b) If the half-life of benzoyl peroxide is 7.30 h, or 438 min, at 70°C, what is the activation energy (in kJ/mol) for the decomposition of benzoyl peroxide? (c) Write the rate laws for the elementary steps in the above

polymerization process, and identify the reactant, product, and intermediates. (d) What condition would favor the growth of long, high-molar-mass polyethylenes?

13.126 The rate constant for the gaseous reaction

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$
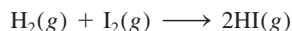
is $2.42 \times 10^{-2}/M \cdot s$ at 400°C. Initially an equimolar sample of H_2 and I_2 is placed in a vessel at 400°C and the total pressure is 1658 mmHg. (a) What is the initial rate (M/min) of formation of HI? (b) What are the rate of formation of HI and the concentration of HI (in molarity) after 10.0 min?

13.127 A protein molecule, P, of molar mass $\mathcal{M}$ dimerizes when it is allowed to stand in solution at room temperature. A plausible mechanism is that the protein molecule is first denatured (that is, loses its activity due to a change in overall structure) before it dimerizes:

$$P \xrightarrow{k} P^*(\text{denatured}) \qquad \text{slow}$$
$$2P^* \longrightarrow P_2 \qquad \text{fast}$$

where the asterisk denotes a denatured protein molecule. Derive an expression for the average molar mass (of P and P_2), $\overline{\mathcal{M}}$, in terms of the initial protein concentration $[P]_0$ and the concentration at time t, $[P]_t$, and $\mathcal{M}$. Describe how you would determine k from molar mass measurements.

13.128 When the concentration of A in the reaction $A \longrightarrow B$ was changed from $1.20\ M$ to $0.60\ M$, the half-life increased from 2.0 min to 4.0 min at 25°C. Calculate the order of the reaction and the rate constant. (*Hint:* Use the equation in Problem 13.124.)

13.129 At a certain elevated temperature, ammonia decomposes on the surface of tungsten metal as follows:

$$NH_3 \longrightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2$$
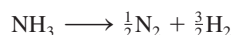
The kinetic data are expressed as the variation of the half-life with the initial pressure of NH_3:

P (mmHg)	264	130	59	16
$t_{\frac{1}{2}}$ (s)	456	228	102	60

(a) Determine the order of the reaction. (b) How does the order depend on the initial pressure? (c) How does the mechanism of the reaction vary with pressure? (*Hint:* You need to use the equation in Problem 13.124 and plot $\log t_{\frac{1}{2}}$ versus $\log P$.)

13.130 The activation energy for the reaction

$$N_2O(g) \longrightarrow N_2(g) + O(g)$$
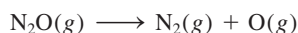
is 2.4×10^2 kJ/mol at 600 K. Calculate the percentage of the increase in rate from 600 K to 606 K. Comment on your results.

13.131 The rate of a reaction was followed by the absorption of light by the reactants and products as a function of wavelengths ($\lambda_1, \lambda_2, \lambda_3$) as time progresses.

Which of the following mechanisms is consistent with the experimental data?

(a) $A \longrightarrow B, A \longrightarrow C$
(b) $A \longrightarrow B + C$
(c) $A \longrightarrow B, B \longrightarrow C + D$
(d) $A \longrightarrow B, B \longrightarrow C$
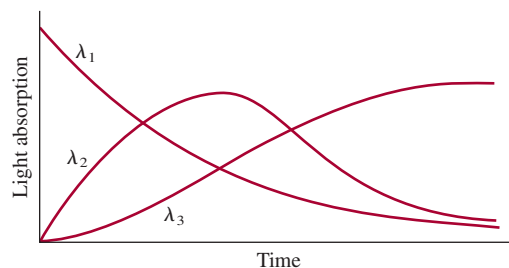
13.132 A gas mixture containing CH_3 fragments, C_2H_6 molecules, and an inert gas (He) was prepared at 600 K with a total pressure of 5.42 atm. The elementary reaction

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$$
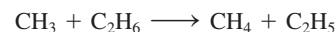
has a second-order rate constant of $3.0 \times 10^4/M \cdot s$. Given that the mole fractions of CH_3 and C_2H_6 are 0.00093 and 0.00077, respectively, calculate the initial rate of the reaction at this temperature.

13.133 To prevent brain damage, a drastic medical procedure is to lower the body temperature of someone who has suffered cardiac arrest. What is the physiochemical basis for this treatment?

13.134 The activation energy (E_a) for the reaction

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g) \quad \Delta H° = -164 \text{ kJ/mol}$$
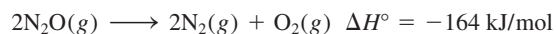
is 240 kJ/mol. What is E_a for the reverse reaction?

