Chemical Kinetics

14

The brilliant colors seen in fireworks displays result from extremely fast, highly exothermic chemical reactions.

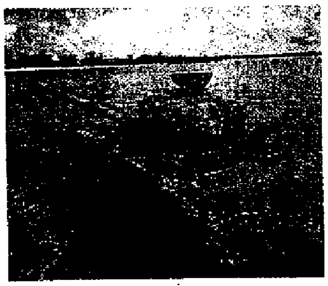
mistry is, by its very nature, concerned with change. Chemical reac- convert substances with well-defined properties into other materials different properties. Much of our study of chemical reactions is con- with the formation of new substances from a given set of reactants. ver, it is equally important to understand how rapidly chemical re- s occur. Our everyday experience tells us that some reactions are fast others are slow (Figure 14.1 ▶), and we wish to understand the fac- at control their rates. For example, what factors determine how rapid- d spoils? How does one design a fast-setting material for dental s? What determines the rate at which steel rusts? What controls the which fuel burns in an automobile engine?

e area of chemistry that is concerned with the speeds, or rates, at reactions occur is called **chemical kinetics.** In this chapter we will ow to determine the rates at which reactions occur and how these n be expressed mathematically. We will see that the rates of chem- ctions are affected by several factors, most notably:

concentrations of the reactants: Most chemical reactions proceed ter if the concentration of one or more of the reactants is increased. example, steel wool burns with difficulty in air, which contains percent O_2, but bursts into a brilliant white flame in pure oxygen gure 14.2 ▶).

temperature at which the reaction occurs: The rates of chemical reac- s increase as temperature is increased. It is for this reason that we igerate perishable foods such as milk. The bacterial reactions that d to the spoiling of milk proceed much more rapidly at room tem- ature than they do at the lower temperatures of a refrigerator.

presence of a catalyst: The rates of many reactions can be increased adding a substance known as a *catalyst*. We will see that a catalyst eases the rate of a reaction without being consumed in the reac- . The physiology of most living species depends crucially on *en- es*, protein molecules that act as catalysts, which increase the rates elected biochemical reactions.



▲ **Figure 14.1** The rates of chemical reactions span a range of time scales. They can be very fast, as in many combustion reactions (see the chapter-opening photograph). They can also be very slow, taking years or more, as in the corrosion of metals in the atmosphere. In the laboratory portion of your course you will probably carry out reactions that are complete on the time scale of minutes to hours.

4. *The surface area of solid or liquid reactants or catalysts*: Reactions that involve so[lids] often proceed faster as the surface area of the solid is increased. For exam[ple,] a medicine in the form of a tablet will dissolve in the stomach and ente[r the] bloodstream more slowly than the same medicine in the form of a fine pow[der.]

We will consider these factors as we proceed through this chapter. We will [al]so see that chemical kinetics can teach us much about how reactions occur a[t the] molecular level.

14.1 Reaction Rates

The *speed* of an event is defined as the *change* that occurs in a given interv[al of] *time*: Whenever we talk about speed, we necessarily bring in the notion of ti[me.] For example, the speed of a car is expressed as the change in the car's posi[tion] over a certain period of time. The units of this speed are usually miles pe[r hour] (mi/hr), that is, the quantity that is changing (position, measured in miles) [di]vided by a time interval (hours).

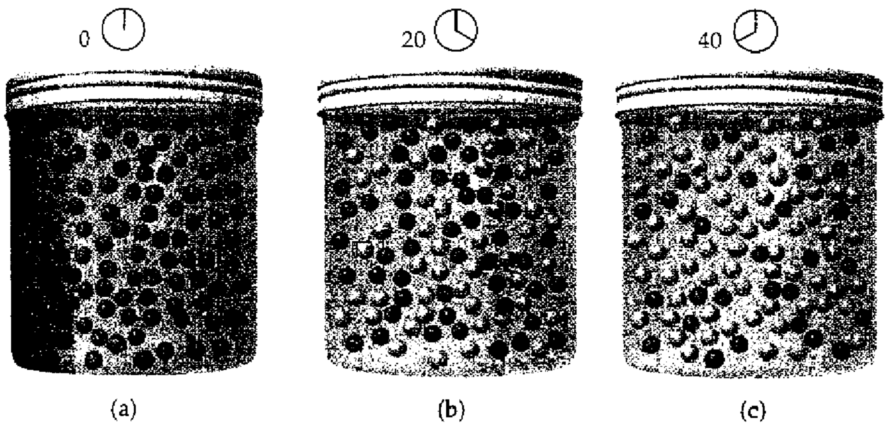
Similarly, we can speak about the speed of a chemical reaction, or its rea[ction] **rate**. Let's consider a simple hypothetical reaction, $A \longrightarrow B$. We will depi[ct the] quantity of A with red spheres and the quantity of B with blue spheres, [with] each sphere representing 0.01 mol (Figure 14.3 ▶). Suppose that we start wit[h 1.00] mol of A in a container of fixed volume, as shown in Figure 14.3(a). We [then] monitor the quantities of A and B at later times. For this hypothetical reactio[n, we] see that after 20 minutes there are 0.54 mol of A and 0.46 mol of B in the con[tainer] [Figure 14.3(b)]; notice that the sum of the quantities of A and B is still 1.00 [mol] because one molecule of B is produced for each molecule of A that reacts. [After] 40 minutes we have 0.30 mol of A and 0.70 mol of B [Figure 14.3(c)]. Figure 1[4.3(d)] is a plot of the number of moles of A and B measured every 10 minutes [for one] hour after the start of the reaction (which we call *time zero* and denote $t = 0$).

