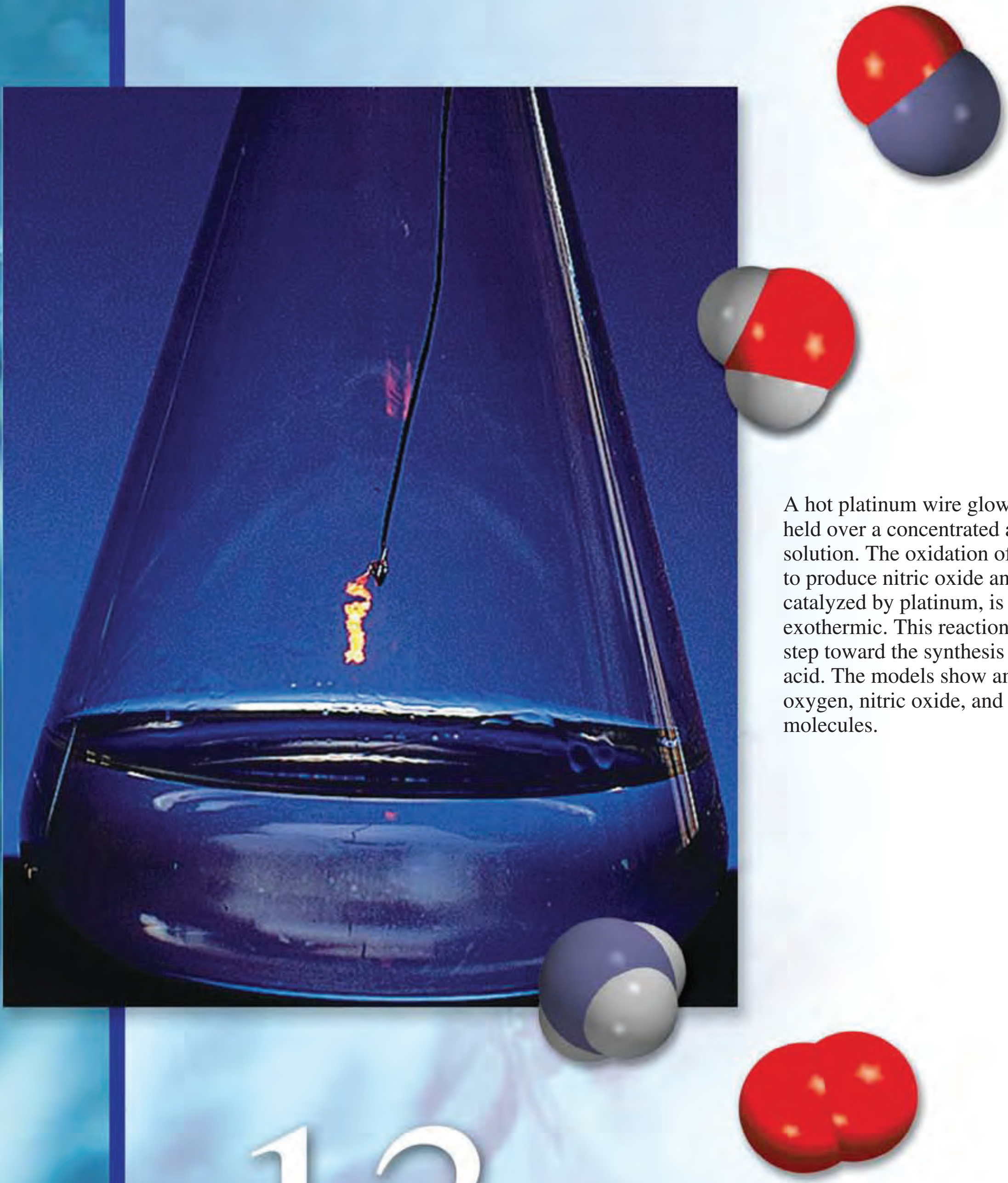
Chemical Kinetics



A hot platinum wire glows when held over a concentrated ammonia solution. The oxidation of ammonia to produce nitric oxide and water, catalyzed by platinum, is highly exothermic. This reaction is the first step toward the synthesis of nitric acid. The models show ammonia, oxygen, nitric oxide, and water molecules.

13

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 18) 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:

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

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 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

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

where $\Delta[\text{A}]$ and $\Delta[\text{B}]$ are the changes in concentration (molarity) over a time period Δt. Because the concentration of A *decreases* during the time interval, $\Delta[\text{A}]$ 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

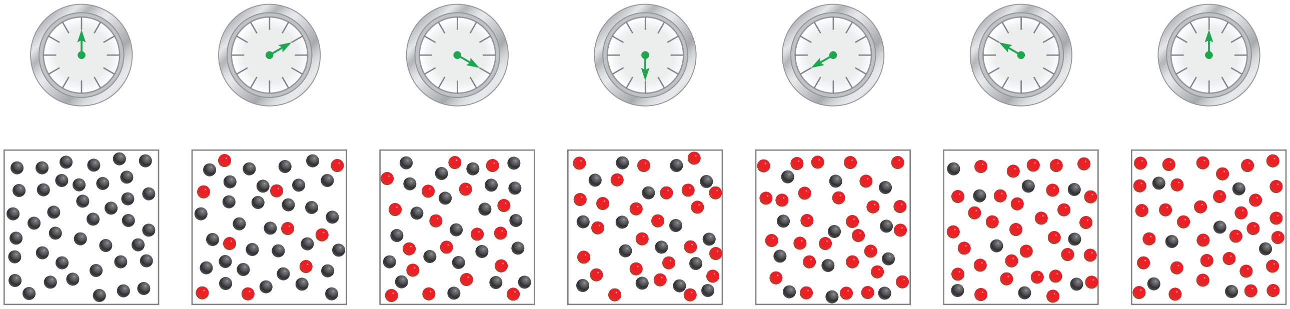


Figure 13.1 *The progress of reaction A ⟶ B at 10-s intervals over a period of 60 s. Initially, only A molecules (gray spheres) are present. As time progresses, B molecules (red spheres) are formed.*

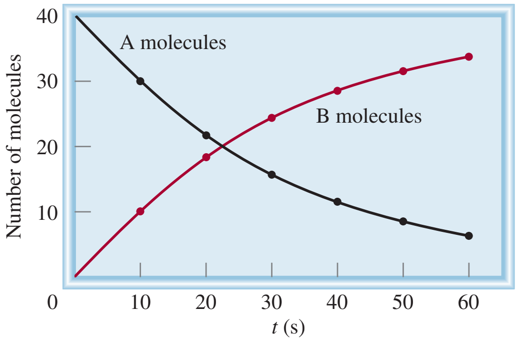


Figure 13.2 *The rate of reaction A $\longrightarrow$ B, represented as the decrease of A molecules with time and as the increase of B molecules with time.*

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).

