11 Rate of Reaction

The rate at which the speeding train is traveling can be expressed in km/h. Similarly, the rate of a reaction can be expressed in *M*/h.

Not every collision,
not every punctilious trajectory
by which billiard-ball complexes
arrive at their calculable meeting
places leads to reaction.

Men (and women) are not as
different from molecules as they
think.

—ROALD HOFFMANN
Excerpt from *Men and Molecules*

Chapter Outline

For a chemical reaction to be feasible, it must occur at a reasonable rate. Consequently, it is important to be able to control the rate of reaction. Most often, this means making it occur more rapidly. When you carry out a reaction in the general chemistry laboratory, you want it to take place quickly. A research chemist trying to synthesize a new drug has the same objective. Sometimes, though, it is desirable to reduce the rate of reaction. The aging process, a complex series of biological oxidations, believed to involve "free radicals" with unpaired electrons such as

is one we would all like to slow down.

This chapter sets forth the principles of **chemical kinetics,** the study of reaction rates. The main emphasis is on those factors that influence rate. These include

- the concentrations of reactants (Sections 11-2 and 11-3).
- the process by which the reaction takes place (Section 11-4).
- the temperature (Section 11-5).
- the presence of a catalyst (Section 11-6).
- the reaction mechanism (Section 11-7).

11-1 Meaning of Reaction Rate

To discuss **reaction rate** meaningfully, it must be defined precisely. ***The rate of reaction is a positive quantity that expresses how the concentration of a reactant or product changes with time.*** To illustrate what this means, consider the reaction

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

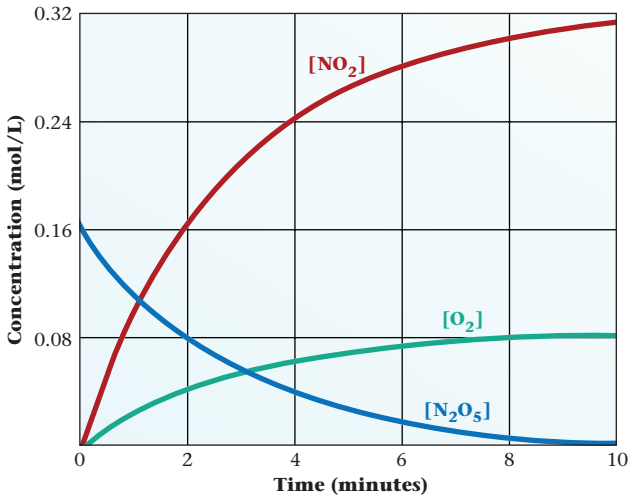


Figure 11.1 Changes in reactant and product concentrations with time. For the reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$, the concentrations of NO_2 and O_2 increase with time, whereas that of N_2O_5 decreases. The reaction rate is defined as $-\Delta[N_2O_5]/\Delta t = \Delta[NO_2]/2\Delta t = \Delta[O_2]/\frac{1}{2}\Delta t$.

As you can see from Figure 11.1, the concentration of N_2O_5 decreases with time; the concentrations of NO_2 and O_2 increase. Because these species have different coefficients in the balanced equation, their concentrations do not change at the same rate. When *one* mole of N_2O_5 decomposes, *two* moles of NO_2 and *one-half* mole of O_2 are formed. This means that

Δ [reactants] $<$ O.
Δ [products] $>$ O.

$$-\Delta[N_2O_5] = \frac{\Delta[NO_2]}{2} = \frac{\Delta[O_2]}{\frac{1}{2}}$$

where $\Delta[\ ]$ refers to the change in concentration in moles per liter. The minus sign in front of the N_2O_5 term is necessary because $[N_2O_5]$ decreases as the reaction takes place; the numbers in the denominator of the terms on the right ($2, \frac{1}{2}$) are the coefficients of these species in the balanced equation. The rate of reaction can now be defined by dividing by the change in time, Δt:

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

More generally, for the reaction

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

where A, B, C, and D represent substances in the gas phase (g) or in aqueous solution (aq), and a, b, c, d are their coefficients in the balanced equation,

$$\text{rate} = \frac{-\Delta[A]}{a\,\Delta t} = \frac{-\Delta[B]}{b\,\Delta t} = \frac{\Delta[C]}{c\,\Delta t} = \frac{\Delta[D]}{d\,\Delta t} \qquad (11.1)$$

This is the defining equation for rate.

To illustrate the use of this expression, suppose that for the formation of ammonia,

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

molecular nitrogen is disappearing at the rate of 0.10 mol/L per minute, that is, $\Delta[N_2]/\Delta t = -0.10$ mol/L·min. From the coefficients of the balanced equation, we see that the concentration of H_2 must be decreasing three times as fast: $\Delta[H_2]/\Delta t = -0.30$ mol/L·min. By the same token, the concentration of NH_3 must be increasing at the rate of 2×0.10 mol/L·min: $\Delta[NH_3]/\Delta t = 0.20$ mol/L·min. It follows that

$$\text{rate} = \frac{-\Delta[N_2]}{\Delta t} = \frac{-\Delta[H_2]}{3\Delta t} = \frac{\Delta[NH_3]}{2\Delta t} = \frac{0.10\ \text{mol}}{\text{L}\cdot\text{min}}$$

By defining rate this way, it is independent of which species we focus on: N_2, H_2, or NH_3.

Notice that reaction rate has the units of concentration divided by time. We will always express concentration in moles per liter. Time, on the other hand, can be expressed in seconds, minutes, hours, ... A rate of 0.10 mol/L · min corresponds to

$$0.10\ \frac{\text{mol}}{\text{L}\cdot\text{min}} \times \frac{1\ \text{min}}{60\ \text{s}} = 1.7 \times 10^{-3}\ \frac{\text{mol}}{\text{L}\cdot\text{s}}$$

or

$$0.10\ \frac{\text{mol}}{\text{L}\cdot\text{min}} \times \frac{60\ \text{min}}{1\ \text{h}} = 6.0\ \frac{\text{mol}}{\text{L}\cdot\text{h}}$$

EXAMPLE 11.1

Consider the following balanced hypothetical equation.

$$A(g) + 3B(g) \longrightarrow C(g) + 2D(g)$$

a Express the average rate of the reaction with respect to each of the products and reactants.

SOLUTION

$$\text{rate} = \frac{-\Delta[A]}{\Delta t} = \frac{-\Delta[B]}{3\Delta t} = \frac{\Delta[C]}{\Delta t} = \frac{\Delta[D]}{2\Delta t}$$

b In the first 20 seconds of the reaction, the concentration of B dropped from 0.100 *M* to 0.0357 *M*. What is the average rate of the reaction in the first 20 seconds of the reaction?

ANALYSIS

Information given:	time, t (20 s) $[B]_o$ (0.100 *M*); [B] after 20 seconds (0.0357 *M*) from part (a): the reaction rate for B $\left(\frac{-\Delta[B]}{3\Delta t}\right)$
Asked for:	average rate of the reaction

STRATEGY

Substitute into the rate equation obtained in part (a).

SOLUTION

average rate	$\text{rate} = \left(\frac{-\Delta[B]}{3\Delta t}\right) = -\frac{(0.0357\ M - 0.100\ M)}{3(20\ \text{s})} = 1.07 \times 10^{-3}\ M/\text{s}$

c Predict the change in the concentration of D during the first 20 seconds of the reaction.

ANALYSIS

Information given:	from part (a): the rate equation for D $\left(\frac{-\Delta[D]}{2\Delta t}\right)$; from part (b): the rate of reaction (1.07×10^{-3} *M*/s)
Asked for:	change in the concentration of D after 20 s, (Δ[D])

STRATEGY

Substitute into the rate equation obtained in part (a).

SOLUTION

Δ[D]	$\text{rate} = \frac{\Delta[D]}{2\Delta t}$; $\Delta[D] = (1.07 \times 10^{-3}\ M/\text{s})(2)(20\ \text{s}) = 0.0428\ M$

END POINT

The answer obtained in part (c) is not the concentration of D after 20 s but rather the change in the concentration of D. If you were given an initial concentration of D ($[D]_o$), then you would be able to obtain [D] after 20 s.

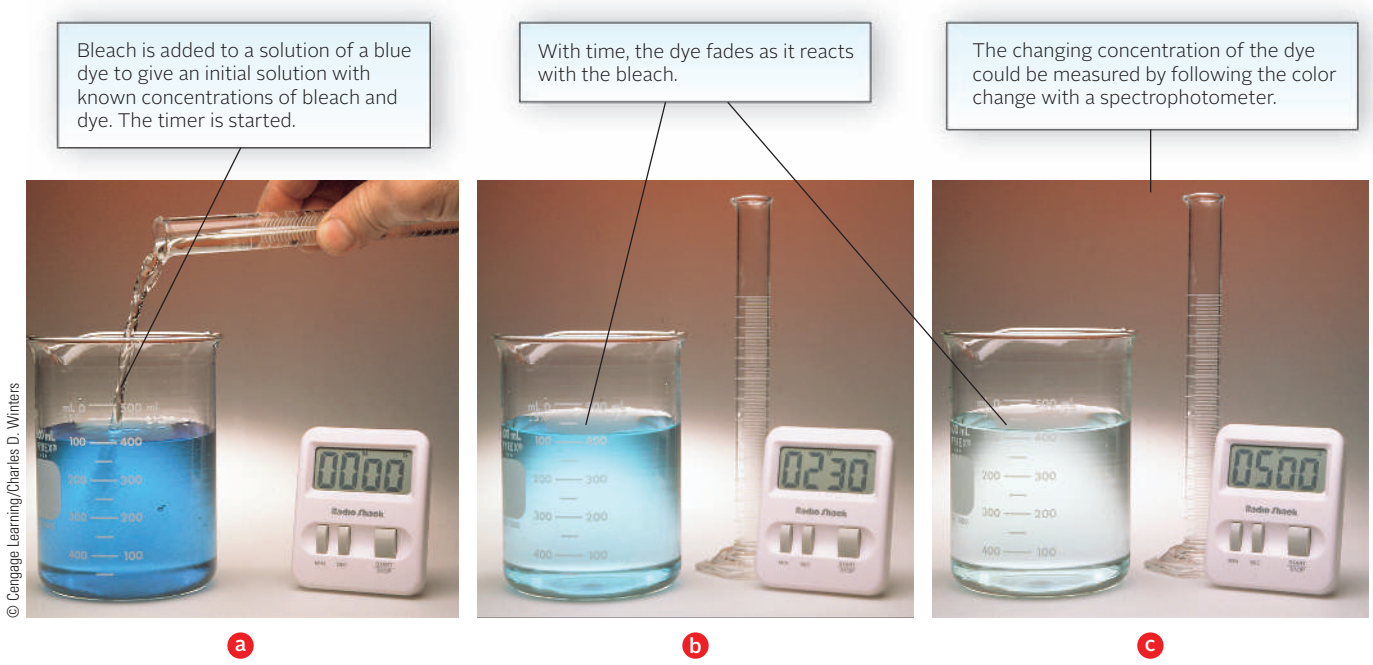


Figure 11.2 Measurement of reaction rate by observing color change.

Measurement of Rate

Rate is often measured by following the color change that occurs in a reaction (Figure 11.2).

For the reaction

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

the rate could be determined by measuring

- the absorption of visible light by the NO_2 formed; this species has a reddish-brown color, whereas N_2O_5 and O_2 are colorless.
- the change in pressure that results from the increase in the number of moles of gas (1 mol reactant $\rightarrow 2\frac{1}{2}$ mol product).

The graphs in Figure 11.1 show plots of data from measurements of this type.

To find the rate of decomposition of N_2O_5, it is convenient to use Figure 11.3, which is a magnified version of a portion of Figure 11.1. If a tangent is drawn to the curve of concentration versus time, its slope at that point must equal $\Delta[N_2O_5]/\Delta t$. But because the reaction rate is $-\Delta[N_2O_5]/\Delta t$, it follows that

$$\text{rate} = -\text{slope of tangent}$$

From Figure 11.3 it appears that the slope of the tangent at $t = 2$ min is -0.028 mol/L · min. Hence

$$\text{rate at 2 min} = -(-0.028 \text{ mol/L} \cdot \text{min}) = 0.028 \text{ mol/L} \cdot \text{min}$$

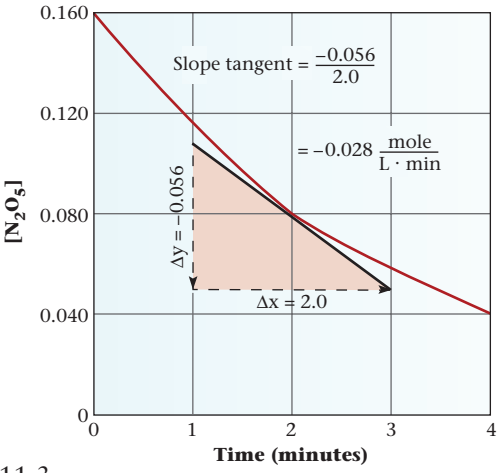


Figure 11.3 Determination of the instantaneous rate at a particular concentration. To determine the rate of reaction, plot concentration versus time and take the tangent to the curve at the desired point. For the reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$, it appears that the reaction rate at $[N_2O_5] = 0.080\ M$ is 0.028 mol/L · min.

11-2 Reaction Rate and Concentration

Ordinarily, reaction rate is directly related to reactant concentration (Figure 11.4). The higher the concentration of starting materials, the more rapidly a reaction takes place. Pure hydrogen peroxide, in which the concentration of H_2O_2 molecules is about 40 mol/L, is an extremely dangerous substance. In the presence of trace impurities, it decomposes explosively

$$H_2O_2(l) \longrightarrow H_2O(g) + \tfrac{1}{2}O_2(g)$$

a

b

Figure 11.4 Reaction rate and concentration. The rate of the reaction of potassium permanganate with hydrogen peroxide depends on the concentration of the permanganate. With dilute $KMnO_4$ the reaction is slow (a), but it is more rapid in more concentrated $KMnO_4$ (b).

at a rate too rapid to measure. The hydrogen peroxide you buy in a drugstore is a dilute aqueous solution in which $[H_2O_2] \approx 1\ M$. At this relatively low concentration, decomposition is so slow that the solution is stable for several months.