The reaction rate is a measure of how quickly A is consumed or how qu[ick]ly B is produced. Thus, for a given interval of time, we can express the av[erage] rate of the reaction as the increase in the number of moles of B over that int[erval:]

$$\text{Average rate} = \frac{\text{change in the number of moles of B}}{\text{change in time}} = \frac{\Delta(\text{moles of B})}{\Delta t}$$

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

(a) (b)



◀ **Figure 14.3** Progress of a hypothetical reaction A ⟶ B, starting with 1.00 mol A. Each red sphere represents 0.01 mol A, and each blue sphere represents 0.01 mol B. (a) At time zero, the vessel contains 1.00 mol A (100 red spheres) and 0 mol B (0 blue spheres). (b) After 20 min, the vessel contains 0.54 mol A and 0.46 mol B. (c) After 40 min, the vessel contains 0.30 mol A and 0.70 mol B. These data, and those at other times, are graphed in Figure 14.4.

Recall that the Greek letter delta, Δ, is read "change in." (Section 5.2) Thus, Δt is the change in time between the beginning and end of any specific time interval: Δt = (time at end of interval) − (time at beginning of interval). The quantity Δ(moles of B) is the difference in the number of moles of B measured at the final and initial times:

$$\Delta(\text{moles of B}) = (\text{moles of B at final time}) - (\text{moles of B at initial time}) \quad [14.2]$$

Because the number of moles of B is increasing as the reaction proceeds, Δ(moles of B) is a positive number.

We can use Equation 14.1 and the data in Figure 14.4 to calculate the average rate of the reaction at different time intervals. For example, the average rate over the interval $t = 0$ min to $t = 10$ min is given by:

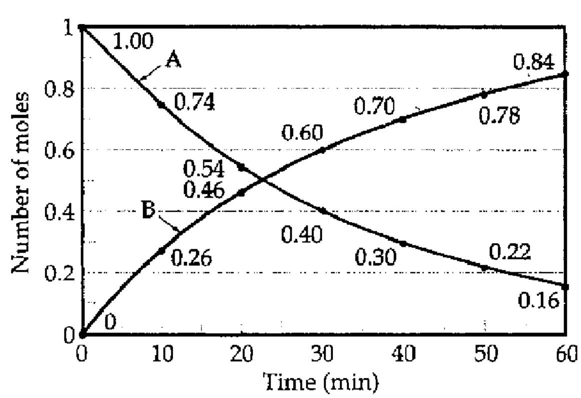
$$\text{Average rate} = \frac{\Delta(\text{moles of B})}{\Delta t}$$

$$= \frac{(\text{moles of B at } t = 10) - (\text{moles of B at } t = 0)}{10 \text{ min} - 0 \text{ min}}$$

$$= \frac{0.26 \text{ mol} - 0 \text{ mol}}{10 \text{ min} - 0 \text{ min}} = 0.026 \text{ mol/min}$$

We can similarly calculate the average reaction rate for each successive 10-min period, as shown in Table 14.1 ▶. Notice that the average rate steadily decreases as the reaction proceeds.

The rate expression in Equation 14.1 focuses on the number of moles of B that are produced during the reaction; it is the *rate of appearance of B*. We could have



◀ **Figure 14.4** Plot of the numbers of moles of A and B as a function of reaction time for the hypothetical reaction A ⟶ B discussed in the text. At $t = 0$ (time zero), there are 1.00 mol A and 0 mol B. The number of moles of A decreases and the number of moles of B increases as the reaction proceeds.

TABLE 14.1 Rate Data for the Hypothetical Reaction A ⟶ B

Time, t (min)	Moles of A	Moles of B	Average Rate (mol/min) per 10-min-interval
0	1.00	0	
			0.026
10	0.74	0.26	
			0.020
20	0.54	0.46	
			0.014
30	0.40	0.60	
			0.010
40	0.30	0.70	
			0.008
50	0.22	0.78	
			0.006
60	0.16	0.84	

expressed the rate of the reaction equally well in terms of the change in the num-ber of moles of A. The stoichiometry of this reaction tells us that one molecule of A disappears for each molecule of B that appears. Thus, for any time interval the change in the number of moles of A, Δ(moles of A), is a negative number that is equal in magnitude but opposite in sign to Δ(moles of B):

$$\Delta(\text{moles of A}) = (\text{moles of A at final time}) - (\text{moles of A at initial time}) = -\Delta(\text{moles of B}) \quad [14.3]$$

We can combine Equations 14.1 and 14.3 to write the average rate in terms of the change in the number of moles of A:

$$\text{Average rate} = -\frac{\text{change in the number of moles of A}}{\text{change in time}} = -\frac{\Delta(\text{moles of A})}{\Delta t} \quad [14.4]$$

This rate is the *rate of disappearance of A*. Notice the negative sign in Equation 14.4; this is present because A is a reactant that is consumed during the reaction.

Because of the 1:1 stoichiometry of the reaction, the rate of disappearance of A equals the rate of appearance of B. Later in this section we will generalize the stoichiometric relationship between rates of disappearance of reactants and rates of appearance of products.

Rates in Terms of Concentrations

In our discussion of the hypothetical reaction A ⟶ B we monitored the progress of the reaction by counting the number of moles of both A and B. Because the vol-ume of the container is fixed, plots of the *concentrations* of A and B, in units of moles per volume, would parallel those that we saw in Figure 14.4. In fact, for most chemical reactions we will determine the reaction rate by following changes in concentration. The units of reaction rates are therefore usually chosen to be molarity per second (M/s). We will now use these units to examine reaction rates more thoroughly.