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).*

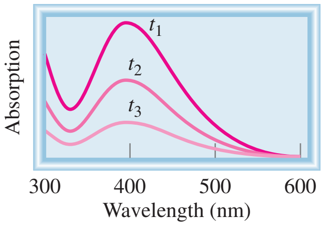


Figure 13.4 *Plot of absorption of bromine versus wavelength. The maximum absorption of visible light by bromine occurs at 393 nm. As the reaction progresses (t_1 to t_3), the absorption, which is proportional to $[Br_2]$, decreases.*

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:

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

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 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

TABLE 13.1 **Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C**

Time (s)	$[Br_2]$ (M)	Rate (M/s)	$k = \frac{\text{rate}}{[Br_2]}$ (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}

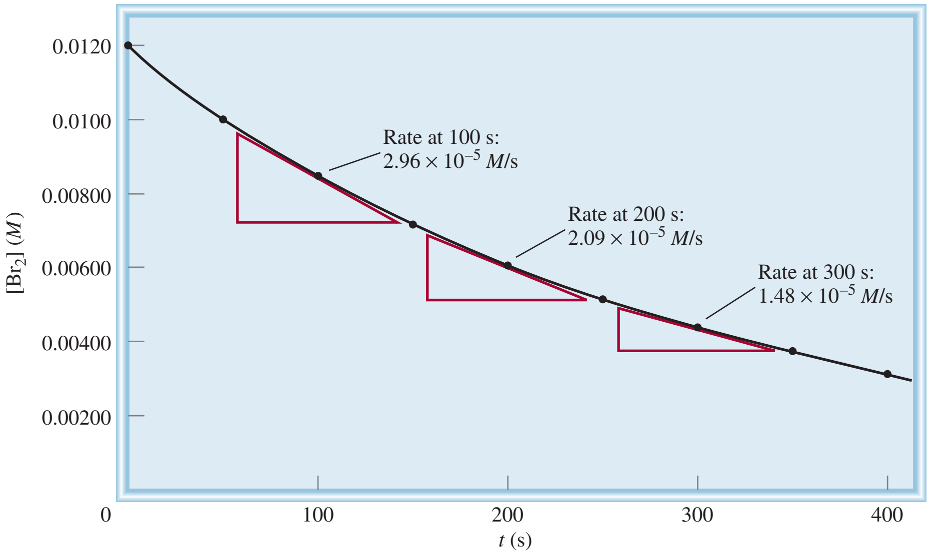


Figure 13.5 *The instantaneous rates of the reaction between molecular bromine and formic acid at t = 100 s, 200 s, and 300 s are given by the slopes of the tangents at these times.*

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 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

$$\begin{aligned} \text{rate} &\propto [\mathrm{Br_2}] \\ &= k[\mathrm{Br_2}] \end{aligned}$$

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.

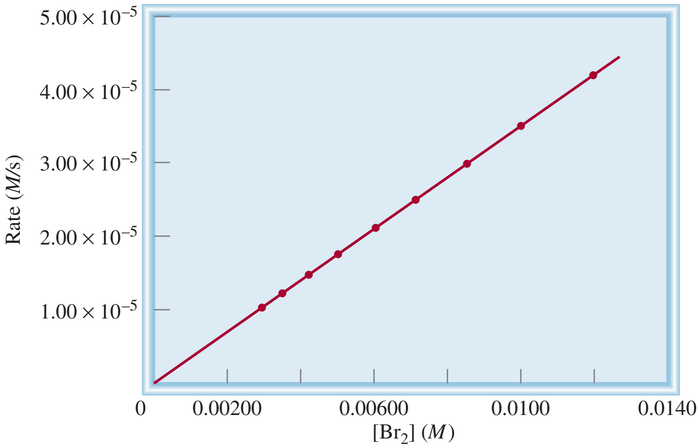
Figure 13.6 is a plot of the rate versus Br_2 concentration. The fact that this graph is a straight line shows that the rate is directly proportional to the concentration; the higher the concentration, the higher the rate. Rearranging the last equation gives

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

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

As we will see, for a given reaction, *k* is affected only by a change in temperature.

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.*



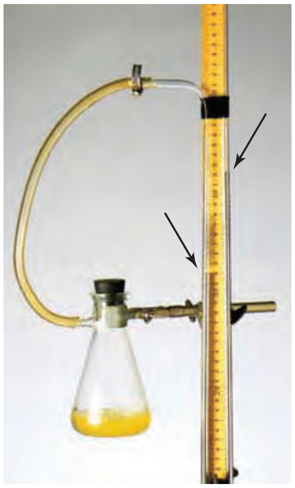


Figure 13.7 *The rate of hydrogen peroxide decomposition can be measured with a manometer, which shows the increase in the oxygen gas pressure with time. The arrows show the mercury levels in the U tube.*

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

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{Br}_2]} \\ &= \frac{3.52 \times 10^{-5}\ M/\text{s}}{0.0101\ M} = 3.49 \times 10^{-3}\ \text{s}^{-1} \end{aligned}$$

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.

Reaction Rates and Stoichiometry

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

$$2\mathrm{A} \longrightarrow \mathrm{B}$$

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

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

In general, for the reaction

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

the rate is given by

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

Use reaction stoichiometry to determine relative rates of reactions between species in a reaction. See the outline for examples.

EXAMPLE 13.2

Consider the reaction

$$4\text{NO}_2(g) + \text{O}_2(g) \longrightarrow 2\text{N}_2\text{O}_5(g)$$

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:

We are given

$$\frac{\Delta[\text{O}_2]}{\Delta t} = -0.024\ M/\text{s}$$

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

(Continued)

so

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

Practice Exercise Consider the reaction

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

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?

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

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

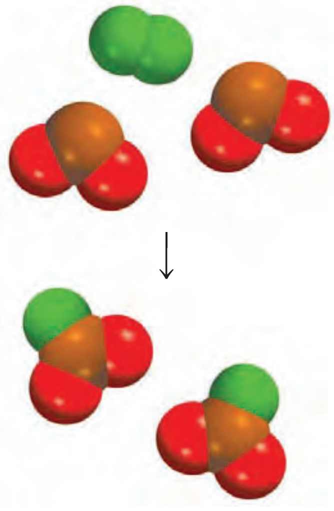
the rate law takes the form

$$\boxed{\text{rate} = k[\mathrm{A}]^x[\mathrm{B}]^y} \qquad (13.1)$$

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:



$F_2 + 2ClO_2 \longrightarrow 2FClO_2$

$$F_2(g) + 2ClO_2(g) \longrightarrow 2FClO_2(g)$$

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 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

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

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}

Reaction order enables us to understand how the reaction depends on reactant concentrations. Suppose, for example, that for the general reaction $a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$ we have $x = 1$ and $y = 2$. The rate law for the reaction is [see Equation (13.1)]

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

This reaction is first order in A, second order in B, and third order overall ($1 + 2 = 3$). Let us assume that initially $[\text{A}] = 1.0\ M$ and $[\text{B}] = 1.0\ M$. 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 $[\text{A}] = 1.0\ M$ $$\begin{aligned}\text{rate}_1 &= k(1.0\ M)(1.0\ M)^2\\ &= k(1.0\ M^3)\end{aligned}$$

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

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 $[\text{A}] = 1\ M$, the rate will increase by a factor of 4 because of the power 2 in the exponent:

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

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

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

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

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

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.