The dependence of reaction rate on concentration is readily explained. Ordinarily, ***reactions occur as the result of collisions between reactant molecules.*** The higher the concentration of molecules, the greater the number of collisions in unit time and hence the faster the reaction. As reactants are consumed, their concentrations drop, collisions occur less frequently, and reaction rate decreases. This explains the common observation that reaction rate drops off with time, eventually going to zero when the limiting reactant is consumed.

Rate Expression and Rate Constant

The dependence of reaction rate on concentration is readily determined for the decomposition of N_2O_5. Figure 11.5 shows what happens when reaction rate is plotted versus $[N_2O_5]$. As you would expect, rate increases as concentration increases, going from zero when $[N_2O_5] = 0$ to about 0.06 mol/L · min when $[N_2O_5] = 0.16\ M$. Moreover, as you can see from the figure, the plot of rate versus concentration is a straight line through the origin, which means that rate must be directly proportional to the concentration.

$$\text{rate} = k[N_2O_5]$$

This equation is referred to as the **rate expression** for the decomposition of N_2O_5. It tells how the rate of the reaction

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

depends on the concentration of reactant. The proportionality constant k is called a **rate constant.** It is independent of the other quantities in the equation.

Rate depends on concentration, but the rate constant does not.

As we will see shortly, the rate expression can take various forms, depending on the nature of the reaction. It can be quite simple, as in the N_2O_5 decomposition, or exceedingly complex.

Order of Reaction Involving a Single Reactant

Rate expressions have been determined by experiment for a large number of reactions. For the process

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

the rate expression has the general form

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

Remember, [A] means the concentration of A in moles per liter.

The power to which the concentration of reactant A is raised in the rate expression is called the **order of reaction,** m. If m is 0, the reaction is said to be "zero-order." If $m = 1$, the reaction is "first-order"; if $m = 2$, it is "second-order"; and

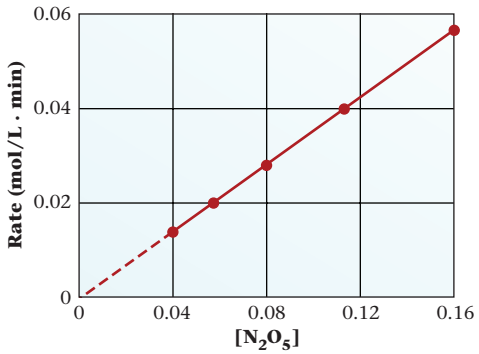


Figure 11.5 A plot of rate versus concentration for the decomposition of N_2O_5 is a straight line. The line, if extrapolated, passes through the origin. This means that rate is directly proportional to concentration; that is, rate = $k\,[N_2O_5]$.

so on. Ordinarily, the reaction order is integral (0, 1, 2, . . .), but fractional orders such as $\frac{3}{2}$ are possible.

The order of a reaction must be determined experimentally; ***it cannot be deduced from the coefficients in the balanced equation.*** This must be true because there is only one reaction order, but there are many different ways in which the equation for the reaction can be balanced. For example, although we wrote

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

to describe the decomposition of N_2O_5, it could have been written

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

The reaction is still first-order no matter how the equation is written.

One way to find the order of a reaction is to measure the initial rate (i.e., the rate at $t = 0$) as a function of the concentration of reactant. Suppose, for example, that we make up two different reaction mixtures differing only in the concentration of reactant A. We now measure the rates at the beginning of reaction, before the concentration of A has decreased appreciably. This gives two different initial rates (rate_1, rate_2) corresponding to two different starting concentrations of A, $[A]_1$ and $[A]_2$. From the rate expression,

$$\text{rate}_2 = k[A]_2^m \qquad \text{rate}_1 = k[A]_1^m$$

Dividing the second rate by the first,

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{[A]_2^m}{[A]_1^m} = \left(\frac{[A]_2}{[A]_1}\right)^m$$

Because all the quantities in this equation are known except m, the reaction order can be calculated (Example 11.2).

EXAMPLE 11.2

Acetaldehyle, CH_3CHO, occurs naturally in oak and tobacco leaves, and also is present in automobile and diesel exhaust. The initial rate of decomposition of acetaldehyde at 600°C

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

was measured at a series of concentrations with the following results:

$[CH_3CHO]$	0.20 *M*	0.30 *M*	0.40 *M*	0.50 *M*
Rate (mol/L·s)	0.34	0.76	1.4	2.1

Using these data, determine the reaction order; that is, determine the value of m in the equation

$$\text{rate} = k[CH_3CHO]^m$$

ANALYSIS

Information given:	experiments with intial concentrations and rates
Asked for:	order of the reaction

STRATEGY

1. Choose two initial concentrations and their corresponding rates.
2. Calculate the rate ratio.
3. Calculate the concentration ratio.
4. Substitute into the following equation to obtain the order of the reaction, m.

$$\frac{\text{rate}_2}{\text{rate}_1} = \left(\frac{[A]_2}{[A]_1}\right)^m$$

continued

SOLUTION

1. Choose the first two experiments	$\text{rate}_1 = 0.34$ mol/L·s; $\text{rate}_2 = 0.76$ mol/L·s; $[CH_3CHO]_1 = 0.20\ M$; $[CH_3CHO]_2 = 0.30\ M$
2. Rate ratio	$\dfrac{\text{rate}_2}{\text{rate}_1} = \dfrac{0.76}{0.34} = 2.2$
3. Concentration ratio	$\dfrac{[CH_3CHO]_2}{[CH_3CHO]_1} = \dfrac{0.30}{0.20} = 1.5$
4. m	$\dfrac{\text{rate}_2}{\text{rate}_1} = \left(\dfrac{[CH_3CHO]_2}{[CH_3CHO]_1}\right)^m \longrightarrow 2.2 = (1.5)^m \longrightarrow m = 2$ The reaction is second-order.

END POINTS

1. If m is not obvious, then solve for m algebraically by taking the log of both sides:

$$2.2 = (1.5)^m \text{ becomes } \log 2.2 = m(\log 1.5);\ m = \frac{\log 2.2}{\log 1.5} = \frac{0.34}{0.18} = 1.9 \longrightarrow 2$$

2. You would get the same result ($m = 2$) if you used any two experiments. Try it!

Once the order of the reaction is known, the rate constant is readily calculated. Consider, for example, the decomposition of acetaldehyde, where we have shown that the rate expression is

$$\text{rate} = k[CH_3CHO]^2$$

There are two variables in this equation, rate and concentration, and two constants, k and reaction order.

The data in Example 11.2 show that the rate at 600°C is 0.34 mol/L·s when the concentration is 0.20 mol/L. It follows that

$$k = \frac{\text{rate}}{[CH_3CHO]^2} = \frac{0.34 \text{ mol/L}\cdot\text{s}}{(0.20 \text{ mol/L})^2} = 8.5 \text{ L/mol}\cdot\text{s}$$

The same value of k would be obtained, within experimental error, using any other data pair.

Having established the value of k and the reaction order, the rate is readily calculated at any concentration. Again, using the decomposition of acetaldehyde as an example, we have established that

$$\text{rate} = 8.5\frac{\text{L}}{\text{mol}\cdot\text{s}}[CH_3CHO]^2$$

If the concentration of acetaldehyde were 0.60 M,

$$\text{rate} = 8.5\ \frac{\text{L}}{\text{mol}\cdot\text{s}}(0.60 \text{ mol/L})^2 = 3.1 \text{ mol/L}\cdot\text{s}$$

Order of Reaction with More Than One Reactant

Many (indeed, most) reactions involve more than one reactant. For a reaction between two species A and B,

$$a\text{A} + b\text{B} \longrightarrow \text{products}$$

the general form of the rate expression is

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

In this equation m is referred to as "the order of the reaction with respect to A." Similarly, n is "the order of the reaction with respect to B." The *overall order* of the reaction is the sum of the exponents, $m + n$. If $m = 1, n = 2$, then the reaction is first-order in A, second-order in B, and third-order overall.

When more than one reactant is involved, the order can be determined by holding the initial concentration of one reactant constant while varying that of the other reactant. From rates measured under these conditions, it is possible to deduce the order of the reaction with respect to the reactant whose initial concentration is varied.

To see how to do this, consider the reaction between A and B referred to above. Suppose we run two different experiments in which the initial concentrations of A differ ($[A]_1$, $[A]_2$) but that of B is held constant at [B]. Then

$$\text{rate}_1 = k[A]_1^m \times [B]^n \qquad \text{rate}_2 = k[A]_2^m \times [B]^n$$

Dividing the second equation by the first

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]_2^m \times [B]^n}{k[A]_1^m \times [B]^n} = \frac{[A]_2^m}{[A]_1^m} = \left(\frac{[A]_2}{[A]_1}\right)^m$$

This way, the concentration terms cancel for that reactant.

Knowing the two rates and the ratio of the two concentrations, we can readily find the value of m.

EXAMPLE 11.3

Consider the reaction between t-butylbromide and a base at 55°C:

$$(CH_3)_3CBr(aq) + OH^-(aq) \longrightarrow (CH_3)_3COH(aq) + Br^-(aq)$$

A series of experiments is carried out with the following results:

	Expt. 1	Expt. 2	Expt. 3	Expt. 4	Expt. 5
$[(CH_3)_3CBr]$	0.50	1.0	1.5	1.0	1.0
$[OH^-]$	0.050	0.050	0.050	0.10	0.20
Rate (mol/L·s)	0.0050	0.010	0.015	0.010	0.010

a Find the order of the reaction with respect to both $(CH_3)_3CBr$ and OH^-.

ANALYSIS

Information given:	results of initial state experiments
Asked for:	order of the reaction with respect to $(CH_3)_3CBr$ and OH^-

STRATEGY

For m:
1. Choose two experiments where $[OH^-]$ is constant.
2. Find the rate and concentration ratios for $(CH_3)_3CBr$.
3. Substitute into the rate equation

   rate ratio = ([$(CH_3)_3CBr$] ratio)^m

For n:
1. Choose two experiments where $[(CH_3)_3CBr]$ is constant.
2. Find the rate and concentration ratios for OH^-.
3. Substitute into the rate equation

   rate ratio = ($[OH^-]$ ratio)^n

continued

SOLUTION

For m:	**1.** Experiments	Experiments 1 and 3
	2. ratios	rate ratio: $\frac{\text{rate}_3}{\text{rate}_1} = \frac{0.015}{0.005} = 3$
		concentration ratio: $\frac{[(CH_3)_3CBr]_3}{[(CH_3)_3CBr]_1} = \frac{1.5}{0.50} = 3$
	3. m	$3 = (3)^m$; $m = 1$
For n:	**1.** Experiments	Experiments 2 and 5
	2. ratios	rate ratio: $\frac{\text{rate}_5}{\text{rate}_2} = \frac{0.010}{0.010} = 1$
		concentration ratio: $\frac{[OH^-]_5}{[OH^-]_2} = \frac{0.20}{0.050} = 4$
	3. n	$1 = (4)^n$; $n = 0$
reaction order		The reaction is first-order with respect to $(CH_3)_3CBr$ and zero-order with respect to OH^-.

b Write the rate expression for the reaction.

ANALYSIS

Information given:	from part (a): m (1), n (0)
Asked for:	rate expression for the reaction

SOLUTION

rate expression	rate $= k[(CH_3)_3CBr]^1\,[OH^-]^0 = k[(CH_3)_3CBr]$

c Calculate the rate constant at 55°C.

ANALYSIS

Information given:	from part (b): rate expression (rate $= k[(CH_3)_3CBr]$) experiments with rates and concentrations at initial states
Asked for:	k

STRATEGY

1. Substitute a rate and a concentration for $(CH_3)_3CBr$ and OH^- into the rate expression.

2. Use any rate/concentration pair from any experiment. (We choose experiment 3.)

SOLUTION

k	rate $= k[(CH_3)_3CBr] \longrightarrow 0.015\ \frac{\text{mol}}{\text{L}\cdot\text{s}} = k\left(1.5\ \frac{\text{mol}}{\text{L}}\right) \longrightarrow k = 0.010\ \text{s}^{-1}$

d What effect does doubling the concentration of OH^- have on the reaction if $[(CH_3)_3CBr]$ is kept at 1.0 *M*?

SOLUTION

Changing $[OH^-]$ has no effect on the rate of the reaction. The reaction is zero-order ($n = 0$) with respect to OH^-, which means that the rate is independent of its concentration.

11-3 Reactant Concentration and Time

The rate expression

$$\text{rate} = k[N_2O_5]$$

shows how the rate of decomposition of N_2O_5 changes with concentration. From a practical standpoint, however, it is more important to know the relation between concentration and *time* rather than between concentration and rate. Suppose, for example, you are studying the decomposition of dinitrogen pentoxide. Most likely, you would want to know how much N_2O_5 is left after 5 min, 1 h, or several days. An equation relating *rate* to concentration does not provide that information.

There are no speedometers for reactions, but every lab has a clock.

Using calculus, it is possible to develop integrated rate equations relating reactant concentration to time. We now examine several such equations, starting with first-order reactions.

First-Order Reactions

For the decomposition of N_2O_5 and any other **first-order reaction** of the type

$$A \longrightarrow \text{products} \qquad \text{rate} = k[A]$$

it can be shown by using calculus that the relationship between concentration and time is*

$$\ln \frac{[A]_o}{[A]} = kt \tag{11.2a}$$

where $[A]_o$ is the original concentration of reactant, [A] is its concentration at time t, k is the first-order rate constant, and the abbreviation "ln" refers to the natural logarithm.

Because $\ln a/b = \ln a - \ln b$, the first-order equation can be written in the form

$$\ln [A]_o - \ln [A] = kt \tag{11.2b}$$

Solving for ln [A],

$$\ln [A] = \ln [A]_o - kt$$

Comparing this equation with the general equation of a straight line,

$$y = b + mx \qquad (b = y\text{-intercept}, m = \text{slope})$$

it is clear that a plot of ln [A] versus t should be a straight line with a y-intercept of $\ln [A]_o$ and a slope of $-k$. This is indeed the case, as you can see from Figure 11.6, in which we have plotted $\ln [N_2O_5]$ versus t for the decomposition of N_2O_5. Drawing the best straight line through the points and taking the slope based on a point on the x-axis ($y_2 = -3.5$, $x_2 = 4.9$) and another on the y-axis ($y_1 = -1.8$, $x_1 = 0$)

$$\text{slope} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{-3.5 + 1.8}{4.9 - 0} = \frac{-1.7}{4.9} = -0.35$$

It follows that the rate constant is 0.35/min; the integrated first-order equation for the decomposition of N_2O_5 is

The slope is negative but k is always positive.

$$\ln \frac{[N_2O_5]_o}{[N_2O_5]} = \frac{0.35}{\text{min}}\, t \qquad (\text{at } 67^\circ\text{C})$$

*Throughout Section 11-3, balanced chemical equations are written in such a way that the coefficient of the reactant is 1. In general, if the coefficient of the reactant is a, where a may be 2 or 3 or . . . , then k in each integrated rate equation must be replaced by the product ak. (See Problem 101.)