13.135 The rate constants for the first-order decomposition of an organic compound in solution are measured at several temperatures:

k (s^{-1})	0.00492	0.0216	0.0950	0.326	1.15
T (K)	278	288	298	308	318

Determine graphically the activation energy and frequency factor for the reaction.

13.136 Assume that the formation of nitrogen dioxide:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
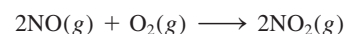
is an elementary reaction. (a) Write the rate law for this reaction. (b) A sample of air at a certain temperature is contaminated with 2.0 ppm of NO by volume. Under these conditions, can the rate law be simplified? If so, write the simplified rate law. (c) Under the condition described in (b), the half-life of the reaction has been estimated to be 6.4×10^3 min. What would be the half-life if the initial concentration of NO were 10 ppm?

Interpreting, Modeling & Estimating

13.137 An instructor performed a lecture demonstration of the thermite reaction (see p. 259). He mixed aluminum with iron(III) oxide in a metal bucket placed on a block of ice. After the extremely exothermic reaction started, there was an enormous bang, which was not characteristic of thermite reactions. Give a plausible chemical explanation for the unexpected sound effect. The bucket was open to air.

13.138 Account for the variation of the rate of an enzyme-catalyzed reaction versus temperature shown here. What is the approximate temperature that corresponds to the maximum rate in the human body?
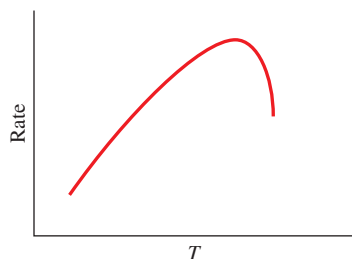
13.139 Is the rate constant (k) of a reaction more sensitive to changes in temperature if E_a is small or large?

13.140 Shown here is a plot of $[A]_t$ versus t for the reaction A $\longrightarrow$ product. (a) Determine the order and the rate constant of the reaction. (b) Estimate the initial rate and the rate at 30 s.
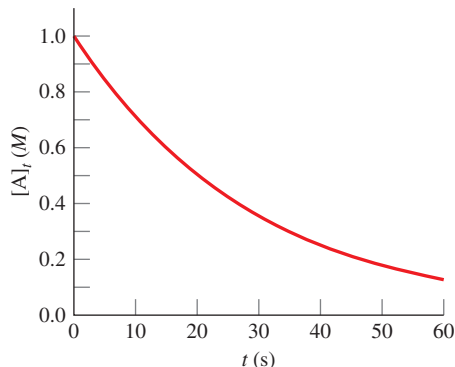
13.141 What are the shortest and longest times (in years) that can be estimated by carbon-14 dating?

13.142 In addition to chemical and biological systems, kinetic treatments can sometimes be applied to behavioral and social processes such as the evolution of technology. For example, in 1965, Gordon Moore, a co-founder of Intel, described a trend that the number of transistors on an integrated circuit (N) roughly doubles every 1.5 yr. Now referred to as *Moore's law,* this trend has persisted for the past several decades. A plot of ln N versus year is shown here. (a) Determine the rate constant for the growth in the number of transistors on an integrated circuit. (b) Based on the rate constant, how long does it take for N to double? (c) If *Moore's law* continues until the end of the century, what will be the number of transistors on an integrated circuit in the year 2100? Comment on your result.
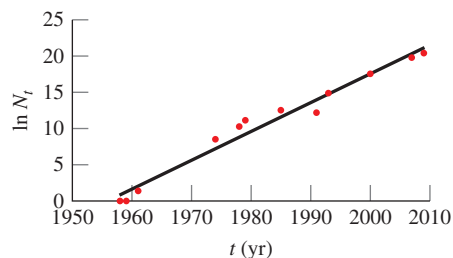
Answers to Practice Exercises

13.1
$$\text{rate} = -\frac{\Delta[CH_4]}{\Delta t} = -\frac{1}{2}\frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[CO_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}$$
13.2 (a) 0.013 M/s. (b) −0.052 M/s. **13.3** rate = $k[S_2O_8^{2-}][I^-]$; $k = 8.1 \times 10^{-2}/M \cdot$ s. **13.4** 66 s.

13.5 First order. 1.4×10^{-2} min^{-1}. **13.6** 1.2×10^3 s. **13.7** (a) 3.2 min. (b) 2.1 min. **13.8** 240 kJ/mol. **13.9** 3.13×10^{-9} s^{-1}. **13.10** (a) NO$_2$ + CO $\longrightarrow$ NO + CO$_2$. (b) NO$_3$. (c) The first step is rate-determining.