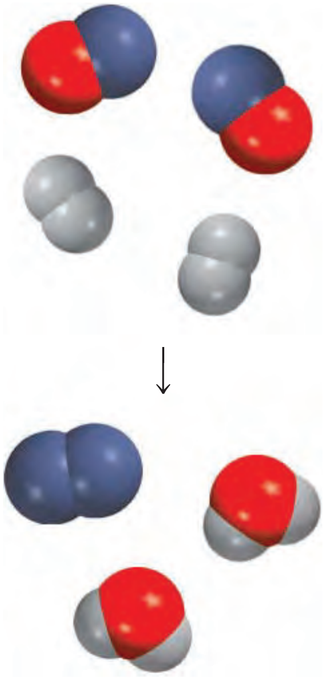
Example 13.3 illustrates the procedure for determining the rate law of a reaction.

EXAMPLE 13.3

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

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

(Continued)



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

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

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

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

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

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

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

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

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

(Continued)

The data from experiment 2 give us

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

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

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

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}

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

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

the rate is

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

From the rate law we also know that

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

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

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

Combining the first two equations for the rate we get

$$-\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}] \qquad (13.2)$$

In differential form, Equation (13.2) becomes

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]$$

Rearranging, we get

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

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

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

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

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

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

$$\boxed{\ln \frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt} \qquad (13.3)$$

where ln is the natural logarithm, and $[\mathrm{A}]_0$ and $[\mathrm{A}]_t$ 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:

$$\boxed{\ln [\mathrm{A}]_t = -kt + \ln [\mathrm{A}]_0} \qquad (13.4)$$

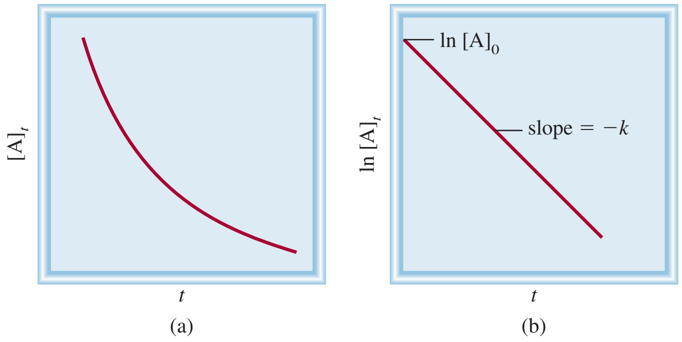
Equation (13.4) has the form of the linear equation $y = mx + b$, in which m is the slope of the line that is the graph of the equation:

$$\begin{array}{ccccccc} \ln [\mathrm{A}]_t & = & (-k) & (t) & + & \ln [\mathrm{A}]_0 \\ \updownarrow & & \updownarrow & \updownarrow & & \updownarrow \\ y & = & m & x & + & b \end{array}$$

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 $\ln [\mathrm{A}]_t$ versus time (y versus x), we obtain a straight line with a slope equal to $-k$ and a y intercept equal to $\ln [\mathrm{A}]_0$ [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):

$$C_2H_6 \longrightarrow 2CH_3$$



(a) (b)

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 $-k$.*

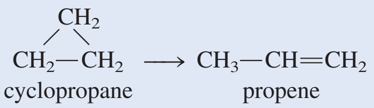
The decomposition of N_2O_5 is also a first-order reaction

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

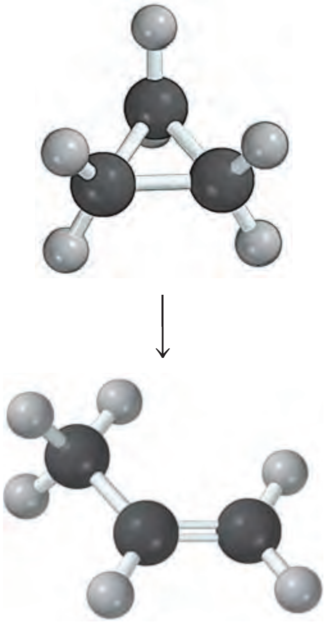
In Example 13.4 we apply Equation (13.3) to an organic reaction.

EXAMPLE 13.4

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



$$\text{cyclo-}(CH_2)_3 \longrightarrow CH_3{-}CH{=}CH_2$$



(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.

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

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

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

(Continued)

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

(b) Using Equation (13.3),

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

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

$$= 13\ \mathrm{min}$$

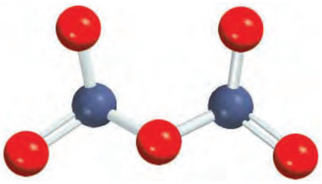
(c) From Equation (13.3),

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

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

Similar problem: 13.88.

Practice Exercise The reaction 2A ⟶ B is first order in A with a rate constant of $2.8 \times 10^{-2}\ \mathrm{s}^{-1}$ 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 nitrogen pentoxide in carbon tetrachloride (CCl_4) solvent at 45°C:

$$2\mathrm{N_2O_5}(\mathrm{CCl_4}) \longrightarrow 4\mathrm{NO_2}(g) + \mathrm{O_2}(g)$$

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

t (s)	$[\mathrm{N_2O_5}]$ (M)	ln $[\mathrm{N_2O_5}]$
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, 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:

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

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

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

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

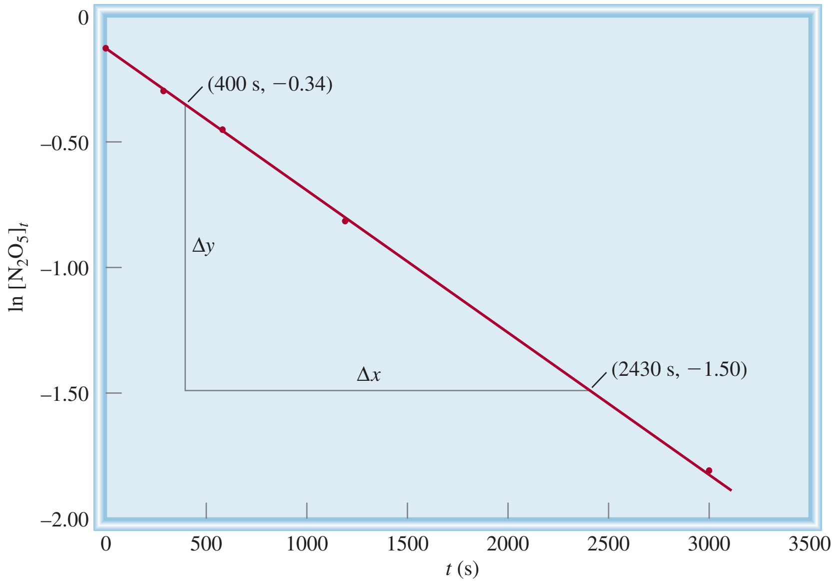
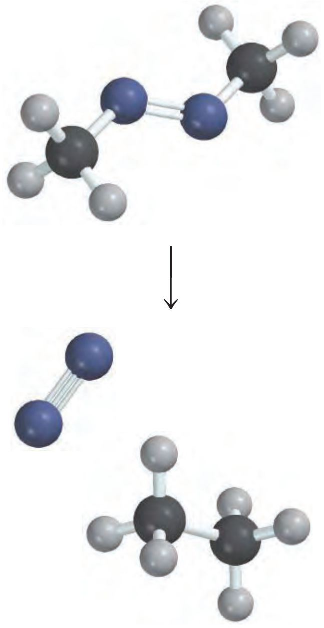


Figure 13.10 *Plot of ln* $[N_2O_5]_t$ *versus time. The rate constant can be determined from the slope of the straight line.*



$C_2H_6N_2 \longrightarrow N_2 + C_2H_6$

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 $k = 2.55 \times 10^{-3}\ \text{s}^{-1}$.

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

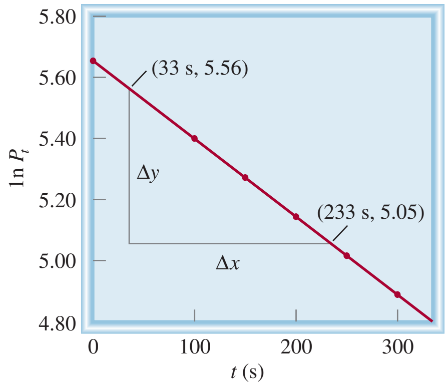


Figure 13.11 *Plot of ln P_t versus time for the decomposition of azomethane.*

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

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

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

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

or

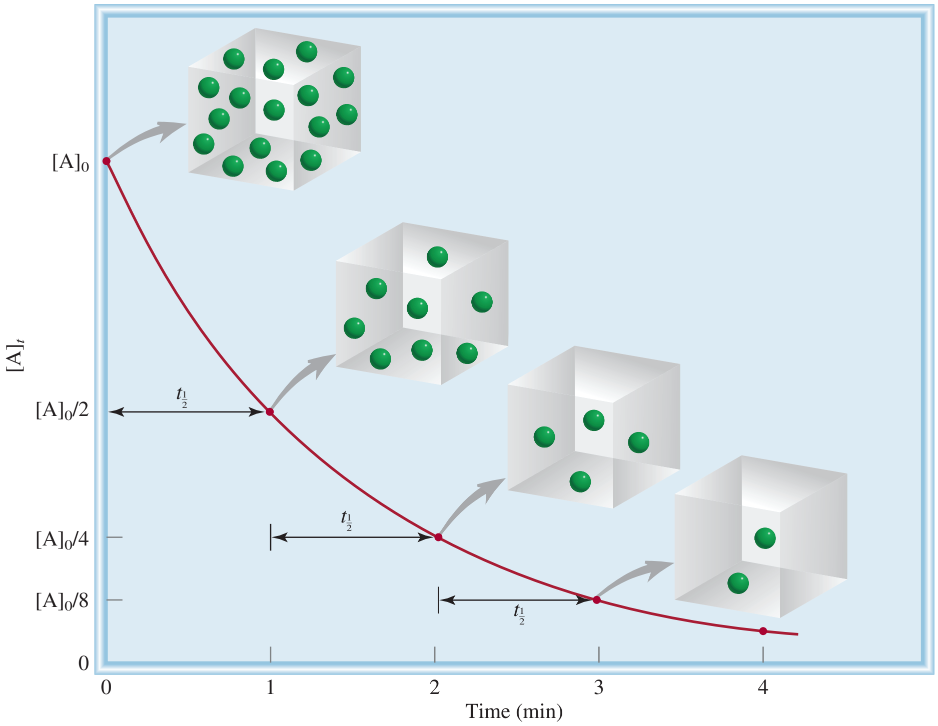
$$t_{\frac{1}{2}} = \frac{1}{k} \ln 2 = \frac{0.693}{k} \tag{13.6}$$

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 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.

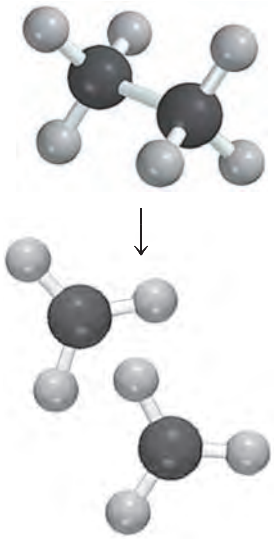
The following analogy may be helpful for understanding Equation (13.6). If a college student takes 4 yr to graduate, the half-life of his or her stay at the college is 2 yr. Thus, half-life is not affected by how many other students are present. Similarly, the half-life of a first-order reaction is concentration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

The usefulness of $t_{\frac{1}{2}}$ is that it gives us an estimate of the magnitude of the rate constant—the shorter the half-life, the larger the k. Consider, for example, two radioactive 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.

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.*



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



$C_2H_6 \longrightarrow 2CH_3$

EXAMPLE 13.6

The decomposition of ethane (C_2H_6) to methyl radicals is a first-order reaction with a rate constant of $5.36 \times 10^{-4}\ s^{-1}$ 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.

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

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{0.693}{k} \\ &= \frac{0.693}{5.36 \times 10^{-4}\ s^{-1}} \\ &= 1.29 \times 10^{3}\ s \times \frac{1\ min}{60\ s} \\ &= \boxed{21.5\ min} \end{aligned}$$

Practice Exercise Calculate the half-life of the decomposition of N_2O_5, discussed on p. 572.

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:

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

where

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

From the rate law,

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

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

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

Another type of second-order reaction is

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

and the rate law is given by

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

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:

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

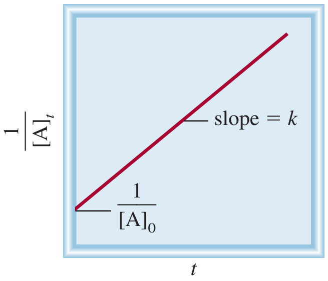


Figure 13.13 *A plot of 1/[A]$_t$ versus t for a second-order reaction. The slope of the line is equal to k.*

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 $= 1/[A]_0$. (The corresponding equation for "A + B $\longrightarrow$ product" reactions is too complex for our discussion.)