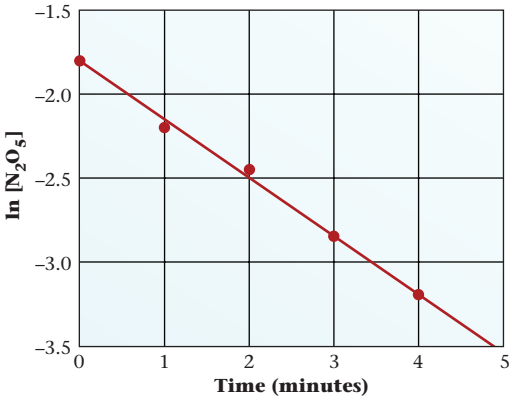


Figure 11.6 A first-order reaction plot. The rate constant for a first-order reaction can be determined from the slope of a plot of ln[A] versus time. The reaction illustrated, at 67°C, is $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$. Using two points on the line, one can find the slope of the line, which is the rate constant. In this case, k is found to be about 0.35/min.

EXAMPLE 11.4

Consider the first-order decomposition of N_2O_5 at 67°C, where $k = 0.35$/min.

a What is the concentration after six minutes, starting at 0.200 *M*?

ANALYSIS

Information given:	k(0.35/min); t(6.00 min); $[N_2O_5]_o$ (0.200 *M*) reaction order (first-order)
Asked for:	$[N_2O_5]$ after 6 minutes

STRATEGY

Substitute into Equation 11.2a or 11.2b.

$$\ln \frac{[N_2O_5]_o}{[N_2O_5]} = kt \quad \text{or} \quad \ln [N_2O_5]_o - \ln [N_2O_5] = kt$$

SOLUTION

$[N_2O_5]$	$\ln (0.200 \text{ mol/L}\cdot\text{min}) - \ln [N_2O_5] = -1.609 - \ln(N_2O_5) = 0.35 \frac{1}{\text{min}} \times 6.00 \text{ min}$ $\ln [N_2O_5] = -1.609 - 2.1 = -3.7 \longrightarrow [N_2O_5] = e^{-3.7} =$ 0.024 mol/L

b How long does it take for the concentration to drop from 0.200 *M* to 0.150 *M*?

ANALYSIS

Information given:	k(0.35/min); $[N_2O_5]_o$ (0.200 *M*); $[N_2O_5]_t$ (0.150 *M*)
Asked for:	t

STRATEGY

Substitute into Equation 11.2a or 11.2b.

SOLUTION

t	$\ln(0.200\ M) - \ln(0.150\ M) = \frac{0.35}{\text{min}} \times t \longrightarrow -1.61 - (-1.90) = 0.35\ t$ $t =$ 0.82 min

c How long does it take for half a sample of N_2O_5 to decompose?

ANALYSIS

Information given:	k(0.35/min); $[N_2O_5] = (\frac{1}{2})\ [N_2O_5]_o$
Asked for:	t

continued

STRATEGY	
Substitute into Equation 11.2a or 11.2b.	
SOLUTION	
t	$\ln \dfrac{[N_2O_5]_o}{\frac{1}{2}[N_2O_5]_o} = (0.35/\text{min})\, t \longrightarrow \ln 2 = (0.35/\text{min})t \longrightarrow t = 0.693/0.35$ $t = 2.0$ min

The analysis of Example 11.4c reveals an important feature of a first-order reaction: ***The time required for one half of a reactant to decompose via a first-order reaction has a fixed value, independent of concentration.*** This quantity, called the **half-life,** is given by the expression

This relation holds only for a first-order reaction.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \qquad \text{first-order reaction} \qquad (11.3)$$

where k is the rate constant. For the decomposition of N_2O_5, where $k = 0.35$/min, $t_{1/2} = 2.0$ min. Thus every two minutes, one half of a sample of N_2O_5 decomposes (Table 11.1).

Notice that for a first-order reaction the rate constant has the units of reciprocal time, for example, min^{-1}. This suggests a simple physical interpretation of k (at least where k is small); it is the fraction of reactant decomposing in unit time. For a first-order reaction in which

$$k = 0.010/\text{min} = 0.010\ \text{min}^{-1}$$

we can say that 0.010 (i.e., 1.0%) of the sample decomposes per minute.

Perhaps the most important first-order reaction is that of radioactive decay, in which an unstable nucleus decomposes (Chapter 2). Letting X be the amount of a radioactive isotope present at time t,

$$\text{rate} = kX$$

and

$$\ln \frac{X_o}{X} = kt$$

where X_o is the initial amount. The amount of a radioactive isotope can be expressed in terms of moles, grams, or number of atoms.

Table 11.1 Decomposition of N_2O_5 at 67°C ($t_{1/2} = 2.0$ min)

t (min)	0.0	2.0	4.0	6.0	8.0
$[N_2O_5]$	0.160	0.080	0.040	0.020	0.010
Fraction of N_2O_5 decomposed	0	$\frac{1}{2}$	$\frac{3}{4}$	$\frac{7}{8}$	$\frac{15}{16}$
Fraction of N_2O_5 left	1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$
Number of half-lives	0	1	2	3	4

EXAMPLE 11.5 GRADED

Plutonium-240 (Pu-240) is a by-product of the nuclear reaction that takes place in a reactor. It takes one thousand years for 10.0% of a 4.60-g sample to decay.

a What is the half-life of Pu-240?

ANALYSIS

Information given:	time, t (1000 y); $[\text{Pu-240}]_o$ (4.60 g); rate of decay (10%/1000 years)
Information implied:	reaction order; k; [Pu-240] after 1000 years
Asked for:	$t_{1/2}$

STRATEGY

1. Find [Pu-240] after 1000 years.

   $[\text{Pu-240}] = [\text{Pu-240}]_o - 0.10([\text{Pu-240}]_o)$

2. All nuclear reactions are first-order. Find k by substituting into Equation 11.2a or 11.2b.
3. Find $t_{1/2}$ by substituting into Equation 11.3.

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

SOLUTION

[Pu-240]	$[\text{Pu-240}] = 4.60\text{ g} - (0.10)(4.60\text{ g}) = 4.14\text{ g}$
k	$\ln 4.60 - \ln 4.14 = k(1000\text{ y}) \longrightarrow k = 1.05 \times 10^{-4}\text{ y}^{-1}$
$t_{1/2}$	$t_{1/2} = \dfrac{0.693}{1.05 \times 10^{-4}\text{ y}^{-1}} = 6.60 \times 10^3\text{ y}$

b How long will it take to reduce a 2.00-g sample to 15% of its original amount?

ANALYSIS

Information given:	$[\text{Pu-240}]_o$ (2.00 g); [Pu-240] (15% of 2.00 g) from part (a): $k(1.05 \times 10^{-4}\text{ y}^{-1})$
Asked for:	t

STRATEGY

1. Find [Pu-240].
2. Find t by substituting into Equation 11.2a or 11.2b.

SOLUTION

[Pu-240]	$[\text{Pu-240}] = 0.15(2.00\text{ g}) = 0.30\text{ g}$
t	$\ln 2.00 - \ln 0.30 = (1.05 \times 10^{-4}\text{ y}^{-1})t \longrightarrow t = 1.8 \times 10^4\text{ y}$

c What is the rate of decay of a 5.00-g sample in g/year?

ANALYSIS

Information given:	$[\text{Pu-240}]_o$ (5.00 g); from part (a): $k(1.05 \times 10^{-4}\text{ y}^{-1})$
Information implied:	reaction order ($m = 1$)
Asked for:	rate of decay

STRATEGY

Since the question is now to relate concentration and rate, you must substitute into the general rate expression for Pu-240 decay.

$\text{rate} = k[\text{Pu-240}]_o^1$

continued

SOLUTION	
Rate	rate = $(1.05 \times 10^{-4}\ y^{-1})(5.00\ g) = 5.25 \times 10^{-4}\ g/y$

END POINT

In part (c) the rate is dependent on the initial mass unlike in part (a), where the half-life is independent of the original amount.

Half-lives can be interpreted in terms of the level of radiation of the corresponding isotopes. Uranium has a very long half-life (4.5×10^9 y), so it gives off radiation very slowly. At the opposite extreme is fermium-258, which decays with a half-life of 3.8×10^{-4} s. You would expect the rate of decay to be quite high. Within a second virtually all the radiation from fermium-258 is gone. Species such as this produce very high radiation during their brief existence.

Zero- and Second-Order Reactions

A **zero-order reaction** is a reaction whose rate is independent of reactant concentration. This is because any non-zero quantity raised to the zero power, including [A], is equal to 1.

$$\text{A} \longrightarrow \text{products} \qquad \text{rate} = k[\text{A}]^0 = k$$

In other words, the rate of a zero-order reaction is constant, independent of concentration. As you might expect from our earlier discussion, zero-order reactions are relatively rare. Most of them take place at solid surfaces, where the rate is independent of concentration in the gas phase. A typical example is the thermal decomposition of hydrogen iodide on gold:

In a zero-order reaction, all the reactant is consumed in a finite time, which is $2t_{1/2}$.

$$\text{HI}(g) \xrightarrow{\text{Au}} \tfrac{1}{2}\text{H}_2(g) + \tfrac{1}{2}\text{I}_2(g)$$

When the gold surface is completely covered with HI molecules, increasing the concentration of HI(g) has no effect on reaction rate.

It can be shown using the integrated rate law that the concentration-time relation for a zero-order reaction is

$$[\text{A}] = [\text{A}]_\text{o} - kt \qquad (11.4)$$

Comparing this equation with that for a straight line,

$$y = b + mx \qquad (b = y\text{-intercept}, m = \text{slope})$$

it should be clear that a plot of [A] versus t should be a straight line with a slope of $-k$. Putting it another way, if a plot of concentration versus time is linear, the reaction must be zero-order; the rate constant k is numerically equal to the slope of that line but has the opposite sign.

For a **second-order reaction** (a reaction whose rate depends on the second power of the reactant concentration) involving a single reactant, such as acetaldehyde (recall Example 11.2),

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

it is again necessary to resort to calculus* to obtain the concentration-time relationship

$$\frac{1}{[\text{A}]} - \frac{1}{[\text{A}]_\text{o}} = kt \qquad (11.5)$$

*If you are taking a course in calculus, you may be surprised to learn how useful it can be in the real world (e.g., chemistry). The general rate expressions for zero-, first-, and second-order reactions are

$$-d[\text{A}]/dt = k \qquad -d[\text{A}]/dt = k[\text{A}] \qquad -d[\text{A}]/dt = k[\text{A}]^2$$

Integrating these equations from 0 to t and from $[\text{A}]_\text{o}$ to [A], you should be able to derive the equations for zero-, first-, and second-order reactions.

Table 11.2 Characteristics of Zero-, First-, and Second-Order Reactions for A (*g*) ⟶ products, where [A] = conc. A at *t*, $[A]_o$ = conc. A at *t* = 0

Order	Rate Expression	Conc.-Time Relation	Half-Life	Linear Plot
0	rate = k	$[A]_o - [A] = kt$	$[A]_o/2k$	[A] vs. t
1	rate = $k[A]$	$\ln\frac{[A]_o}{[A]} = kt$	$0.693/k$	ln [A] vs. t
2	rate = $k[A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$	$1/k\,[A]_o$	$\frac{1}{[A]}$ vs. t

where the symbols [A], $[A]_o$, t, and k have their usual meanings. For a second-order reaction, a plot of 1/[A] versus t should be linear.

The characteristics of zero-, first-, and second-order reactions are summarized in Table 11.2. To determine reaction order, the properties in either of the last two columns at the right of the table can be used (Example 11.6).

EXAMPLE 11.6

The following data were obtained for the gas-phase decomposition of hydrogen iodide:

Time (h)	0	2	4	6
[HI]	1.00	0.50	0.33	0.25

Is this reaction zero-, first-, or second-order in HI?

STRATEGY

1. Prepare a table listing [HI], ln[HI], and 1/[HI] as a function of time from the experimental data given.
2. Make a plot of each concentration-time relationship.
3. See Table 11.2 for the order of the reaction based on the linear plot that you obtain.

SOLUTION

concentration-time table

t	[HI]	ln [HI]	1/[HI]
0	1.00	0	1.0
2	0.50	−0.69	2.0
4	0.33	−1.10	3.0
6	0.25	−1.39	4.0

plots — See Figure 11.7 (page 289).

order of the reaction — 1/[HI] vs time gives a linear plot. The reaction is second-order.

END POINTS

1. Note that the concentration drops from 1.00 *M* to 0.500 *M* in 2 hours. If the reaction were zero-order, it would be all over in 2 hours.
2. If the reaction is first-order, the concentration would be 0.25 *M* after 4 hours.

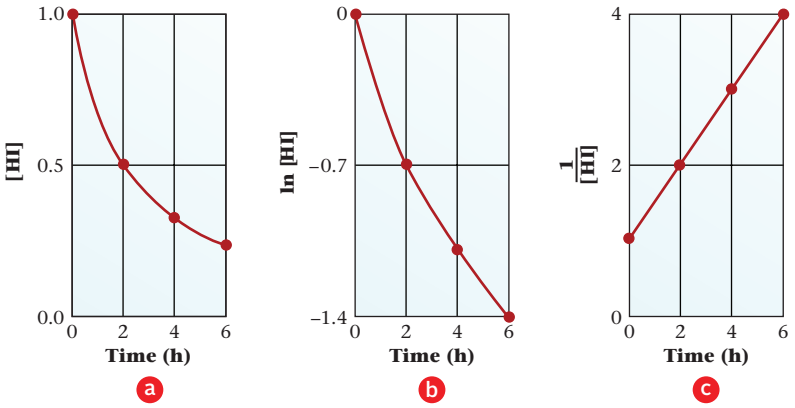
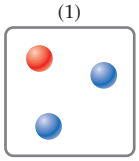


Figure 11.7 Determination of reaction order. One way to determine reaction order is to search for a linear relation between some function of concentration and time (Table 11.2). Because a plot of 1/[HI] versus t (plot c) is linear, the decomposition of HI must be second-order.

