# 12 Chemical Kinetics

Contents

The kinetic energy of these world championship runners is evident in the 800-meter race at Saint-Denis, France.

*T*he applications of chemistry focus largely on chemical reactions, and the commercial use of a reaction requires knowledge of several of its characteristics, including its stoichiometry, energetics, and rate. A reaction is defined by its reactants and products, whose identity must be learned by experiment. Once the reactants and products are known, the equation for the reaction can be written and balanced, and stoichiometric calculations can be carried out. Another very important characteristic of a reaction is its spontaneity. Spontaneity refers to the *inherent tendency* for the process to occur; however, it implies nothing about speed. *Spontaneous does not mean fast.* There are many spontaneous reactions that are so slow that no apparent reaction occurs over a period of weeks or years at normal temperatures. For example, there is a strong inherent tendency for gaseous hydrogen and oxygen to combine, that is,

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$
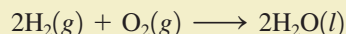
but in fact the two gases can coexist indefinitely at 25°C. Similarly, the gaseous reactions

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$
$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$
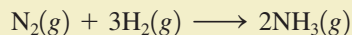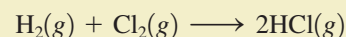
are both highly likely to occur from a thermodynamic standpoint, but we observe no reactions under normal conditions. In addition, the process of changing diamond to graphite is spontaneous but is so slow that it is not detectable.

To be useful, reactions must occur at a reasonable rate. To produce the 20 million tons of ammonia needed each year for fertilizer, we cannot simply mix nitrogen and hydrogen gases at 25°C and wait for them to react. It is not enough to understand the stoichiometry and thermodynamics of a reaction; we also must understand the factors that govern the rate of the reaction. The area of chemistry that concerns reaction rates is called **chemical kinetics.**

One of the main goals of chemical kinetics is to understand the steps by which a reaction takes place. This series of steps is called the *reaction mechanism.* Understanding the mechanism allows us to find ways to facilitate the reaction. For example, the Haber process for the production of ammonia requires high temperatures to achieve commercially feasible reaction rates. However, even higher temperatures (and more cost) would be required without the use of iron oxide, which speeds up the reaction.

In this chapter we will consider the main ideas of chemical kinetics. We will explore rate laws, reaction mechanisms, and simple models for chemical reactions.

12.1 Reaction Rates

To introduce the concept of the rate of a reaction, we will consider the decomposition of nitrogen dioxide, a gas that causes air pollution. Nitrogen dioxide decomposes to nitric oxide and oxygen as follows:

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$
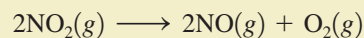
Suppose in a particular experiment we start with a flask of nitrogen dioxide at 300°C and measure the concentrations of nitrogen dioxide, nitric oxide, and oxygen as the nitrogen dioxide decomposes. The results of this experiment are summarized in Table 12.1, and the data are plotted in Fig. 12.1.

The energy required for athletic exertion, the breaching of an Orca whale, and the combustion of fuel in a race car all result from chemical reactions.

Note from these results that the concentration of the reactant (NO_2) decreases with time and the concentrations of the products (NO and O_2) increase with time (see Fig. 12.2). Chemical kinetics deals with the speed at which these changes occur. The speed, or *rate,* of a process is defined as the change in a given quantity over a specific period of time. For chemical reactions, the quantity that changes is the amount or concentration of a reactant or product. So the **reaction rate** of a chemical reaction is defined as the *change in concentration of a reactant or product per unit time:*

$$\text{Rate} = \frac{\text{concentration of A at time } t_2 - \text{concentration of A at time } t_1}{t_2 - t_1}$$

[A] means concentration of A in mol/L.

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

TABLE 12.1 Concentrations of Reactant and Products as a Function of Time for the Reaction $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ (at 300°C)

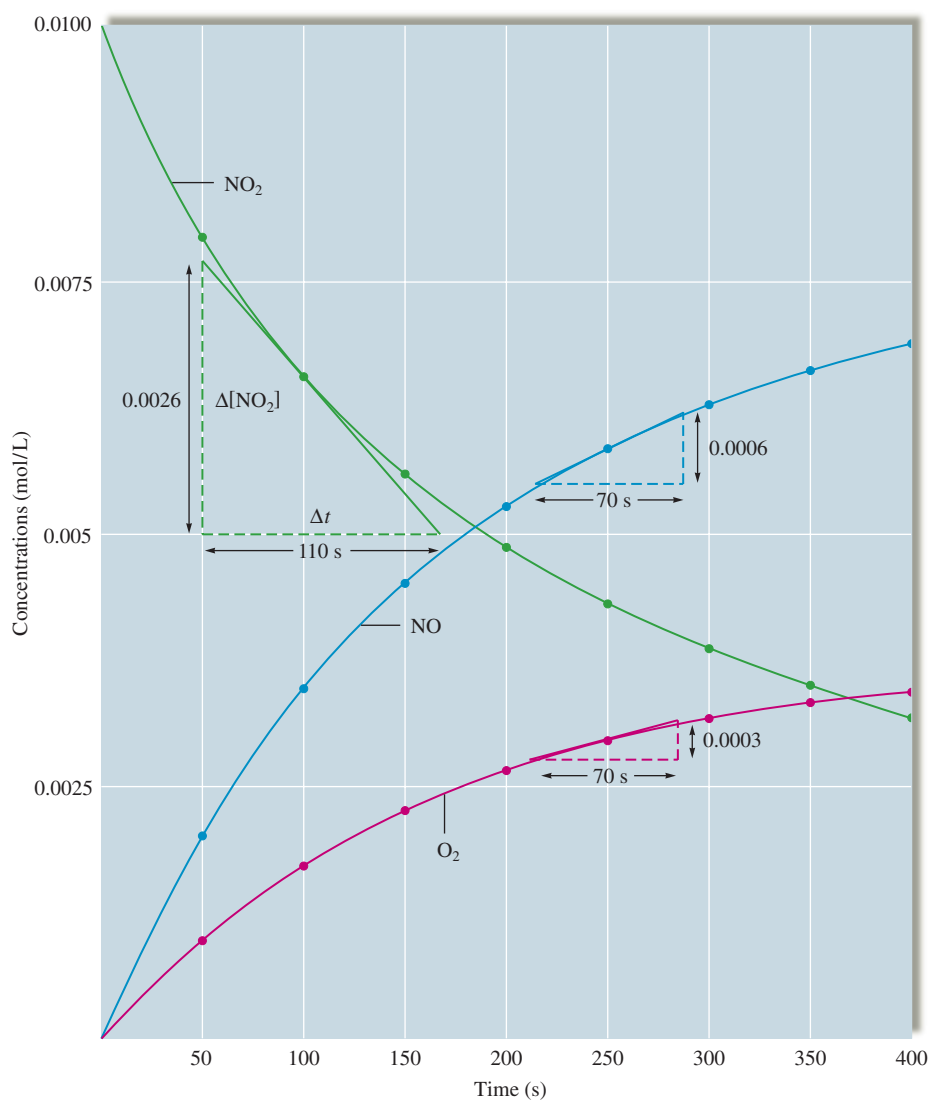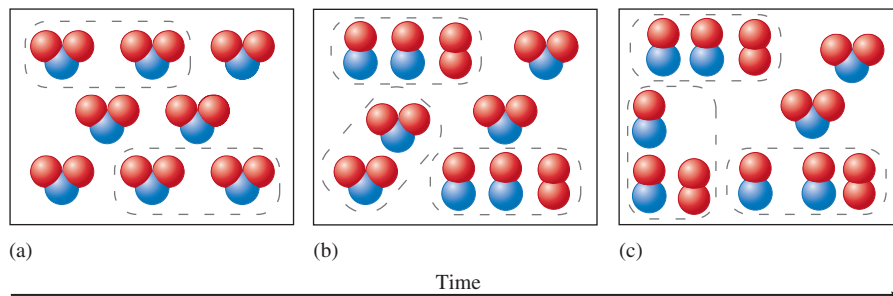| Time (±1 s)	Concentration (mol/L)		
	NO_2	NO	O_2
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

FIGURE 12.1
Starting with a flask of nitrogen dioxide at 300°C, the concentrations of nitrogen dioxide, nitric oxide, and oxygen are plotted versus time.

FIGURE 12.2
Representation of the reaction $2NO_2(g) \rightarrow$ $2NO(g) + O_2(g)$. (a) The reaction at the very beginning ($t = 0$). (b) and (c) As time passes, NO_2 is converted to NO and O_2.

(a)   (b)   (c)

Time

where A is the reactant or product being considered, and the square brackets indicate concentration in mol/L. As usual, the symbol Δ indicates a *change* in a given quantity. Note that a change can be positive (increase) or negative (decrease), thus leading to a positive or negative reaction rate by this definition. However, for convenience, we will always define the rate as a positive quantity, as we will see.

Now let us calculate the average rate at which the concentration of NO_2 changes over the first 50 seconds of the reaction using the data given in Table 12.1.

$$\frac{\text{Change in } [NO_2]}{\text{Time elapsed}} = \frac{\Delta[NO_2]}{\Delta t}$$

$$= \frac{[NO_2]_{t=50} - [NO_2]_{t=0}}{50.\text{ s} - 0\text{ s}}$$

$$= \frac{0.0079\text{ mol/L} - 0.0100\text{ mol/L}}{50.\text{ s}}$$

$$= -4.2 \times 10^{-5}\text{ mol/L} \cdot \text{s}$$

Note that since the concentration of NO_2 decreases with time, $\Delta[NO_2]$ is a negative quantity. Because it is customary to work with *positive* reaction rates, we define the rate of this particular reaction as

$$\text{Rate} = -\frac{\Delta[NO_2]}{\Delta t}$$

Appendix 1.3 reviews slopes of straight lines.

Since the concentrations of reactants always decrease with time, any rate expression involving a reactant will include a negative sign. The average rate of this reaction from 0 to 50 seconds is then

$$\text{Rate} = -\frac{\Delta[NO_2]}{\Delta t}$$

$$= -(-4.2 \times 10^{-5}\text{ mol/L} \cdot \text{s})$$

$$= 4.2 \times 10^{-5}\text{ mol/L} \cdot \text{s}$$

The average rates for this reaction during several other time intervals are given in Table 12.2. *Note that the rate is not constant but decreases with time.* The rates given in Table 12.2 are *average rates* over 50-second time intervals. The value of the rate at a particular time (the **instantaneous rate**) can be obtained by computing the slope of a line tangent to the curve at that point. Figure 12.1 shows a tangent drawn at $t = 100$ seconds. The *slope* of this line gives the rate at $t = 100$ seconds as follows:

$$\text{Slope of the tangent line} = \frac{\text{change in } y}{\text{change in } x}$$

$$= \frac{\Delta[NO_2]}{\Delta t}$$

TABLE 12.2 Average Rate (in mol/L · s) of Decomposition of Nitrogen Dioxide as a Function of Time*

| $\dfrac{\Delta[NO_2]}{\Delta t}$	Time Period (s)
4.2×10^{-5}	$0 \rightarrow 50$
2.8×10^{-5}	$50 \rightarrow 100$
2.0×10^{-5}	$100 \rightarrow 150$
1.4×10^{-5}	$150 \rightarrow 200$
1.0×10^{-5}	$200 \rightarrow 250$

*Note that the *rate* decreases with time.

Los Angeles on a clear day, and on a day when air pollution is significant.

But

$$\text{Rate} = -\frac{\Delta[NO_2]}{\Delta t}$$

Therefore,

$$\text{Rate} = -(\text{slope of the tangent line})$$
$$= -\left(\frac{-0.0026 \text{ mol/L}}{110 \text{ s}}\right)$$
$$= 2.4 \times 10^{-5} \text{ mol/L} \cdot \text{s}$$

So far we have discussed the rate of this reaction only in terms of the reactant. The rate also can be defined in terms of the products. However, in doing so we must take into account the coefficients in the balanced equation for the reaction, because the stoichiometry determines the relative rates of consumption of reactants and generation of products. For example, in the reaction we are considering,

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$
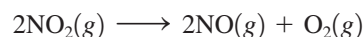
both the reactant NO_2 and the product NO have a coefficient of 2, so NO is produced at the same rate as NO_2 is consumed. We can verify this from Fig. 12.1. Note that the curve for NO is the same shape as the curve for NO_2, except that it is inverted, or flipped over. This means that, at any point in time, the slope of the tangent to the curve for NO will be the negative of the slope to the curve for NO_2. (Verify this at the point $t = 100$ seconds on both curves.) In the balanced equation, the product O_2 has a coefficient of 1, which means it is produced half as fast as NO, since NO has a coefficient of 2. That is, the rate of NO production is twice the rate of O_2 production.

We also can verify this fact from Fig. 12.1. For example, at $t = 250$ seconds,

$$\text{Slope of the tangent to the NO curve} = \frac{6.0 \times 10^{-4} \text{ mol/L}}{70. \text{ s}}$$
$$= 8.6 \times 10^{-6} \text{ mol/L} \cdot \text{s}$$
$$\text{Slope of the tangent to the } O_2 \text{ curve} = \frac{3.0 \times 10^{-4} \text{ mol/L}}{70. \text{ s}}$$
$$= 4.3 \times 10^{-6} \text{ mol/L} \cdot \text{s}$$

The slope at $t = 250$ seconds on the NO curve is twice the slope of that point on the O_2 curve, showing that the rate of production of NO is twice that of O_2.

The rate information can be summarized as follows:

| Rate of consumption of NO_2 | $=$ | rate of production of NO | $=$ | 2(rate of production of O_2) |

$$-\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[NO]}{\Delta t} = 2\left(\frac{\Delta[O_2]}{\Delta t}\right)$$

We have seen that the rate of a reaction is not constant, but that it changes with time. This is so because the concentrations change with time (Fig. 12.1).

Because the reaction rate changes with time, and because the rate is different (by factors that depend on the coefficients in the balanced equation) depending on which reactant or product is being studied, we must be very specific when we describe a rate for a chemical reaction.
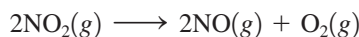
12.2 Rate Laws: An Introduction

Chemical reactions are *reversible.* In our discussion of the decomposition of nitrogen dioxide, we have so far considered only the *forward reaction,* as shown here:

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

However, the *reverse reaction* also can occur. As NO and O_2 accumulate, they can react to re-form NO_2:

$$O_2(g) + 2NO(g) \longrightarrow 2NO_2(g)$$
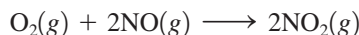
When gaseous NO_2 is placed in an otherwise empty container, initially the dominant reaction is

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

When forward and reverse reaction rates are equal, there will be no changes in the concentrations of reactants or products. This is called *chemical equilibrium* and is discussed fully in Chapter 13.

and the change in the concentration of NO_2 ($\Delta[NO_2]$) depends only on the forward reaction. However, after a period of time, enough products accumulate so that the reverse reaction becomes important. Now $\Delta[NO_2]$ depends on the *difference in the rates of the forward and reverse reactions.* This complication can be avoided if we study the rate of a reaction under conditions where the reverse reaction makes only a negligible contribution. Typically, this means that we must study a reaction at a point soon after the reactants are mixed, before the products have had time to build up to significant levels.

If we choose conditions where the reverse reaction can be neglected, the *reaction rate will depend only on the concentrations of the reactants.* For the decomposition of nitrogen dioxide, we can write

$$\text{Rate} = k[NO_2]^n \tag{12.1}$$

Such an expression, which shows how the rate depends on the concentrations of reactants, is called a **rate law.** The proportionality constant k, called the **rate constant,** and n, called the **order** of the reactant, must both be determined by experiment. The order of a reactant can be an integer (including zero) or a fraction. For the relatively simple reactions we will consider in this book, the orders will often be positive integers.

Note two important points about Equation (12.1):

1. The concentrations of the products do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate.

2. The value of the exponent n must be determined by experiment; it cannot be written from the balanced equation.

Before we go further we must define exactly what we mean by the term *rate* in Equation (12.1). In Section 12.1 we saw that reaction rate means a change in concentration per unit time. However, which reactant or product concentration do we choose in defining the rate? For example, for the decomposition of NO_2 to produce O_2 and NO considered in Section 12.1, we could define the rate in terms of any of these three species. However, since O_2 is produced only half as fast as NO, we must be careful to specify which species we are talking about in a given case. For instance, we might choose to define the reaction rate in terms of the consumption of NO_2:

$$\text{Rate} = -\frac{\Delta[NO_2]}{\Delta t} = k[NO_2]^n$$

On the other hand, we could define the rate in terms of the production of O_2:

$$\text{Rate}' = \frac{\Delta[O_2]}{\Delta t} = k'[NO_2]^n$$

Note that because $2NO_2$ molecules are consumed for every O_2 molecule produced,

$$\text{Rate} = 2 \times \text{rate}'$$

or

$$k[NO_2]^n = 2k'[NO_2]^n$$

and

$$k = 2 \times k'$$

Thus the value of the rate constant depends on how the rate is defined.

In this text we will always be careful to define exactly what is meant by the rate for a given reaction so that there will be no confusion about which specific rate constant is being used.

Types of Rate Laws

Notice that the rate law we have used to this point expresses rate as a function of concentration. For example, for the decomposition of NO_2 we have defined

$$\text{Rate} = -\frac{\Delta[NO_2]}{\Delta t} = k[NO_2]^n$$

The name *differential rate law* comes from a mathematical term. We will regard it simply as a label. The terms *differential rate law* and *rate law* will be used interchangeably in this text.

which tells us (once we have determined the value of *n*) exactly how the rate depends on the concentration of the reactant, NO_2. A rate law that expresses how the *rate depends on concentration* is technically called the **differential rate law,** but it is often simply called the **rate law.** Thus when we use the term *the rate law* in this text, we mean the expression that gives the rate as a function of concentration.

A second kind of rate law, the **integrated rate law,** also will be important in our study of kinetics. The integrated rate law expresses how the *concentrations depend on time.* Although we will not consider the details here, a given differential rate law is always related to a certain type of integrated rate law, and vice versa. That is, if we determine the differential rate law for a given reaction, we automatically know the form of the integrated rate law for the reaction. This means that once we determine experimentally either type of rate law for a reaction, we also know the other one.

Which rate law we choose to determine by experiment often depends on what types of data are easiest to collect. If we can conveniently measure how the rate changes as the concentrations are changed, we can readily determine the differential (rate/concentration) rate law. On the other hand, if it is more convenient to measure the concentration as a function of time, we can determine the form of the integrated (concentration/time) rate law. We will discuss how rate laws are actually determined in the next several sections.

Why are we interested in determining the rate law for a reaction? How does it help us? It helps us because we can work backward from the rate law to infer the steps by

which the reaction occurs. Most chemical reactions do not take place in a single step but result from a series of sequential steps. To understand a chemical reaction, we must learn what these steps are. For example, a chemist who is designing an insecticide may study the reactions involved in the process of insect growth to see what type of molecule might interrupt this series of reactions. Or an industrial chemist may be trying to make a given reaction occur faster. To accomplish this, he or she must know which step is slowest, because it is that step that must be speeded up. Thus a chemist is usually not interested in a rate law for its own sake but because of what it reveals about the steps by which a reaction occurs. We will develop a process for finding the reaction steps in this chapter.

> **Rate Laws: A Summary**
>
> - There are two types of rate laws.
>
>   1. The *differential rate law* (often called simply the *rate law*) shows how the rate of a reaction depends on concentrations.
>
>   2. The *integrated rate law* shows how the concentrations of species in the reaction depend on time.
>
> - Because we typically consider reactions only under conditions where the reverse reaction is unimportant, our rate laws will involve only concentrations of reactants.
>
> - Because the differential and integrated rate laws for a given reaction are related in a well-defined way, the experimental determination of *either* of the rate laws is sufficient.
>
> - Experimental convenience usually dictates which type of rate law is determined experimentally.
>
> - Knowing the rate law for a reaction is important mainly because we can usually infer the individual steps involved in the reaction from the specific form of the rate law.