As an example, let's consider the reaction that occurs when butyl chloride, C_4H_9Cl, is placed in water. The products formed are butyl alcohol, C_4H_9OH, and hydrochloric acid:

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq) \quad [14.5]$$

Suppose that we prepare a 0.1000 M solution of C_4H_9Cl in water and then mea-sure the concentration of C_4H_9Cl at various times after time zero (Table 14.2)

TABLE 14.2 Rate Data for Reaction of C_4H_9Cl with Water

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

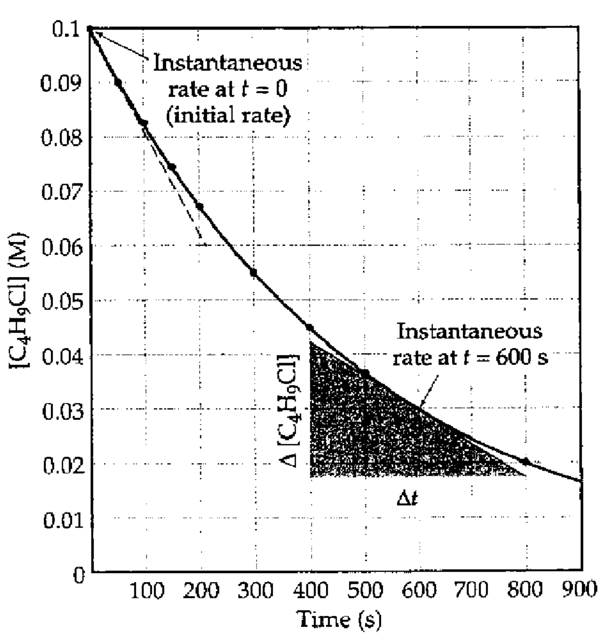
We can use these data to calculate the average rate of disappearance of C_4H_9Cl in units of M/s:

$$\text{Average rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t}$$

$$= -\left(\frac{[C_4H_9Cl]_{\text{final time}} - [C_4H_9Cl]_{\text{initial time}}}{(\text{final time}) - (\text{initial time})}\right) \quad [14.6]$$

Brackets around a chemical substance, such as those around C_4H_9Cl in Equation 14.6, indicate the concentration of the substance, often expressed as molarity. As before, the minus sign in Equation 14.6 indicates that this is a rate of disappearance of a reactant. The calculated average rate for each time interval is shown in the third column of Table 14.2.

The data for $[C_4H_9Cl]$ versus time from Table 14.2 are plotted graphically in Figure 14.5 ▼. Using this curve, we can determine the **instantaneous rate** of the reaction at any point. This is the rate *at a particular time* as opposed to the average rate over an interval of time. The instantaneous rate is obtained from the straight-



◀ **Figure 14.5** Concentration of butyl chloride, C_4H_9Cl, as a function of time. The dots represent the experimental data from the first two columns of Table 14.2, and the red curve is drawn to smoothly connect the data points. Lines are drawn that are tangent to the curve at $t = 0$ and $t = 600$ s. The slope of each of these tangents is defined as the vertical change divided by the horizontal change, that is, $\Delta[C_4H_9Cl]/\Delta t$. The reaction rate at any time is related to the slope of the tangent to the curve at that time. Because C_4H_9Cl is disappearing, the rate is equal to the negative of the slope.

line tangent that touches the curve at the point of interest. We have drawn two such tangents in Figure 14.5, one at $t = 0$ and the other at $t = 600$ s. The slopes of these tangents give the instantaneous rates at these times.* For example, to determine the instantaneous rate at 600 s, we draw the tangent to the curve at this time, then construct horizontal and vertical lines to form the right triangle shown. The slope is the ratio of the height of the vertical side to the horizontal side:

$$\text{Instantaneous rate} = \frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.017 - 0.042)\,M}{(800 - 400)\text{ s}}$$
$$= 6.2 \times 10^{-5}\,M/\text{s}$$

In what follows, the term "rate," means "instantaneous rate," unless indicated otherwise.

SAMPLE EXERCISE 14.1

(a) Using the data in Table 14.2, calculate the average rate of disappearance of C_4H_9Cl over the time interval from 50.0 to 150.0 s. **(b)** Using Figure 14.5, estimate the instantaneous rate of disappearance of C_4H_9Cl at $t = 0$ (the initial rate).

Solution (a) Using data from Table 14.2, we have

$$\text{Average rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t}$$
$$= -\frac{(0.0741 - 0.0905)\,M}{(150.0 - 50.0)\text{ s}} = 1.64 \times 10^{-4}\,M/\text{s}$$

(b) The initial rate is given by the slope of the dashed line in Figure 14.5. The slope of a straight line is given by the change in the vertical axis divided by the corresponding change in the horizontal axis. The straight line falls from $[C_4H_9Cl] = 0.100\,M$ to $0.060\,M$ in the time change from 0 to 200 s. Thus, the initial instantaneous rate is

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.060 - 0.100)\,M}{(200 - 0)\text{ s}} = 2.0 \times 10^{-4}\,M/\text{s}$$

PRACTICE EXERCISE

Using Figure 14.5, estimate the instantaneous rate of disappearance of C_4H_9Cl at $t = 300$ s. *Answer:* $1.1 \times 10^{-4}\,M/\text{s}$

Reaction Rates and Stoichiometry

During our earlier discussion of the hypothetical reaction $A \longrightarrow B$, we saw that the stoichiometry requires that the rate of disappearance of A be equal to the rate of appearance of B. Likewise, the stoichiometry of the reaction in Equation 14.5 tells us that one mole of C_4H_9OH is produced for each mole of C_4H_9Cl consumed. Therefore, the rate of appearance of C_4H_9OH equals the rate of disappearance of C_4H_9Cl:

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

What happens when the stoichiometric relationships are not one-to-one? For example, in the reaction

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

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

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

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

In general, for the reaction

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

the rate is given by

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\text{D}]}{\Delta t} \qquad [14.7]$$

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

SAMPLE EXERCISE 14.2

(a) How is the rate of disappearance of ozone related to the rate of appearance of oxygen in the following equation: $2O_3(g) \longrightarrow 3O_2(g)$? **(b)** If the rate of appearance of O_2, $\Delta[O_2]/\Delta t$, is $6.0 \times 10^{-5}\ M/s$ at a particular instant, what is the value of the rate of disappearance of O_3, $-\Delta[O_3]/\Delta t$ at this same time?

Solution **(a)** Using the coefficients in the balanced equation, we have

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

(b) Using the relationship from part (a), we have

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

PRACTICE EXERCISE

The decomposition of N_2O_5 proceeds according to the equation

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

If the rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is $4.2 \times 10^{-7}\ M/s$, what is the rate of appearance of **(a)** NO_2; **(b)** O_2? *Answers:* **(a)** $8.4 \times 10^{-7}\ M/s$; **(b)** $2.1 \times 10^{-7}\ M/s$

14.2 The Dependence of Rate on Concentration

The decreasing rate of reaction with passing time that is evident in Figures 14.4 and 14.5 is quite typical of reactions. Reaction rates diminish as the concentrations of reactants diminish. Conversely, rates generally increase when reactant concentrations are increased.

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*Equation 14.7 does not hold true if substances other than C and D are formed in significant amounts during the course of the reaction. For example, sometimes intermediate substances build in concentration before forming the final products. In that case the relationship between the rate of disappearance of reactants and the rate of appearance of products will not be given by Equation 14.7. All reactions whose rates we consider in this chapter obey Equation 14.7.

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

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$$

We might study the rate of this reaction by measuring the concentration of NH_4^+ or NO_2^- as a function of time or by measuring the volume of N_2 collected. Because the stoichiometric coefficients on NH_4^+, NO_2^-, and N_2 are all the same, all of these rates will be equal.

Once we determine the initial reaction rate (the instantaneous rate at $t = 0$) for various starting concentrations of NH_4^+ and NO_2^-, we can tabulate the data as shown in Table 14.3 ▼. These data indicate that changing either $[NH_4^+]$ or $[NO_2^-]$ changes the reaction rate. Notice that if we double $[NH_4^+]$ while holding $[NO_2^-]$ constant, the rate doubles (compare experiments 1 and 2). If $[NH_4^+]$ is increased by a factor of 4 (compare experiments 1 and 3), the rate changes by a factor of 4, and so forth. These results indicate that the rate is proportional to $[NH_4^+]$ raised to the first power. When $[NO_2^-]$ is similarly varied while $[NH_4^+]$ is held constant, the rate is affected in the same manner. We conclude that the rate is also directly proportional to the concentration of NO_2^-. We can express the overall concentration dependence as follows:

$$\text{Rate} = k[NH_4^+][NO_2^-]$$

Such an expression, which shows how the rate depends on the concentrations of reactants, is called a **rate law**. The constant k in the rate law is called the **rate constant**. The magnitude of k provides us with extremely important information about reactions, as we will see later in this chapter.

If we know the rate law for a reaction and its rate for a set of reactant concentrations, we can calculate the value of the rate constant, k. For example, using the data in Table 14.3 and the results from experiment 1, we can substitute into Equation 14.8:

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

Solving for k gives

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

You may wish to satisfy yourself that this same value of k is obtained using any of the other experimental results given in Table 14.3.

TABLE 14.3 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

Once we have both the rate law and the value of the rate constant for a reaction, we can calculate the rate of reaction for any set of concentrations. For example, using Equation 14.8, and $k = 2.7 \times 10^{-4}\ M^{-1}s^{-1}$, we can calculate the rate for $[NH_4^+] = 0.100\ M$ and $[NO_2^-] = 0.100\ M$:

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

Note that if the concentration of either NH_4^+ or NO_2^- were doubled, the rate of production of N_2 and H_2O likewise would double.

Reaction Order

The rate laws for most reactions have the general form

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \ldots \qquad [14.9]$$

The exponents m and n in Equation 14.9 are called **reaction orders**, and their sum is the **overall reaction order**. For example, the rate law for the reaction of NH_4^+ with NO_2^- (Equation 14.8) contains the concentration of NH_4^+ raised to the first power. Thus, the reaction order in NH_4^+ is 1; the reaction is *first order* in NH_4^+. It is also first order in NO_2^-. The overall reaction order is 1 + 1 = 2; we say the reaction is *second order overall*.

The following are some further examples of rate laws:

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g) \quad \text{Rate} = k[N_2O_5] \qquad [14.10]$$

$$CHCl_3(g) + Cl_2(g) \longrightarrow CCl_4(g) + HCl(g) \quad \text{Rate} = k[CHCl_3][Cl_2]^{1/2} \qquad [14.11]$$

$$H_2(g) + I_2(g) \longrightarrow 2HI(g) \quad \text{Rate} = k[H_2][I_2] \qquad [14.12]$$

Rates of Reaction simulation

Notice that the reaction orders do not necessarily correspond to the coefficients in the balanced chemical equation. *The values of these exponents are determined experimentally.* In most rate laws, reaction orders are 0, 1, or 2. However, we also occasionally encounter rate laws in which the reaction order is fractional (such as Equation 14.11) or even negative.