EXAMPLE 11.7 CONCEPTUAL

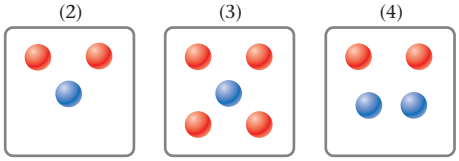
A certain reaction is first-order in A and second-order in B. In the box shown below, which is assumed to have a volume of one liter, a mole of A is represented by ●, a mole of B by ●.

(1)



In which of the three boxes shown below is the rate of reaction the same as that in the box shown above?

(2) (3) (4)



ANALYSIS

Information given:	order of the reaction with respect to A (first-order) and to B (second-order) concentrations of A and B
Asked for:	Which box has the same reaction rate as box (1)?

STRATEGY

Write the reaction rate for each box and compare.

SOLUTION

Box (1)	rate $= k(1)(2)^2 = 4k$
Box (2)	rate $= k(2)(1)^2 = 2k$
Box (3)	rate $= k(4)(1)^2 = 4k$
Box (4)	rate $= k(2)(2)^2 = 8k$
	The rates in boxes (1) and (3) are the same.

11-4 Models for Reaction Rate

So far in this chapter we have approached reaction rate from an experimental point of view, describing what happens in the laboratory or the world around us. Now we change emphasis and try to explain why certain reactions occur rapidly

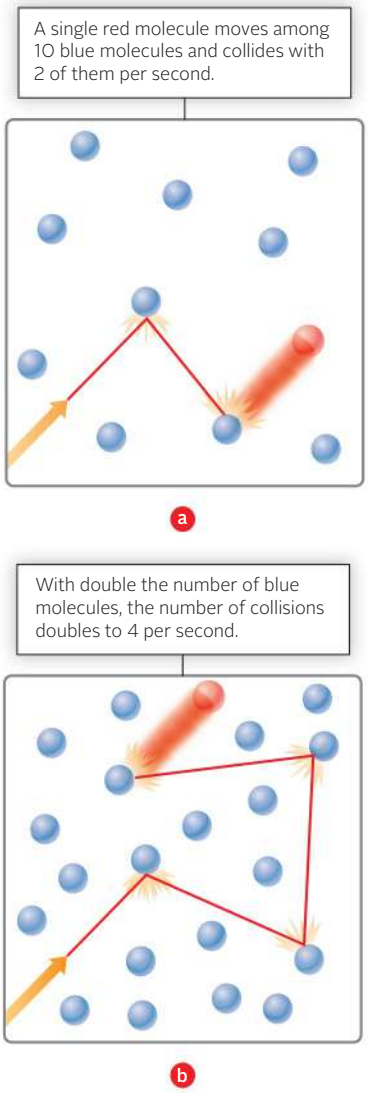


Figure 11.8 Concentration and molecular collisions. A red molecule must collide with a blue molecule for a reaction to take place.

There would be an explosion.

while others take place slowly. To do this, we look at a couple of models that chemists have developed to predict rate constants for reactions.

Collision Model; Activation Energy

Consider the reaction

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

Above 600 K, this reaction takes place as a direct result of collisions between CO and NO_2 molecules. When the concentration of CO doubles (Figure 11.8), the number of these collisions in a given time increases by a factor of 2; doubling the concentration of NO_2 has the same effect. Assuming that reaction rate is directly proportional to the collision rate, the following relation should hold:

$$\text{reaction rate} = k[CO] \times [NO_2]$$

Experimentally, this prediction is confirmed; the reaction is first-order in both carbon monoxide and nitrogen dioxide.

There is a restriction on this simple model for the CO-NO_2 reaction. According to the kinetic theory of gases, for a reaction mixture at 700 K and concentrations of 0.10 *M*, every CO molecule should collide with about 10^9 NO_2 molecules in one second. If every collision were effective, the reaction should be over in a fraction of a second. In reality, this does not happen; under these conditions, the half-life is about 10 s. This implies that not every CO-NO_2 collision leads to reaction.

There are a couple of reasons why collision between reactant molecules does not always lead to reaction. For one thing, the molecules have to be properly oriented with respect to one another when they collide. Suppose, for example, that the carbon atom of a CO molecule strikes the nitrogen atom of an NO_2 molecule (Figure 11.9). This is very unlikely to result in the transfer of an oxygen atom from NO_2 to CO, which is required for reaction to occur.

A more important factor that reduces the number of effective collisions has to do with the kinetic energy of reactant molecules. These molecules are held together by strong chemical bonds. Only if the colliding molecules are moving very rapidly will the kinetic energy be large enough to supply the energy required to break these bonds. Molecules with small kinetic energies bounce off one another without reacting. As a result, only a small fraction of collisions are effective.

For every reaction, there is a certain minimum energy that molecules must possess for collision to be effective. This is referred to as the **activation energy.** It has the symbol E_a and is expressed in kilojoules/mol. For the reaction between one mole of CO and one mole of NO_2, E_a is 134 kJ/mol. The colliding molecules (CO and NO_2) must have a total kinetic energy of at least 134 kJ/mol if they are to react. The activation energy for a reaction is a positive quantity ($E_a > 0$) whose value depends on the nature of the reaction.

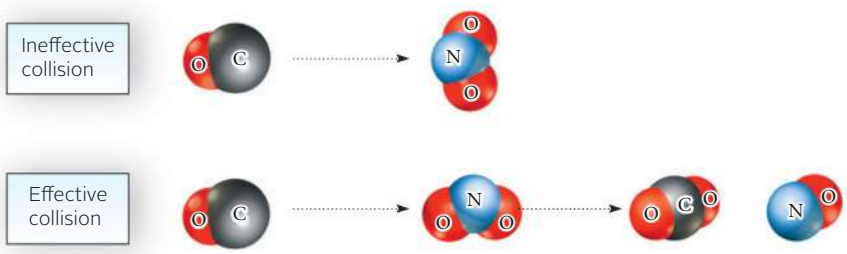


Figure 11.9 Effective and ineffective molecular collisions. For a collision to result in reaction, the molecules must be properly oriented. For the reaction $CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$, the carbon atom of the CO molecule must strike an oxygen atom of the NO_2 molecule, forming CO_2 as one product, NO as the other.

The collision model of reaction rates just developed can be made quantitative. We can say that the rate constant for a reaction, k, is a product of three factors:

$$k = p \times Z \times \mathrm{f}$$

where

- p, called a *steric factor*, takes into account the fact that only certain orientations of colliding molecules are likely to lead to reaction (recall Figure 11.9). Unfortunately, the collision model cannot predict the value of p; about all we can say is that it is less than 1, sometimes much less.
- Z, the *collision frequency*, which gives the number of molecular collisions occurring in unit time at unit concentrations of reactants. This quantity can be calculated quite accurately from the kinetic theory of gases, but we will not describe that calculation.
- f, the *fraction of collisions in which the energy of the colliding molecules is equal to or greater than* E_a. It can be shown that

$$\mathrm{f} = e^{-E_a/RT}$$

where e is the base of natural logarithms, R is the gas constant, and T is the absolute temperature in K.

Substituting this expression for f into the equation written above for k, we obtain the basic equation for the collision model:

$$k = p \times Z \times e^{-E_a/RT}$$

This equation tells us, among other things, that *the larger the value of* E_a, *the smaller the rate constant*. Thus

$$\begin{aligned} \text{if } E_a &= 0,\ e^{-E_a/RT} = e^0 = 1 \\ E_a &= RT,\ e^{-E_a/RT} = e^{-1} = 0.37 \\ E_a &= 2RT,\ e^{-E_a/RT} = e^{-2} = 0.14 \end{aligned}$$

and so on. This makes sense; the larger the activation energy, the smaller the fraction of molecules having enough energy to react on collision, so the slower the rate of reaction.

High-energy molecules get the job done.

Table 11.3 compares observed rate constants for several reactions with those predicted by collision theory, arbitrarily taking $p = 1$. As you might expect, the calculated k's are too high, suggesting that the steric factor is indeed less than 1.

Transition-State Model; Activation Energy Diagrams

Figure 11.10 is an energy diagram for the CO-NO_2 reaction. Reactants CO and NO_2 are shown at the left. Products CO_2 and NO are at the right; they have an energy 226 kJ less than that of the reactants. The enthalpy change, ΔH, for the reaction is −226 kJ. In the center of the figure is an intermediate called an **activated complex**. This is an unstable, high-energy species that must be formed before the reaction can occur. It has an energy 134 kJ greater than that of the

In the activated complex, electrons are often in excited states.

Table 11.3 Observed and Calculated Rate Constants for Second-Order Gas-Phase Reactions

Reaction	k Observed	Collision Model	Transition-State Model
$NO + O_3 \longrightarrow NO_2 + O_2$	6.3×10^7	4.0×10^9	3.2×10^7
$NO + Cl_2 \longrightarrow NOCl + Cl$	5.2	130	1.6
$NO_2 + CO \longrightarrow NO + CO_2$	1.2×10^{-4}	6.4×10^{-4}	1.0×10^{-4}
$2NO_2 \longrightarrow 2NO + O_2$	5.0×10^{-3}	1.0×10^{-1}	1.2×10^{-2}

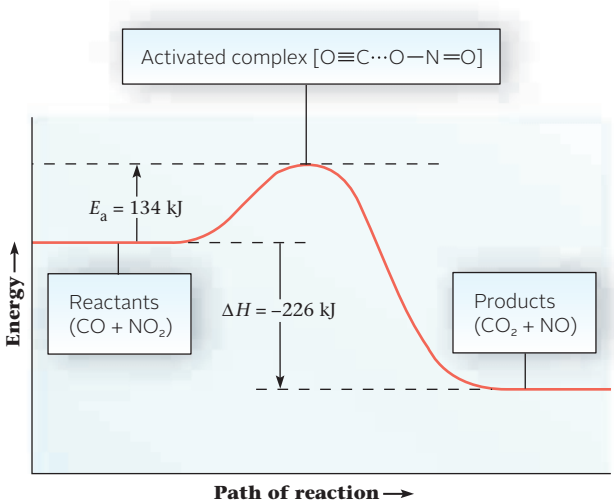


Figure 11.10 Reaction energy diagram. During the reaction initiation, 134 kJ—the activation energy E_a—must be furnished to the reactants for every mole of CO that reacts. This energy activates each CO—NO_2 complex to the point at which reaction can occur.

reactants and 360 kJ greater than that of the products. The state of the system at this point is often referred to as a *transition state*, intermediate between reactants and products.

The exact nature of the activated complex is difficult to determine. For this reaction, the activated complex might be a "pseudomolecule" made up of CO and NO_2 molecules in close contact. The path of the reaction might be more or less as follows:

$$O{\equiv}C + O{-}N{=}O \longrightarrow O{\equiv}C{\cdots}O{\cdots}N{=}O \longrightarrow O{=}C{=}O + N{=}O$$

reactants — activated complex — products

The dotted lines stand for "partial bonds" in the activated complex. The N—O bond in the NO_2 molecule has been partially broken. A new bond between carbon and oxygen has started to form.

The idea of the activated complex was developed by, among others, Henry Eyring at Princeton in the 1930s. It forms the basis of the *transition-state model* for reaction rate, which assumes that the activated complex

- is in equilibrium, at low concentrations, with the reactants.
- may either decompose to products by "climbing" over the energy barrier or, alternatively, revert back to reactants.

With these assumptions, it is possible to develop an expression for the rate constant k. Although the expression is too complex to discuss here, we show some of the results in Table 11.3.

The transition-state model is generally somewhat more accurate than the collision model (at least with $p = 1$). Another advantage is that it explains why

CHEMISTRY THE **HUMAN** SIDE

Chemical kinetics, the subject of this chapter, evolved from an art into a science in the first half of the twentieth century. One person more than any other was responsible for that change: Henry Eyring. Born in a Mormon settlement in Mexico, Henry immigrated to Arizona with his parents in 1912, when the Mexican revolution broke out. Many years later, he became a U.S. citizen, appearing before a judge who had just naturalized Albert Einstein.

Eyring's first exposure to kinetics came as a young chemistry instructor at the University of Wisconsin in the 1920s. There he worked on the thermal decomposition of N_2O_5 (Section 11-2). In 1931 Eyring came to Princeton, where he developed the transition-state model of reaction rates. Using this model and making reasonable guesses about the nature of the activated complex, Eyring calculated rate constants that agreed well with experiment. After 15 productive years at Princeton, Eyring returned to his Mormon roots at the University of Utah in Salt Lake City. While serving as dean of the graduate school, he found time to do ground-breaking research on the kinetics of life processes, including the mechanism of aging.

Henry Eyring's approach to research is best described in his own words:

> I perceive myself as rather uninhibited, with a certain mathematical facility and more interest in the broad aspects of a problem than the delicate nuances. I am more interested in discovering what is over the next rise than in assiduously cultivating the beautiful garden close at hand.

Courtesy of Allyson Mower

Henry Eyring
(1901–1981)

Henry's enthusiasm for chemistry spilled over into just about every other aspect of his life. Each year he challenged his students to a 50-yard dash held at the stadium of the University of Utah. He continued these races until he was in his mid-seventies. Henry never won, but on one occasion he did make the *CBS Evening News*.

the activation energy is ordinarily much smaller than the bond enthalpies in the reactant molecules. Consider, for example, the reaction

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

where E_a = 134 kJ/mol. This is considerably smaller than the amount of energy required to break any of the bonds in the reactants.

C≡O 1075 kJ N═O 607 kJ N—O 222 kJ

Forming the activated complex shown in Figure 11.10 requires the absorption of relatively little energy, because it requires only the weakening of reactant bonds rather than their rupture.

11-5 Reaction Rate and Temperature

The rates of most reactions increase as the temperature rises (Figure 11.11). A person in a hurry to prepare dinner applies this principle by turning the dial on the oven to the highest possible setting. By storing the leftovers in a refrigerator, the chemical reactions responsible for food spoilage are slowed down. As a general and very approximate rule, it is often stated that an increase in temperature of 10°C doubles the reaction rate. If this rule holds, foods should deteriorate four times as rapidly at room temperature (25°C) as they do in a refrigerator at 5°C.

Hibernating animals lower their body temperature, slowing down life processes.