12.3 Determining the Form of the Rate Law

The first step in understanding how a given chemical reaction occurs is to determine the *form* of the rate law. That is, we need to determine experimentally the power to which each reactant concentration must be raised in the rate law. In this section we will explore ways to obtain the differential rate law for a reaction. First, we will consider the decomposition of dinitrogen pentoxide in carbon tetrachloride solution:

$$2N_2O_5(soln) \longrightarrow 4NO_2(soln) + O_2(g)$$
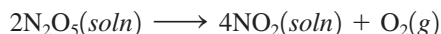
Data for this reaction at 45°C are listed in Table 12.3 and plotted in Fig. 12.3. In this reaction the oxygen gas escapes from the solution and thus does not react with the nitrogen dioxide, so we do not have to be concerned about the effects of the reverse reaction at any time over the life of the reaction. That is, the reverse reaction is negligible at all times over the course of this reaction.

Evaluation of the reaction rates at concentrations of N_2O_5 of 0.90 M and 0.45 M, by taking the slopes of the tangents to the curve at these points (see Fig. 12.3), yields the following data:

TABLE 12.3 Concentration/Time Data for the Reaction $2N_2O_5(soln) \rightarrow 4NO_2(soln) + O_2(g)$ (at 45°C)

$[N_2O_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000

$[N_2O_5]$	Rate (mol/L · s)
0.90 M	5.4×10^{-4}
0.45 M	2.7×10^{-4}

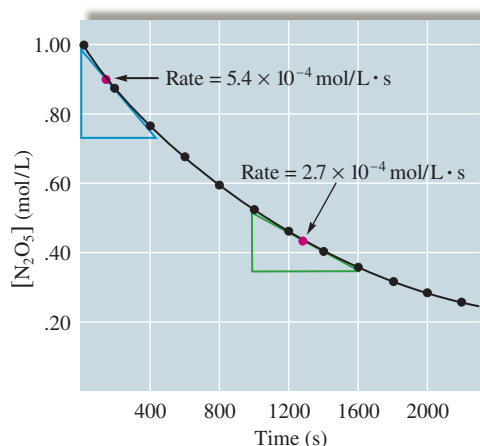**FIGURE 12.3**
A plot of the concentration of N_2O_5 as a function of time for the reaction $2N_2O_5(soln) \rightarrow 4NO_2(soln) + O_2(g)$ (at 45°C). Note that the reaction rate at $[N_2O_5] = 0.90\ M$ is twice that at $[N_2O_5] = 0.45\ M$.

Visualization: Decomposition of N_2O_5

First order: rate = $k[A]$. Doubling the concentration of A doubles the reaction rate.

Note that when $[N_2O_5]$ is halved, the rate is also halved. This means that the rate of this reaction depends on the concentration of N_2O_5 to the *first power*. In other words, the (differential) rate law for this reaction is

$$\text{Rate} = -\frac{\Delta[N_2O_5]}{\Delta t} = k[N_2O_5]^1 = k[N_2O_5]$$

Thus the reaction is *first order* in N_2O_5. Note that for this reaction the order is *not* the same as the coefficient of N_2O_5 in the balanced equation for the reaction. This reemphasizes the fact that the order of a particular reactant must be obtained by *observing* how the reaction rate depends on the concentration of that reactant.

We have seen that by determining the instantaneous rate at two different reactant concentrations, the rate law for the decomposition of N_2O_5 is shown to have the form

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

where A represents N_2O_5.

Method of Initial Rates

The value of the initial rate is determined for each experiment at the same value of t as close to $t = 0$ as possible.

One common method for experimentally determining the form of the rate law for a reaction is the **method of initial rates.** The **initial rate** of a reaction is the instantaneous rate determined just after the reaction begins (just after $t = 0$). The idea is to determine the instantaneous rate before the initial concentrations of reactants have changed significantly. Several experiments are carried out using different initial concentrations, and the initial rate is determined for each run. The results are then compared to see how the initial rate depends on the initial concentrations. This allows the form of the rate law to be determined. We will illustrate the method of initial rates using the following equation:

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

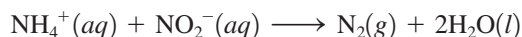Visualization: Reaction Rate and Concentration

Table 12.4 gives initial rates obtained from three experiments involving different initial concentrations of reactants. The general form of the rate law for this reaction is

$$\text{Rate} = -\frac{\Delta[NH_4^+]}{\Delta t} = k[NH_4^+]^n[NO_2^-]^m$$

We can determine the values of n and m by observing how the initial rate depends on the initial concentrations of NH_4^+ and NO_2^-. In Experiments 1 and 2, where the initial

	TABLE 12.4 Initial Rates from Three Experiments for the Reaction $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$		
Experiment	**Initial Concentration of NH_4^+**	**Initial Concentration of NH_2^-**	**Initial Rate (mol/L · s)**
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

concentration of NH_4^+ remains the same but the initial concentration of NO_2^- doubles, the observed initial rate also doubles. Since

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

we have for Experiment 1

$$\text{Rate} = 1.35 \times 10^{-7}\ \text{mol/L} \cdot \text{s} = k(0.100\ \text{mol/L})^n(0.0050\ \text{mol/L})^m$$

and for Experiment 2

$$\text{Rate} = 2.70 \times 10^{-7}\ \text{mol/L} \cdot \text{s} = k(0.100\ \text{mol/L})^n(0.010\ \text{mol/L})^m$$

The ratio of these rates is

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \underbrace{\frac{2.70 \times 10^{-7}\ \text{mol/L} \cdot \text{s}}{1.35 \times 10^{-7}\ \text{mol/L} \cdot \text{s}}}_{2.00} = \frac{k(\cancel{0.100\ \text{mol/L}})^n(0.010\ \text{mol/L})^m}{k(\cancel{0.100\ \text{mol/L}})^n(0.0050\ \text{mol/L})^m}$$

$$= \frac{(0.010\ \text{mol/L})^m}{(0.0050\ \text{mol/L})^m} = (2.0)^m$$

Thus

$$\frac{\text{Rate 2}}{\text{Rate 1}} = 2.00 = (2.0)^m$$

which means the value of m is 1. The rate law for this reaction is first order in the reactant NO_2^-.

A similar analysis of the results for Experiments 2 and 3 yields the ratio

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{5.40 \times 10^{-7}\ \text{mol/L} \cdot \text{s}}{2.70 \times 10^{-7}\ \text{mol/L} \cdot \text{s}} = \frac{(0.200\ \text{mol/L})^n}{(0.100\ \text{mol/L})^n}$$

$$= 2.00 = \left(\frac{0.200}{0.100}\right)^n = (2.00)^n$$

The value of n is also 1.

We have shown that the values of n and m are both 1 and the rate law is

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

This rate law is first order in both NO_2^- and NH_4^+. Note that it is merely a coincidence that n and m have the same values as the coefficients of NH_4^+ and NO_2^- in the balanced equation for the reaction.

Overall reaction order is the sum of the orders for the various reactants.

The **overall reaction order** is the sum of n and m. For this reaction, $n + m = 2$. The reaction is second order overall.

The value of the rate constant k can now be calculated using the results of *any* of the three experiments shown in Table 12.4. From the data for Experiment 1, we know that

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

$$1.35 \times 10^{-7}\,\text{mol/L} \cdot \text{s} = k(0.100\,\text{mol/L})(0.0050\,\text{mol/L})$$

Then

$$k = \frac{1.35 \times 10^{-7}\,\text{mol/L} \cdot \text{s}}{(0.100\,\text{mol/L})(0.0050\,\text{mol/L})} = 2.7 \times 10^{-4}\,\text{L/mol} \cdot \text{s}$$

Sample Exercise 12.1   ## Determining a Rate Law

The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the equation

$$\text{BrO}_3^-(aq) + 5\text{Br}^-(aq) + 6\text{H}^+(aq) \longrightarrow 3\text{Br}_2(l) + 3\text{H}_2\text{O}(l)$$
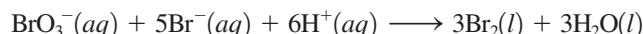
Table 12.5 gives the results from four experiments. Using these data, determine the orders for all three reactants, the overall reaction order, and the value of the rate constant.

Solution

The general form of the rate law for this reaction is

$$\text{Rate} = k[\text{BrO}_3^-]^n[\text{Br}^-]^m[\text{H}^+]^p$$

We can determine the values of n, m, and p by comparing the rates from the various experiments. To determine the value of n, we use the results from Experiments 1 and 2, in which only $[\text{BrO}_3^-]$ changes:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{1.6 \times 10^{-3}\,\text{mol/L} \cdot \text{s}}{8.0 \times 10^{-4}\,\text{mol/L} \cdot \text{s}} = \frac{k(0.20\,\text{mol/L})^n(0.10\,\text{mol/L})^m(0.10\,\text{mol/L})^p}{k(0.10\,\text{mol/L})^n(0.10\,\text{mol/L})^m(0.10\,\text{mol/L})^p}$$

$$2.0 = \left(\frac{0.20\,\text{mol/L}}{0.10\,\text{mol/L}}\right)^n = (2.0)^n$$

Thus n is equal to 1.

To determine the value of m, we use the results from Experiments 2 and 3, in which only $[\text{Br}^-]$ changes:

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{3.2 \times 10^{-3}\,\text{mol/L} \cdot \text{s}}{1.6 \times 10^{-3}\,\text{mol/L} \cdot \text{s}} = \frac{k(0.20\,\text{mol/L})^n(0.20\,\text{mol/L})^m(0.10\,\text{mol/L})^p}{k(0.20\,\text{mol/L})^n(0.10\,\text{mol/L})^m(0.10\,\text{mol/L})^p}$$

$$2.0 = \left(\frac{0.20\,\text{mol/L}}{0.10\,\text{mol/L}}\right)^m = (2.0)^m$$

Thus m is equal to 1.

TABLE 12.5   The Results from Four Experiments to Study the Reaction
$\text{BrO}_3^-(aq) + 5\text{Br}^-(aq) + 6\text{H}^+(aq) \rightarrow 3\text{Br}_2(l) + 3\text{H}_2\text{O}(l)$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol/L · s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

To determine the value of p, we use the results from Experiments 1 and 4, in which $[BrO_3^-]$ and $[Br^-]$ are constant but $[H^+]$ differs:

$$\frac{\text{Rate 4}}{\text{Rate 1}} = \frac{3.2 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}} = \frac{k(0.10 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.20 \text{ mol/L})^p}{k(0.10 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p}$$

$$4.0 = \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}}\right)^p$$

$$4.0 = (2.0)^p = (2.0)^2$$

Thus p is equal to 2.

The rate of this reaction is first order in BrO_3^- and Br^- and second order in H^+. The overall reaction order is $n + m + p = 4$.

The rate law can now be written

$$\text{Rate} = k[BrO_3^-][Br^-][H^+]^2$$

The value of the rate constant k can be calculated from the results of any of the four experiments. For Experiment 1, the initial rate is 8.0×10^{-4} mol/L $\cdot$ s and $[BrO_3^-] = 0.100\,M$, $[Br^-] = 0.10\,M$, and $[H^+] = 0.10\,M$. Using these values in the rate law gives

$$8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s} = k(0.10 \text{ mol/L})(0.10 \text{ mol/L})(0.10 \text{ mol/L})^2$$

$$8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s} = k(1.0 \times 10^{-4} \text{ mol}^4/\text{L}^4)$$

$$k = \frac{8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}}{1.0 \times 10^{-4} \text{ mol}^4/\text{L}^4} = 8.0 \text{ L}^3/\text{mol}^3 \cdot \text{s}$$

***Reality Check:*** Verify that the same value of k can be obtained from the results of the other experiments.

See Exercises 12.25 through 12.28.

12.4 The Integrated Rate Law

The rate laws we have considered so far express the rate as a function of the reactant concentrations. It is also useful to be able to express the reactant concentrations as a function of time, given the (differential) rate law for the reaction. In this section we show how this is done.

We will proceed by first looking at reactions involving a single reactant:

$$aA \longrightarrow \text{products}$$
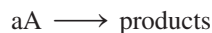
all of which have a rate law of the form

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

We will develop the integrated rate laws individually for the cases $n = 1$ (first order), $n = 2$ (second order), and $n = 0$ (zero order).

First-Order Rate Laws

For the reaction

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

we have found that the rate law is

$$\text{Rate} = -\frac{\Delta[N_2O_5]}{\Delta t} = k[N_2O_5]$$

Since the rate of this reaction depends on the concentration of N_2O_5 to the first power, it is a **first-order reaction.** This means that if the concentration of N_2O_5 in a flask were suddenly doubled, the rate of production of NO_2 and O_2 also would double. This rate law can be put into a different form using a calculus operation known as integration, which yields the expression

$$\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$$

Appendix 1.2 contains a review of logarithms.

where ln indicates the natural logarithm, t is the time, $[N_2O_5]$ is the concentration of N_2O_5 at time t, and $[N_2O_5]_0$ is the initial concentration of N_2O_5 (at $t = 0$, the start of the experiment). Note that such an equation, called the *integrated rate law,* expresses the *concentration of the reactant as a function of time.*

For a chemical reaction of the form

$$aA \longrightarrow \text{products}$$
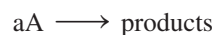
where the kinetics are first order in [A], the rate law is

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

and the **integrated first-order rate law** is

$$\ln[A] = -kt + \ln[A]_0 \tag{12.2}$$

There are several important things to note about Equation (12.2):

An integrated rate law relates concentration to reaction time.

1. The equation shows how the concentration of A depends on time. If the initial concentration of A and the rate constant k are known, the concentration of A at any time can be calculated.

2. Equation (12.2) is of the form $y = mx + b$, where a plot of y versus x is a straight line with slope m and intercept b. In Equation (12.2),

$$y = \ln[A] \qquad x = t \qquad m = -k \qquad b = \ln[A]_0$$

For a first-order reaction, a plot of ln[A] versus t is always a straight line.

Thus, for a first-order reaction, plotting the natural logarithm of concentration versus time always gives a straight line. This fact is often used to test whether a reaction is first order. For the reaction

$$aA \longrightarrow \text{products}$$
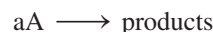
the *reaction is first order in A if a plot of ln[A] versus t is a straight line.* Conversely, if this plot is not a straight line, the reaction is not first order in A.

3. This integrated rate law for a first-order reaction also can be expressed in terms of a *ratio* of [A] and $[A]_0$ as follows:

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

Sample Exercise 12.2 **First-Order Rate Laws I**

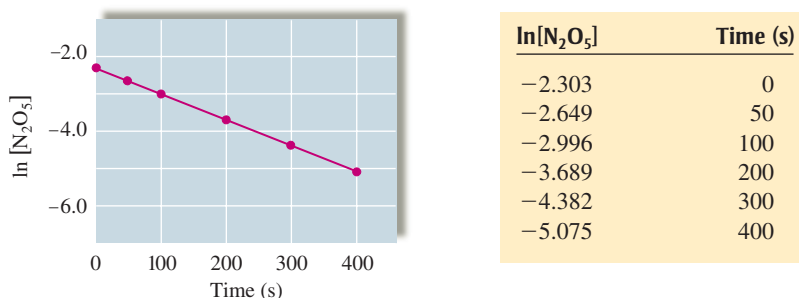The decomposition of N_2O_5 in the gas phase was studied at constant temperature.

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

ln[N$_2$O$_5$]	Time (s)
−2.303	0
−2.649	50
−2.996	100
−3.689	200
−4.382	300
−5.075	400

FIGURE 12.4
A plot of ln[N$_2$O$_5$] versus time.

The following results were collected:

[N$_2$O$_5$] (mol/L)	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

Using these data, verify that the rate law is first order in [N$_2$O$_5$], and calculate the value of the rate constant, where the rate $= -\Delta[N_2O_5]/\Delta t$.

Solution

We can verify that the rate law is first order in [N$_2$O$_5$] by constructing a plot of ln[N$_2$O$_5$] versus time. The values of ln[N$_2$O$_5$] at various times are given in the table above and the plot of ln[N$_2$O$_5$] versus time is shown in Fig. 12.4. The fact that the plot is a straight line confirms that the reaction is first order in N$_2$O$_5$, since it follows the equation ln[N$_2$O$_5$] $= -kt + \ln[N_2O_5]_0$.

Since the reaction is first order, the slope of the line equals $-k$, where

$$\text{Slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta(\ln[N_2O_5])}{\Delta t}$$

Since the first and last points are exactly on the line, we will use these points to calculate the slope:

$$\text{Slope} = \frac{-5.075 - (-2.303)}{400.\ \text{s} - 0\ \text{s}} = \frac{-2.772}{400.\ \text{s}} = -6.93 \times 10^{-3}\ \text{s}^{-1}$$

$$k = -(\text{slope}) = 6.93 \times 10^{-3}\ \text{s}^{-1}$$

See Exercise 12.31.

Sample Exercise 12.3   **First-Order Rate Laws II**

Using the data given in Sample Exercise 12.2, calculate [N$_2$O$_5$] at 150 s after the start of the reaction.

Solution

We know from Sample Exercise 12.2 that [N$_2$O$_5$] $= 0.0500$ mol/L at 100 s and [N$_2$O$_5$] $= 0.0250$ mol/L at 200 s. Since 150 s is halfway between 100 and 200 s, it is tempting to

assume that we can simply use an arithmetic average to obtain $[N_2O_5]$ at that time. This is incorrect because it is $\ln[N_2O_5]$, not $[N_2O_5]$, that is directly proportional to t. To calculate $[N_2O_5]$ after 150 s, we use Equation (12.2):

$$\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$$

where $t = 150.$ s, $k = 6.93 \times 10^{-3}\,\text{s}^{-1}$ (as determined in Sample Exercise 12.2), and $[N_2O_5]_0 = 0.1000$ mol/L.

$$\ln([N_2O_5])_{t=150} = -(6.93 \times 10^{-3}\,\text{s}^{-1})(150.\ \text{s}) + \ln(0.100)$$
$$= -1.040 - 2.303 = -3.343$$
$$[N_2O_5]_{t=150} = \text{antilog}(-3.343) = 0.0353 \text{ mol/L}$$

The antilog operation means to exponentiate (see Appendix 1.2).

Note that this value of $[N_2O_5]$ is *not* halfway between 0.0500 and 0.0250 mol/L.

See Exercise 12.31.

Half-Life of a First-Order Reaction

The time required for a reactant to reach half its original concentration is called the **half-life of a reactant** and is designated by the symbol $t_{1/2}$. For example, we can calculate the half-life of the decomposition reaction discussed in Sample Exercise 12.2. The data plotted in Fig. 12.5 show that the half-life for this reaction is 100 seconds. We can see this by considering the following numbers:

Visualization: Half-Life of Reactions

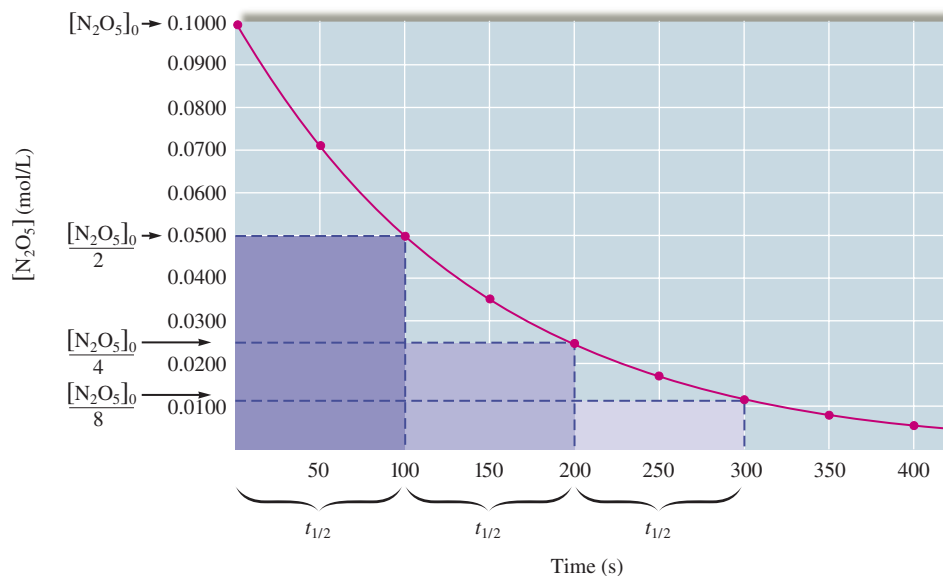| $[N_2O_5]$ (mol/L)	t (s)		
0.100	0	$\Delta t = 100$ s;	$\dfrac{[N_2O_5]_{t=100}}{[N_2O_5]_{t=0}} = \dfrac{0.050}{0.100} = \dfrac{1}{2}$
0.0500	100	$\Delta t = 100$ s;	$\dfrac{[N_2O_5]_{t=200}}{[N_2O_5]_{t=100}} = \dfrac{0.025}{0.050} = \dfrac{1}{2}$
0.0250	200	$\Delta t = 100$ s;	$\dfrac{[N_2O_5]_{t=300}}{[N_2O_5]_{t=200}} = \dfrac{0.0125}{0.0250} = \dfrac{1}{2}$
0.0125	300		

FIGURE 12.5
A plot of $[N_2O_5]$ versus time for the decomposition reaction of N_2O_5.