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

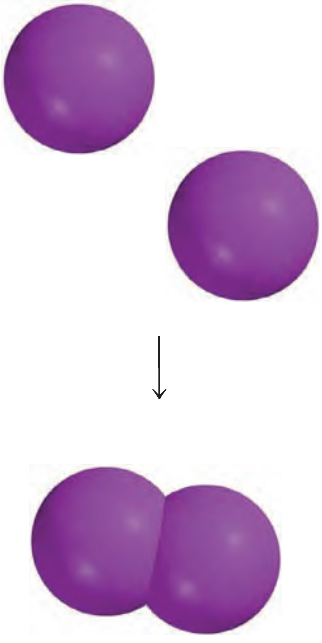
$$\frac{1}{[A]_0/2} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

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

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0} \qquad (13.8)$$

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.

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)

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

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

the rate law is given by

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

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

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

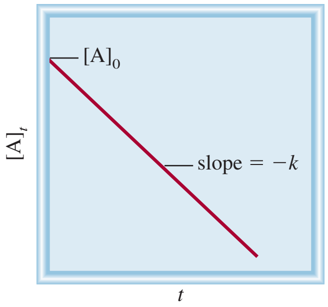


Figure 13.14 *A plot of [A]$_t$ versus t for a zero-order reaction. The slope of the line is equal to $-k$.*

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 $= [A]_0$.

Many of the known zero-order reactions take place on a metal surface. An exam-ple is the decomposition of nitrous oxide (N2O) to nitrogen and oxygen in the presence of platinum (Pt):

2N2O(g) ¡ 2N2(g) 1 O2(g)

When all the binding sites on Pt are occupied, the rate becomes constant regardless of the amount of N2O 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.

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.

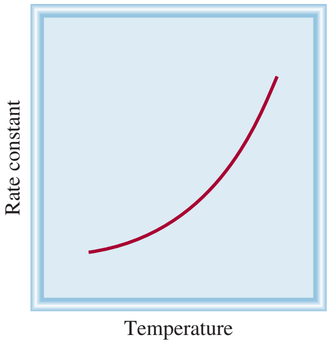


Figure 13.15 *Dependence of rate constant on temperature. The rate constants of most reactions increase with increasing temperature.*

The Collision Theory of Chemical Kinetics

The kinetic molecular theory of gases (p. 201) 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:

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

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

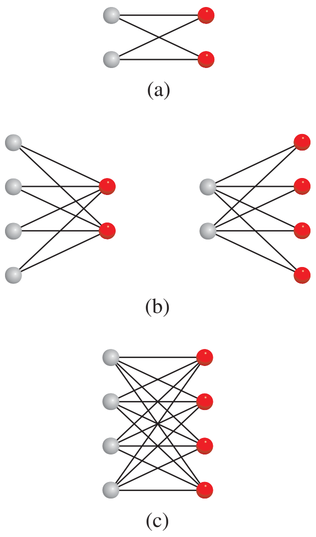


Figure 13.16 *Dependence of number of collisions on concentration. We consider here only A-B collisions, which can lead to formation of products. (a) There are four possible collisions among two A and two B molecules. (b) Doubling the number of either type of molecule (but not both) increases the number 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.*

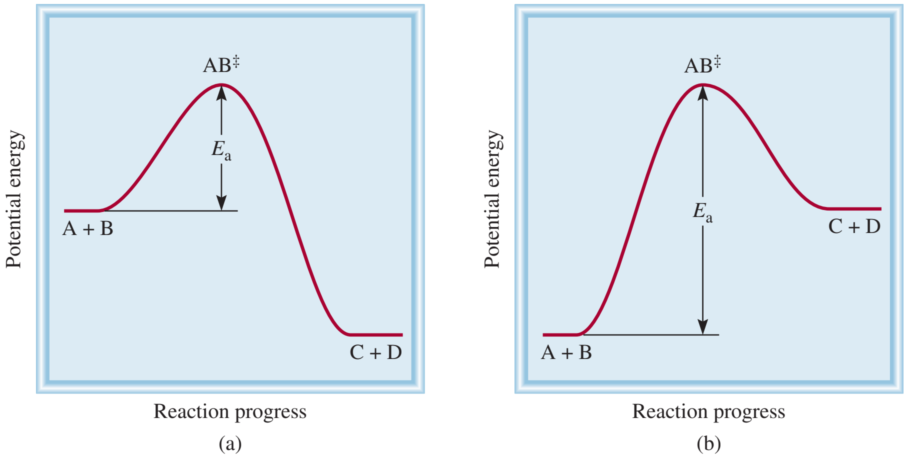


Figure 13.17 *Potential energy profiles for (a) exothermic and (b) endothermic reactions. These plots show the change in potential energy as reactants A and B are converted to products C and D. The activated complex ($AB^{\ddagger}$) is a highly unstable species with a high potential energy. The activation 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

$$A + B \longrightarrow AB^{\ddagger} \longrightarrow C + D$$

where $AB^{\ddagger}$ 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 therefore 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 temperature, the rate of product formation is also greater at the higher temperature.

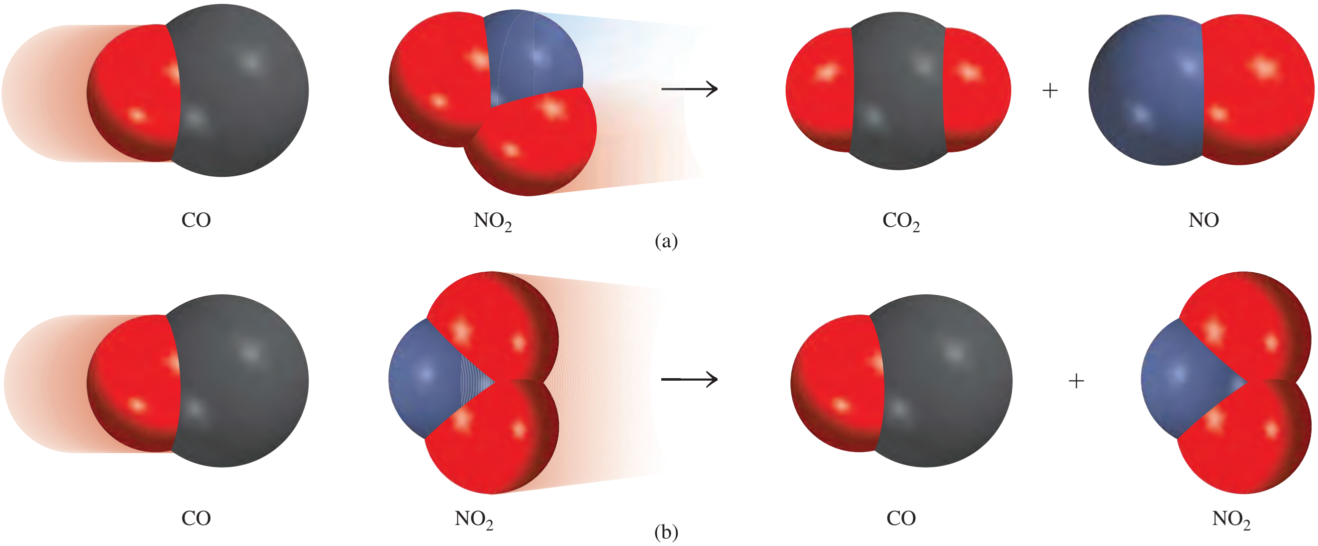


Figure 13.19 *The orientations of the molecules shown in (a) are effective and will likely lead to formation of products. The orientations shown in (b) are ineffective and no products will be formed.*