The effect of temperature on reaction rate can be explained in terms of kinetic theory. Recall from Chapter 5 that raising the temperature greatly increases the fraction of molecules having very high speeds and hence high kinetic energies (kinetic energy = $mu^2/2$). These are the molecules that are most likely to react when they collide. The higher the temperature, the larger the fraction of molecules that can provide the activation energy required for reaction. This effect is apparent from Figure 11.12 where the distribution of kinetic energies is shown at two different temperatures. Notice that the fraction of molecules having a kinetic energy equal to or greater than the activation energy E_a (shaded area) is considerably larger at the

$T \uparrow \rightarrow k \uparrow \rightarrow$ rate $\uparrow$

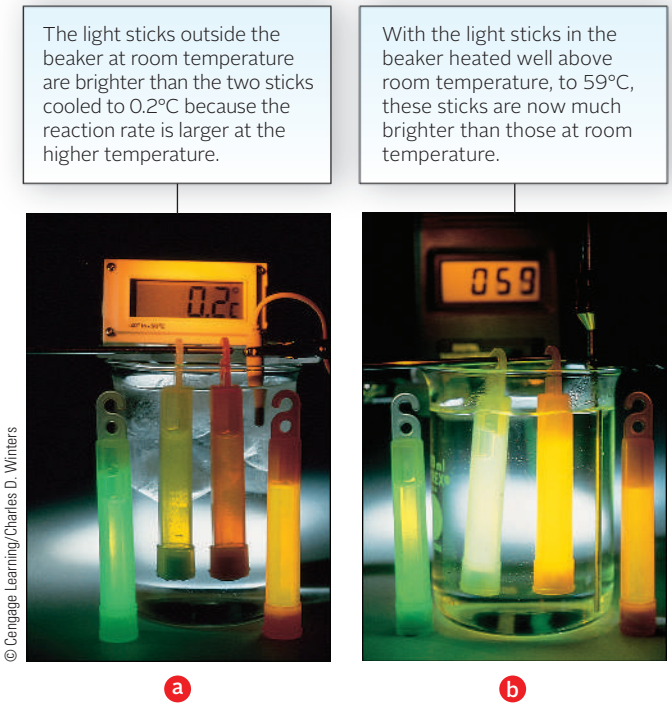


Figure 11.11 Temperature and reaction rate. A chemical reaction in the Cyalume® light sticks produces light as it takes place.

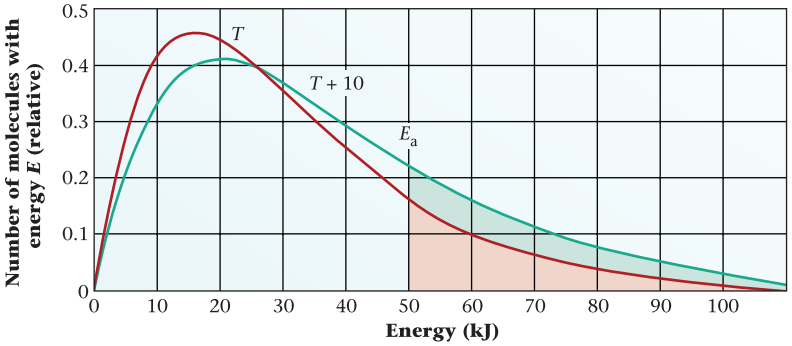


Figure 11.12 Temperature and activation energy. When T is increased to $T + 10$, the number of molecules with high energies increases. Hence, many more molecules possess sufficient energy to react and the reaction occurs more rapidly. If E_a is 50 kJ/mol, any molecule with this or a higher energy can react. The number of molecules that react at T is represented by the red area under the T curve, and the number that react at $T + 10$ is represented by the sum of the red and blue areas under the $T + 10$ curve.

higher temperature. Hence the fraction of effective collisions increases; this is the major factor causing reaction rate to increase with temperature.

The Arrhenius Equation

You will recall from Section 11-4 that the collision model yields the following expression for the rate constant:

$$k = p \times Z \times e^{-E_a/RT} \tag{11.6}$$

The steric factor, p, is presumably temperature-independent. The collision number, Z, is relatively insensitive to temperature. For example, when the temperature increases from 500 to 600 K, Z increases by less than 10%. Hence to a good degree of approximation we can write, as far as temperature dependence is concerned,

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

where A is a constant. Taking the natural logarithm of both sides of this equation,

$$\ln k = \ln A - E_a/RT$$

This equation was first shown to be valid by Svante Arrhenius (Chapter 4) in 1889. It is commonly referred to as the **Arrhenius equation**. This equation expresses the temperature dependence of the rate constant.

Comparing the Arrhenius equation with the general equation for a straight line,

$$y = b + mx$$

it should be clear that a plot of $\ln k$ ("y") versus $1/T$ ("x") should be linear. The slope of the straight line, m, is equal to $-E_a/R$. Figure 11.13 shows such a plot for

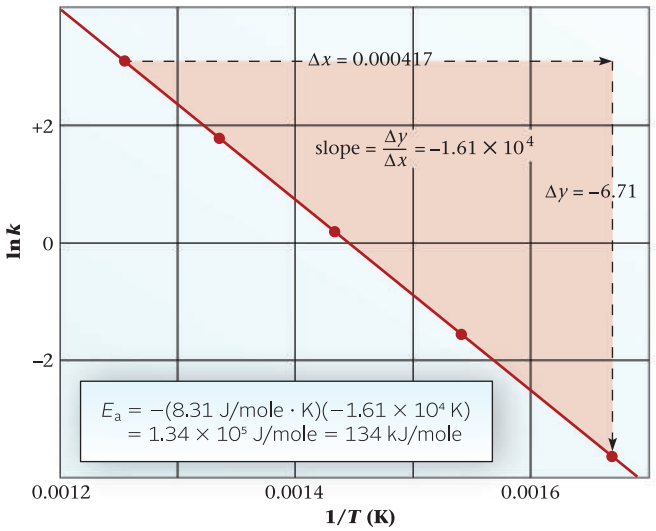


Figure 11.13 Arrhenius plot. A plot of $\ln k$ versus $1/T$ (k = rate constant, T = Kelvin temperature) is a straight line. From the slope of this line, the activation energy can be determined: $E_a = -R \times$ slope.

the CO-NO_2 reaction. The slope appears to be about -1.61×10^4 K. Hence

$$\frac{-E_a}{R} = -1.61 \times 10^4 \text{ K}$$

$$E_a = 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}} (1.61 \times 10^4 \text{ K}) = 1.34 \times 10^5 \text{ J/mol} = 134 \text{ kJ/mol}$$

Two-Point Equation Relating *k* and *T*

The Arrhenius equation can be expressed in a different form by following the procedure used with the Clausius-Clapeyron equation in Chapter 9. At two different temperatures, T_2 and T_1,

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

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

Subtracting the second equation from the first eliminates ln *A*, and we obtain

$$\ln k_2 - \ln k_1 = \frac{-E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad \textbf{(11.7a)}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \textbf{(11.7b)}$$

Taking $R = 8.31$ J/mol·K, the activation energy is expressed in joules per mole.

EXAMPLE 11.8 GRADED

Consider the first-order decomposition of A. The following is known about it:

- the rate constant doubles when the temperature increases from 15°C to 25°C.
- the rate constant for the decomposition at 40°C is 0.0125 s^{-1}.

a What is the activation energy for the decomposition?

ANALYSIS

Information given:	*k* at 15°C(k_1); *k* at 25°C($k_2 = 2k_1$)
Information implied:	*R* value
Asked for:	E_a

STRATEGY

1. Take 15°C (288 K) as T_1 where the rate constant is k_1.
2. Take 25°C (298 K) as T_2 where the rate constant is $k_2 = 2k_1$.
3. Substitute into Equation 11.7b.

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

SOLUTION

E_a

$$\ln \frac{2k_1}{k_1} = \frac{E_a}{8.31 \text{ J/mol} \cdot \text{K}}\left[\frac{1}{288} - \frac{1}{298}\right] \longrightarrow (0.693)(8.31) = E_a\left[\frac{1}{288} - \frac{1}{298}\right]$$

$$E_a = 4.9 \times 10^4 \text{ J/mol} = 49 \text{ kJ/mol}$$

continued

b What is the half-life of A at 78°C?

ANALYSIS

Information given:	from part (a): E_a(4.9 × 10^4 J/mol) k_1 (0.0125 s^{-1}) at T_1 (40°C); T_2 (78°C)
Information implied:	R value
Asked for:	$t_{1/2}$ at 78°C

STRATEGY

1. Find k_2 at 78°C (T_2) by substituting into Equation 11.7b. Recall that k_1 and T_1 are given.
2. Find $t_{1/2}$ at 78°C by substituting into Equation 11.3.

SOLUTION

k_2 at 78°C

$$\ln k_2 - \ln(0.0125) = \frac{4.9 \times 10^4 \text{ J/mol}}{8.31 \text{ J/mol·K}}\left(\frac{1}{313 \text{ K}} - \frac{1}{351 \text{ K}}\right)$$

$$\ln k_2 = 2.04 + (-4.38) = -2.34 \longrightarrow k_2 = e^{-2.34} = 0.0963 \text{ s}^{-1}$$

$t_{1/2}$

$$t_{1/2} = \frac{0.693}{0.0963 \text{ s}^{-1}} = 7.20 \text{ s}$$

c At what temperature will the rate of the decomposition of 0.165 M be 0.124 mol/L·s?

ANALYSIS

Information given:	from part (a): E_a(4.9 × 10^4 J/mol); from part (b): k_1 (0.0125 s^{-1}) at T_1 (40°C) rate (0.124 mol/L·s) for [A] (0.165 M)
Information implied:	R value
Asked for:	T at the given rate for A.

STRATEGY

1. Find k (k_2) for the decomposition at T_2 by substituting into the rate expression.
2. Substitute into the Arrhenius equation (11.7b).

SOLUTION

k

$$0.124 \text{ mol/L·s} = k(0.165 \text{ mol/L}) \longrightarrow k = 0.752 \text{ s}^{-1}$$

T_2

$$\ln(0.752 \text{ s}^{-1}) - \ln(0.0125 \text{ s}^{-1}) = \frac{4.9 \times 10^4 \text{ J/mol}}{8.31 \text{ J/mol·K}}\left(\frac{1}{313 \text{ K}} - \frac{1}{T_2}\right)$$

$$4.10 = 5.9 \times 10^3\left(\frac{1}{313 \text{ K}} - \frac{1}{T_2}\right) \longrightarrow T_2 = 4.0 \times 10^2 \text{ K} = 1.3 \times 10^2\text{°C}$$

11-6 Catalysis

A* catalyst *is a substance that increases the rate of a reaction without being consumed by it. It does this by changing the reaction path to one with a lower activation energy. Frequently the catalyzed path consists of two or more steps. In this case, the activation energy for the uncatalyzed reaction exceeds that for any of the steps in the catalyzed reaction (Figure 11.14).

Heterogeneous Catalysis

A *heterogeneous catalyst* is one that is in a different phase from the reaction mixture. Most commonly, the catalyst is a solid that increases the rate of a gas-phase or liquid-phase reaction. An example is the decomposition of N_2O on gold:

$$N_2O(g) \xrightarrow{Au} N_2(g) + \tfrac{1}{2}O_2(g)$$

In the catalyzed decomposition, N_2O is chemically adsorbed on the surface of the solid. A chemical bond is formed between the oxygen atom of an N_2O molecule and a gold atom on the surface. This weakens the bond joining nitrogen to oxygen, making it easier for the N_2O molecule to break apart. Symbolically, this process can be shown as

$$N{\equiv}N{-}O(g) + Au(s) \longrightarrow N{\equiv}N{---}O{---}Au(s) \longrightarrow N{\equiv}N(g) + O(g) + Au(s)$$

where the broken lines represent weak covalent bonds.

Perhaps the most familiar example of heterogeneous catalysis is the series of reactions that occur in the catalytic converter of an automobile (Figure 11.15). Typically this device contains 1 to 3 g of platinum metal mixed with rhodium. The platinum catalyzes the oxidation of carbon monoxide and unburned hydrocarbons such as benzene, C_6H_6:

$$2CO(g) + O_2(g) \xrightarrow{Pt} 2CO_2(g)$$

$$C_6H_6(g) + \tfrac{15}{2}O_2(g) \xrightarrow{Pt} 6CO_2(g) + 3H_2O(g)$$

The rhodium acts as a catalyst to destroy nitrogen oxide by the reaction

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

One problem with heterogeneous catalysis is that the solid catalyst is easily "poisoned." Foreign materials deposited on the catalytic surface during the reaction reduce or even destroy its effectiveness. A major reason for using unleaded gasoline is that lead metal poisons the Pt-Rh mixture in the catalytic converter.

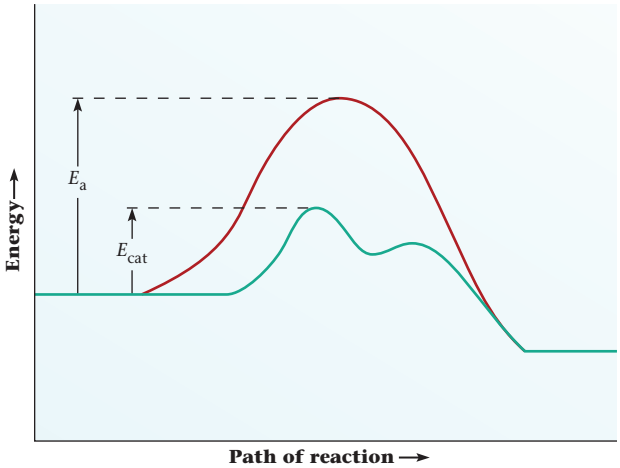


Figure 11.14 Catalysis and activation energy. By changing the path by which a reaction occurs, a catalyst can lower the activation energy that is required and so speed up a reaction.

Many industrial processes use heterogeneous catalysts.

Homogeneous Catalysis

A *homogeneous catalyst* is one that is present in the same phase as the reactants. It speeds up the reaction by forming a reactive intermediate that decomposes to give products. In this way, the catalyst provides an alternative process of lower activation energy.