Units of Rate Constants

The units of the rate constant depend on the overall reaction order of the rate law. For example, in a reaction that is second order overall, the units of the rate constant must satisfy

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

Hence, in our usual units of concentration and time,

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

SAMPLE EXERCISE 14.3

(a) What are the overall reaction orders for the reactions described in Equations 14.10 and 14.11? **(b)** What are the usual units of the rate constant for the rate law for Equation 14.10?

Solution **(a)** The overall reaction order is the sum of the powers to which all the concentrations of reactants are raised in the rate law. The reaction in Equation 14.10 is first order in N_2O_5 and first order overall. The reaction in Equation 14.11 is first order in $CHCl_3$ and one-half order in Cl_2. The overall reaction order is three halves.

(b) For the rate law for Equation 14.10 we have

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

So

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

Notice that the units of the rate constant for the first-order reaction are different fr those for the second-order reaction discussed above.

PRACTICE EXERCISE

(a) What is the reaction order of the reactant H_2 in Equation 14.12? **(b)** What a units of the rate constant for Equation 14.11? *Answers:* **(a)** 1; **(b)** $M^{-1/2}\text{s}^{-1}$

Using Initial Rates to Determine Rate Laws

The rate law for any chemical reaction must be determined experimentall cannot be predicted by merely looking at the chemical equation. We often termine the rate law for a reaction by the same method we applied to the da Table 14.3: We observe the effect of changing the initial concentrations of th actants on the initial rate of the reaction. If a reaction is zero order in a par lar reactant, changing its concentration will have no effect on rate (as lon some of the reactant is present). If the reaction is first order in a reactant, cha in the concentration of that substance will produce proportional changes i rate. Thus, doubling the concentration will double the rate, and so forth. Wh the rate law is second order in a particular reactant, doubling its concentr increases the rate by a factor of $2^2 = 4$, tripling its concentration caus rate to increase by a factor of $3^2 = 9$, and so forth.

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

SAMPLE EXERCISE 14.4

The initial rate of a reaction $A + B \longrightarrow C$ was measured for several different concentrations of A and B, with the results given here:

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

Using these data, determine **(a)** the rate law for the reaction; **(b)** the magnitu rate constant; **(c)** the rate of the reaction when [A] = 0.050 M and [B] = 0.10

Solution **(a)** We may assume that the rate law has the following form $k[A]^m[B]^n$. Our task is to deduce the values of m and n. Notice that when [A] is stant and [B] is doubled, the rate remains the same (compare experiments 1 a conclude that the concentration of B has no effect on the reaction rate. The therefore zero order in B. Experiments 1 and 3 indicate that doubling [A] incr from

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rate fou ...old. This result indicates that rate is proportional to $[A]^2$; the reaction is second ord... in A. The rate law is

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

This sa... conclusion could be reached in a more formal way by taking the ratio of the rates fr... two experiments:

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

Using th... rate law, then, we have

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

But 2^n eq...s 1 only if $n = 0$. We can deduce the value of m in a similar fashion:

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

Using th... ate law gives

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

The fact t... $2^m = 4$ indicates that $m = 2$.

(b) U...g the rate law and the data from experiment 1, we have

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

(c) U...; the rate law from part (a) and the rate constant from part (b), we have

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

Because [... not part of the rate law, it is immaterial to the rate, provided that there is at least ...e B present to react with A.

PRACTIC... ...RCISE

A particul... ...action was found to depend on the concentration of the hydrogen ion, $[H^+]$. The ...al rates varied as a function of $[H^+]$ as follows:

...$[H^+]$ (M)	0.0500	0.100	0.200
...itial rate (M/s)	6.4×10^{-7}	3.2×10^{-7}	1.6×10^{-7}

(a) What i... order of the reaction in $[H^+]$? **(b)** Predict the initial reaction rate when $[H^+] = 0.4$... *Answers:* **(a)** −1 (the rate is *inversely* proportional to $[H^+]$); **(b)** 0.80 $\times 10^{-7}$ M/...

14.3 T... ...hange of Concentration with Time

A rate law ... how the rate of a reaction changes at a particular temperature as we ... reactant concentrations. Rate laws can be converted into equations that ... that the concentrations of the reactants or products are at any time durin... ...urse of a reaction. The mathematics required involves calculus. We do ... you to be able to perform the calculus operations; however, you sh... ...ble to use the resulting equations. We will apply this conversion ... simplest rate laws: those that are first-order overall and those that ... ...-order overall.

First-Order Reactions

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

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

Using calculus, this equation can be transformed into an equation that relates the concentration of A at the start of the reaction, $[\text{A}]_0$, to its concentration at any other time t, $[\text{A}]_t$:

First Order Process movie

$$\ln[\text{A}]_t - \ln[\text{A}]_0 = -kt \quad \text{or} \quad \ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt \qquad [14.13]$$

The function "ln" is the natural logarithm (Appendix A.2).*

Equation 14.13 can be rearranged:

$$\ln[\text{A}]_t = -kt + \ln[\text{A}]_0 \qquad [14.14]$$

This equation has the form of the general equation for a straight line, $y = mx + b$, in which m is the slope and b is the y-intercept of the line (see Appendix A.4):

$$\begin{array}{ccccc} \ln[\text{A}]_t & = & -k \cdot t & + & \ln[\text{A}]_0 \\ \updownarrow & & \updownarrow\ \updownarrow & & \updownarrow \\ y & = & m \cdot x & + & b \end{array}$$

Thus, for a first-order reaction a graph of $\ln[\text{A}]_t$ versus time gives a straight line with a slope of $-k$ and a y-intercept of $\ln[\text{A}]_0$.