Note that it *always* takes 100 seconds for $[N_2O_5]$ to be halved in this reaction.

A general formula for the half-life of a first-order reaction can be derived from the integrated rate law for the general reaction

$$aA \longrightarrow products$$
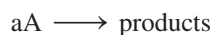
If the reaction is first order in $[A]$,

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

By definition, when $t = t_{1/2}$,

$$[A] = \frac{[A]_0}{2}$$

Then, for $t = t_{1/2}$, the integrated rate law becomes

$$\ln\left(\frac{[A]_0}{[A]_0/2}\right) = kt_{1/2}$$

or

$$\ln(2) = kt_{1/2.}$$

Substituting the value of $\ln(2)$ and solving for $t_{1/2}$ gives

$$t_{1/2} = \frac{0.693}{k} \tag{12.3}$$

For a first-order reaction, $t_{1/2}$ is independent of the initial concentration.

This is the *general equation for the half-life of a first-order reaction.* Equation (12.3) can be used to calculate $t_{1/2}$ if k is known or k if $t_{1/2}$ is known. Note that for a first-order reaction, *the half-life does not depend on concentration.*

| Sample Exercise 12.4 | **Half-Life for First-Order Reaction** |

A certain first-order reaction has a half-life of 20.0 minutes.

a. Calculate the rate constant for this reaction.
b. How much time is required for this reaction to be 75% complete?

Solution

a. Solving Equation (12.3) for k gives

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20.0 \text{ min}} = 3.47 \times 10^{-2} \text{ min}^{-1}$$

b. We use the integrated rate law in the form

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

If the reaction is 75% complete, 75% of the reactant has been consumed, leaving 25% in the original form:

$$\frac{[A]}{[A]_0} \times 100\% = 25\%$$

This means that

$$\frac{[A]}{[A]_0} = 0.25 \quad \text{or} \quad \frac{[A]_0}{[A]} = \frac{1}{0.25} = 4.0$$

Then

$$\ln\left(\frac{[A]_0}{[A]}\right) = \ln(4.0) = kt = \left(\frac{3.47 \times 10^{-2}}{\text{min}}\right)t$$

and
$$t = \frac{\ln(4.0)}{\dfrac{3.47 \times 10^{-2}}{\text{min}}} = 40.\ \text{min}$$
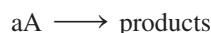
Thus it takes 40. minutes for this particular reaction to reach 75% completion.

Let's consider another way of solving this problem using the definition of half-life. After one half-life the reaction has gone 50% to completion. If the initial concentration were 1.0 mol/L, after one half-life the concentration would be 0.50 mol/L. One more half-life would produce a concentration of 0.25 mol/L. Comparing 0.25 mol/L with the original 1.0 mol/L shows that 25% of the reactant is left after two half-lives. This is a general result. (What percentage of reactant remains after three half-lives?) Two half-lives for this reaction is 2(20.0 min), or 40.0 min, which agrees with the preceding answer.

See Exercises 12.32 and 12.42 through 12.44.

Second-Order Rate Laws

For a general reaction involving a single reactant, that is,

$$aA \longrightarrow \text{products}$$

that is second order in A, the rate law is

Second order: rate $= k[A]^2$. Doubling the concentration of A quadruples the reaction rate; tripling the concentration of A increases the rate by nine times.

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2 \qquad (12.4)$$

The **integrated second-order rate law** has the form

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \qquad (12.5)$$

Note the following characteristics of Equation (12.5):

For second-order reactions, a plot of $1/[A]$ versus t will be linear.

1. A plot of $1/[A]$ versus t will produce a straight line with a slope equal to k.

2. Equation (12.5) shows how [A] depends on time and can be used to calculate [A] at any time t, provided k and $[A]_0$ are known.

When one half-life of the second-order reaction has elapsed ($t = t_{1/2}$), by definition,

$$[A] = \frac{[A]_0}{2}$$

Equation (12.5) then becomes

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

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

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

Solving for $t_{1/2}$ gives *the expression for the half-life of a second-order reaction:*

$$t_{1/2} = \frac{1}{k[A]_0} \qquad (12.6)$$

Sample Exercise 12.5 **Determining Rate Laws**

When two identical molecules combine, the resulting molecule is called a *dimer*.

Butadiene reacts to form its dimer according to the equation

$$2C_4H_6(g) \longrightarrow C_8H_{12}(g)$$

The following data were collected for this reaction at a given temperature:

$[C_4H_6]$ (mol/L)	Time (± 1 s)
0.01000	0
0.00625	1000
0.00476	1800
0.00370	2800
0.00313	3600
0.00270	4400
0.00241	5200
0.00208	6200

a. Is this reaction first order or second order?
b. What is the value of the rate constant for the reaction?
c. What is the half-life for the reaction under the conditions of this experiment?

Solution

a. To decide whether the rate law for this reaction is first order or second order, we must see whether the plot of $\ln[C_4H_6]$ versus time is a straight line (first order) or the plot of $1/[C_4H_6]$ versus time is a straight line (second order). The data necessary to make these plots are as follows:

t (s)	$\dfrac{1}{[C_4H_6]}$	$\ln[C_4H_4]$
0	100	-4.605
1000	160	-5.075
1800	210	-5.348
2800	270	-5.599
3600	320	-5.767
4400	370	-5.915
5200	415	-6.028
6200	481	-6.175

The resulting plots are shown in Fig. 12.6. Since the $\ln[C_4H_6]$ versus t plot [Fig. 12.6(a)] is not a straight line, the reaction is *not* first order. The reaction is, however, second order, as shown by the linearity of the $1/[C_4H_6]$ versus t plot [Fig. 12.6(b)]. Thus we can now write the rate law for this second-order reaction:

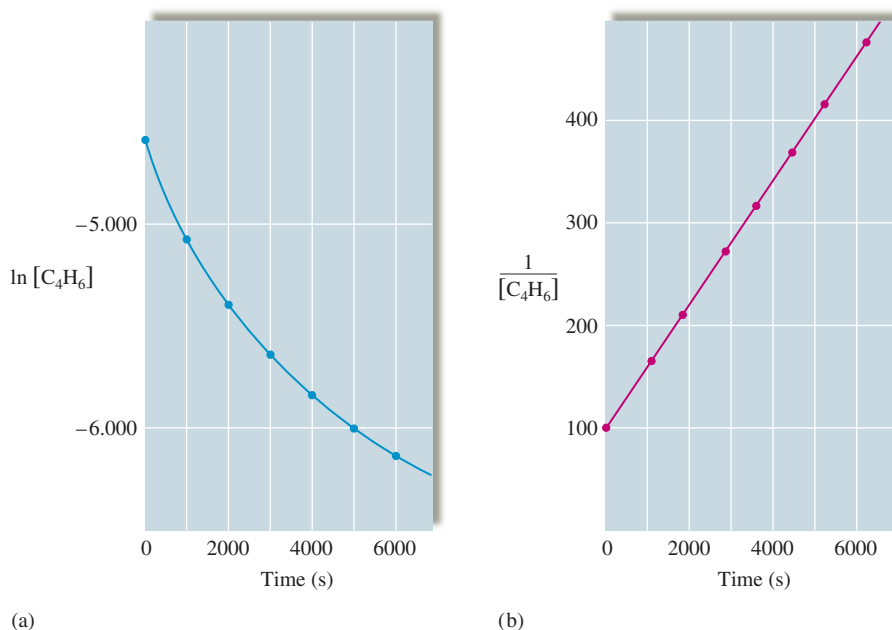$$\text{Rate} = -\frac{\Delta[C_4H_6]}{\Delta t} = k[C_4H_6]^2$$

b. For a second-order reaction, a plot of $1/[C_4H_6]$ versus t produces a straight line of slope k. In terms of the standard equation for a straight line, $y = mx + b$, we have $y = 1/[C_4H_6]$ and $x = t$. Thus the slope of the line can be expressed as follows:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{\Delta\left(\dfrac{1}{[C_4H_6]}\right)}{\Delta t}$$
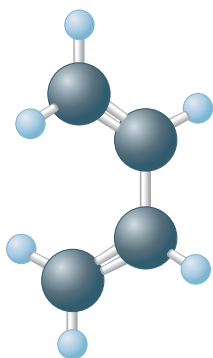
Butadiene (C_4H_6)

FIGURE 12.6
(a) A plot of $\ln[C_4H_6]$ versus t. (b) A plot of $1/[C_4H_6]$ versus t.

Using the points at $t = 0$ and $t = 6200$, we can find the rate constant for the reaction:

$$k = \text{slope} = \frac{(481 - 100)\,\text{L/mol}}{(6200. - 0)\,\text{s}} = \frac{381}{6200.}\,\text{L/mol} \cdot \text{s} = 6.14 \times 10^{-2}\,\text{L/mol} \cdot \text{s}$$

c. The expression for the half-life of a second-order reaction is

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

In this case $k = 6.14 \times 10^{-2}\,\text{L/mol} \cdot \text{s}$ (from part b) and $[A]_0 = [C_4H_6]_0 = 0.01000\,M$ (the concentration at $t = 0$). Thus

$$t_{1/2} = \frac{1}{(6.14 \times 10^{-2}\,\text{L/mol} \cdot \text{s})(1.000 \times 10^{-2}\,\text{mol/L})} = 1.63 \times 10^3\,\text{s}$$

The initial concentration of C_4H_6 is halved in 1630 s.

See Exercises 12.33, 12.34, 12.45, and 12.46.

For a second-order reaction, $t_{1/2}$ is dependent on $[A]_0$. For a first-order reaction, $t_{1/2}$ is independent of $[A]_0$.

It is important to recognize the difference between the half-life for a first-order reaction and the half-life for a second-order reaction. For a second-order reaction, $t_{1/2}$ depends on both k and $[A]_0$; for a first-order reaction, $t_{1/2}$ depends only on k. For a first-order reaction, a constant time is required to reduce the concentration of the reactant by half, and then by half again, and so on, as the reaction proceeds. From Sample Exercise 12.5 we can see that this is *not* true for a second-order reaction. For that second-order reaction, we found that the first half-life (the time required to go from $[C_4H_6] = 0.010\,M$ to $[C_4H_6] = 0.0050\,M$) is 1630 seconds. We can estimate the second half-life from the concentration data as a function of time. Note that to reach 0.0024 M C_4H_6 (approximately 0.0050/2) requires 5200 seconds of reaction time. Thus to get from 0.0050 M C_4H_6 to 0.0024 M C_4H_6 takes 3570 seconds (5200 − 1630). The second half-life is much longer than the first. This pattern is characteristic of second-order reactions. In fact, *for a second-order reaction, each successive half-life is double the preceding one* (provided the effects

(a)   (b)

Suppose we run this reaction under conditions where $[BrO_3^-]_0 = 1.0 \times 10^{-3} \, M$, $[Br^-]_0 = 1.0 \, M$, and $[H^+]_0 = 1.0 \, M$. As the reaction proceeds, $[BrO_3^-]$ decreases significantly, but because the Br^- ion and H^+ ion concentrations are so large initially, relatively little of these two reactants is consumed. Thus $[Br^-]$ and $[H^+]$ remain *approximately constant.* In other words, under the conditions where the Br^- ion and H^+ ion concentrations are much larger than the BrO_3^- ion concentration, we can assume that throughout the reaction

$$[Br^-] = [Br^-]_0 \quad \text{and} \quad [H^+] = [H^+]_0$$

This means that the rate law can be written

$$\text{Rate} = k[Br^-]_0[H^+]_0^2[BrO_3^-] = k'[BrO_3^-]$$

where, since $[Br^-]_0$ and $[H^+]_0$ are constant,

$$k' = k[Br^-]_0[H^+]_0^2$$

The rate law

$$\text{Rate} = k'[BrO_3^-]$$

is first order. However, since this law was obtained by simplifying a more complicated one, it is called a **pseudo-first-order rate law.** Under the conditions of this experiment, a plot of $\ln[BrO_3^-]$ versus t will give a straight line where the slope is equal to $-k'$. Since $[Br^-]_0$ and $[H^+]_0$ are known, the value of k can be calculated from the equation

$$k' = k[Br^-]_0[H^+]_0^2$$

which can be rearranged to give

$$k = \frac{k'}{[Br^-]_0[H^+]_0^2}$$

Note that the kinetics of complicated reactions can be studied by observing the behavior of one reactant at a time. If the concentration of one reactant is much smaller than the concentrations of the others, then the amounts of those reactants present in large concentrations will not change significantly and can be regarded as constant. The change in concentration with time of the reactant present in a relatively small amount can then be used to determine the order of the reaction in that component. This technique allows us to determine rate laws for complex reactions.

12.5 Rate Laws: A Summary

In the last several sections we have developed the following important points:

1. To simplify the rate laws for reactions, we have always assumed that the rate is being studied under conditions where only the forward reaction is important. This produces rate laws that contain only reactant concentrations.

2. There are two types of rate laws.
   a. The *differential rate law* (often called the *rate law*) shows how the rate depends on the concentrations. The forms of the rate laws for zero-order, first-order, and second-order kinetics of reactions with single reactants are shown in Table 12.6.
   b. The *integrated rate law* shows how concentration depends on time. The integrated rate laws corresponding to zero-order, first-order, and second- order kinetics of one-reactant reactions are given in Table 12.6.

3. Whether we determine the differential rate law or the integrated rate law depends on the type of data that can be collected conveniently and accurately. Once we have experimentally determined either type of rate law, we can write the other for a given reaction.

4. The most common method for experimentally determining the differential rate law is the method of initial rates. In this method several experiments are run at different initial concentrations and the instantaneous rates are determined for each at the same value of t (as close to $t = 0$ as possible). The point is to evaluate the rate before the concentrations change significantly from the initial values. From a comparison of the initial rates and the initial concentrations the dependence of the rate on the concentrations of various reactants can be obtained—that is, the order in each reactant can be determined.

5. To experimentally determine the integrated rate law for a reaction, concentrations are measured at various values of t as the reaction proceeds. Then the job is to see which integrated rate law correctly fits the data. Typically this is done visually by ascertaining which type of plot gives a straight line. A summary for one-reactant reactions is given in Table 12.6. Once the correct straight-line plot is found, the correct integrated rate law can be chosen and the value of k obtained from the slope. Also, the (differential) rate law for the reaction can then be written.

Visualization: Rate Laws

TABLE 12.6   Summary of the Kinetics for Reactions of the Type aA → Products That Are Zero, First, or Second Order in [A]

	Order		
	Zero	*First*	*Second*
Rate Law:	$\text{Rate} = k$	$\text{Rate} = k[A]$	$\text{Rate} = k[A]^2$
Integrated Rate Law:	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\dfrac{1}{[A]} = kt + \dfrac{1}{[A]_0}$
Plot Needed to Give a Straight Line:	$[A]$ versus t	$\ln[A]$ versus t	$\dfrac{1}{[A]}$ versus t
Relationship of Rate Constant to the Slope of Straight Line:	$\text{Slope} = -k$	$\text{Slope} = -k$	$\text{Slope} = k$
Half-Life:	$t_{1/2} = \dfrac{[A]_0}{2k}$	$t_{1/2} = \dfrac{0.693}{k}$	$t_{1/2} = \dfrac{1}{k[A]_0}$

6. The integrated rate law for a reaction that involves several reactants can be treated by choosing conditions such that the concentration of only one reactant varies in a given experiment. This is done by having the concentration of one reactant remain small compared with the concentrations of all the others, causing a rate law such as

$$\text{Rate} = k[A]^n[B]^m[C]^p$$

to reduce to

$$\text{Rate} = k'[A]^n$$

where $k' = k[B]_0^m[C]_0^p$ and $[B]_0 \gg [A]_0$ and $[C]_0 \gg [A]_0$. The value of n is obtained by determining whether a plot of $[A]$ versus t is linear ($n = 0$), a plot of $\ln[A]$ versus t is linear ($n = 1$), or a plot of $1/[A]$ versus t is linear ($n = 2$). The value of k' is determined from the slope of the appropriate plot. The values of m, p, and k can be found by determining the value of k' at several different concentrations of B and C.

12.6 Reaction Mechanisms

Visualization: Oscillating Reaction

Most chemical reactions occur by a *series of steps* called the **reaction mechanism.** To understand a reaction, we must know its mechanism, and one of the main purposes for studying kinetics is to learn as much as possible about the steps involved in a reaction. In this section we explore some of the fundamental characteristics of reaction mechanisms.

Consider the reaction between nitrogen dioxide and carbon monoxide:

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

The rate law for this reaction is known from experiment to be

$$\text{Rate} = k[NO_2]^2$$

A balanced equation does not tell us *how* the reactants become products.

As we will see below, this reaction is more complicated than it appears from the balanced equation. This is quite typical; the balanced equation for a reaction tells us the reactants, the products, and the stoichiometry but gives no direct information about the reaction mechanism.

For the reaction between nitrogen dioxide and carbon monoxide, the mechanism is thought to involve the following steps:

$$NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g)$$
$$NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g)$$

An intermediate is formed in one step and used up in a subsequent step and so is never seen as a product.
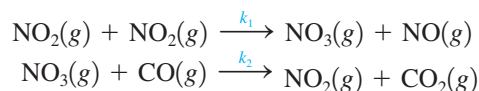
where k_1 and k_2 are the rate constants of the individual reactions. In this mechanism, gaseous NO_3 is an **intermediate,** a species that is neither a reactant nor a product but that is formed and consumed during the reaction sequence. This reaction is illustrated in Fig. 12.9.

Step 1

Step 2

FIGURE 12.9
A molecular representation of the elementary steps in the reaction of NO_2 and CO.

TABLE 12.7   Examples of Elementary Steps

Elementary Step	Molecularity	Rate Law
A → products	*Uni*molecular	Rate = $k[A]$
A + A → products	*Bi*molecular	Rate = $k[A]^2$
(2A → products)		
A + B → products	*Bi*molecular	Rate = $k[A][B]$
A + A + B → products	*Ter*molecular	Rate = $k[A]^2[B]$
(2A + B → products)		
A + B + C → products	*Ter*molecular	Rate = $k[A][B][C]$

Each of these two reactions is called an **elementary step,** *a reaction whose rate law can be written from its molecularity.* **Molecularity** is defined as the number of species that must collide to produce the reaction indicated by that step. A reaction involving one molecule is called a **unimolecular step.** Reactions involving the collision of two and three species are termed **bimolecular** and **termolecular,** respectively. Termolecular steps are quite rare, because the probability of three molecules colliding simultaneously is very small. Examples of these three types of elementary steps and the corresponding rate laws are shown in Table 12.7. Note from Table 12.7 that the rate law for an elementary step follows *directly* from the molecularity of that step. For example, for a bimolecular step the rate law is always second order, either of the form $k[A]^2$ for a step with a single reactant or of the form $k[A][B]$ for a step involving two reactants.

The prefix *uni-* means one, *bi-* means two, and *ter-* means three.
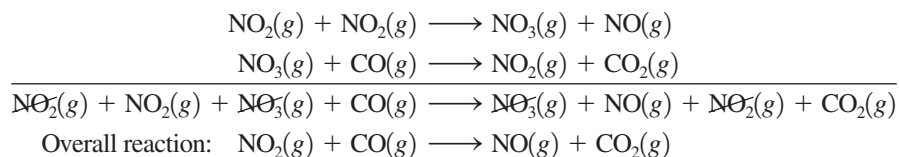
A unimolecular elementary step is always first order, a bimolecular step is always second order, and so on.