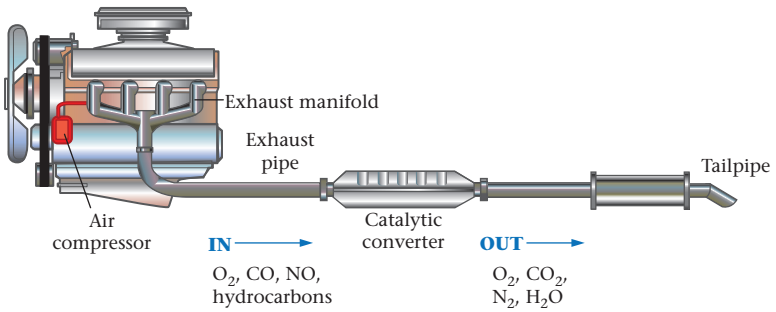


Figure 11.15 Automobile catalytic converter. Catalytic converters contain a "three-way" catalyst designed to convert CO to CO_2, unburned hydrocarbons to CO_2 and H_2O, and NO to N_2. The active components of the catalysts are the precious metals platinum and rhodium; palladium is sometimes used as well.

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Figure 11.16 Enzyme catalysis. An enzyme in the potato is catalyzing the decomposition of a hydrogen peroxide solution, as shown by the bubbles of oxygen.

An example of a reaction that is subject to homogeneous catalysis is the decomposition of hydrogen peroxide in aqueous solution:

$$2H_2O_2(aq) \longrightarrow 2H_2O + O_2(g)$$

Under ordinary conditions, this reaction occurs very slowly. However, if a solution of sodium iodide, NaI, is added, reaction occurs almost immediately; you can see the bubbles of oxygen forming.

The catalyzed decomposition of hydrogen peroxide is believed to take place by a two-step path:

$$\text{Step 1: } H_2O_2(aq) + I^-(aq) \longrightarrow H_2O + IO^-(aq)$$

$$\text{Step 2: } H_2O_2(aq) + IO^-(aq) \longrightarrow H_2O + O_2(g) + I^-(aq)$$

$$2H_2O_2(aq) \longrightarrow 2H_2O + O_2(g)$$

Notice that the end result is the same as in the direct reaction.

The I^- ions are not consumed in the reaction. For every I^- ion used up in the first step, one is produced in the second step. The activation energy for this two-step process is much smaller than for the uncatalyzed reaction.

Enzymes

Many reactions that take place slowly under ordinary conditions occur readily in living organisms in the presence of catalysts called *enzymes*. Enzymes are protein molecules of high molar mass. An example of an enzyme-catalyzed reaction is the decomposition of hydrogen peroxide:

$$2H_2O_2(aq) \longrightarrow 2H_2O + O_2(g)$$

In blood or tissues, this reaction is catalyzed by an enzyme called catalase (Figure 11.16). When 3% hydrogen peroxide is used to treat a fresh cut or wound, oxygen gas is given off rapidly. The function of catalase in the body is to prevent the build-up of hydrogen peroxide, a powerful oxidizing agent.

Many enzymes are extremely specific. For example, the enzyme maltase catalyzes the hydrolysis of maltose:

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}(aq)} + H_2O \xrightarrow{\text{maltase}} \underset{\text{glucose}}{2C_6H_{12}O_6(aq)}$$

This is the only function of maltase, but it is one that no other enzyme can perform. Many such digestive enzymes are required for the metabolism of carbohydrates, proteins, and fats. It has been estimated that without enzymes, it would take upward of 50 years to digest a meal.

That would make dieting a lot easier.

Enzymes, like all other catalysts, lower the activation energy for reaction. They can be enormously effective; it is not uncommon for the rate constant to increase by a factor of 10^{12} or more. However, from a commercial standpoint, enzymes have some drawbacks. A particular enzyme operates best over a narrow range of temperature. An increase in temperature frequently deactivates an enzyme by causing the molecule to "unfold," changing its characteristic shape. Recently, chemists have discovered that this effect can be prevented if the enzyme is immobilized by bonding to a solid support. Among the solids that have been used are synthetic polymers, porous glass, and even stainless steel. The development of immobilized enzymes has led to a host of new products. The sweetener aspartame, used in many diet soft drinks, is made using the enzyme aspartase in immobilized form.

11-7 Reaction Mechanisms

A **reaction mechanism** is a description of a path, or a sequence of steps, by which a reaction occurs at the molecular level. In the simplest case, only a single step is involved. This is a collision between two reactant molecules. This is the mech-

anism for the reaction of CO with NO_2 at high temperatures, above about 600 K:

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

At lower temperatures the reaction between carbon monoxide and nitrogen dioxide takes place by a quite different mechanism. Two steps are involved:

$$\begin{aligned} NO_2(g) + NO_2(g) &\longrightarrow NO_3(g) + NO(g) \\ CO(g) + NO_3(g) &\longrightarrow CO_2(g) + NO_2(g) \\ \hline CO(g) + NO_2(g) &\longrightarrow NO(g) + CO_2(g) \end{aligned}$$

Reaction mechanisms frequently change with *T*, sometimes with *P*.

Notice that the overall reaction, obtained by summing the individual steps, is identical with that for the one-step process. The rate expressions are quite different, however:

high temperatures: $\text{rate} = k[CO][NO_2]$

low temperatures: $\text{rate} = k[NO_2]^2$

In general, the nature of the rate expression and hence ***the reaction order depends on the mechanism by which the reaction takes place.***

Elementary Steps

The individual steps that constitute a reaction mechanism are referred to as **elementary steps.** These steps may be *unimolecular*

$$A \longrightarrow B + C \qquad \text{rate} = k[A]$$

bimolecular

$$A + B \longrightarrow C + D \qquad \text{rate} = k[A][B]$$

or, in rare cases, *termolecular*

$$A + B + C \longrightarrow D + E \qquad \text{rate} = k[A][B][C]$$

Notice from the rate expressions just written that ***the rate of an elementary step is equal to a rate constant k multiplied by the concentration of each reactant molecule.*** This rule is readily explained. Consider, for example, a step in which two molecules, A and B, collide effectively with each other to form C and D. As pointed out earlier, the rate of collision and hence the rate of reaction will be directly proportional to the concentration of each reactant.

Slow Steps

Often, one step in a mechanism is much slower than any other. If this is the case, *the slowest step is a* **rate-determining step.** That is, the rate of the overall reaction can be taken to be that of the slow step. Consider, for example, a three-step reaction:

$$\begin{aligned} &\text{Step 1: } A \longrightarrow B \quad \text{(fast)} \\ &\text{Step 2: } B \longrightarrow C \quad \text{(slow)} \\ &\text{Step 3: } C \longrightarrow D \quad \text{(fast)} \\ \hline &\qquad A \longrightarrow D \end{aligned}$$

The rate at which A is converted to D (the overall reaction) is approximately equal to the rate of conversion of B to C (the slow step).

To understand the rationale behind this rule, and its limitations, consider an analogous situation. Suppose three people (A, B, and C) are assigned to grade general chemistry examinations that contain three questions. On the average, A spends 10 s grading question 1 and B spends 15 s grading question 2. In contrast,

Maybe questions 1 and 2 were multiple-choice.

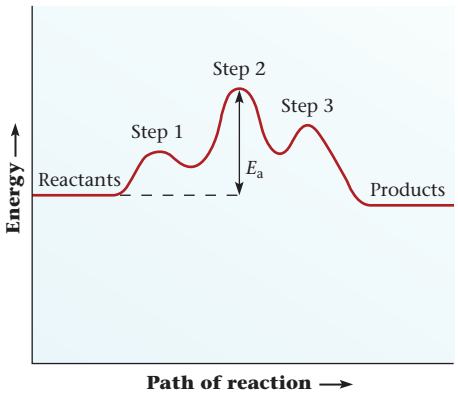


Figure 11.17 Reaction plot for a reaction with a three-step mechanism. The second of the three steps is rate-determining.

C, the ultimate procrastinator, takes 5 min to grade question 3. The rate at which exams are graded is

$$\frac{1 \text{ exam}}{10 \text{ s} + 15 \text{ s} + 300 \text{ s}} = \frac{1 \text{ exam}}{325 \text{ s}} = 0.00308 \text{ exam/s}$$

This is approximately equal to the rate of the slower grader:

$$\frac{1 \text{ exam}}{300 \text{ s}} = 0.00333 \text{ exam/s}$$

Extrapolating from general chemistry exams to chemical reactions, we can say that

- the overall rate of the reaction cannot exceed that of the slowest step.
- if that step is by far the slowest, its rate will be approximately equal to that of the overall reaction.
- the slowest step in a mechanism is ordinarily the one with the highest activation energy (Figure 11.17).

Deducing a Rate Expression from a Proposed Mechanism

As we have seen, rate expressions for reactions must be determined experimentally. Once this has been done, it is possible to derive a plausible mechanism compatible with the observed rate expression. This, however, is a rather complex process and we will not attempt it here. Instead, we will consider the reverse process, which is much more straightforward. *Given a mechanism for a several-step reaction, how can you deduce the rate expression corresponding to that mechanism?*

In principle, at least, all you have to do is to apply the rules just cited.

1. ***Find the slowest step and equate the rate of the overall reaction to the rate of that step.***
2. ***Find the rate expression for the slowest step.***

To illustrate this process, consider the two-step mechanism for the low-temperature reaction between CO and NO_2.

$$\begin{array}{rll} NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g) & & \text{(slow)} \\ CO(g) + NO_3(g) \longrightarrow CO_2(g) + NO_2(g) & & \text{(fast)} \\ \hline CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g) & & \end{array}$$

Applying the above rules in order,

$$\text{rate of overall reaction} = \text{rate of first step} = k[NO_2]^2$$

This analysis explains why the rate expression for the two-step mechanism is different from that for the direct, one-step reaction.

Elimination of Intermediates

Sometimes the rate expression obtained by the process just described involves a reactive intermediate, that is, a species produced in one step of the mechanism and consumed in a later step. Ordinarily, concentrations of such species are too small to be determined experimentally. Hence they must be eliminated from the rate expression if it is to be compared with experiment. The final rate expression usually includes only those species that appear in the balanced equation for the

reaction. Sometimes, the concentration of a catalyst is included, but never that of a reactive intermediate.

To illustrate this situation, consider the reaction between nitric oxide and chlorine, which is believed to proceed by a two-step mechanism:

$$\text{Step 1:} \quad \text{NO}(g) + \text{Cl}_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{NOCl}_2(g) \qquad \text{(fast)}$$

$$\text{Step 2:} \quad \text{NOCl}_2(g) + \text{NO}(g) \xrightarrow{k_2} 2\text{NOCl}(g) \qquad \text{(slow)}$$

$$\text{2NO}(g) + \text{Cl}_2(g) \longrightarrow 2\text{NOCl}(g)$$

The first step occurs rapidly and reversibly; a dynamic equilibrium is set up in which the rates of forward and reverse reactions are equal. Because the second step is slow and rate-determining, it follows that

$$\text{rate of overall reaction} = \text{rate of step 2} = k_2[\text{NOCl}_2][\text{NO}]$$

The rate expression just written is unsatisfactory in that it cannot be checked against experiment. The species NOCl_2 is a reactive intermediate whose concentration is too small to be measured accurately, if at all. To eliminate the $[\text{NOCl}_2]$ term from the rate expression, recall that the rates of forward and reverse reactions in step 1 are equal, which means that

If the concentration of a species can't be measured, it had better not appear in the rate expression.

$$k_1[\text{NO}] \times [\text{Cl}_2] = k_{-1}[\text{NOCl}_2]$$

Solving for $[\text{NOCl}_2]$ and substituting in this rate expression,

$$[\text{NOCl}_2] = \frac{k_1[\text{NO}][\text{Cl}_2]}{k_{-1}}$$

$$\text{rate of overall reaction} = k_2[\text{NOCl}_2] \times [\text{NO}] = \frac{k_2k_1[\text{NO}]^2[\text{Cl}_2]}{k_{-1}}$$

The quotient k_2k_1/k_{-1} is the experimentally observed rate constant for the reaction, which is found to be second-order in NO and first-order in Cl_2, as predicted by this mechanism.

EXAMPLE 11.9

The decomposition of ozone, O_3, to diatomic oxygen, O_2, is believed to occur by a two-step mechanism:

$$\text{Step 1:} \quad \text{O}_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{O}_2(g) + \text{O}(g) \qquad \text{(fast)}$$

$$\text{Step 2:} \quad \text{O}_3(g) + \text{O}(g) \xrightarrow{k_2} 2\text{O}_2(g) \qquad \text{(slow)}$$

$$2\text{O}_3(g) \longrightarrow 3\text{O}_2(g)$$

Obtain the rate expression corresponding to this mechanism.

STRATEGY

1. The rate-limiting step is the slow step (step 2). Write its rate expression.
2. Write the rate expressions for the forward and reverse reactions of step 1. Since step 1 is in equilibrium, rate forward reaction = rate backward reaction.
3. Express the rates of step 1 in terms of [O] and substitute into the rate expression for step 2.
4. Combine all constants into a single constant k.

continued

SOLUTION

1. Rate expression for step 2	$\text{rate} = k_2[O_3][O]$
2. Rate of forward reaction	$\text{rate} = k_1[O_3]$
Rate of reverse reaction	$\text{rate} = k_{-1}[O_2][O]$
Rate forward reaction = rate reverse reaction	$k_1[O_3] = k_{-1}[O_2][O]$
3. [O]	$[O] = \dfrac{k_1[O_3]}{k_{-1}[O_2]}$
Overall rate	$\text{rate} = k_2[O_3]\left(\dfrac{k_1[O_3]}{k_{-1}[O_2]}\right)$
4. Combine all constants	$k = \dfrac{k_2k_1}{k_{-1}}$
	$\text{rate} = k\dfrac{[O_3]^2}{[O_2]}$

It is important to point out one of the limitations of mechanism studies. Usually more than one mechanism is compatible with the same experimentally obtained rate expression. To make a choice between alternative mechanisms, other evidence must be considered. A classic example of this situation is the reaction between hydrogen and iodine

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

for which the observed rate expression is

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

For many years, it was assumed that the H_2-I_2 reaction occurs in a single step, a collision between an H_2 molecule and an I_2 molecule. That would, of course, be compatible with the rate expression above. However, there is now evidence to indicate that a quite different and more complex mechanism is involved (see Problem 77).

CHEMISTRY **BEYOND** THE CLASSROOM

The Ozone Story

In recent years, a minor component of the atmosphere, ozone, has received a great deal of attention. Ozone, molecular formula O_3, is a pale blue gas with a characteristic odor that can be detected after lightning activity, in the vicinity of electric motors, or near a subway train.