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

13.5 Reaction Mechanisms

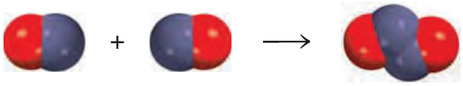
As we mentioned earlier, an overall balanced chemical equation does not tell us much about how a reaction actually takes place. In many cases, it merely represents the sum of several ***elementary steps,*** or *elementary reactions, a series of simple reactions that represent the progress of the overall 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:

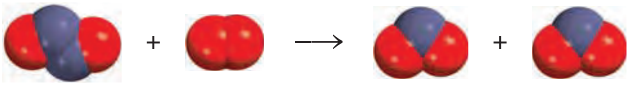
$$2\mathrm{NO}(g) + \mathrm{O}_2(g) \longrightarrow 2\mathrm{NO}_2(g)$$

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:

$$2\mathrm{NO}(g) \longrightarrow \mathrm{N}_2\mathrm{O}_2(g)$$



$$\mathrm{N}_2\mathrm{O}_2(g) + \mathrm{O}_2(g) \longrightarrow 2\mathrm{NO}_2(g)$$



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:

$$\begin{array}{ll} \text{Step 1:} & \mathrm{NO} + \mathrm{NO} \longrightarrow \mathrm{N}_2\mathrm{O}_2 \\ \text{Step 2:} & \mathrm{N}_2\mathrm{O}_2 + \mathrm{O}_2 \longrightarrow 2\mathrm{NO}_2 \\ \hline \text{Overall reaction:} & 2\mathrm{NO} + \cancel{\mathrm{N}_2\mathrm{O}_2} + \mathrm{O}_2 \longrightarrow \cancel{\mathrm{N}_2\mathrm{O}_2} + 2\mathrm{NO}_2 \end{array}$$

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:

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

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:

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

For a bimolecular elementary reaction involving A and B molecules

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

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

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

Similarly, for a bimolecular elementary reaction of the type

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

or

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

the rate becomes

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

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:

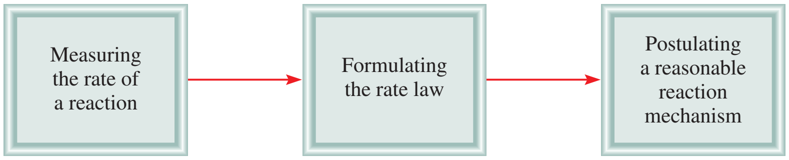


Figure 13.20 *Sequence of steps in the study of a reaction mechanism.*

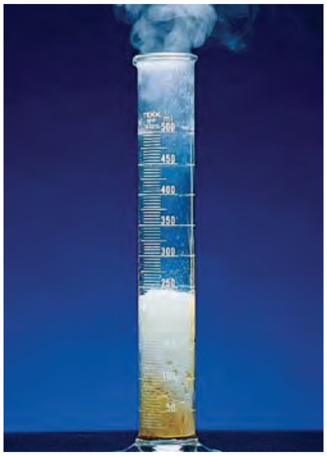


Figure 13.21 *The decomposition of hydrogen peroxide is catalyzed by the iodide ion. A few drops of liquid soap have been added to the solution to dramatize the evolution of oxygen gas. (Some of the iodide ions are oxidized to molecular iodine, which then reacts with iodide ions to form the brown triiodide*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

- 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.

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:

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

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

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.

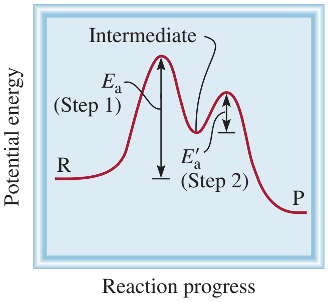


Figure 13.22 *Potential energy profile for a two-step reaction in which the first step is rate-determining. R and P represent reactants and products, respectively.*

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

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

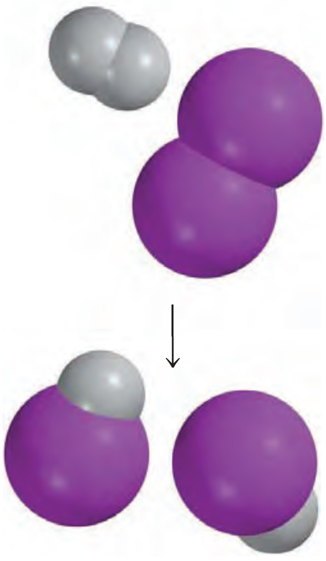
For many years it was thought that the reaction occurred just as written; that is, it is a bimolecular reaction involving a hydrogen molecule and an iodine molecule, as shown on p. 590. However, in the 1960s chemists found that the actual mechanism is more complicated. A two-step mechanism was proposed:

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

$$\text{Step 2:} \qquad H_2 + 2I \xrightarrow{k_2} 2HI$$

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.


$H_2 + I_2 \longrightarrow 2HI$

Chemical equilibrium will be discussed in Chapter 14.

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

$$\begin{aligned}\text{rate} &= \frac{k_1k_2}{k_{-1}}[H_2][I_2] \\ &= k[H_2][I_2]\end{aligned}$$

where $k = k_1k_2/k_{-1}$. 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.

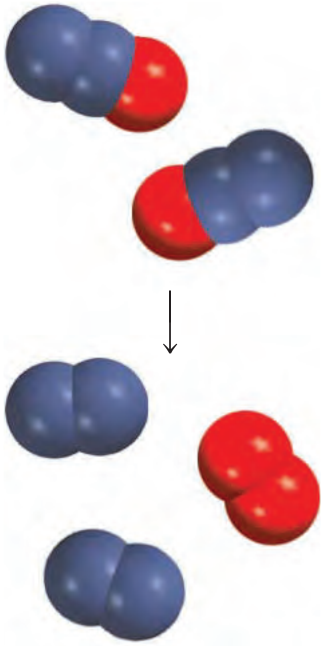
EXAMPLE 13.10

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)



$2N_2O \longrightarrow 2N_2 + O_2$

Similar problem: 13.51.