We can now define a reaction mechanism more precisely. It is a *series of elementary steps that must satisfy two requirements:*

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

2. The mechanism must agree with the experimentally determined rate law.

To see how these requirements are applied, we will consider the mechanism given above for the reaction of nitrogen dioxide and carbon monoxide. First, note that the sum of the two steps gives the overall balanced equation:

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)$$
$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$$
$$\overline{\rule{0pt}{1.2em}\cancel{NO_2}(g) + NO_2(g) + \cancel{NO_3}(g) + CO(g) \longrightarrow \cancel{NO_3}(g) + NO(g) + \cancel{NO_2}(g) + CO_2(g)}$$
$$\text{Overall reaction:} \quad NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

The first requirement for a correct mechanism is met. To see whether the mechanism meets the second requirement, we need to introduce a new idea: the **rate-determining step.** Multistep reactions often have one step that is much slower than all the others. Reactants can become products only as fast as they can get through this slowest step. That is, the overall reaction can be no faster than the slowest, or rate-determining, step in the sequence. An analogy for this situation is the pouring of water rapidly into a container through a funnel. The water collects in the container at a rate that is essentially determined by the size of the funnel opening and not by the rate of pouring.

A reaction is only as fast as its slowest step.

Which is the rate-determining step in the reaction of nitrogen dioxide and carbon monoxide? Let's *assume* that the first step is rate-determining and the second step is relatively fast:

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + ONO(g) \qquad \text{Slow (rate-determining)}$$
$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g) \qquad \text{Fast}$$

What we have really assumed here is that the formation of NO_3 occurs much more slowly than its reaction with CO. The rate of CO_2 production is then controlled by the rate of formation of NO_3 in the first step. Since this is an elementary step, we can write the rate law from the molecularity. The bimolecular first step has the rate law

$$\text{Rate of formation of } NO_3 = \frac{\Delta[NO_3]}{\Delta t} = k_1[NO_2]^2$$

Since the overall reaction rate can be no faster than the slowest step,

$$\text{Overall rate} = k_1[NO_2]^2$$

Note that this rate law agrees with the experimentally determined rate law given earlier. The mechanism we assumed above satisfies the two requirements stated earlier and *may* be the correct mechanism for the reaction.

How does a chemist deduce the mechanism for a given reaction? The rate law is always determined first. Then, using chemical intuition and following the two rules given on the previous page, the chemist constructs possible mechanisms and tries, with further experiments, to eliminate those that are least likely. *A mechanism can never be proved absolutely.* We can only say that a mechanism that satisfies the two requirements is *possibly* correct. Deducing mechanisms for chemical reactions can be difficult and requires skill and experience. We will only touch on this process in this text.

Sample Exercise 12.6	**Reaction Mechanisms**

The balanced equation for the reaction of the gases nitrogen dioxide and fluorine is

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$
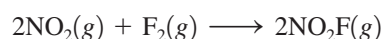
The experimentally determined rate law is

$$\text{Rate} = k[NO_2][F_2]$$

A suggested mechanism for this reaction is

$$NO_2 + F_2 \xrightarrow{k_1} NO_2F + F \qquad \text{Slow}$$
$$F + NO_2 \xrightarrow{k_2} NO_2F \qquad \text{Fast}$$
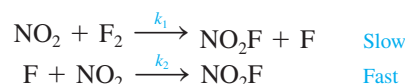
Is this an acceptable mechanism? That is, does it satisfy the two requirements?

Solution

The first requirement for an acceptable mechanism is that the sum of the steps should give the balanced equation:

$$NO_2 + F_2 \longrightarrow NO_2F + F$$
$$\underline{F + NO_2 \longrightarrow NO_2F}$$
$$2NO_2 + F_2 + \cancel{F} \longrightarrow 2NO_2F + \cancel{F}$$

Overall reaction: $2NO_2 + F_2 \longrightarrow 2NO_2F$
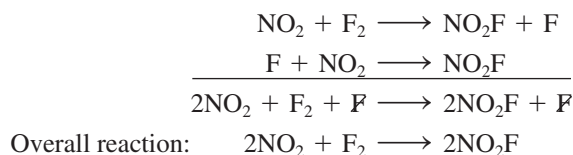
The first requirement is met.

The second requirement is that the mechanism must agree with the experimentally determined rate law. Since the proposed mechanism states that the first step is rate-determining, the overall reaction rate must be that of the first step. The first step is bimolecular, so the rate law is

$$\text{Rate} = k_1[NO_2][F_2]$$
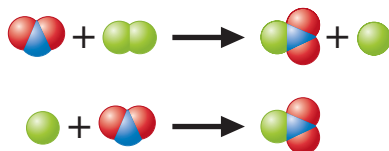
This has the same form as the experimentally determined rate law. The proposed mechanism is acceptable because it satisfies both requirements. (Note that we have not proved that it is *the correct* mechanism.)

Although the mechanism given in Sample Exercise 12.6 has the correct stoichiometry and fits the observed rate law, other mechanisms may also satisfy these requirements. For example, the mechanism might be

$$NO_2 + F_2 \longrightarrow NOF_2 + O \qquad \text{Slow}$$
$$NO_2 + O \longrightarrow NO_3 \qquad \text{Fast}$$
$$NOF_2 + NO_2 \longrightarrow NO_2F + NOF \qquad \text{Fast}$$
$$NO_3 + NOF \longrightarrow NO_2F + NO_2 \qquad \text{Fast}$$

To decide on the most probable mechanism for the reaction, the chemist doing the study would have to perform additional experiments.

12.7 A Model for Chemical Kinetics

How do chemical reactions occur? We already have given some indications. For example, we have seen that the rates of chemical reactions depend on the concentrations of the reacting species. The initial rate for the reaction

$$aA + bB \longrightarrow \text{products}$$
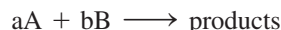
can be described by the rate law

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

where the order of each reactant depends on the detailed reaction mechanism. This explains why reaction rates depend on concentration. But what about some of the other factors affecting reaction rates? For example, how does temperature affect the speed of a reaction?

We can answer this question qualitatively from our experience. We have refrigerators because food spoilage is retarded at low temperatures. The combustion of wood occurs at a measurable rate only at high temperatures. An egg cooks in boiling water much faster at sea level th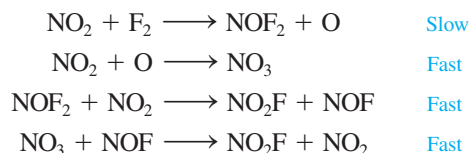an in Leadville, Colorado (elevation 10,000 ft), where the boiling point of water is approximately 90°C. These observations and others lead us to conclude that *chemical reactions speed up when the temperature is increased.* Experiments have shown that virtually all rate constants show an exponential increase with absolute temperature, as represented in Fig. 12.10.

In this section we discuss a model used to account for the observed characteristics of reaction rates. This model, called the **collision model,** is built around the central idea that *molecules must collide to react.* We have already seen how this assumption explains the concentration dependence of reaction rates. Now we need to consider whether this model can account for the observed temperature dependence of reaction rates.

The kinetic molecular theory of gases predicts that an increase in temperature raises molecular velocities and so increases the frequency of collisions between molecules. This idea agrees with the observation that reaction rates are greater at higher temperatures. Thus there is qualitative agreement between the collision model and experimental observations. However, it is found that the rate of reaction is much smaller than the calculated collision frequency in a collection of gas particles. This must mean that *only a small fraction of the collisions produces a reaction.* Why?
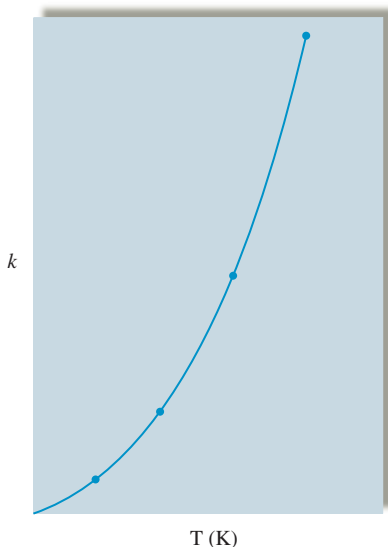

k

T (K)

FIGURE 12.10
A plot showing the exponential dependence of the rate constant on absolute temperature. The exact temperature dependence of k is different for each reaction. This plot represents the behavior of a rate constant that doubles for every increase in temperature of 10 K.
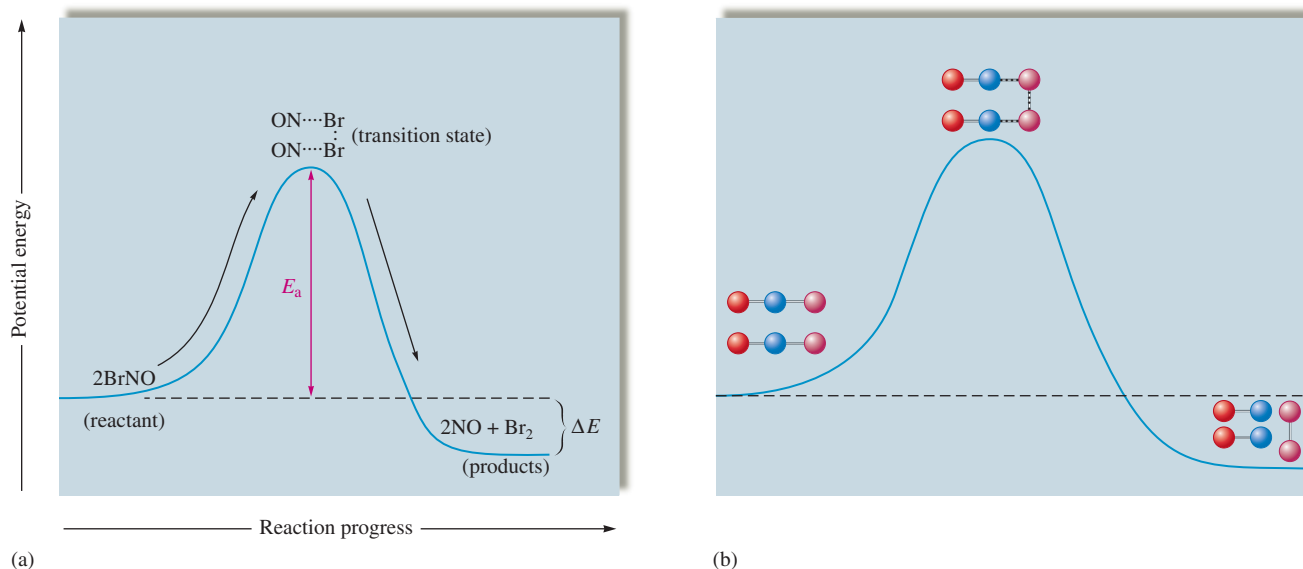
FIGURE 12.11
(a) The change in potential energy as a function of reaction progress for the reaction 2BrNO → 2NO + Br$_2$. The activation energy E_a represents the energy needed to disrupt the BrNO molecules so that they can form products. The quantity ΔE represents the net change in energy in going from reactant to products. (b) A molecular representation of the reaction.

This question was first addressed in the 1880s by Svante Arrhenius. He proposed the existence of a *threshold energy,* called the **activation energy,** that must be overcome to produce a chemical reaction. Such a proposal makes sense, as we can see by considering the decomposition of BrNO in the gas phase:

$$2BrNO(g) \longrightarrow 2NO(g) + Br_2(g)$$
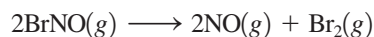
In this reaction two Br—N bonds must be broken and one Br—Br bond must be formed. Breaking a Br—N bond requires considerable energy (243 kJ/mol), which must come from somewhere. The collision model postulates that the energy comes from the kinetic energies possessed by the reacting molecules before the collision. This kinetic energy is changed into potential energy as the molecules are distorted during a collision to break bonds and rearrange the atoms into the product molecules.

We can envision the reaction progress as shown in Fig. 12.11. The arrangement of atoms found at the top of the potential energy "hill," or barrier, is called the **activated complex,** or **transition state.** The conversion of BrNO to NO and Br$_2$ is exothermic, as indicated by the fact that the products have lower potential energy than the reactant. However, ΔE has no effect on the rate of the reaction. Rather, the rate depends on the size of the activation energy E_a.

The main point here is that a certain minimum energy is required for two BrNO molecules to "get over the hill" so that products can form. This energy is furnished by the energy of the collision. A collision between two BrNO molecules with small kinetic energies will not have enough energy to get over the barrier. At a given temperature only a certain fraction of the collisions possesses enough energy to be effective (to result in product formation).

We can be more precise by recalling from Chapter 5 that a distribution of velocities exists in a sample of gas molecules. Therefore, a distribution of collision energies also exists, as shown in Fig. 12.12 for two different temperatures. Figure 12.12 also shows the activation energy for the reaction in question. Only collisions with energy greater than

Visualization: Transition States and Activation Energy

The higher the activation energy, the slower the reaction at a given temperature.
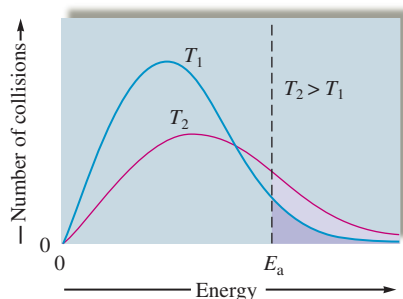
FIGURE 12.12
Plot showing the number of collisions with a particular energy at T_1 and T_2, where $T_2 > T_1$.

the activation energy are able to react (get over the barrier). At the lower temperature, T_1, the fraction of effective collisions is quite small. However, as the temperature is increased to T_2, the fraction of collisions with the required activation energy increases dramatically. When the temperature is doubled, the fraction of effective collisions much more than doubles. In fact, the fraction of effective collisions increases *exponentially* with temperature. This is encouraging for our theory; remember that rates of reactions are observed to increase exponentially with temperature. Arrhenius postulated that the number of collisions having an energy greater than or equal to the activation energy is given by the expression:

Number of collisions with the activation energy $= $ (total number of collisions)$e^{-E_a/RT}$

where E_a is the activation energy, R is the universal gas constant, and T is the Kelvin temperature. The factor $e^{-E_a/RT}$ represents the fraction of collisions with energy E_a or greater at temperature T.

We have seen that not all molecular collisions are effective in producing chemical reactions because a minimum energy is required for the reaction to occur. There is, however, another complication. Experiments show that the *observed reaction rate is considerably smaller than the rate of collisions with enough energy to surmount the barrier.* This means that many collisions, even though they have the required energy, still do not produce a reaction. Why not?

The answer lies in the **molecular orientations** during collisions. We can illustrate this using the reaction between two BrNO molecules, as shown in Fig. 12.13. Some collision orientations can lead to reaction, and others cannot. Therefore, we must include a correction factor to allow for collisions with nonproductive molecular orientations.

To summarize, two requirements must be satisfied for reactants to collide successfully (to rearrange to form products):

1. The collision must involve enough energy to produce the reaction; that is, the collision energy must equal or exceed the activation energy.

2. The relative orientation of the reactants must allow formation of any new bonds necessary to produce products.

Taking these factors into account, we can represent the rate constant as
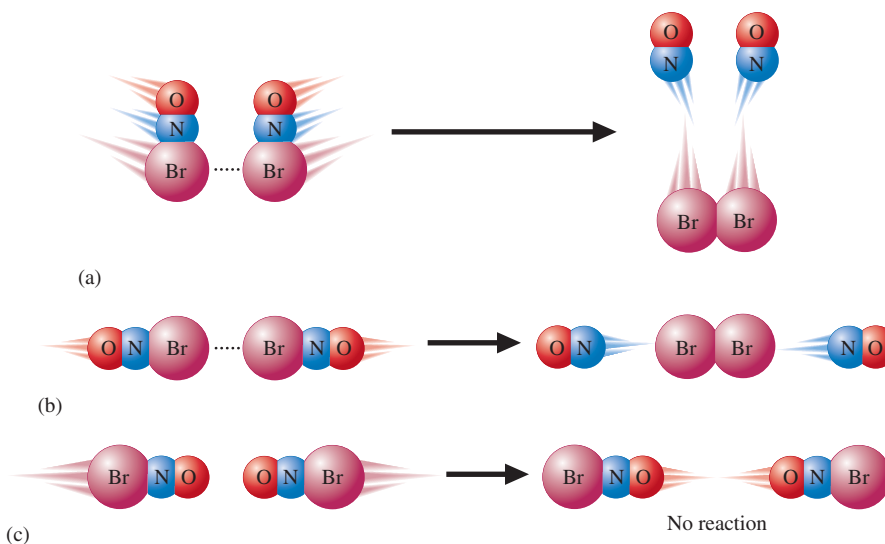
$$k = zpe^{-E_a/RT}$$

FIGURE 12.13
Several possible orientations for a collision between two BrNO molecules. Orientations (a) and (b) can lead to a reaction, but orientation (c) cannot.

where z is the collision frequency, p is called the **steric factor** (always less than 1) and reflects the fraction of collisions with effective orientations, and $e^{-E_a/RT}$ represents the fraction of collisions with sufficient energy to produce a reaction. This expression is most often written in form

$$k = Ae^{-E_a/RT} \tag{12.9}$$

which is called the **Arrhenius equation.** In this equation, A replaces zp and is called the **frequency factor** for the reaction.

Taking the natural logarithm of each side of the Arrhenius equation gives

$$\ln(k) = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln(A) \tag{12.10}$$

Equation (12.10) is a linear equation of the type $y = mx + b$, where $y = \ln(k)$, $m = -E_a/R = $ slope, $x = 1/T$, and $b = \ln(A) = $ intercept. Thus, for a reaction where the rate constant obeys the Arrhenius equation, a plot of $\ln(k)$ versus $1/T$ gives a straight line. The slope and intercept can be used to determine, respectively, the values of E_a and A characteristic of that reaction. The fact that most rate constants obey the Arrhenius equation to a good approximation indicates that the collision model for chemical reactions is physically reasonable.

A snowy tree cricket. The frequency of a cricket's chirps depends on the temperature of the cricket.

Sample Exercise 12.7 | **Determining Activation Energy I**

The reaction

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$
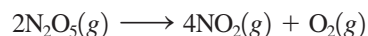
was studied at several temperatures, and the following values of k were obtained:

k (s^{-1})	T (°C)
2.0×10^{-5}	20
7.3×10^{-5}	30
2.7×10^{-4}	40
9.1×10^{-4}	50
2.9×10^{-3}	60

Calculate the value of E_a for this reaction.

Solution

To obtain the value of E_a, we need to construct a plot of $\ln(k)$ versus $1/T$. First, we must calculate values of $\ln(k)$ and $1/T$, as shown below:

T (°C)	T (K)	$1/T$ (K)	k (s^{-1})	$\ln(k)$
20	293	3.41×10^{-3}	2.0×10^{-5}	-10.82
30	303	3.30×10^{-3}	7.3×10^{-5}	-9.53
40	313	3.19×10^{-3}	2.7×10^{-4}	-8.22
50	323	3.10×10^{-3}	9.1×10^{-4}	-7.00
60	333	3.00×10^{-3}	2.9×10^{-3}	-5.84
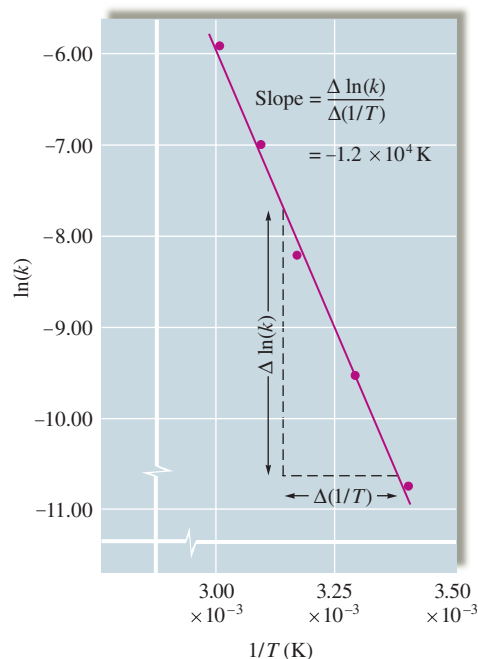
FIGURE 12.14
Plot of ln(k) versus 1/T for the reaction
$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. The value of
the activation energy for this reaction can
be obtained from the slope of the line,
which equals $-E_a/R$.