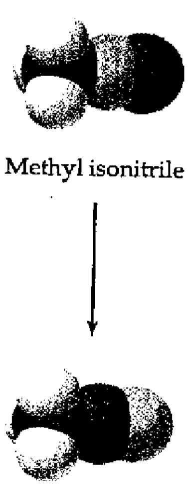
As an example of a first-order reaction, we can consider the conversion of methyl isonitrile, CH_3NC, to acetonitrile, CH_3CN (Figure 14.6 ◀). Because experiments show that the reaction is first order, we can write the rate law:

$$\text{Rate} = -\frac{\Delta[CH_3NC]}{\Delta t} = k[CH_3NC]$$

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

For a first-order reaction, Equation 14.13 or 14.14 can be used to determine (1) the concentration of a reactant remaining at any time after the reaction has started, (2) the time required for a given fraction of a sample to react, or (3) the time required for a reactant concentration to reach a certain level.

▼ **Figure 14.6** The transformation of methyl isonitrile, CH_3NC, to acetonitrile, CH_3CN, is a first-order process. Methylisonitrile and acetonitrile are isomers, molecules that have the same atoms arranged differently. This reaction is called an isomerization reaction.



* In terms of base-10 or common logarithms, Equation 14.13 can be written as

$$\log[\text{A}]_t - \log[\text{A}]_0 = -\frac{kt}{2.303} \quad \text{or} \quad \log\frac{[\text{A}]_t}{[\text{A}]_0} = -\frac{kt}{2.303}$$

The factor 2.303 arises from the conversion of natural logarithms to base-10 logarithms.

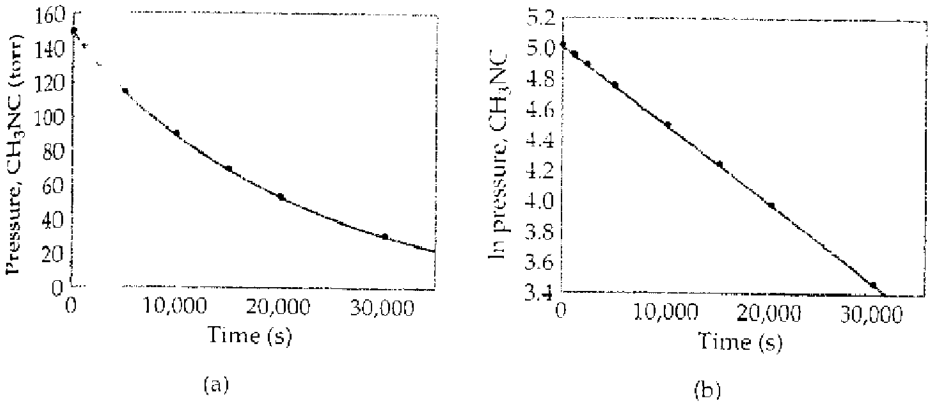


Figure 14.7
(a) Variation in the partial pressure of methyl isonitrile, CH_3NC, with time at 198.9°C during the reaction $CH_3NC \longrightarrow CH_3CN$. (b) A plot of the natural logarithm of the CH_3NC pressure as a function of time.

SAMPL ERCISE 14.5

The first rder rate constant for the decomposition of a certain insecticide in water at 12°C is 1 5 yr^{-1}. A quantity of this insecticide is washed into a lake on June 1, leading to a conc tration of 5.0×10^{-7} g/cm^3 of water. Assume that the effective temperature of the lak is 12°C. **(a)** What is the concentration of the insecticide on June 1 of the following y ar? **(b)** How long will it take for the concentration of the insecticide to drop to 3.0 × ^{7} g/cm^3?

Solutio **(a)** Substituting $k = 1.45\ yr^{-1}$, $t = 1.00$ yr, and $[\text{insecticide}]_0 = 5.0 \times 10^{-7}$ g/cm^3 in Equation 14.14 gives

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

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

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

To obtai nsecticide]$_{t=1\,yr}$ we use the inverse natural logarithm, or e^x, function on the calculat

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

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

(b) gain substituting into Equation 14.14, with $[\text{insecticide}]_t = 3.0 \times 10^{-7}$ g/cm^3, gives

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

Solving r t gives

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

PRACTI EXERCISE

The dec position of dimethyl ether, $(CH_3)_2O$, at 510 °C is a first-order process with a rate co tant of $6.8 \times 10^{-4}\ s^{-1}$.

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

If the in l pressure of $(CH_3)_2O$ is 135 torr, what is its partial pressure after 1420 s?
Answer: 1 torr

Half-lif

The **hal** e of a reaction, $t_{1/2}$, is the time required for the concentration of a react to drop to one half of its initial value, $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$. We can determine the half-life of a first-order reaction by substituting $[A]_{t_{1/2}}$ into Equation 14.13:

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

$$\ln \tfrac{1}{2} = -kt_{1/2}$$

$$t_{1/2} = -\frac{\ln \frac{1}{2}}{k} = \frac{0.693}{k} \qquad [14.15]$$

Rates of Reaction simulation

Notice that $t_{1/2}$ for a first-order rate law is independent of the initial concentration of reactant. Thus, the half-life is the same at any time during the reaction. If, for example, the concentration of the reactant is 0.120 M at some moment in the reaction, it will be $\frac{1}{2}(0.120\ M) = 0.060\ M$ one half-life later. After one more half-life passes, the concentration will drop to 0.030 M, and so on. The concept of half-life is widely used in describing radioactive decay. This application is discussed in detail in Section 21.4.