Depending on its location in the atmosphere, ozone can be a villain or a beleaguered hero. In the lower atmosphere (the *troposphere*), ozone is bad news; it is a major component of photochemical smog, formed by the reaction sequence

$$\begin{aligned} NO_2(g) &\longrightarrow NO(g) + O(g) \\ O_2(g) + O(g) &\longrightarrow O_3(g) \\ \hline NO_2(g) + O_2(g) &\longrightarrow NO(g) + O_3(g) \end{aligned}$$

Ozone is an extremely powerful oxidizing agent, which explains its toxicity to animals and humans. At partial pressures as low as 10^{-7} atm, it can cut in half the rate of photosynthesis by plants.

In the upper atmosphere (the *stratosphere*), the situation is quite different. There the partial pressure of ozone goes through a maximum of about 10^{-5} atm at an altitude of 30 km. From 95% to 99% of sunlight in the ultraviolet region between 200 and 300 nm is absorbed by ozone in this region, commonly referred to as the "ozone layer." The mechanism by which this occurs can be represented by the following pair of equations:

$$\begin{aligned} O_3(g) + \text{UV radiation} &\longrightarrow O_2(g) + O(g) \\ O_2(g) + O(g) &\longrightarrow O_3(g) + \text{heat} \\ \hline \text{UV radiation} &\longrightarrow \text{heat} \end{aligned}$$

The net effect is simply the conversion of ultraviolet to thermal energy.

If the UV radiation were to reach the surface of the earth, it could have several adverse effects. A 5% decrease in ozone concentration could increase the incidence of skin cancer by 10% to 20%. Ultraviolet radiation is also a factor in diseases of the eye, including cataract formation.

Ozone molecules in the stratosphere can decompose by the reaction

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

This reaction takes place rather slowly by direct collision between an O_3 molecule and an O atom. It can occur more rapidly by a two-step process in which a chlorine atom acts as a catalyst:

$$O_3(g) + Cl(g) \longrightarrow O_2(g) + ClO(g) \quad k = 5.2 \times 10^9 \text{ L/mol} \cdot \text{s at 220 K}$$
$$ClO(g) + O(g) \longrightarrow Cl(g) + O_2(g) \quad k = 2.6 \times 10^{10} \text{ L/mol} \cdot \text{s at 220 K}$$
$$\overline{O_3(g) + O(g) \longrightarrow 2O_2(g)}$$

A single chlorine atom can bring about the decomposition of tens of thousands of ozone molecules. Bromine atoms can substitute for chlorine; indeed the rate constant for the Br-catalyzed reaction is larger than that for the reaction just cited.

The chlorine atoms that catalyze the decomposition of ozone come from chlorofluorocarbons (CFCs) used in many refrigerators and air conditioners. A major culprit is CF_2Cl_2, Freon, which forms Cl atoms when exposed to ultraviolet radiation at 200 nm:

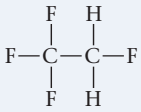
$$CF_2Cl_2(g) \longrightarrow CF_2Cl(g) + Cl(g)$$

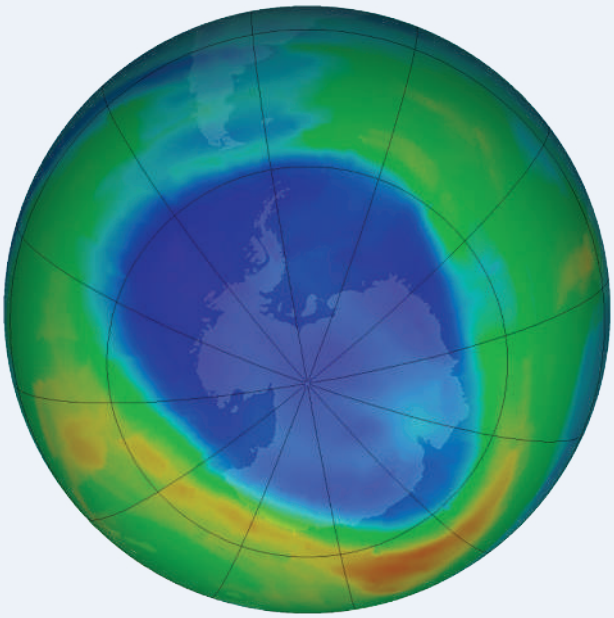
The two scientists who first suggested (in 1974) that CFCs could deplete the ozone layer, F. Sherwood Rowland (1927–2012) and Mario Molina (1943–), won the 1995 Nobel Prize in chemistry, along with Paul Crutzen (1933–), who first suggested that oxides of nitrogen in the atmosphere could catalyze the decomposition of ozone.

Recent research suggests that ozone depletion has affected Antarctica's climate, cooling the interior and warming the extremities. The catalyzed decomposition of ozone is known to be responsible for the ozone hole (Figure A) that develops in Antarctica each year in September and October, at the end of winter in the Southern Hemisphere. No ozone is generated during the long, dark Antarctic winter. Meanwhile, a heterogeneous reaction occurring on clouds of ice crystals at −85°C produces species such as Cl_2, Br_2, and HOCl. When the Sun reappears in September, these molecules decompose photochemically to form Cl or Br atoms, which catalyze the decomposition of ozone, lowering its concentration.

Ozone depletion is by no means restricted to the Southern Hemisphere. In the extremely cold winter of 1994–1995, a similar "ozone hole" was found in the Arctic. Beyond that, the concentration of ozone in the atmosphere over parts of Siberia dropped by 40%.

In 1987 an international treaty was signed in Montreal to cut back on the use of CFCs. Production of Freon in the United States ended in 1996. It has been replaced in automobile air conditioners by a related compound with no chlorine atoms, $C_2H_2F_4$:





NASA Ozone Watch

Figure A The ozone (O_3) layer over the southern hemisphere stratosphere August 30, 2013. The thickness is measured in Dobsons (= 0.01 mm thick). The normal ozone layer for the stratosphere is 360 Dobsons. The ozone "hole" is 200–220 Dobsons.

Key Concepts

1. Determine the rate expression (reaction order) from
   - initial rate data.
   (Examples 11.1, 11.2, 11.3; Problems 19–28)
   - concentration-time data, using Table 11.2.
   (Example 11.6; Problems 29, 30)
   - reaction mechanism.
   (Example 11.9; Problems 77, 78)
2. Relate concentration to time for a first-order reaction. **(Examples 11.4, 11.5; Problems 35–48)**
3. Use the Arrhenius equation to relate rate constant to temperature. **(Example 11.8; Problems 57–70)**

Key Equations

Rate of reaction $aA + bB \longrightarrow cC + dD$

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

Zero-order reaction $\text{rate} = k \qquad [A] = [A]_o - kt$

First-order reaction $\text{rate} = k[A] \qquad \ln[A]_o/[A] = kt \qquad t_{1/2} = 0.693/k$

Second-order reaction $\text{rate} = k[A]^2 \quad 1/[A] - 1/[A]_o = kt$

Rate constant $\text{rate} = p \times Z \times e^{-E_a/RT}$

Arrhenius equation $$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Key Terms

activation energy
catalyst
elementary steps
first-order reaction
half-life
order of reaction
rate constant
rate-determining step
rate expression
reaction mechanism
reaction rate
second-order reaction
zero-order reaction

Summary Problem

Hydrogen peroxide decomposes to water and oxygen according to the following reaction:

$H_2O_2(aq) \longrightarrow H_2O + \frac{1}{2}O_2(g)$

Its rate of decomposition is measured by titrating samples of the solution with potassium permanganate ($KMnO_4$) at certain timed intervals.

(a) At what rate is H_2O_2 decomposing if O_2 is being formed at the rate of 0.0215 mol/L · min? At what rate is H_2O being produced?

(b) Initial rate experiments at 25°C for the decomposition give the following data:

$[H_2O_2]$	Initial rate (mol/L · min)
0.200	1.04×10^{-4}
0.300	1.55×10^{-4}
0.500	2.59×10^{-4}

1. What is the order of the reaction?
2. Write the rate equation for the decomposition.
3. Calculate the rate constant and the half-life for the reaction at 25°C.

(c) Hydrogen peroxide is sold commercially as a 30.0% solution. If the solution is kept at room temperature (25°C), how long will it take for the solution to become 10.0% H_2O_2?

(d) It has been determined that at 40°C, the rate constant for the reaction is 1.93×10^{-3} min^{-1}. Calculate the activation energy for the decomposition of H_2O_2.

(e) Manufacturers recommend that solutions of hydrogen peroxide be kept in a refrigerator at 4°C. How much longer will it take a 30.0% solution to decompose to 10.0% if one follows the manufacturer's recommendations?

(f) The rate constant for the catalyzed decomposition at 25°C is 2.95×10^8 min^{-1}.

1. What is the half-life of the catalyzed reaction?
2. What is the rate of the catalyzed decomposition of 0.500 *M* H_2O_2?
3. How much faster is the rate of the catalyzed reaction compared to that of the uncatalyzed decomposition?

(g) Hydrogen peroxide in basic solution oxidizes iodide ions to iodine. The proposed mechanism for this reaction is

$H_2O_2(aq) + I^-(aq) \longrightarrow HOI(aq) + OH^-(aq)$ slow
$HOI(aq) + I^-(aq) \rightleftharpoons I_2(aq) + OH^-(aq)$ fast

Write the overall redox reaction. Write a rate law consistent with this proposed mechanism.

Answers

(a) rate H_2O_2 = rate H_2O = 0.0430 mol/L·min
(b) 1. first-order
2. rate = $k[H_2O_2]$
3. $k = 5.17 \times 10^{-4}$ min^{-1}; $t_{1/2}$ = 22.3 hours
(c) 35.4 hours
(d) 68 kJ/mol
(e) 249 hours
(f) 1. 2.35×10^{-9} min
2. 1.48×10^{8} mol/L·min
3. 5.71×10^{11} times faster, or about 500 trillion times faster
(g) $H_2O_2(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2OH^-(aq)$; rate = $k[H_2O_2] \times [I^-]$

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

11-1 Meaning of Reaction Rate

1. Express the rate of the reaction

$$2N_2H_4\,(l) + N_2O_4\,(l) \longrightarrow 3N_2\,(g) + 4H_2O(g)$$

in terms of
(**a**) $\Delta[N_2O_4]$ (**b**) $\Delta[N_2]$

2. Express the rate of the reaction

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$$

in terms of
(**a**) $\Delta[N_2O]$ (**b**) $\Delta[O_2]$

3. Consider the following hypothetical reaction:

$$X(g) \longrightarrow Y(g)$$

A 200.0-mL flask is filled with 0.120 moles of X. The disappearance of X is monitored at timed intervals. Assume that temperature and volume are kept constant. The data obtained are shown in the table below.

Time (min)	0	20	40	60	80
moles of X	0.120	0.103	0.085	0.071	0.066

(**a**) Make a similar table for the appearance of Y.
(**b**) Calculate the average disappearance of X in *M*/s in the first two 20-minute intervals.
(**c**) What is the average rate of appearance of Y between the 20- and 60-minute intervals?

4. Consider the following hypothetical reaction:

$$2AB_2(g) \longrightarrow A_2(g) + 2B_2(g)$$

A 500.0-mL flask is filled with 0.384 mol of AB_2. The appearance of A_2 is monitored at timed intervals. Assume that temperature and volume are kept constant. The data obtained are shown in the table below.

Time (min)	0	10	20	30	40	50
moles of A_2	0	0.0541	0.0833	0.1221	0.1432	0.1567

(**a**) Make a similar table for the disappearance of AB_2.
(**b**) What is the average rate of disappearance of AB_2 over the second and third 10-minute intervals?
(**c**) What is the average rate of appearance of A_2 between $t = 30$ and $t = 50$?

5. Consider the combustion of ethane:

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

If the ethane is burning at the rate of 0.20 mol/L·s, at what rates are CO_2 and H_2O being produced?

6. For the reaction

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O$$

It was found that at a particular instant, bromine was being formed at the rate of 0.029 mol/L·s. At that instant, at what rate
(**a**) are the hydrogen ions being consumed?
(**b**) is water being formed?
(**c**) are the bromide ions being consumed?

7. Nitrosyl chloride (NOCl) decomposes to nitrogen oxide and chlorine gases.
(**a**) Write a balanced equation using smallest whole-number coefficients for the decomposition.
(**b**) Write an expression for the reaction rate in terms of Δ[NOCl].
(**c**) The concentration of NOCl drops from 0.580 *M* to 0.238 *M* in 8.00 min. Calculate the average rate of reaction over this time interval.

8. Ammonia is produced by the reaction between nitrogen and hydrogen gases.
(**a**) Write a balanced equation using smallest whole-number coefficients for the reaction.
(**b**) Write an expression for the rate of reaction in terms of $\Delta[NH_3]$.
(**c**) The concentration of ammonia increases from 0.257 *M* to 0.815 *M* in 15.0 min. Calculate the average rate of reaction over this time interval.

9. Experimental data are listed for the following hypothetical reaction:

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

Time (s)	0	20	40	60	80	100
[B]	0.51	0.43	0.39	0.35	0.33	0.31

(**a**) Plot these data as in Figure 11.3.
(**b**) Draw a tangent to the curve to find the instantaneous rate at 60 seconds.
(**c**) Find the average rate over the 20 to 80 second interval.
(**d**) Compare the instantaneous rate at 60 seconds with the average rate over the 60-second interval.

10. Experimental data are listed for the hypothetical reaction

$$X \longrightarrow Y + Z$$

Time (s)	0	10	20	30	40	50
[X]	0.0038	0.0028	0.0021	0.0016	0.0012	0.00087

(a) Plot these data as in Figure 11.3.
(b) Draw a tangent to the curve to find the instantaneous rate at 40 s.
(c) Find the average rate over the 10 to 50 s interval.
(d) Compare the instantaneous rate at 40 s with the average rate over the 40-s interval.

11-2 Reaction Rate and Concentration

11. A reaction has two reactants X and Y. What is the order with respect to each reactant and the overall order of the reaction described by the following rate expressions?
(a) rate = $k_1[X][Y]^2$ (b) rate = $k_2[X]^2$
(c) rate = $k_3[X][Y]$ (d) rate = k_4

12. A reaction has two reactants Q and P. What is the order with respect to each reactant and the overall order of the reaction described by the following rate expressions?
(a) rate = k_1 (b) rate = $k_2[P]^2[Q]$
(c) rate = $k_3[Q]^2$ (d) rate = $k_4[P][Q]$

13. What will the units of the rate constants in Question 11 be if the rate is expressed in mol/L · min?

14. What will the units of the rate constants in Question 12 be if the rate is expressed in mol/L · min?

15. Consider the reaction

$$Z \longrightarrow \text{products}$$

The data below give the rate of the reaction and the concentration of Z (as *M*).