The plot of ln(k) versus $1/T$ is shown in Fig. 12.14, where the slope

$$\frac{\Delta\ln(k)}{\Delta\left(\dfrac{1}{T}\right)}$$

is found to be -1.2×10^4 K. The value of E_a can be determined by solving the following equation:

$$\text{Slope} = -\frac{E_a}{R}$$

$$E_a = -R(\text{slope}) = -(8.3145 \text{ J/K} \cdot \text{mol})(-1.2 \times 10^4 \text{ K})$$

$$= 1.0 \times 10^5 \text{ J/mol}$$

Thus the value of the activation energy for this reaction is 1.0×10^5 J/mol.

See Exercises 12.57 and 12.58.

The most common procedure for finding E_a for a reaction involves measuring the rate constant k at several temperatures and then plotting ln(k) versus $1/T$, as shown in Sample Exercise 12.7. However, E_a also can be calculated from the values of k at only two temperatures by using a formula that can be derived as follows from Equation (12.10).

At temperature T_1, where the rate constant is k_1,

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

At temperature T_2, where the rate constant is k_2,

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

Subtracting the first equation from the second gives

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

$$= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

And

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{12.11}$$

Therefore, the values of k_1 and k_2 measured at temperatures T_1 and T_2 can be used to calculate E_a, as shown in Sample Exercise 12.8.

Sample Exercise 12.8   **Determining Activation Energy II**

The gas-phase reaction between methane and diatomic sulfur is given by the equation

$$CH_4(g) + 2S_2(g) \longrightarrow CS_2(g) + 2H_2S(g)$$
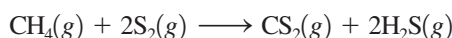
At 550°C the rate constant for this reaction is 1.1 L/mol · s, and at 625°C the rate constant is 6.4 L/mol · s. Using these values, calculate E_a for this reaction.

Solution

The relevant data are shown in the following table:

k (L/mol · s)	T (°C)	T (K)
$1.1 = k_1$	550	$823 = T_1$
$6.4 = k_2$	625	$898 = T_2$

Substituting these values into Equation (12.11) gives

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E_a}{8.3145 \text{ J/K} \cdot \text{mol}}\left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}}\right)$$

Solving for E_a gives

$$E_a = \frac{(8.3145 \text{ J/K} \cdot \text{mol})\ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}}\right)}$$

$$= 1.4 \times 10^5 \text{ J/mol}$$

See Exercises 12.59 through 12.62.

12.8 Catalysis

We have seen that the rate of a reaction increases dramatically with temperature. If a particular reaction does not occur fast enough at normal temperatures, we can speed it up by raising the temperature. However, sometimes this is not feasible. For example, living cells can survive only in a rather narrow temperature range, and the human body is designed to operate at an almost constant temperature of 98.6°F. But many of the complicated biochemical reactions keeping us alive would be much too slow at this temperature without intervention. We exist only because the body contains many substances called **enzymes,** which increase the rates of these reactions. In fact, almost every biologically important reaction is assisted by a specific enzyme.

FIGURE 12.15
Energy plots for a catalyzed and an uncatalyzed pathway for a given reaction.

Visualization: Heterogeneous Catalysis

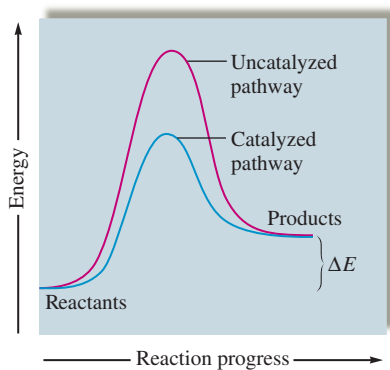These cookies contain partially hydrogenated vegetable oil.

Although it is possible to use higher temperatures to speed up commercially important reactions, such as the Haber process for synthesizing ammonia, this is very expensive. In a chemical plant an increase in temperature means significantly increased costs for energy. The use of an appropriate catalyst allows a reaction to proceed rapidly at a relatively low temperature and can therefore hold down production costs.

A **catalyst** is *a substance that speeds up a reaction without being consumed itself.* Just as virtually all vital biologic reactions are assisted by enzymes (biologic catalysts), almost all industrial processes also involve the use of catalysts. For example, the production of sulfuric acid uses vanadium(V) oxide, and the Haber process uses a mixture of iron and iron oxide.

How does a catalyst work? Remember that for each reaction a certain energy barrier must be surmounted. How can we make a reaction occur faster without raising the temperature to increase the molecular energies? The solution is to provide a new pathway for the reaction, one with a *lower activation energy.* This is what a catalyst does, as is shown in Fig. 12.15. Because the catalyst allows the reaction to occur with a lower activation energy, a much larger fraction of collisions is effective at a given temperature, and the reaction rate is increased. This effect is illustrated in Fig. 12.16. Note from this diagram that although a catalyst lowers the activation energy E_a for a reaction, it does not affect the energy difference ΔE between products and reactants.

Catalysts are classified as homogeneous or heterogeneous. A **homogeneous catalyst** is one that is *present in the same phase as the reacting molecules.* A **heterogeneous catalyst** exists *in a different phase,* usually as a solid.

Heterogeneous Catalysis

Heterogeneous catalysis most often involves gaseous reactants being adsorbed on the surface of a solid catalyst. **Adsorption** refers to the collection of one substance on the surface of another substance; *absorption* refers to the penetration of one substance into another. Water is *absorbed* by a sponge.

An important example of heterogeneous catalysis occurs in the hydrogenation of unsaturated hydrocarbons, compounds composed mainly of carbon and hydrogen with some carbon–carbon double bonds. Hydrogenation is an important industrial process used to change unsaturated fats, occurring as oils, to saturated fats (solid shortenings such as Crisco) in which the C=C bonds have been converted to C—C bonds through addition of hydrogen.

A simple example of hydrogenation involves ethylene:
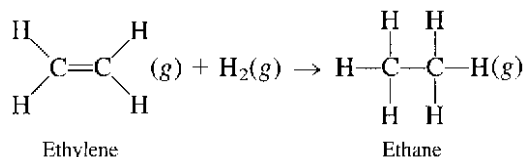
This reaction is quite slow at normal temperatures, mainly because the strong bond in the hydrogen molecule results in a large activation energy for the reaction. However, the

FIGURE 12.16
Effect of a catalyst on the number of reaction-producing collisions. Because a catalyst provides a reaction pathway with a lower activation energy, a much greater fraction of the collisions is effective for the catalyzed pathway (b) than for the uncatalyzed pathway (a) (at a given temperature). This allows reactants to become products at a much higher rate, even though there is no temperature increase.

reaction rate can be greatly increased by using a solid catalyst of platinum, palladium, or nickel. The hydrogen and ethylene adsorb on the catalyst surface, where the reaction occurs. The main function of the catalyst apparently is to allow formation of metal–hydrogen interactions that weaken the H—H bonds and facilitate the reaction. The mechanism is illustrated in Fig. 12.17.

Typically, heterogeneous catalysis involves four steps:

1. Adsorption and activation of the reactants

2. Migration of the adsorbed reactants on the surface

3. Reaction of the adsorbed substances

4. Escape, or *desorption,* of the products

Heterogeneous catalysis also occurs in the oxidation of gaseous sulfur dioxide to gaseous sulfur trioxide. This process is especially interesting because it illustrates both positive and negative consequences of chemical catalysis.

The negative side is the formation of damaging air pollutants. Recall that sulfur dioxide, a toxic gas with a choking odor, is formed whenever sulfur-containing fuels are burned. However, it is sulfur trioxide that causes most of the environmental damage, mainly through the production of acid rain. When sulfur trioxide combines with a droplet of water, sulfuric acid is formed:

$$H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq)$$

This sulfuric acid can cause considerable damage to vegetation, buildings and statues, and fish populations.

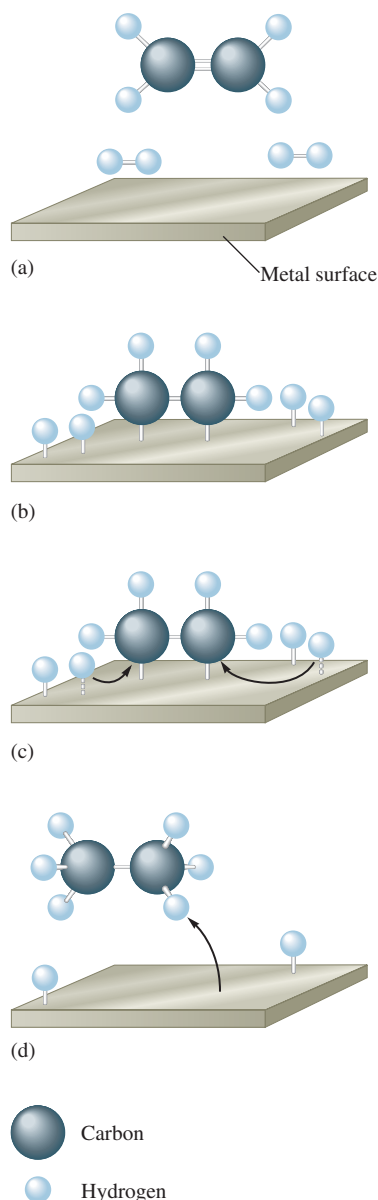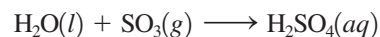Sulfur dioxide is *not* rapidly oxidized to sulfur trioxide in clean, dry air. Why, then, is there a problem? The answer is catalysis. Dust particles and water droplets catalyze the reaction between SO_2 and O_2 in the air.

On the positive side, the heterogeneous catalysis of the oxidation of SO_2 is used to advantage in the manufacture of sulfuric acid, where the reaction of O_2 and SO_2 to form SO_3 is catalyzed by a solid mixture of platinum and vanadium(V) oxide.

Heterogeneous catalysis is also utilized in the catalytic converters in automobile exhaust systems. The exhaust gases, containing compounds such as nitric oxide, carbon monoxide, and unburned hydrocarbons, are passed through a converter containing beads of solid catalyst (see Fig. 12.18). The catalyst promotes the conversion of carbon monoxide to carbon dioxide, hydrocarbons to carbon dioxide and water, and nitric oxide to nitrogen gas to lessen the environmental impact of the exhaust gases. However, this beneficial catalysis can, unfortunately, be accompanied by the unwanted catalysis of the oxidation of SO_2 to SO_3, which reacts with the moisture present to form sulfuric acid.

Because of the complex nature of the reactions that take place in the converter, a mixture of catalysts is used. The most effective catalytic materials are transition metal oxides and noble metals such as palladium and platinum.

Homogeneous Catalysis

A homogeneous catalyst exists in the same phase as the reacting molecules. There are many examples in both the gas and liquid phases. One such example is the unusual catalytic behavior of nitric oxide toward ozone. In the troposphere, that part of the atmosphere closest to earth, nitric oxide catalyzes ozone production. However, in the upper atmosphere it catalyzes the decomposition of ozone. Both these effects are unfortunate environmentally.

In the lower atmosphere, NO is produced in any high-temperature combustion process where N_2 is present. The reaction

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

(a)

Metal surface

(b)

(c)

(d)

Carbon

Hydrogen

FIGURE 12.17
Heterogeneous catalysis of the hydrogenation of ethylene. (a) The reactants above the metal surface. (b) Hydrogen is adsorbed onto the metal surface, forming metal–hydrogen bonds and breaking the H—H bonds. The π bond in ethylene is broken and metal–carbon bonds are formed during adsorption. (c) The adsorbed molecules and atoms migrate toward each other on the metal surface, forming new C—H bonds. (d) The C atoms in ethane (C_2H_6) have completely saturated bonding capacities and so cannot bind strongly to the metal surfaces. The C_2H_6 molecule thus escapes.

CHEMICAL IMPACT

Automobiles: Air Purifiers?

Outlandish as it may seem, a new scheme has been proposed to turn automobiles into air purifiers, devouring the pollutants ozone and carbon monoxide. Engelhard Corporation, an Iselin, New Jersey, company that specializes in the manufacture of catalytic converters for automotive exhaust systems, has developed a catalyst that decomposes ozone to oxygen and converts carbon monoxide to carbon dioxide. Engelhard proposes to paint the catalyst on auto-

mobile radiators and air-conditioner compressors where fans draw large volumes of air for cooling purposes. The catalyst works well at the warm temperatures present on the surfaces of these devices. The idea is to let cars destroy pollutants using nothing but the catalyst and waste radiator heat.

It's an intriguing idea. The residents of Los Angeles drive nearly 300 million miles every day. At that rate, they could process a lot of air.

is very slow at normal temperatures because of the very strong $N\equiv N$ and $O=O$ bonds. However, at elevated temperatures, such as those found in the internal combustion engines of automobiles, significant quantities of NO form. Some of this NO is converted back to N_2 in the catalytic converter, but significant amounts escape into the atmosphere to react with oxygen:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
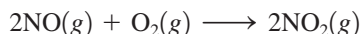
In the atmosphere, NO_2 can absorb light and decompose as follows:

$$NO_2(g) \xrightarrow{\text{Light}} NO(g) + O(g)$$
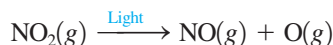
The oxygen atom is very reactive and can combine with oxygen molecules to form ozone:

$$O_2(g) + O(g) \longrightarrow O_3(g)$$

Although O_2 is represented here as the oxidizing agent for NO, the actual oxidizing agent is probably some type of peroxide compound produced by reaction of oxygen with pollutants. The direct reaction of NO and O_2 is very slow.

Ozone is a powerful oxidizing agent that can react with other air pollutants to form substances irritating to the eyes and lungs, and is itself very toxic.

In this series of reactions, nitric oxide is acting as a true catalyst because it assists the production of ozone without being consumed itself. This can be seen by summing the reactions:

$$NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g)$$
$$NO_2(g) \xrightarrow{\text{Light}} NO(g) + O(g)$$
$$\underline{O_2(g) + O(g) \longrightarrow O_3(g)}$$
$$\tfrac{3}{2}O_2(g) \longrightarrow O_3(g)$$

FIGURE 12.18
The exhaust gases from an automobile engine are passed through a catalytic converter to minimize environmental damage.

Engine   Exhaust gases   Exhaust gases

CO →   CO₂ →
NO →   Catalytic converter   N₂ →

In the upper atmosphere, the presence of nitric oxide has the opposite effect—the depletion of ozone. The series of reactions involved is

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$
$$\underline{O(g) + NO_2(g) \longrightarrow NO(g) + O_2(g)}$$
$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$
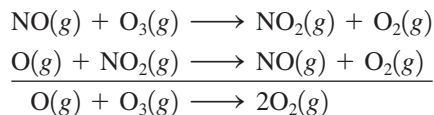
Nitric oxide is again catalytic, but here its effect is to change O_3 to O_2. This is a potential problem because O_3, which absorbs ultraviolet light, is necessary to protect us from the harmful effects of this high-energy radiation. That is, we want O_3 in the upper atmosphere to block ultraviolet radiation from the sun but not in the lower atmosphere, where we would have to breathe it and its oxidation products.

The ozone layer is also threatened by *Freons,* a group of stable, noncorrosive compounds, until recently, used as refrigerants and as propellants in aerosol cans. The most commonly used substance of this type was Freon-12 (CCl_2F_2). The chemical inertness of Freons makes them valuable but also creates a problem, since they remain in the environment a long time. Eventually, they migrate into the upper atmosphere to be decomposed by high-energy light. Among the decomposition products are chlorine atoms:

$$CCl_2F_2(g) \xrightarrow{\text{Light}} CClF_2(g) + Cl(g)$$
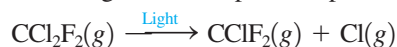
These chlorine atoms can catalyze the decomposition of ozone:
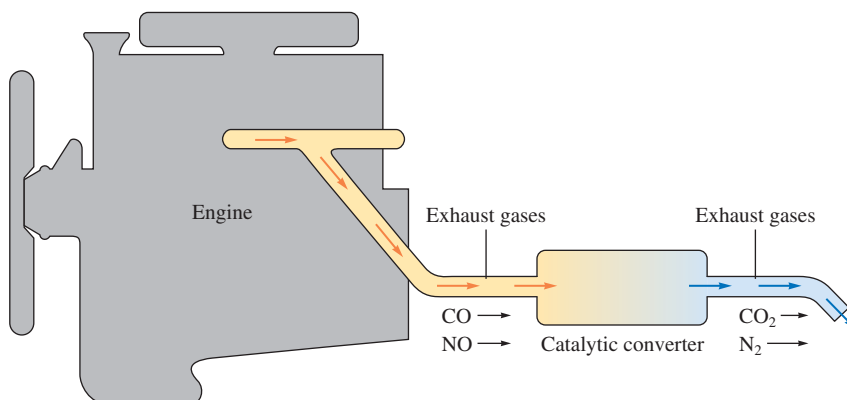
$$Cl(g) + O_3(g) \longrightarrow ClO(g) + O_2(g)$$
$$\underline{O(g) + ClO(g) \longrightarrow Cl(g) + O_2(g)}$$
$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$
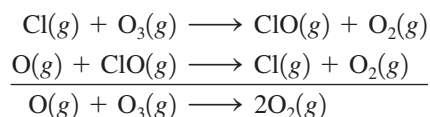
The problem of Freons has been brought into strong focus by the discovery of a mysterious "hole" in the ozone layer in the stratosphere over Antarctica. Studies performed there to find the reason for the hole have found unusually high levels of chlorine monoxide (ClO). This strongly implicates the Freons in the atmosphere as being responsible for the ozone destruction.

Because they pose environmental problems, Freons have been banned by international agreement. Substitute compounds are now being used.

Freon-12

Ozone

Sep 22 2004
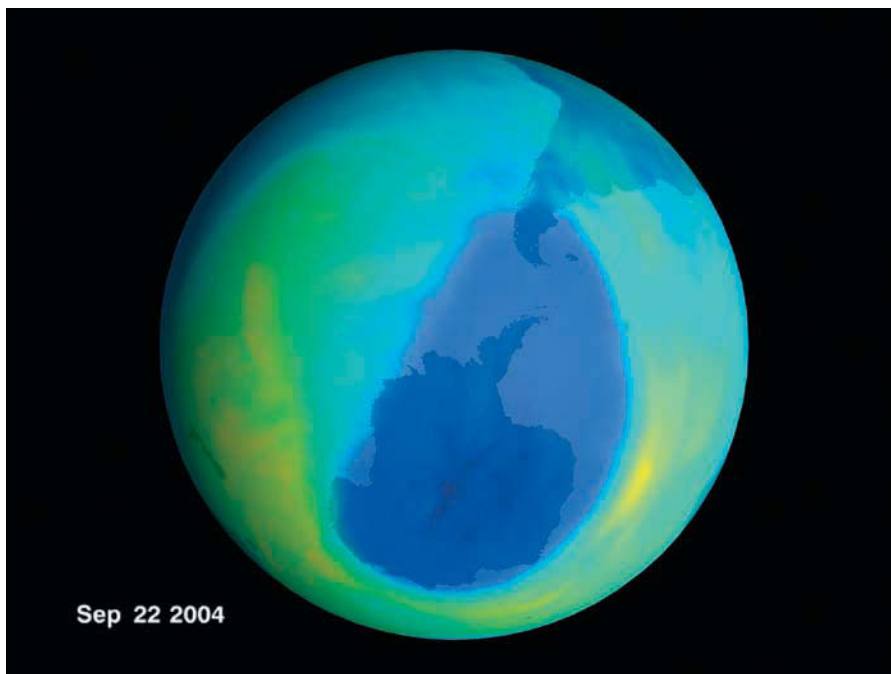
This graphic shows data from the Total Ozone Mapping Spectrometer (TOMS) Earth Probe.