The data for the first-order rearrangement of methyl isonitrile at 198.9°C are graphed in Figure 14.8 ▼. The first half-life is shown at 13,300 s. At a time 13,300 s later, the isonitrile concentration has decreased to one half of one half, or one-fourth the original concentration. *In a first-order reaction the concentration of the reactant decreases by $\frac{1}{2}$ in each of a series of regularly spaced time intervals, namely, $t_{1/2}$.*

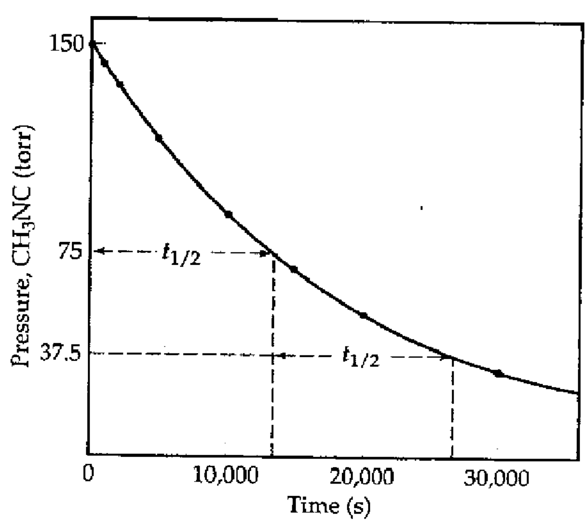
SAMPLE EXERCISE 14.6

From Figure 14.5 estimate the half-life of the reaction of C_4H_9Cl with water.

Solution From the figure we see that the initial value of $[C_4H_9Cl]$ is 0.100 M. The half-life for this first-order reaction is the time required for $[C_4H_9Cl]$ to decrease to 0.050 M. This point occurs at approximately 340 s. At the end of the second half-life, which should occur at 680 s, the concentration should have decreased by yet another factor of 2, to 0.025 M. Inspection of the graph shows that this is indeed the case.

PRACTICE EXERCISE

Using Equation 14.15, calculate $t_{1/2}$ for the reaction described in Practice Exercise 14.
Answer: 1.02×10^3 s



▶ **Figure 14.8** Pressure of methyl isonitrile as a function of time. Two successive half-lives of the isomerization reaction, Figure 14.6, are shown.

ond-Order Reactions

cond-order reaction is one whose rate depends on the reactant concentration d to the second power or on the concentrations of two different reactants, raised to the first power. For simplicity let's consider reactions of the sort → products, or A + B ⟶ products. If such a reaction is second order in just reactant, A, the rate law is given by

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

ing on calculus, this rate law can be used to derive the following equation:

$$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0} \qquad [14.16]$$

equation, like Equation 14.14, has the form of a straight line ($y = mx + b$). reaction is second order, a plot of $1/[\text{A}]_t$ versus t will yield a straight line a slope equal to k and a y-intercept equal to $1/[\text{A}]_0$. One way to distinguish een first- and second-order rate laws is to graph both $\ln[\text{A}]_t$ and $1/[\text{A}]_t$ st t. If the $\ln[\text{A}]_t$ plot is linear, the reaction is first order; if the $1/[\text{A}]_t$ plot is ; the reaction is second order.

sing Equation 14.16, we can show that the half-life of a second-order on is

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

e that, unlike the half-life of first-order reactions, the half-life of a second- reaction is dependent on the initial concentration of reactant.

LE EXERCISE 14.7

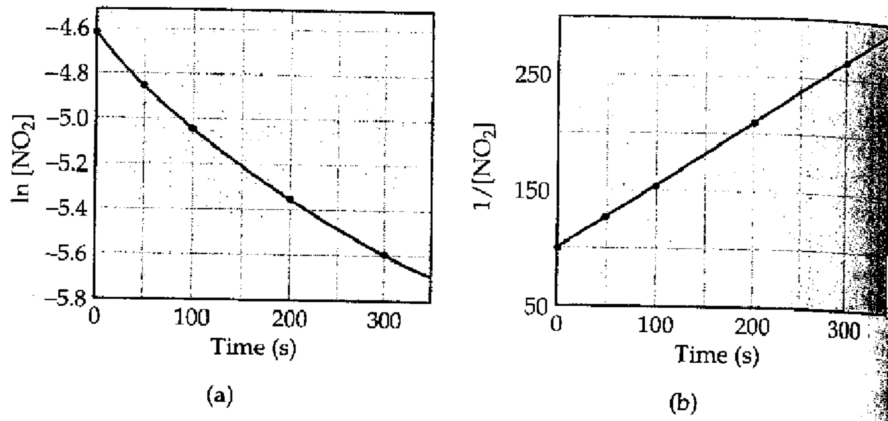
ollowing data were obtained for the gas-phase decomposition of nitrogen le at 300°C, $NO_2(g) \longrightarrow NO(g) + \frac{1}{2}O_2(g)$:

Time (s)	$[NO_2]$ (M)
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

eaction first or second order in NO_2?

on To test whether the reaction is first or second order, we can construct plots $O_2]$ and $1/[NO_2]$ against time. In doing so, we will find it useful to prepare the ng table from the data given:

Time (s)	$[NO_2]$ (M)	$\ln[NO_2]$	$1/[NO_2]$
0.0	0.01000	−4.610	100
50.0	0.00787	−4.845	127
100.0	0.00649	−5.038	154
200.0	0.00481	−5.337	208
300.0	0.00380	−5.573	263



▶ **Figure 14.9** Plots of the kinetic data for the reaction $NO_2(g) \longrightarrow NO(g) + \frac{1}{2}O_2(g)$ at 300°C. A smooth curve connecting the data points in a plot of $\ln[NO_2]$ versus time (a) is not linear; consequently, we can conclude that the reaction is not first order in NO_2. The plot of $1/[NO_2]$ versus time (b) is linear; the reaction is second order in NO_2.