Experimentally the rate law is found to be rate $= k[N_2O]$. (a) Write the equation for the overall reaction. (b) Identify the intermediates. (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

$$\boxed{2N_2O \longrightarrow 2N_2 + O_2}$$

(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

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

and $k = k_1$.

Check Step 1 must be the rate-determining step because the rate law written from this step matches the experimentally determined rate law, that is, rate $= k[N_2O]$.

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

$$\begin{aligned} &\text{Step 1:} \quad NO_2 + NO_2 \longrightarrow NO + NO_3 \\ &\text{Step 2:} \quad NO_3 + CO \longrightarrow NO_2 + CO_2 \end{aligned}$$

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?

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 alter-native 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.

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.

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.

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,

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

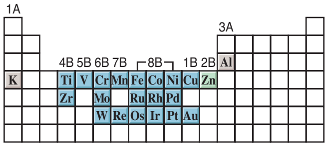
Figure 13.23 shows the potential energy profiles for both reactions. Note that the total energies of the reactants (A and B) and those of the products (C and D) are unaffected by the catalyst; the only difference between the two is a lowering of the activation energy from E_a to E'_a. Because the activation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

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

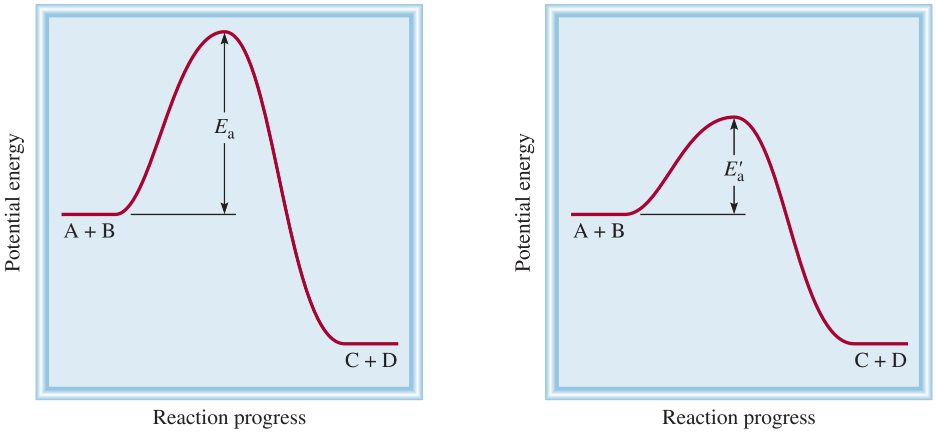
There are three general types of catalysis, depending on the nature of the rate-increasing substance: heterogeneous catalysis, homogeneous catalysis, and enzyme catalysis.

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



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



(a) (b)

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).*

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.

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 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:

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

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

$$N + 3H \longrightarrow NH_3$$

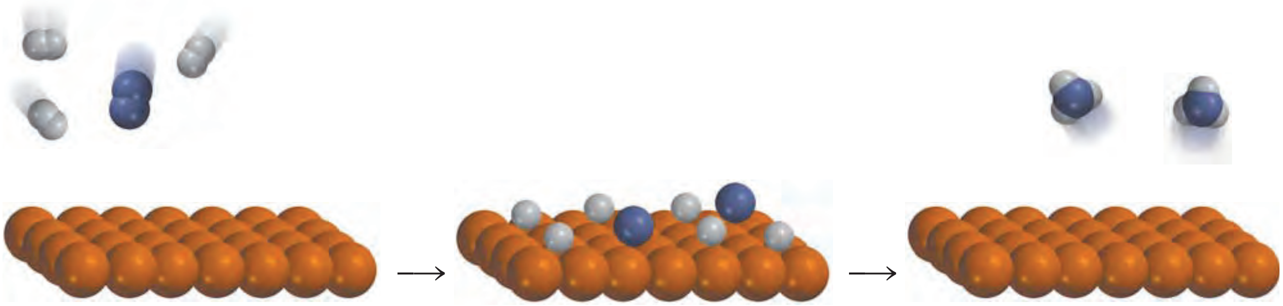


Figure 13.24 *The catalytic action in the synthesis of ammonia. First the H_2 and N_2 molecules bind to the surface of the catalyst. This interaction weakens the covalent bonds within the molecules and eventually causes the molecules to dissociate. The highly reactive H and N atoms combine to form NH_3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

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

Catalytic Converters

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

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

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.

[†] 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.

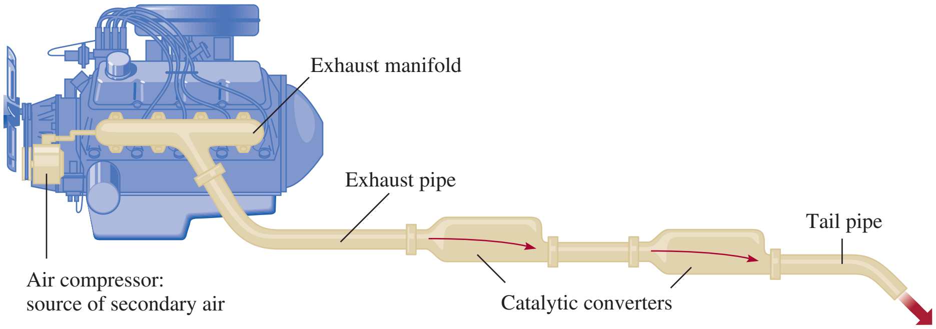
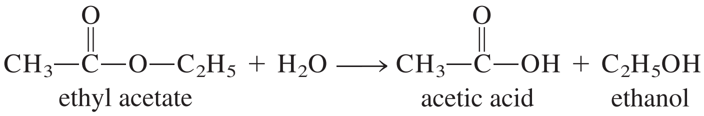


Figure 13.26 *A two-stage catalytic converter for an automobile.*

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.



$$\underset{\text{ethyl acetate}}{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}C_2H_5} + H_2O \longrightarrow \underset{\text{acetic acid}}{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH} + \underset{\text{ethanol}}{C_2H_5OH}$$

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

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

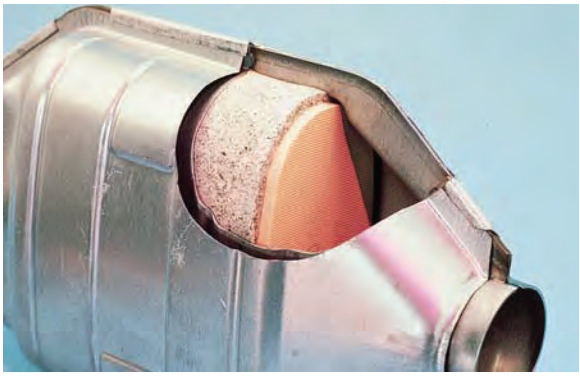


Figure 13.27 *A cross-sectional view of a catalytic converter. The beads contain platinum, palladium, and rhodium, which catalyze the conversion of CO and hydrocarbons to carbon dioxide and water.*