CHEMICAL IMPACT

Enzymes: Nature's Catalysts

The most impressive examples of homogeneous catalysis occur in nature, where the complex reactions necessary for plant and animal life are made possible by enzymes. Enzymes are large molecules specifically tailored to facilitate a given type of reaction. Usually enzymes are proteins, an important class of biomolecules constructed from α-amino acids that have the general structure

where R represents any one of 20 different substituents. These amino acid molecules can be "hooked together" to form a *polymer* (a word meaning "many parts") called a *protein*. The general structure of a protein can be represented as follows:

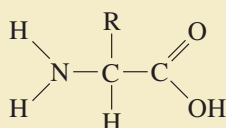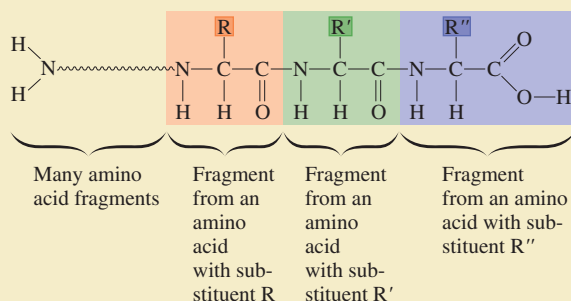

Since specific proteins are needed by the human body, the proteins in food must be broken into their constituent amino acids, which are then used to construct new proteins in the body's cells. The reaction in which a protein is broken down one amino acid at a time is shown in Fig. 12.19. Note that in this reaction a water molecule reacts with a protein molecule to produce an amino acid and a new protein containing one less amino acid. Without the enzymes found in human cells, this reaction would be much too slow to be useful. One of these enzymes is *carboxypeptidase-A,* a zinc-containing protein (Fig. 12.20).

Carboxypeptidase-A captures the protein to be acted on (called the *substrate*) in a special groove and positions the substrate so that the end is in the active site, where the catalysis occurs (Fig. 12.21). Note that the Zn^{2+} ion bonds to the oxygen of the C=O (carbonyl) group. This polarizes the electron density in the carbonyl group, allowing the neigh-
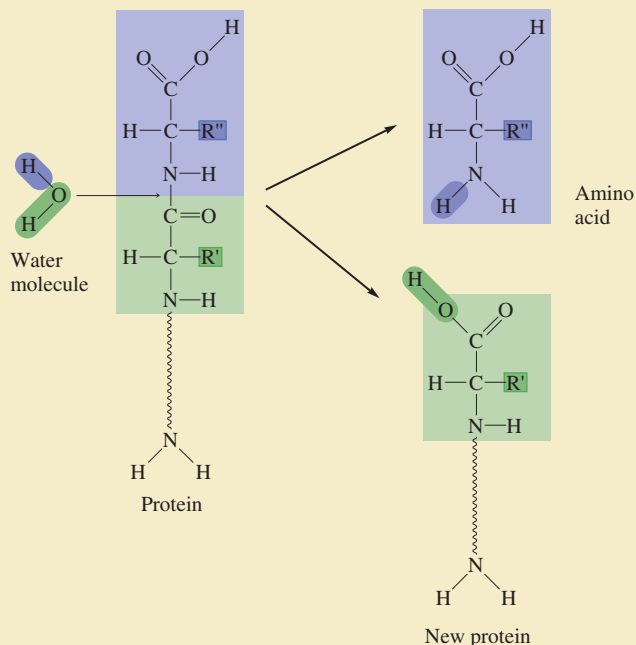
FIGURE 12.19
The removal of the end amino acid from a protein by reaction with a molecule of water. The products are an amino acid and a new, smaller protein.

boring C—N bond to be broken much more easily. When the reaction is completed, the remaining portion of the substrate protein and the newly formed amino acid are released by the enzyme.

The process just described for carboxypeptidase-A is characteristic of the behavior of other enzymes. Enzyme catalysis can be represented by the series of reactions shown below:

$$E + S \longrightarrow E \cdot S$$
$$E \cdot S \longrightarrow E + P$$
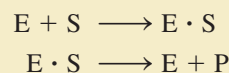
where E represents the enzyme, S represents the substrate, E · S represents the enzyme–substrate complex, and P represents the products. The enzyme and substrate form a complex, where the reaction occurs. The enzyme then releases the product and is ready to repeat the process. The most amazing thing about enzymes is their efficiency. Because an enzyme plays its catalytic role over and over and very rapidly, only a tiny amount of enzyme is required. This makes the isolation of enzymes for study quite difficult.
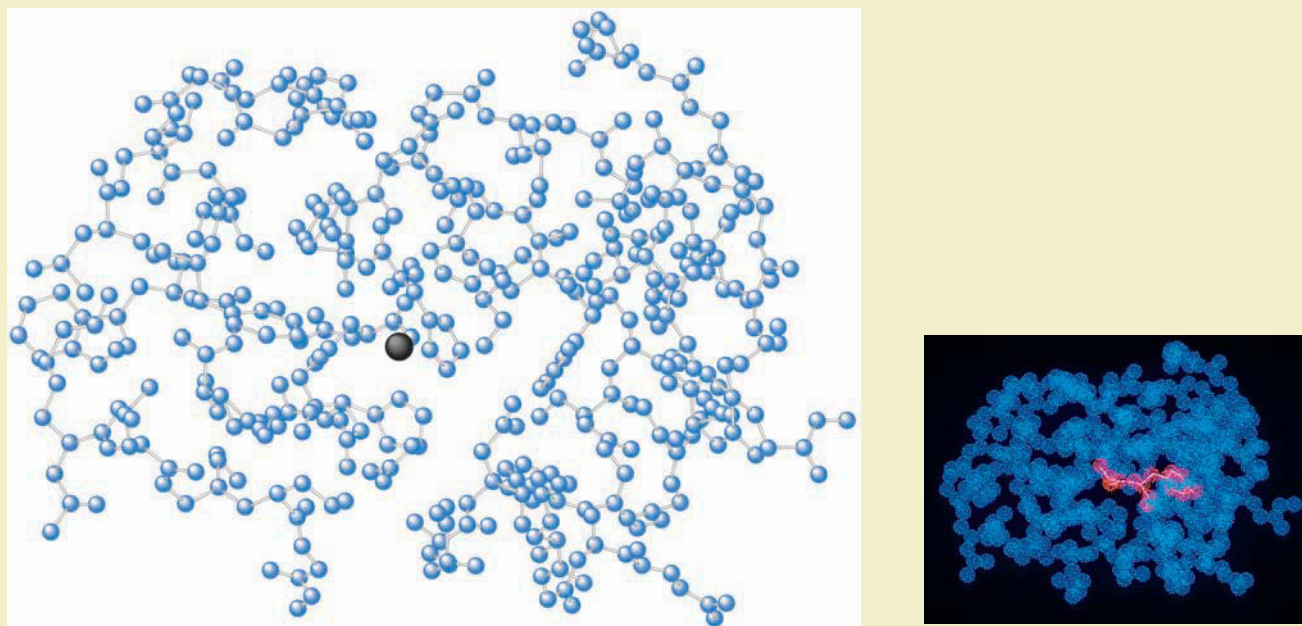
(a)   (b)

FIGURE 12.20
(a) The structure of the enzyme carboxypeptidase-A, which contains 307 amino acids. The zinc ion is shown above as a black sphere in the center. (b) Carboxypeptidase-A with a substrate (pink) in place.

FIGURE 12.21
Protein–substrate interaction. The substrate is shown in black and red, with the red representing the terminal amino acid. Blue indicates side chains from the enzyme that help bind the substrate.
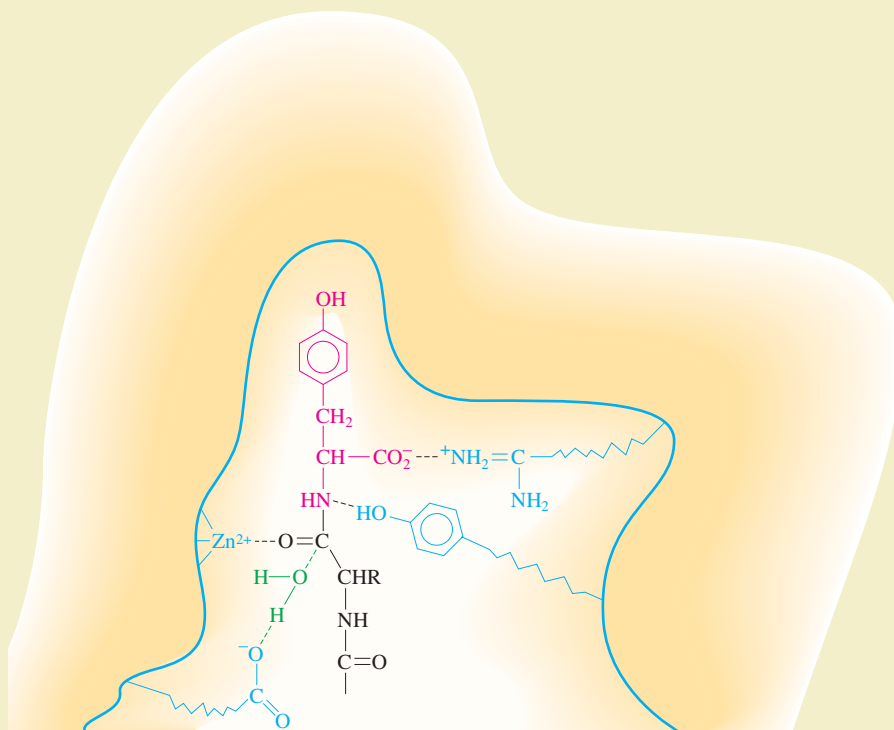
Key Terms

chemical kinetics

Section 12.1
reaction rate
instantaneous rate

Section 12.2
rate law
rate constant
order
(differential) rate law
integrated rate law

Section 12.3
method of initial rates
initial rate
overall reaction order

Section 12.4
first-order reaction
integrated first-order rate law
half-life of a reactant
integrated second-order rate law
zero-order reaction
integrated zero-order rate law
pseudo-first-order rate law

Section 12.6
reaction mechanism
intermediate
elementary step
molecularity
unimolecular step
bimolecular step
termolecular step
rate-determining step

Section 12.7
collision model
activation energy
activated complex (transition state)
molecular orientations
steric factor
Arrhenius equation
frequency factor

Section 12.8
enzyme
catalyst
homogeneous catalyst
heterogeneous catalyst
adsorption

For Review

Chemical kinetics
- The study of the factors that control the rate (speed) of a chemical reaction
  - Rate is defined in terms of the change in concentration of a given reaction component per unit time
  - Kinetic measurements are often made under conditions where the reverse reaction is insignificant
- The kinetic and thermodynamic properties of a reaction are not fundamentally related

Rate laws
- Differential rate law: describes the rate as a function of concentration

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

  - k is the rate constant
  - n is the order; not related to the coefficients in the balanced equation
- Integrated rate law: describes the concentration as a function of time
  - For a reaction of the type

$$aA \longrightarrow \text{products}$$
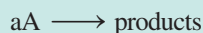
  for which

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

  $n = 0$: $\qquad [A] = -kt + [A]_0$

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

  $n = 1$: $\qquad \ln[A] = -kt + \ln[A]_0$

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

  $n = 2$: $\qquad \dfrac{1}{[A]} = kt + \dfrac{1}{[A]_0}$

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

  - The value of k can be determined from the plot of the appropriate function of [A] versus t

Reaction mechanism
- Series of elementary steps by which an overall reaction occurs
  - Elementary step: rate law for the step can be written from the molecularity of the reaction
- Two requirements for an acceptable mechanism:
  - The elementary steps sum to give the correct overall balanced equation
  - The mechanism agrees with the experimentally determined rate law
- Simple reactions can have an elementary step that is slower than all of the other steps; which is called the rate-determining step.

Kinetic models
- The simplest model to account for reaction kinetics is the collision model
  - Molecules must collide to react
  - The collision kinetic energy furnishes the potential energy needed to enable the reactants to rearrange to form products

- A certain threshold energy called the activation energy (E_a) is necessary for a reaction to occur
- The relative orientations of the colliding reactants are also a determining factor in the reaction rate
- This model leads to the Arrhenius equation:

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

- *A* depends on the collision frequency and relative orientation of the molecules
- The value of E_a can be found by obtaining the values of k at several temperatures

Catalyst
- Speeds up a reaction without being consumed
- Works by providing a lower-energy pathway for the reaction
- Enzymes are biological catalysts
- Catalysts can be classified as homogeneous or heterogeneous
  - Homogeneous: exist in the same phase as the reactants
  - Heterogeneous: exist in a different phase than the reactants

REVIEW QUESTIONS

1. Define *reaction rate*. Distinguish between the initial rate, average rate, and instantaneous rate of a chemical reaction. Which of these rates is usually fastest? The initial rate is the rate used by convention. Give a possible explanation as to why.

2. Distinguish between the differential rate law and the integrated rate law. Which of these is often called just the "rate law"? What is k in a rate law, and what are orders in a rate law? Explain.

3. One experimental procedure that can be used to determine the rate law of a reaction is the method of initial rates. What data are gathered in the method of initial rates, and how are these data manipulated to determine k and the orders of the species in the rate law? Are the units for k, the rate constant, the same for all rate laws? Explain. If a reaction is first order in A, what happens to the rate if [A] is tripled? If the initial rate for a reaction increases by a factor of 16 when [A] is quadrupled, what is the order of n? If a reaction is third order in A and [A] is doubled, what happens to the initial rate? If a reaction is zero order, what effect does [A] have on the initial rate of a reaction?

4. The initial rate for a reaction is equal to the slope of the tangent line at $t \approx 0$ in a plot of [A] versus time. From calculus, initial rate $= \dfrac{-d[A]}{dt}$. Therefore, the differential rate law for a reaction is Rate $= \dfrac{-d[A]}{dt} = k[A]^n$. Assuming you have some calculus in your background, derive the zero-, first-, and second-order integrated rate laws using the differential rate law.

5. Consider the zero-, first-, and second-order integrated rate laws. If you have concentration versus time data for some species in a reaction, what plots would you make to "prove" a reaction is either zero, first, or second order? How would the rate constant, k, be determined from such a plot? What does the y-intercept equal in each plot? When a rate law contains the concentration of two or more species, how can plots be used to determine k and the orders of the species in the rate law?

6. Derive expressions for the half-life of zero-, first-, and second-order reactions using the integrated rate law for each order. How does each half-life depend on

concentration? If the half-life for a reaction is 20. seconds, what would be the second half-life assuming the reaction is either zero, first, or second order?

7. Define each of the following.
   a. elementary step
   b. molecularity
   c. reaction mechanism
   d. intermediate
   e. rate-determining step

   What two requirements must be met to call a mechanism plausible? Why say a "plausible" mechanism instead of the "correct" mechanism? Is it true that most reactions occur by a one-step mechanism? Explain.

8. What is the premise underlying the collision model? How is the rate affected by each of the following?
   a. activation energy
   b. temperature
   c. frequency of collisions
   d. orientation of collisions

   Sketch a potential energy versus reaction progress plot for an endothermic reaction and for an exothermic reaction. Show ΔE and E_a in both plots. When concentrations and temperatures are equal, would you expect the rate of the forward reaction to be equal to, greater than, or less than the rate of the reverse reaction if the reaction is exothermic? Endothermic?

9. Give the Arrhenius equation. Take the natural log of both sides and place this equation in the form of a straight-line equation ($y = mx + b$). What data would you need and how would you graph those data to get a linear relationship using the Arrhenius equation? What does the slope of the straight line equal? What does the y-intercept equal? What are the units of R in the Arrhenius equation? Explain how if you know the rate constant value at two different temperatures, you can determine the activation energy for the reaction.

10. Why does a catalyst increase the rate of a reaction? What is the difference between a homogeneous catalyst and a heterogeneous catalyst? Would a given reaction necessarily have the same rate law for both a catalyzed and an uncatalyzed pathway? Explain.

Active Learning Questions*

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. Define *stability* from both a kinetic and thermodynamic perspective. Give examples to show the differences in these concepts.

2. Describe at least two experiments you could perform to determine a rate law.

3. Make a graph of [A] versus time for zero-, first-, and second-order reactions. From these graphs, compare successive half-lives.

---

*In the Questions and the Exercises, the term *rate law* always refers to the differential rate law.

4. How does temperature affect k, the rate constant? Explain.

5. Consider the following statements: "In general, the rate of a chemical reaction increases a bit at first because it takes a while for the reaction to get 'warmed up.' After that, however, the rate of the reaction decreases because its rate is dependent on the concentrations of the reactants, and these are decreasing." Indicate everything that is correct in these statements, and indicate everything that is incorrect. Correct the incorrect statements and explain.

6. For the reaction A + B → C, explain at least two ways in which the rate law could be zero order in chemical A.

7. A friend of yours states, "A balanced equation tells us how chemicals interact. Therefore, we can determine the rate law directly from the balanced equation." What do you tell your friend?

8. Provide a conceptual rationale for the differences in the half-lives of zero-, first-, and second-order reactions.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide.*

Questions

9. Define what is meant by unimolecular and bimolecular steps. Why are termolecular steps infrequently seen in chemical reactions?

10. Hydrogen reacts explosively with oxygen. However, a mixture of H_2 and O_2 can exist indefinitely at room temperature. Explain why H_2 and O_2 do not react under these conditions.

11. For the reaction

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

the observed rate law is

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

Which of the changes listed below would affect the value of the rate constant k?
a. increasing the partial pressure of hydrogen gas
b. changing the temperature
c. using an appropriate catalyst

12. The rate law for a reaction can be determined only from experiment and not from the balanced equation. Two experimental procedures were outlined in Chapter 12. What are these two procedures? Explain how each method is used to determine rate laws.

13. Table 12.2 illustrates how the average rate of a reaction decreases with time. Why does the average rate decrease with time? How does the instantaneous rate of a reaction depend on time? Why are initial rates used by convention?

14. The type of rate law for a reaction, either the differential rate law or the integrated rate, is usually determined by which data is easiest to collect. Explain.

15. The initial rate of a reaction doubles as the concentration of one of the reactants is quadrupled. What is the order of this reactant? If a reactant has a −1 order, what happens to the initial rate when the concentration of that reactant increases by a factor of two?

16. Reactions that require a metal catalyst are often zero order after a certain amount of reactant(s) are present. Explain.

17. The central idea of the collision model is that molecules must collide in order to react. Give two reasons why not all collisions of reactant molecules result in product formation.

18. Would the slope of a ln k versus $1/T$ (K) plot for a catalyzed reaction be more of less negative than the slope of the ln k versus $1/T$ (K) plot for the uncatalyzed reaction? Explain.

Exercises

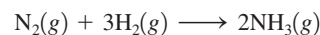In this section similar exercises are paired.

Reaction Rates

19. Consider the reaction

$$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$
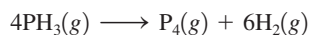
If, in a certain experiment, over a specific time period, 0.0048 mol PH_3 is consumed in a 2.0-L container each second of reaction, what are the rates of production of P_4 and H_2 in this experiment?

20. In the Haber process for the production of ammonia,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

what is the relationship between the rate of production of ammonia and the rate of consumption of hydrogen?

21. At 40°C, $H_2O_2(aq)$ will decompose according to the following reaction:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$
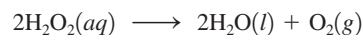
The following data were collected for the concentration of H_2O_2 at various times.

Time (s)	$[H_2O_2]$ (mol/L)
0	1.000
2.16×10^4	0.500
4.32×10^4	0.250

a. Calculate the average rate of decomposition of H_2O_2 between 0 and 2.16×10^4 s. Use this rate to calculate the average rate of production of $O_2(g)$ over the same time period.
b. What are these rates for the time period 2.16×10^4 s to 4.32×10^4 s?

22. Consider the general reaction

$$aA + bB \longrightarrow cC$$

and the following average rate data over some time period Δt:

$$-\frac{\Delta A}{\Delta t} = 0.0080 \text{ mol/L} \cdot \text{s}$$

$$-\frac{\Delta B}{\Delta t} = 0.0120 \text{ mol/L} \cdot \text{s}$$

$$\frac{\Delta C}{\Delta t} = 0.0160 \text{ mol/L} \cdot \text{s}$$

Determine a set of possible coefficients to balance this general reaction.

23. What are the units for each of the following if the concentrations are expressed in moles per liter and the time in seconds?
a. rate of a chemical reaction
b. rate constant for a zero-order rate law
c. rate constant for a first-order rate law
d. rate constant for a second-order rate law
e. rate constant for a third-order rate law

24. The rate law for the reaction

$$Cl_2(g) + CHCl_3(g) \longrightarrow HCl(g) + CCl_4(g)$$

is $\text{Rate} = k[Cl_2]^{1/2}[CHCl_3]$

What are the units for k, assuming time in seconds and concentration in mol/L?