As Figure 14.9 ▲ shows, only the plot of $1/[NO_2]$ versus time is linear. Thus the tion obeys a second-order rate law: Rate = $k[NO_2]^2$. From the slope of this str line graph we have that $k = 0.543\ M^{-1}s^{-1}$ for the disappearance of NO_2.

PRACTICE EXERCISE

What is the half-life from time $t = 0$ for the decomposition of NO_2, as represen the tabular data above? *Answer:* 184 s

Chemistry at Work Methyl Bromide in the Atmosphere

Several small molecules containing carbon-chlorine or carbon-bromine bonds, when present in the stratosphere, are capable of reacting with ozone, O_3, and thus contributing to the destruction of the ozone layer. (The nature of the stratospheric ozone layer and its importance for Earth's ecosystems is discussed in Section 18.3). These small molecules are largely *anthropogenic;* that is, their presence in the atmosphere is due mainly to human activities.

Whether a small halogen-containing molecule contributes significantly to destruction of the ozone layer depends in part on its concentrations near Earth's surface, and on its average lifetime in the atmosphere. It takes quite a long time for molecules formed at Earth's surface to diffuse through the lower atmosphere (called the troposphere) and move into the stratosphere, where the ozone layer is located (Figure 14.10 ▶). Decomposition in the lower atmosphere competes with diffusion into the stratosphere.

The much-discussed chlorofluorocarbons, or CFCs, contribute to the destruction of the ozone layer because they have long lifetimes in the troposphere and thus persist long enough so that a substantial fraction of the molecules formed at the surface find their way to the stratosphere. Another simple molecule that has the potential to contribute to destruction of the stratospheric ozone layer is methyl bromide, CH_3Br. This substance has a wide range of uses, including antifungal treatment of plant seeds, and is thus produced in large quantity, abo million pounds per year. In the stratosphere the bond is broken through absorption of short wave radiation. (Section 18.2) The Br atoms cata composition of O_3.

Methyl bromide is removed from the lower phere by a variety of mechanisms, including a slo tion with ocean water:

$$CH_3Br(g) + H_2O(l) \longrightarrow CH_3OH(l) + HBr(aq)$$

To determine the potential importance of CH_3Br struction of the ozone layer, it is important to kn rapidly reaction 14.18 and all other removal me together remove CH_3Br from the atmosphere befo diffuse into the stratosphere. Professor F. Sherwood land and colleagues have recently carried out res estimate the average lifetime of CH_3Br in Earth's phere.* Such an estimate is difficult to make. It ca done in laboratory-based experiments because the tions that exist all over the planet are too compl

* Professor Rowland, together with R. Molina and P. J. C received the 1995 Nobel Prize in chemistry for atmosph ies that led to understanding how the ozone layer fo decomposes. (Section 18.3)

A reaction may also be second order by having a first-order dependence of the rate on each of two reagents; that is, rate = $k[A][B]$. It is possible to derive an expression for the variation in concentrations of A and B with time. However, we will not consider this and other more complicated rate laws in this text.

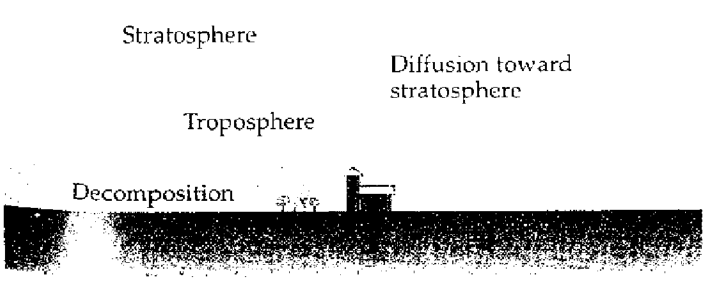
14.4 Temperature and Rate

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

How is this experimental observation of faster reaction at higher temperatures reflected in the rate expression? The faster rate at higher temperature is due to an increase in the rate constant with increasing temperature. For example,

simulated in the laboratory. Instead, these scientists gathered nearly 4000 samples of the atmosphere during aircraft flights all over the Pacific Ocean and analyzed them for the presence of several trace organic substances, including methyl bromide. From a detailed analysis of the patterns of concentrations, it was possible for them to estimate that the *atmospheric residence time* for CH_3Br is 0.8 ± 0.1 year.

The atmospheric residence time is equivalent to the half-life for CH_3Br in the lower atmosphere, assuming that it decomposes by a first-order process. That is, a collection of CH_3Br molecules present at any given time will, on average, be 50 percent decomposed after 0.8 years, 75 percent decomposed after 1.6 years, and so on. These decomposition pathways compete with its diffusion upward through the troposphere and into the stratosphere. A residence time of 0.8 years, while comparatively short, is still sufficiently long so that CH_3Br makes a significant contribution to the destruction of the ozone layer. In 1997 an international agreement was reached to phase out use of methyl bromide in the developed countries worldwide by 2005. A U.S. law banning use of methyl bromide after 2001 was modified by Congress in 1998 to permit use of the substance until 2005. There are presently no good alternatives to methyl bromide as a pesticide against the Asian long-horned beetle, a voracious non-native pest that has recently invaded the United States.



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