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:

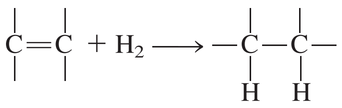
$$\begin{aligned} S(s) + O_2(g) &\longrightarrow SO_2(g) \\ 2SO_2(g) + O_2(g) &\longrightarrow 2SO_3(g) \\ H_2O(l) + SO_3(g) &\longrightarrow H_2SO_4(aq) \end{aligned}$$

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:

$$\begin{array}{ll} & 2SO_2(g) + 2NO_2(g) \longrightarrow 2SO_3(g) + 2NO(g) \\ & \quad 2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \\ \cline{2-2} \text{Overall reaction:} & \quad 2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \end{array}$$

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:



$$>C{=}C< + H_2 \longrightarrow -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{H}{C}}-$$

This reaction is important in the food industry. It converts "unsaturated fats" (compounds containing many C=C bonds) to "saturated fats" (compounds containing few or no C=C bonds).

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

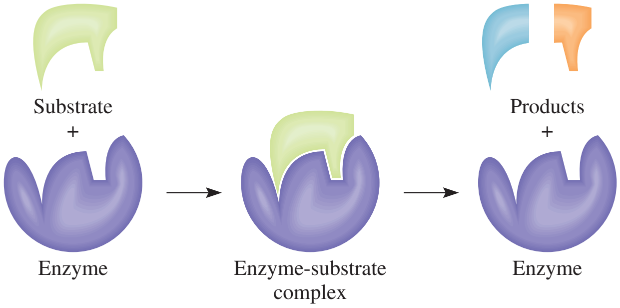


Figure 13.28 *The lock-and-key model of an enzyme's specificity for substrate molecules.*

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.

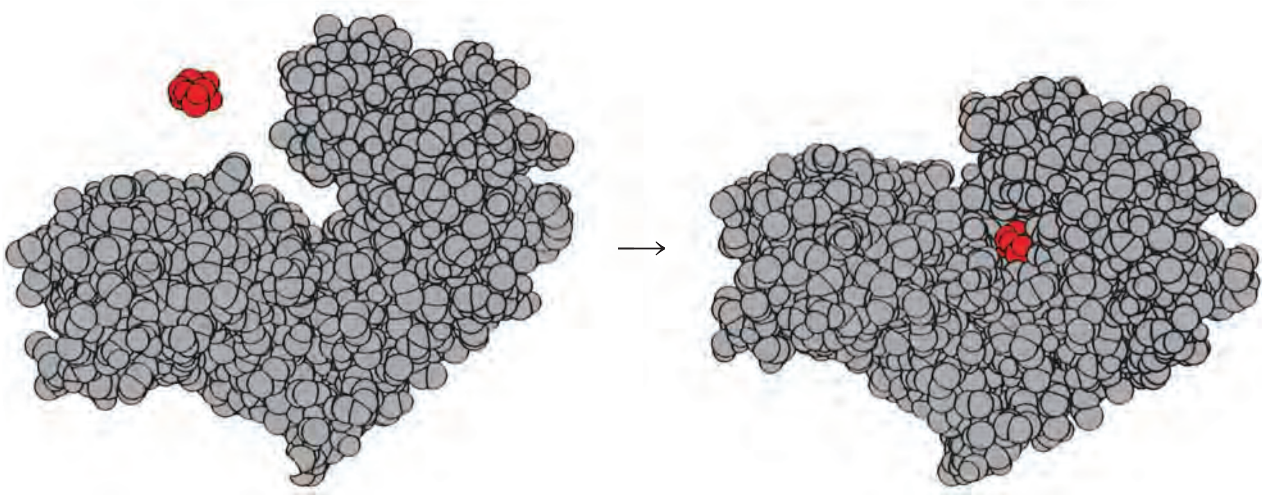


Figure 13.29 *Left to right: The binding of glucose molecule (red) to hexokinase (an enzyme in the metabolic pathway). Note how the region at the active site closes around glucose after binding. Frequently, the geometries of both the substrate and the active site are altered to fit each other.*

Key Equations

$\text{rate} = k[\mathrm{A}]^x[\mathrm{B}]^y$	(13.1)	Rate law expressions. The sum ($x + y$) gives the overall order of the reaction.
$\ln \frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt$	(13.3)	Relationship between concentration and time for a first-orderr eaction.
$\ln [\mathrm{A}]_t = -kt + \ln [\mathrm{A}]_0$	(13.4)	Equation for the graphical determination of k for a first-orderr eaction.
$t_{\frac{1}{2}} = \frac{0.693}{k}$	(13.6)	Half-life for a firstorderreaction.
$\frac{1}{[\mathrm{A}]_t} = kt + \frac{1}{[\mathrm{A}]_0}$	(13.7)	Relationship between concentration and time for a second-order reaction.

Summary of Facts and Concepts

Media Player
Chapter Summary

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. 583
Activation energy (E_a), p. 583
Bimolecular reaction, p. 588
Catalyst, p. 594
Chemical kinetics, p. 558
Elementary step, p. 588
Enzyme, p. 599
First-order reaction, p. 570
Half-life ($t_{\frac{1}{2}}$), p. 575
Intermediate, p. 588
Molecularity of a reaction, p. 588
Rate constant (k), p. 561
Rate-determining step, p. 589
Rate law, p. 565
Reaction mechanism, p. 588
Reaction order, p. 566
Reaction rate, p. 558
Second-order reaction, p. 577
Termolecular reaction, p. 588
Transition state, p. 583
Unimolecular reaction, p. 588

Answers to Practice Exercises

13.1

$$\text{rate} = -\frac{\Delta[\text{CH}_4]}{\Delta t} = -\frac{1}{2}\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

13.2 (a) 0.013 *M*/s. (b) −0.052 *M*/s.
13.3 rate = $k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$; $k = 8.1 \times 10^{-2}/M \cdot \text{s}$.
13.4 66 s. **13.5** First order. $1.4 \times 10^{-2}\ \text{min}^{-1}$.
13.6 1.2×10^3 s. **13.7** (a) 3.2 min. (b) 2.1 min.
13.8 240 kJ/mol. **13.9** $3.13 \times 10^{-9}\ \text{s}^{-1}$.
13.10 (a) $\text{NO}_2 + \text{CO} \longrightarrow \text{NO} + \text{CO}_2$. (b) NO_3.
(c) The first step is rate-determining.