Rate Laws from Experimental Data: Initial Rates Method

25. The reaction

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

was studied at $-10°C$. The following results were obtained where
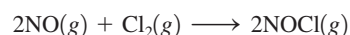
$$\text{Rate} = -\frac{\Delta[Cl_2]}{\Delta t}$$

[NO]$_0$ (mol/L)	[Cl$_2$]$_0$ (mol/L)	Initial Rate (mol/L · min)
0.10	0.10	0.18
0.10	0.20	0.36
0.20	0.20	1.45

a. What is the rate law?
b. What is the value of the rate constant?

26. The reaction

$$2I^-(aq) + S_2O_8^{2-}(aq) \longrightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

was studied at 25°C. The following results were obtained where

$$\text{Rate} = -\frac{\Delta[S_2O_8^{2-}]}{\Delta t}$$

[I$^-$]$_0$ (mol/L)	[S$_2$O$_8^{2-}$]$_0$ (mol/L)	Initial Rate (mol/L · s)
0.080	0.040	12.5×10^{-6}
0.040	0.040	6.25×10^{-6}
0.080	0.020	6.25×10^{-6}
0.032	0.040	5.00×10^{-6}
0.060	0.030	7.00×10^{-6}

a. Determine the rate law.
b. Calculate a value for the rate constant for each experiment and an average value for the rate constant.

27. The decomposition of nitrosyl chloride was studied:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$
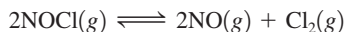
The following data were obtained where

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

[NOCl]$_0$ (molecules/cm^3)	Initial Rate (molecules/cm^3 · s)
3.0×10^{16}	5.98×10^4
2.0×10^{16}	2.66×10^4
1.0×10^{16}	6.64×10^3
4.0×10^{16}	1.06×10^5

a. What is the rate law?
b. Calculate the rate constant.

c. Calculate the rate constant when concentrations are given in moles per liter.

28. The following data were obtained for the gas-phase decomposition of dinitrogen pentoxide,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$
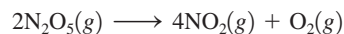
[N$_2$O$_5$]$_0$ (mol/L)	Initial Rate (mol/L · s)
0.0750	8.90×10^{-4}
0.190	2.26×10^{-3}
0.275	3.26×10^{-3}
0.410	4.85×10^{-3}

Defining the rate as $-\Delta[N_2O_5]/\Delta t$, write the rate law and calculate the value of the rate constant.

29. The rate of the reaction between hemoglobin (Hb) and carbon monoxide (CO) was studied at 20°C. The following data were collected with all concentration units in μmol/L. (A hemoglobin concentration of 2.21 μmol/L is equal to 2.21×10^{-6} mol/L.)

[Hb]$_0$ (μmol/L)	[CO]$_0$ (μmol/L)	Initial Rate (μmol/L · s)
2.21	1.00	0.619
4.42	1.00	1.24
4.42	3.00	3.71

a. Determine the orders of this reaction with respect to Hb and CO.
b. Determine the rate law.
c. Calculate the value of the rate constant.
d. What would be the initial rate for an experiment with $[Hb]_0 = 3.36$ μmol/L and $[CO]_0 = 2.40$ μmol/L?

30. The following data were obtained for the reaction

$$2ClO_2(aq) + 2OH^-(aq) \longrightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$$

where

$$\text{Rate} = -\frac{\Delta[ClO_2]}{\Delta t}$$

[ClO$_2$]$_0$ (mol/L)	[OH$^-$]$_0$ (mol/L)	Initial Rate (mol/L · s)
0.0500	0.100	5.75×10^{-2}
0.100	0.100	2.30×10^{-1}
0.100	0.0500	1.15×10^{-1}

a. Determine the rate law and the value of the rate constant.
b. What would be the initial rate for an experiment with $[ClO_2]_0 = 0.175$ mol/L and $[OH^-]_0 = 0.0844$ mol/L?

Integrated Rate Laws

31. The decomposition of hydrogen peroxide was studied, and the following data were obtained at a particular temperature:

Time (s)	[H$_2$O$_2$] (mol/L)
0	1.00
120 ± 1	0.91
300 ± 1	0.78
600 ± 1	0.59
1200 ± 1	0.37
1800 ± 1	0.22
2400 ± 1	0.13
3000 ± 1	0.082
3600 ± 1	0.050

Assuming that

$$\text{Rate} = -\frac{\Delta[H_2O_2]}{\Delta t}$$

determine the rate law, the integrated rate law, and the value of the rate constant. Calculate [H$_2$O$_2$] at 4000. s after the start of the reaction.

32. A certain reaction has the following general form:

$$aA \longrightarrow bB$$

At a particular temperature and $[A]_0 = 2.00 \times 10^{-2}\,M$, concentration versus time data were collected for this reaction, and a plot of ln[A] versus time resulted in a straight line with a slope value of $-2.97 \times 10^{-2}\,min^{-1}$.
  a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
  b. Calculate the half-life for this reaction.
  c. How much time is required for the concentration of A to decrease to $2.50 \times 10^{-3}\,M$?

33. The rate of the reaction

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$
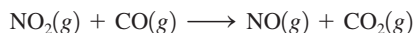
depends only on the concentration of nitrogen dioxide below 225°C. At a temperature below 225°C, the following data were collected:

Time (s)	[NO$_2$] (mol/L)
0	0.500
1.20 × 10^3	0.444
3.00 × 10^3	0.381
4.50 × 10^3	0.340
9.00 × 10^3	0.250
1.80 × 10^4	0.174

Determine the rate law, the integrated law, and the value of the rate constant. Calculate [NO$_2$] at 2.70×10^4 s after the start of the reaction.

34. A certain reaction has the following general form:

$$aA \longrightarrow bB$$
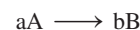
At a particular temperature and $[A]_0 = 2.80 \times 10^{-3}\,M$, concentration versus time data were collected for this reaction, and a plot of 1/[A] versus time resulted in a straight line with a slope value of $+3.60 \times 10^{-2}$ L/mol · s.
  a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
  b. Calculate the half-life for this reaction.
  c. How much time is required for the concentration of A to decrease to $7.00 \times 10^{-4}\,M$?

35. The decomposition of ethanol (C$_2$H$_5$OH) on an alumina (Al$_2$O$_3$) surface

$$C_2H_5OH(g) \longrightarrow C_2H_4(g) + H_2O(g)$$
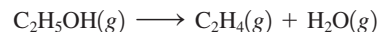
was studied at 600 K. Concentration versus time data were collected for this reaction, and a plot of [A] versus time resulted in a straight line with a slope of -4.00×10^{-5} mol/L · s.
  a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
  b. If the initial concentration of C$_2$H$_5$OH was $1.25 \times 10^{-2}\,M$, calculate the half-life for this reaction.
  c. How much time is required for all the $1.25 \times 10^{-2}\,M$ C$_2$H$_5$OH to decompose?

36. At 500 K in the presence of a copper surface, ethanol decomposes according to the equation

$$C_2H_5OH(g) \longrightarrow CH_3CHO(g) + H_2(g)$$

The pressure of C$_2$H$_5$OH was measured as a function of time and the following data were obtained:

Time (s)	$P_{C_2H_5OH}$ (torr)
0	250.
100.	237
200.	224
300.	211
400.	198
500.	185

Since the pressure of a gas is directly proportional to the concentration of gas, we can express the rate law for a gaseous reaction in terms of partial pressures. Using the above data, deduce the rate law, the integrated rate law, and the value of the rate constant, all in terms of pressure units in atm and time in seconds. Predict the pressure of C$_2$H$_5$OH after 900. s from the start of the reaction. (*Hint:* To determine the order of the reaction with respect to C$_2$H$_5$OH, compare how the pressure of C$_2$H$_5$OH decreases with each time listing.)

37. The dimerization of butadiene

$$2C_4H_6(g) \longrightarrow C_8H_{12}(g)$$

was studied at 500. K, and the following data were obtained:

Time (s)	$[C_4H_6]$ (mol/L)
195	1.6×10^{-2}
604	1.5×10^{-2}
1246	1.3×10^{-2}
2180	1.1×10^{-2}
6210	0.68×10^{-2}

Assuming that

$$\text{Rate} = -\frac{\Delta[C_4H_6]}{\Delta t}$$

determine the form of the rate law, the integrated rate law, and the rate constant for this reaction. (These are actual experimental data, so they may not give a perfectly straight line.)

38. The rate of the reaction

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

was studied at a certain temperature.
a. In the first set of experiments, NO_2 was in large excess, at a concentration of 1.0×10^{13} molecules/cm^3 with the following data collected:

| Time (s)	$[O]$ (atoms/cm^3)
0	5.0×10^9
1.0×10^{-2}	1.9×10^9
2.0×10^{-2}	6.8×10^8
3.0×10^{-2}	2.5×10^8

What is the order of the reaction with respect to oxygen atoms?
b. The reaction is known to be first order with respect to NO_2. Determine the overall rate law and the value of the rate constant.

39. Experimental data for the reaction

$$A \longrightarrow 2B + C$$
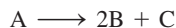
have been plotted in the following three different ways (with concentration units in mol/L):
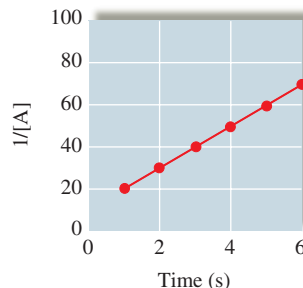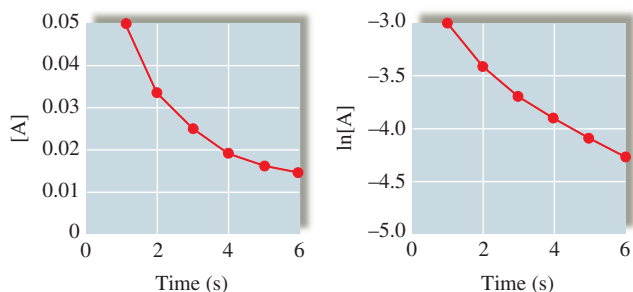
What is the order of the reaction with respect to A and what is the initial concentration of A?

40. Consider the data plotted in Exercise 39 when answering the following questions.
a. What is the concentration of A after 9 s?
b. What are the first three half-lives for this experiment?

41. The reaction

$$A \longrightarrow B + C$$
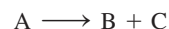
is known to be zero order in A and to have a rate constant of 5.0×10^{-2} mol/L $\cdot$ s at 25°C. An experiment was run at 25°C where $[A]_0 = 1.0 \times 10^{-3}$ M.
a. Write the integrated rate law for this reaction.
b. Calculate the half-life for the reaction.
c. Calculate the concentration of B after 5.0×10^{-3} s has elapsed.

42. The radioactive isotope ^{32}P decays by first-order kinetics and has a half-life of 14.3 days. How long does it take for 95.0% of a sample of ^{32}P to decay?

43. A first-order reaction is 75.0% complete in 320. s.
a. What are the first and second half-lives for this reaction?
b. How long does it take for 90.0% completion?

44. The rate law for the decomposition of phosphine (PH_3) is

$$\text{Rate} = -\frac{\Delta[PH_3]}{\Delta t} = k[PH_3]$$

It takes 120. s for 1.00 M PH_3 to decrease to 0.250 M. How much time is required for 2.00 M PH_3 to decrease to a concentration of 0.350 M?

45. Consider the following initial rate data for the decomposition of compound AB to give A and B:

$[AB]_0$ (mol/L)	Initial Rate (mol/L $\cdot$ s)
0.200	3.20×10^{-3}
0.400	1.28×10^{-2}
0.600	2.88×10^{-2}

Determine the half-life for the decomposition reaction initially having 1.00 M AB present.

46. The rate law for the reaction

$$2NOBr(g) \longrightarrow 2NO(g) + Br_2(g)$$
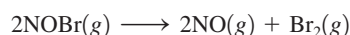
at some temperature is

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

a. If the half-life for this reaction is 2.00 s when $[\text{NOBr}]_0 = 0.900\ M$, calculate the value of k for this reaction.

b. How much time is required for the concentration of NOBr to decrease to 0.100 M?

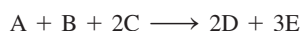**47.** For the reaction A $\rightarrow$ products, successive half-lives are observed to be 10.0, 20.0, and 40.0 min for an experiment in which $[\text{A}]_0 = 0.10\ M$. Calculate the concentration of A at the following times.

a. 80.0 min

b. 30.0 min

48. Consider the hypothetical reaction

$$\text{A} + \text{B} + 2\text{C} \longrightarrow 2\text{D} + 3\text{E}$$

where the rate law is

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

An experiment is carried out where $[\text{A}]_0 = 1.0 \times 10^{-2}\ M$, $[\text{B}]_0 = 3.0\ M$, and $[\text{C}]_0 = 2.0\ M$. The reaction is started, and after 8.0 seconds, the concentration of A is $3.8 \times 10^{-3}\ M$.

a. Calculate k for this reaction.

b. Calculate the half-life for this experiment.

c. Calculate the concentration of A after 13.0 seconds.
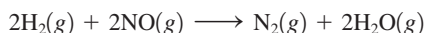
d. Calculate the concentration of C after 13.0 seconds.

Reaction Mechanisms

49. Write the rate laws for the following elementary reactions.
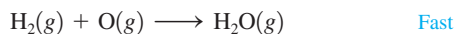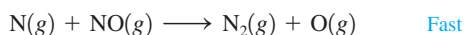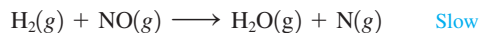
a. $\text{CH}_3\text{NC}(g) \rightarrow \text{CH}_3\text{CN}(g)$

b. $\text{O}_3(g) + \text{NO}(g) \rightarrow \text{O}_2(g) + \text{NO}_2(g)$

c. $\text{O}_3(g) \rightarrow \text{O}_2(g) + \text{O}(g)$

c. $\text{O}_3(g) + \text{O}(g) \rightarrow 2\text{O}_2(g)$

50. The mechanisms shown below have been proposed to explain the kinetics of the reaction considered in Question 11. Which of the following are acceptable mechanisms? Explain.
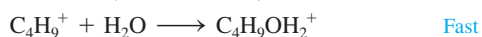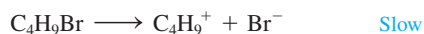
Mechanism I:

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

Mechanism II:

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

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

$\text{H}_2(g) + \text{O}(g) \longrightarrow \text{H}_2\text{O}(g)$ Fast

Mechanism III:

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

$\text{N}_2\text{O}(g) + \text{H}_2(g) \longrightarrow \text{N}_2(g) + \text{H}_2\text{O}(g)$ Fast

51. A proposed mechanism for a reaction is

$\text{C}_4\text{H}_9\text{Br} \longrightarrow \text{C}_4\text{H}_9^+ + \text{Br}^-$ Slow

$\text{C}_4\text{H}_9^+ + \text{H}_2\text{O} \longrightarrow \text{C}_4\text{H}_9\text{OH}_2^+$ Fast

$\text{C}_4\text{H}_9\text{OH}_2^+ + \text{H}_2\text{O} \longrightarrow \text{C}_4\text{H}_9\text{OH} + \text{H}_3\text{O}^+$ Fast

Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction? What are the intermediates in the proposed mechanism?

52. The mechanism for the reaction of nitrogen dioxide with carbon monoxide to form nitric oxide and carbon dioxide is thought to be

$\text{NO}_2 + \text{NO}_2 \longrightarrow \text{NO}_3 + \text{NO}$ Slow

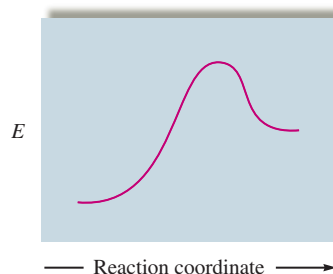$\text{NO}_3 + \text{CO} \longrightarrow \text{NO}_2 + \text{CO}_2$ Fast

Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction?

Temperature Dependence of Rate Constants and the Collision Model

53. For the following reaction profile, indicate

a. the positions of reactants and products.

b. the activation energy.

c. ΔE for the reaction.

54. Draw a rough sketch of the energy profile for each of the following cases:

a. $\Delta E = +10$ kJ/mol, $E_a = 25$ kJ/mol

b. $\Delta E = -10$ kJ/mol, $E_a = 50$ kJ/mol

c. $\Delta E = -50$ kJ/mol, $E_a = 50$ kJ/mol

55. The activation energy for the reaction

$$\text{NO}_2(g) + \text{CO}(g) \longrightarrow \text{NO}(g) + \text{CO}_2(g)$$

is 125 kJ/mol, and ΔE for the reaction is -216 kJ/mol. What is the activation energy for the reverse reaction [$\text{NO}(g) + \text{CO}_2(g) \longrightarrow \text{NO}_2(g) + \text{CO}(g)$]?

56. For a certain process, the activation energy is greater for the forward reaction than for the reverse reaction. Does this reaction have a positive or negative value for ΔE?

57. The rate constant for the gas-phase decomposition of N_2O_5,

$$\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \tfrac{1}{2}\text{O}_2$$
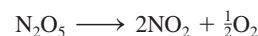
has the following temperature dependence:

T (K)	k (s^{-1})
338	4.9×10^{-3}
318	5.0×10^{-4}
298	3.5×10^{-5}

Make the appropriate graph using these data, and determine the activation energy for this reaction.

58. The reaction

$$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$$
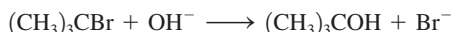
in a certain solvent is first order with respect to $(CH_3)_3CBr$ and zero order with respect to OH^-. In several experiments, the rate constant k was determined at different temperatures. A plot of $\ln(k)$ versus $1/T$ was constructed resulting in a straight line with a slope value of -1.10×10^4 K and y-intercept of 33.5. Assume k has units of s^{-1}.

a. Determine the activation energy for this reaction.
b. Determine the value of the frequency factor A.
c. Calculate the value of k at 25°C.

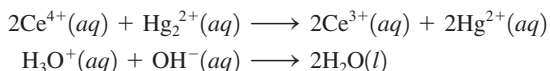**59.** The activation energy for the decomposition of $HI(g)$ to $H_2(g)$ and $I_2(g)$ is 186 kJ/mol. The rate constant at 555 K is 3.52×10^{-7} L/mol · s. What is the rate constant at 645 K?

60. A first-order reaction has rate constants of $4.6 \times 10^{-2}\,s^{-1}$ and $8.1 \times 10^{-2}\,s^{-1}$ at 0°C and 20.°C, respectively. What is the value of the activation energy?
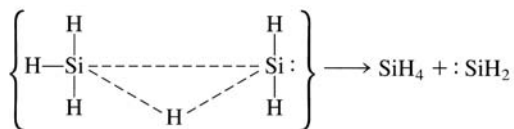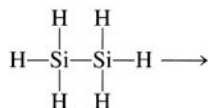
61. A certain reaction has an activation energy of 54.0 kJ/mol. As the temperature is increased from 22°C to a higher temperature, the rate constant increases by a factor of 7.00. Calculate the higher temperature.

62. Chemists commonly use a rule of thumb that an increase of 10 K in temperature doubles the rate of a reaction. What must the activation energy be for this statement to be true for a temperature increase from 25 to 35°C?

63. Which of the following reactions would you expect to proceed at a faster rate at room temperature? Why? (*Hint:* Think about which reaction would have the lower activation energy.)

$$2Ce^{4+}(aq) + Hg_2^{2+}(aq) \longrightarrow 2Ce^{3+}(aq) + 2Hg^{2+}(aq)$$
$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$$

64. One reason suggested for the instability of long chains of silicon atoms is that the decomposition involves the transition state shown below:

$$\begin{array}{cc} H & H \\ | & | \\ H-Si-Si-H \longrightarrow \\ | & | \\ H & H \end{array}$$

$$\left\{ \begin{array}{cc} H & H \\ | & | \\ H-Si------Si: \\ | & | \\ H & H \end{array} \right\} \longrightarrow SiH_4 + :SiH_2$$

The activation energy for such a process is 210 kJ/mol, which is less than either the Si—Si or the Si—H bond energy. Why would a similar mechanism not be expected to play a very important role in the decomposition of long chains of carbon atoms as seen in organic compounds?
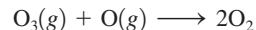
Catalysts

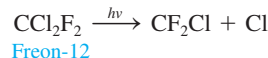**65.** One mechanism for the destruction of ozone in the upper atmosphere is

$$O_3(g) + NO(g) \longrightarrow NO_2(g) + O_2(g) \qquad \text{Slow}$$
$$NO_2(g) + O(g) \longrightarrow NO(g) + O_2(g) \qquad \text{Fast}$$
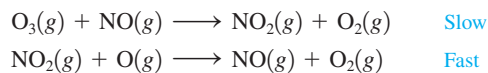
Overall reaction $O_3(g) + O(g) \longrightarrow 2O_2(g)$

a. Which species is a catalyst?
b. Which species is an intermediate?
c. E_a for the uncatalyzed reaction

$$O_3(g) + O(g) \longrightarrow 2O_2$$

is 14.0 kJ. E_a for the same reaction when catalyzed is 11.9 kJ. What is the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25°C? Assume that the frequency factor A is the same for each reaction.

66. One of the concerns about the use of Freons is that they will migrate to the upper atmosphere, where chlorine atoms can be generated by the following reaction:

$$CCl_2F_2 \xrightarrow{hv} CF_2Cl + Cl$$
Freon-12

Chlorine atoms can act as a catalyst for the destruction of ozone. The activation energy for the reaction

$$Cl + O_3 \longrightarrow ClO + O_2$$
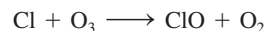
is 2.1 kJ/mol. Which is the more effective catalyst for the destruction of ozone, Cl or NO? (See Exercise 65.)

67. Assuming that the mechanism for the hydrogenation of C_2H_4 given in Section 12.8 is correct, would you predict that the product of the reaction of C_2H_4 with D_2 would be CH_2D—CH_2D or CHD_2—CH_3? How could the reaction of C_2H_4 with D_2 be used to confirm the mechanism for the hydrogenation of C_2H_4 given in Section 12.8?

68. The decomposition of NH_3 to N_2 and H_2 was studied on two surfaces:

Surface	E_a (kJ/mol)
W	163
Os	197

Without a catalyst, the activation energy is 335 kJ/mol.

a. Which surface is the better heterogeneous catalyst for the decomposition of NH_3? Why?
b. How many times faster is the reaction at 298 K on the W surface compared with the reaction with no catalyst present? Assume that the frequency factor A is the same for each reaction.
**c.** The decomposition reaction on the two surfaces obeys a rate law of the form

$$\text{Rate} = k\frac{[NH_3]}{[H_2]}$$

How can you explain the inverse dependence of the rate on the H_2 concentration?

69. A famous chemical demonstration is the "magic genie" procedure, in which hydrogen peroxide decomposes to water and oxygen gas with the aid of a catalyst. The activation energy of this (uncatalyzed) reaction is 70.0 kJ/mol. When the catalyst is added, the activation energy (at 20.°C) is 42.0 kJ/mol. Theoretically, to what temperature (°C) would one have to heat the hydrogen peroxide solution so that the rate of the uncatalyzed reaction is equal to the rate of the catalyzed reaction at 20.°C? Assume the frequency factor A is constant and assume the initial concentrations are the same.

70. The activation energy for a reaction is changed from 184 kJ/mol to 59.0 kJ/mol at 600. K by the introduction of a catalyst. If the uncatalyzed reaction takes about 2400 years to occur, about how long will the catalyzed reaction take? Assume the frequency factor A is constant and assume the initial concentrations are the same.

Additional Exercises

71. The reaction

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
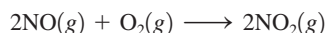
was studied, and the following data were obtained where

$$Rate = -\frac{\Delta[O_2]}{\Delta t}$$

$[NO]_0$ (molecules/cm³)	$[O_2]_0$ (molecules/cm³)	Initial Rate (molecules/cm³ · s)
1.00×10^{18}	1.00×10^{18}	2.00×10^{16}
3.00×10^{18}	1.00×10^{18}	1.80×10^{17}
2.50×10^{18}	2.50×10^{18}	3.13×10^{17}

What would be the initial rate for an experiment where $[NO]_0 = 6.21 \times 10^{18}$ molecules/cm³ and $[O_2]_0 = 7.36 \times 10^{18}$ molecules/cm³?

72. Sulfuryl chloride (SO_2Cl_2) decomposes to sulfur dioxide (SO_2) and chlorine (Cl_2) by reaction in the gas phase. The following pressure data were obtained when a sample containing 5.00×10^{-2} mol sulfuryl chloride was heated to 600. K in a 5.00×10^{-1}-L container.

Time (hours):	0.00	1.00	2.00	4.00	8.00	16.00
$P_{SO_2Cl_2}$ (atm):	4.93	4.26	3.52	2.53	1.30	0.34

Defining the rate as $-\dfrac{\Delta[SO_2Cl_2]}{\Delta t}$,

a. determine the value of the rate constant for the decomposition of sulfuryl chloride at 600. K.
b. what is the half-life of the reaction?
**c.** what fraction of the sulfuryl chloride remains after 20.0 h?

73. For the reaction

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$
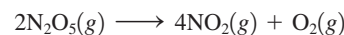
the following data were collected, where

$$Rate = -\frac{\Delta[N_2O_5]}{\Delta t}$$

Time (s)	$T = 338$ K $[N_2O_5]$	$T = 318$ K $[N_2O_5]$
0	1.00×10^{-1} M	1.00×10^{-1} M
100.	6.14×10^{-2} M	9.54×10^{-2} M
300.	2.33×10^{-2} M	8.63×10^{-2} M
600.	5.41×10^{-3} M	7.43×10^{-2} M
900.	1.26×10^{-3} M	6.39×10^{-2} M

Calculate E_a for this reaction.

74. Experimental values for the temperature dependence of the rate constant for the gas-phase reaction

$$NO + O_3 \longrightarrow NO_2 + O_2$$
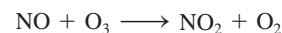
are as follows:

T (K)	k (L/mol · s)
195	1.08×10^9
230.	2.95×10^9
260.	5.42×10^9
298	12.0×10^9
369	35.5×10^9

Make the appropriate graph using these data, and determine the activation energy for this reaction.

75. For enzyme-catalyzed reactions that follow the mechanism

$$E + S \rightleftharpoons E \cdot S$$
$$E \cdot S \rightleftharpoons E + P$$
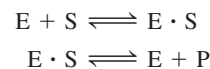
a graph of the rate as a function of [S], the concentration of the substrate, has the following appearance:
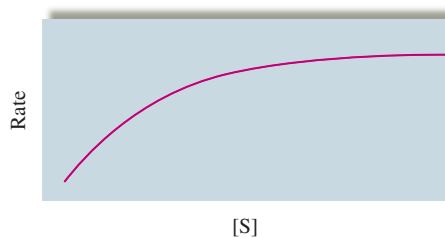
Note that at higher substrate concentrations the rate no longer changes with [S]. Suggest a reason for this.

76. The activation energy of a certain uncatalyzed biochemical re-action is 50.0 kJ/mol. In the presence of a catalyst at 37°C, the rate constant for the reaction increases by a factor of 2.50×10^3 as compared with the uncatalyzed reaction. Assuming the frequency factor A is the same for both the catalyzed and uncatalyzed reactions, calculate the activation energy for the catalyzed reaction.

77. Consider the reaction

$$3A + B + C \rightarrow D + E$$

where the rate law is defined as

$$-\frac{\Delta[A]}{\Delta t} = k[A]^2[B][C]$$

An experiment is carried out where $[B]_0 = [C]_0 = 1.00\ M$ and $[A]_0 = 1.00 \times 10^{-4}\ M$.

a. If after 3.00 min, $[A] = 3.26 \times 10^{-5}\ M$, calculate the value of k.

b. Calculate the half-life for this experiment.

c. Calculate the concentration of B and the concentration of A after 10.0 min.

Challenge Problems

78. Consider a reaction of the type aA → products, in which the rate law is found to be rate $= k[A]^3$ (termolecular reactions are improbable but possible). If the first half-life of the reaction is found to be 40. s, what is the time for the second half-life? *Hint:* Using your calculus knowledge, derive the integrated rate law from the differential rate law for a termolecular reaction:

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]^3$$

79. A study was made of the effect of the hydroxide concentration on the rate of the reaction

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

The following data were obtained:

$[I^-]_0$ (mol/L)	$[OCl^-]_0$ (mol/L)	$[OH^-]_0$ (mol/L)	Initial Rate (mol/L · s)
0.0013	0.012	0.10	9.4×10^{-3}
0.0026	0.012	0.10	18.7×10^{-3}
0.0013	0.0060	0.10	4.7×10^{-3}
0.0013	0.018	0.10	14.0×10^{-3}
0.0013	0.012	0.050	18.7×10^{-3}
0.0013	0.012	0.20	4.7×10^{-3}
0.0013	0.018	0.20	7.0×10^{-3}

Determine the rate law and the value of the rate constant for this reaction.

80. Two isomers (A and B) of a given compound dimerize as follows:

$$2A \xrightarrow{k_1} A_2$$
$$2B \xrightarrow{k_2} B_2$$
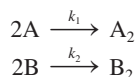
Both processes are known to be second order in reactant, and k_1 is known to be 0.250 L/mol · s at 25°C. In a particular experiment A and B were placed in separate containers at 25°C, where $[A]_0 = 1.00 \times 10^{-2}\ M$ and $[B]_0 = 2.50 \times 10^{-2}\ M$. It was found that after each reaction had progressed for 3.00 min, $[A] = 3.00[B]$. In this case the rate laws are defined as

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k_1[A]^2$$

$$\text{Rate} = -\frac{\Delta[B]}{\Delta t} = k_2[B]^2$$

a. Calculate the concentration of A_2 after 3.00 min.

b. Calculate the value of k_2.

c. Calculate the half-life for the experiment involving A.

81. The reaction

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$
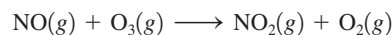
was studied by performing two experiments. In the first experiment the rate of disappearance of NO was followed in the presence of a large excess of O_3. The results were as follows ($[O_3]$ remains effectively constant at 1.0×10^{14} molecules/cm³):

Time (ms)	[NO] (molecules/cm³)
0	6.0×10^8
100 ± 1	5.0×10^8
500 ± 1	2.4×10^8
700 ± 1	1.7×10^8
1000 ± 1	9.9×10^7

In the second experiment [NO] was held constant at 2.0×10^{14} molecules/cm³. The data for the disappearance of O_3 are as follows:

| Time (ms)	[O₃] (molecules/cm³)
0	1.0×10^{10}
50 ± 1	8.4×10^9
100 ± 1	7.0×10^9
200 ± 1	4.9×10^9
300 ± 1	3.4×10^9

a. What is the order with respect to each reactant?

b. What is the overall rate law?

c. What is the value of the rate constant from each set of experiments?

$$\text{Rate} = k'[NO]^x \qquad \text{Rate} = k''[O_3]^y$$

d. What is the value of the rate constant for the overall rate law?

$$\text{Rate} = k[NO]^x[O_3]^y$$

82. Most reactions occur by a series of steps. The energy profile for a certain reaction that proceeds by a two-step mechanism is
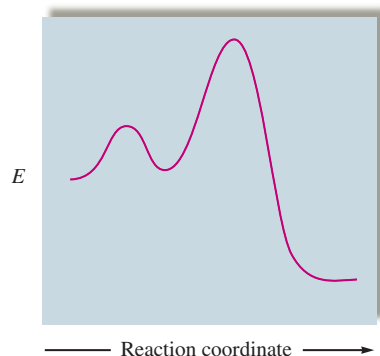

On the energy profile, indicate
a. The positions of reactants and products.
b. The activation energy for the overall reaction.
c. ΔE for the reaction.
d. Which point on the plot represents the energy of the intermediate in the two-step reaction?
e. Which step in the mechanism for this reaction is rate determining, the first or the second step? Explain.

83. Experiments during a recent summer on a number of fireflies (small beetles, *Lampyridaes photinus*) showed that the average interval between flashes of individual insects was 16.3 s at 21.0°C and 13.0 s at 27.8°C.
**a.** What is the apparent activation energy of the reaction that controls the flashing?
b. What would be the average interval between flashes of an individual firefly at 30.0°C?
c. Compare the observed intervals and the one you calculated in part b to the rule of thumb that the Celsius temperature is 54 minus twice the interval between flashes.

84. The decomposition of $NO_2(g)$ occurs by the following bimolecular elementary reaction:

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$
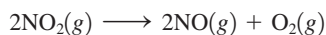
The rate constant at 273 K is 2.3×10^{-12} L/mol · s, and the activation energy is 111 kJ/mol. How long will it take for the concentration of $NO_2(g)$ to decrease from an initial partial pressure of 2.5 atm to 1.5 atm at 500. K? Assume ideal gas behavior.

85. The following data were collected in two studies of the reaction

$$2A + B \longrightarrow C + D$$
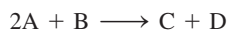
Time (s)	Experiment 1 [A] (mol/L) × 10⁻²	Experiment 2 [A] (mol/L) × 10⁻²
0	10.0	10.0
20.	6.67	5.00
40.	5.00	3.33
60.	4.00	2.50
80.	3.33	2.00
100.	2.86	1.67
120.	2.50	1.43

In experiment 1, $[B]_0 = 5.0\ M$.
In experiment 2, $[B]_0 = 10.0\ M$.

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

a. Why is [B] much greater than [A]?
b. Give the rate law and value for k for this reaction.

**86.** The following data were collected in two studies of the reaction

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

Time (s)	Experiment 1 [H₂] (mol/L)	Experiment 2 [H₂] (mol/L)
0.	1.0×10^{-2}	1.0×10^{-2}
10.	8.4×10^{-3}	5.0×10^{-3}
20.	7.1×10^{-3}	2.5×10^{-3}
30.	?	1.3×10^{-3}
40.	5.0×10^{-3}	6.3×10^{-4}

In experiment 1, $[NO]_0 = 10.0\ M$.
In experiment 2, $[NO]_0 = 20.0\ M$.

$$\text{Rate} = \frac{-\Delta[H_2]}{\Delta t}$$

a. Use the concentration versus time data to determine the rate law for the reaction.
b. Solve for the rate constant (k) for the reaction. Include units.
c. Calculate the concentration of H_2 in experiment 1 at $t = 30.$ s.

87. Consider the hypothetical reaction

$$A + B + 2C \longrightarrow 2D + 3E$$
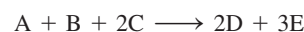
In a study of this reaction three experiments were run at the same temperature. The rate is defined as $-\Delta[B]/\Delta t$.

Experiment 1:

$$[A]_0 = 2.0\ M \quad [B]_0 = 1.0 \times 10^{-3}\ M \quad [C]_0 = 1.0\ M$$

[B] (mol/L)	Time (s)
2.7×10^{-4}	1.0×10^5
1.6×10^{-4}	2.0×10^5
1.1×10^{-4}	3.0×10^5
8.5×10^{-5}	4.0×10^5
6.9×10^{-5}	5.0×10^5
5.8×10^{-5}	6.0×10^5

Experiment 2:

$$[A]_0 = 1.0 \times 10^{-2}\ M \quad [B]_0 = 3.0\ M \quad [C]_0 = 1.0\ M$$

[A] (mol/L)	Time (s)
8.9×10^{-3}	1.0
7.1×10^{-3}	3.0
5.5×10^{-3}	5.0
3.8×10^{-3}	8.0
2.9×10^{-3}	10.0
2.0×10^{-3}	13.0

Experiment 3:

$$[A]_0 = 10.0\,M \quad [B]_0 = 5.0\,M \quad [C]_0 = 5.0 \times 10^{-1}\,M$$

[C] (mol/L)	Time (s)
0.43	1.0×10^{-2}
0.36	2.0×10^{-2}
0.29	3.0×10^{-2}
0.22	4.0×10^{-2}
0.15	5.0×10^{-2}
0.08	6.0×10^{-2}

Write the rate law for this reaction, and calculate the rate constant.

88. Hydrogen peroxide and the iodide ion react in acidic solution as follows:

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \longrightarrow I_3^-(aq) + 2H_2O(l)$$
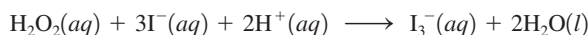
The kinetics of this reaction were studied by following the decay of the concentration of H_2O_2 and constructing plots of $\ln[H_2O_2]$ versus time. All the plots were linear and all solutions had $[H_2O_2]_0 = 8.0 \times 10^{-4}$ mol/L. The slopes of these straight lines depended on the initial concentrations of I^- and H^+. The results follow:

$[I^-]_0$ (mol/L)	$[H^+]_0$ (mol/L)	Slope (min^{-1})
0.1000	0.0400	-0.120
0.3000	0.0400	-0.360
0.4000	0.0400	-0.480
0.0750	0.0200	-0.0760
0.0750	0.0800	-0.118
0.0750	0.1600	-0.174

The rate law for this reaction has the form

$$\text{Rate} = \frac{-\Delta[H_2O_2]}{\Delta t} = (k_1 + k_2[H^+])[I^-]^m[H_2O_2]^n$$

a. Specify the order of this reaction with respect to $[H_2O_2]$ and $[I^-]$.
b. Calculate the values of the rate constants, k_1 and k_2.

c. What reason could there be for the two-term dependence of the rate on $[H^+]$?

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

89. Sulfuryl chloride undergoes first-order decomposition at 320.°C with a half-life of 8.75 h.

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$
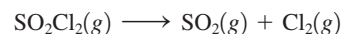
What is the value of the rate constant, k, in s^{-1}? If the initial pressure of SO_2Cl_2 is 791 torr and the decomposition occurs in a 1.25-L container, how many molecules of SO_2Cl_2 remain after 12.5 h?

90. Upon dissolving InCl(s) in HCl, In$^+$(aq) undergoes a disproportionation reaction according to the following unbalanced equation:

$$In^+(aq) \longrightarrow In(s) + In^{3+}(aq)$$
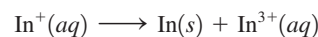
This disproportionation follows first-order kinetics with a half-life of 667 s. What is the concentration of In$^+$(aq) after 1.25 h if the initial solution of In$^+$(aq) was prepared by dissolving 2.38 g of InCl(s) in 5.00×10^2 mL of dilute HCl? What mass of In(s) is formed after 1.25 h?

91. The decomposition of iodoethane in the gas phase proceeds according to the following equation:

$$C_2H_5I(g) \longrightarrow C_2H_4(g) + HI(g)$$
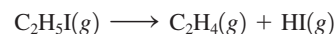
At 660. K, $k = 7.2 \times 10^{-4}$ s^{-1}; at 720. K, $k = 1.7 \times 10^{-2}$ s^{-1}. What is the rate constant for this first-order decomposition at 325°C? If the initial pressure of iodoethane is 894 torr at 245°C, what is the pressure of iodoethane after three half-lives?

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

92. Consider the following reaction:

$$CH_3X + Y \longrightarrow CH_3Y + X$$
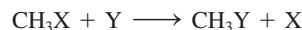
At 25°C, the following two experiments were run, yielding the following data:

Experiment 1: $[Y]_0 = 3.0\,M$

[CH$_3$X] (mol/L)	Time (h)
7.08×10^{-3}	1.0
4.52×10^{-3}	1.5
2.23×10^{-3}	2.3
4.76×10^{-4}	4.0
8.44×10^{-5}	5.7
2.75×10^{-5}	7.0

Experiment 2: $[Y]_0 = 4.5\ M$

[CH$_3$X] (mol/L)	Time (h)
4.50×10^{-3}	0
1.70×10^{-3}	1.0
4.19×10^{-4}	2.5
1.11×10^{-4}	4.0
2.81×10^{-5}	5.5

Experiments also were run at 85°C. The value of the rate constant at 85°C was found to be 7.88×10^{8} (with the time in units of hours), where $[CH_3X]_0 = 1.0 \times 10^{-2}\ M$ and $[Y]_0 = 3.0\ M$.

a. Determine the rate law and the value of k for this reaction at 25°C.
b. Determine the half-life at 85°C.
c. Determine E_a for the reaction.
d. Given that the C—X bond energy is known to be about 325 kJ/mol, suggest a mechanism that explains the results in parts a and c.

Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at **college.hmco.com/ PIC/zumdahl7e.**