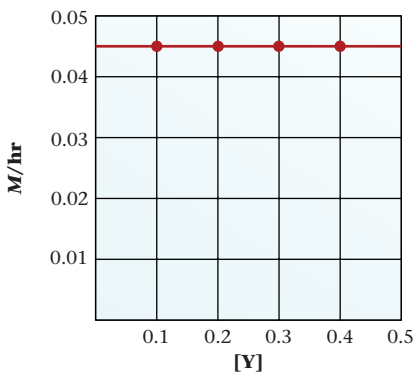
rate (*M*/min)	[Z]
0.02	0.1
0.08	0.2
0.32	0.4
1.28	0.8

(a) What is the order of the reaction with respect to Z?
(b) What is the rate expression for the reaction?
(c) Estimate the value of *k*.

16. Consider the reaction

$$Y \longrightarrow \text{products}$$

The graph below plots the rate of the reaction versus the concentration of Y.
(a) What is the order of the reaction with respect to Y?
(b) Write the rate expression for the reaction.
(c) Estimate the value of *k*.



17. Complete the following table for the reaction

$$2R(g) + 3S(g) \longrightarrow \text{products}$$

that is first-order in R and second-order in S.

	[R]	[S]	*k* (L²/mol² · min)	Rate (mol/L · min)
(a)	0.200	0.200	1.49	_____
(b)	_____	0.633	0.42	0.833
(c)	0.100	_____	0.298	0.162
(d)	0.0500	0.0911	_____	0.00624

18. Complete the following table for the reaction below. It is first-order in both X and Y.

$$2X(g) + Y(g) \longrightarrow \text{products}$$

	[X]	[Y]	k (L/mol · h)	rate (mol/L · h)
(a)	0.100	0.400	1.89	_____
(b)	0.600	_____	0.884	0.159
(c)	_____	0.250	13.4	0.0479
(d)	0.600	0.233	_____	0.00112

19. The decomposition of nitrogen dioxide is a second-order reaction. At 550 K, a 0.250 *M* sample decomposes at the rate of 1.17 mol/L · min.
(a) Write the rate expression.
(b) What is the rate constant at 550 K?
(c) What is the rate of decomposition when $[NO_2] = 0.800$ *M*?

20. The decomposition of ammonia on tungsten at 1100°C is zero-order with a rate constant of 2.5×10^{-4} mol/L · min.
(a) Write the rate expression.
(b) Calculate the rate when $[NH_3] = 0.075$ *M*.
(c) At what concentration of ammonia is the rate equal to the rate constant?

21. The reaction

$$ICl(g) + \tfrac{1}{2}H_2(g) \longrightarrow \tfrac{1}{2}I_2(g) + HCl(g)$$

is first-order in both reactants. At a certain temperature, the rate of the reaction is 2.86×10^{-5} mol/L · s when [ICl] = 0.0500 *M* and $[H_2] = 0.0150$ *M*.
(a) What is the value of *k* at that temperature?
(b) At what concentration of hydrogen is the rate 2.66×10^{-4} mol/L · s and [ICl] = 0.100 *M*?
(c) What is [ICl] when the rate is 0.0715 mol/L · s and $H_2 = 3[ICl]$?

22. The hypothetical reaction

$$X(g) + \tfrac{1}{2}Y(g) \longrightarrow \text{products}$$

is first-order in X and second-order in Y. The rate of the reaction is 0.00389 mol/L · min when [X] is 0.150 *M* and [Y] is 0.0800 *M*.
(a) What is the value for *k*?
(b) At what concentration of [Y] is the rate 0.00948 mol/L · min and [X] is 0.0441 *M*?
(c) At what concentration of [X] is the rate 0.0124 mol/L · min and [Y] = 2[X]?

11-3 Reaction Concentration and Time

Determination of Reaction Order

23. For a reaction involving the decomposition of Z at a certain temperature, the following data are obtained:

Rate (mol/ L ·min)	6.27×10^{-3}	5.33×10^{-3}	4.58×10^{-3}	3.54×10^{-3}
[Z]	0.700	0.645	0.598	0.526

(**a**) What is the order of the reaction?
(**b**) Write the rate expression for the decomposition of Z.
(**c**) Calculate k for the decomposition at that temperature.

24. For a reaction involving the decomposition of Y, the following data are obtained:

Rate (mol/L ·min)	0.288	0.245	0.202	0.158
[Y]	0.200	0.170	0.140	0.110

(**a**) Determine the order of the reaction.
(**b**) Write the rate expression for the decomposition of Y.
(**c**) Calculate k for the experiment above.

25. When boron trifluoride reacts with ammonia, the following reaction occurs:

$$BF_3(g) + NH_3(g) \longrightarrow BF_3NH_3(g)$$

The following data are obtained at a particular temperature:

Expt.	$[BF_3]$	$[NH_3]$	Initial Rate (mol/L ·s)
1	0.100	0.100	0.0341
2	0.200	0.233	0.159
3	0.200	0.0750	0.0512
4	0.300	0.100	0.102

(**a**) What is the order of the reaction with respect to BF_3, NH_3, and overall?
(**b**) Write the rate expression for the reaction.
(**c**) Calculate k for the reaction.
(**d**) When $[BF_3] = 0.533\ M$ and $NH_3 = 0.300\ M$, what is the rate of the reaction at the temperature of the experiment?

26. When nitrogen dioxide reacts with carbon monoxide, the following reaction occurs.

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

The following data are obtained at a certain temperature:

Expt.	$[NO_2]$	[CO]	Initial Rate (mol/L ·s)
1	0.138	0.100	0.00565
2	0.189	0.200	0.0106
3	0.276	0.100	0.0226
4	0.276	0.300	0.0226

(**a**) What is the order of the reaction with respect to NO_2, CO, and overall?
(**b**) Write the rate expression of the reaction.
(**c**) Calculate k for the reaction.
(**d**) When $[NO_2] = 0.421\ M$ and $[CO] = 0.816\ M$, what is the rate of the reaction at the temperature of the experiments?

27. Hydrogen bromide is a highly reactive and corrosive gas used mainly as a catalyst for organic reactions. It is produced by reacting hydrogen and bromine gases together.

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

The rate is followed by measuring the intensity of the orange color of the bromine gas. The following data are obtained:

Expt.	$[H_2]$	$[Br_2]$	Initial Rate (mol/L ·s)
1	0.100	0.100	4.74×10^{-3}
2	0.100	0.200	6.71×10^{-3}
3	0.250	0.200	1.68×10^{-2}

(**a**) What is the order of the reaction with respect to hydrogen, bromine, and overall?
(**b**) Write the rate expression for the reaction.
(**c**) Calculate k for the reaction. What are the units for k?
(**d**) When $[H_2] = 0.455\ M$ and $[Br_2] = 0.215\ M$, what is the rate of the reaction?

28. Diethylhydrazine reacts with iodine according to the following equation:

$$(C_2H_5)_2(NH)_2(l) + I_2(aq) \longrightarrow (C_2H_5)_2\,N_2(l) + 2HI(aq)$$

The rate of the reaction is followed by monitoring the disappearance of the purple color due to iodine. The following data are obtained at a certain temperature.

Expt.	$[(C_2H_5)_2(NH)_2]$	$[I_2]$	Initial Rate (mol/L ·h)
1	0.150	0.250	1.08×10^{-4}
2	0.150	0.3620	1.56×10^{-4}
3	0.200	0.400	2.30×10^{-4}
4	0.300	0.400	3.44×10^{-4}

(**a**) What is the order of the reaction with respect to diethylhydrazine, iodine, and overall?
(**b**) Write the rate expression for the reaction.
(**c**) Calculate k for the reaction.
(**d**) What must $[(C_2H_5)_2(NH)_2]$ be so that the rate of the reaction is 5.00×10^{-4} mol/L ·h when $[I_2] = 0.500\ M$?

29. The equation for the reaction between iodide and bromate ions in acidic solution is

$$6I^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3I_2(aq) + Br^-(aq) + 3H_2O$$

The rate of the reaction is followed by measuring the appearance of I_2. The following data are obtained:

$[I^-]$	$[BrO_3^-]$	$[H^+]$	Initial Rate (mol/L ·s)
0.0020	0.0080	0.020	8.89×10^{-5}
0.0040	0.0080	0.020	1.78×10^{-4}
0.0020	0.0160	0.020	1.78×10^{-4}
0.0020	0.0080	0.040	3.56×10^{-4}
0.0015	0.0040	0.030	7.51×10^{-5}

(a) What is the order of the reaction with respect to each reactant?
(b) Write the rate expression for the reaction.
(c) Calculate k.
(d) What is the hydrogen ion concentration when the rate is 5.00×10^{-4} mol/L·s and $[I^-] = [BrO_3^-] = 0.0075\ M$?

30. Consider the reaction between nitrogen oxide and oxygen.

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

The rate of the reaction is followed by measuring the appearance of NO_2. The following data are obtained:

Expt.	[NO]	$[O_2]$	Initial Rate (mol/L·min)
1	0.0244	0.0372	2.20×10^{-3}
2	0.0244	0.0122	7.23×10^{-4}
3	0.0244	0.0262	1.55×10^{-3}
4	0.0732	0.0372	1.98×10^{-2}

(a) What is the order of the reaction with respect to each reactant?
(b) Write the rate expression for the reaction.
(c) Calculate k for the reaction. What are the units for k?
(d) What is the rate of the reaction at the temperature of the experiment when [NO] = 0.0100 M and $[O_2] = 0.0462\ M$?

31. In a solution at a constant H^+ concentration, iodide ions react with hydrogen peroxide to produce iodine.

$$H^+(aq) + I^-(aq) + \tfrac{1}{2}H_2O_2(aq) \longrightarrow \tfrac{1}{2}I_2(aq) + H_2O$$

The reaction rate can be followed by monitoring the appearance of I_2. The following data are obtained:

$[I^-]$	$[H_2O_2]$	Initial Rate (mol/L·min)
0.015	0.030	0.0022
0.035	0.030	0.0052
0.055	0.030	0.0082
0.035	0.050	0.0087

(a) Write the rate expression for the reaction.
(b) Calculate k.
(c) What is the rate of the reaction when 25.0 mL of a 0.100 M solution of KI is added to 25.0 mL of a 10.0% by mass solution of H_2O_2 (d = 1.00 g/mL)? Assume volumes are additive.

32. Consider the reaction

$$CH_3CO_2CH_3(aq) + OH^-(aq) \longrightarrow CH_3CO_2^-(aq) + CH_3OH(aq)$$

The following data are obtained at a certain temperature:

Expt.	$[CH_3CO_2CH_3]$	$[OH^-]$	Initial Rate (mol/L·s)
1	0.050	0.120	0.00158
2	0.050	0.154	0.00203
3	0.084	0.154	0.00340
4	0.084	0.200	0.00442

(a) Write the rate expression for the reaction.
(b) Calculate k.
(c) What is the rate of the reaction when 10.00 mL of CH_3COOCH_3 (d = 0.932 g/mL) is added to 75.00 mL of 1.50 M NaOH? (Assume that volumes are additive.)

33. Nitrosyl bromide decomposes to nitrogen oxide and bromine. Use the following data to determine the order of the decomposition of nitrosyl bromide.

Time (s)	0	6	12	18	24
[NOBr]	0.0286	0.0253	0.0229	0.0208	0.0190

34. Consider the decomposition of Q. Use the following data to determine the order of the decomposition.

Time (min)	0	4	8	12	16
[Q]	0.334	0.25	0.20	0.167	0.143

First-Order Reactions

35. Azomethane decomposes into nitrogen and ethane at high temperatures according to the following equation:

$$(CH_3)_2N_2(g) \longrightarrow N_2(g) + C_2H_6(g)$$

The following data are obtained in an experiment:

Time (h)	$[(CH_3)_2N_2]$
1.00	0.905
2.00	0.741
3.00	0.607
4.00	0.497

(a) By plotting the data, show that the reaction is first-order.
(b) From the graph, determine k.
(c) Using k, find the time (in hours) that it takes to decrease the concentration to 0.100 M.
(d) Calculate the rate of the reaction when $[(CH_3)_2N_2] = 0.415\ M$.

36. The decomposition of sulfuryl chloride, SO_2Cl_2, to sulfur dioxide and chlorine gases is a first-order reaction. The following kinetic data for the decomposition at a certain temperature are given below:

Time (min)	0	10	30	50	70
$[SO_2Cl_2]$	0.0100	0.00987	0.00962	0.00937	0.00913

(a) Plot the data to show that the reaction is first-order.
(b) From the graph, determine k.
(c) What is the half-life of the decomposition?
(d) Using k from (b), find the time it takes to decrease the concentration to 0.00427 M.
(e) What is the rate of decomposition when $[SO_2Cl_2] = 0.0153\ M$?

37. The first-order rate constant for the decomposition of a certain hormone in water at 25°C is $3.42 \times 10^{-4}\ day^{-1}$.
(a) If a 0.0200 M solution of the hormone is stored at 25°C for two months, what will its concentration be at the end of that period?
(b) How long will it take for the concentration of the solution to drop from 0.0200 M to 0.00350 M?
(c) What is the half-life of the hormone?

38. Consider the first-order decomposition of phosgene at a certain temperature.

$$COCl_2(g) \longrightarrow \text{products}$$

It is found that the concentration of phosgene is 0.0450 *M* after 300 seconds and 0.0200 *M* after 500 seconds. Calculate the following:

(**a**) the rate constant at the temperature of the decomposition

(**b**) the half-life of the decomposition

(**c**) the intial concentration of phosgene

39. The decomposition of azomethane, $(CH_3)_2N_2$, to nitrogen and ethane gases is a first-order reaction,

$$(CH_3)_2N_2\,(g) \rightarrow N_2\,(g) + C_2H_6\,(g).$$

At a certain temperature, a 29-mg sample of azomethane is reduced to 12 mg in 1.4 s.

(**a**) What is the rate constant *k* for the decomposition at that temperature?

(**b**) What is the half-life of the decomposition?

(**c**) How long will it take to decompose 78% of the azomethane?

40. The first-order rate constant for the decomposition of a certain drug at 25°C is 0.215 $month^{-1}$.

(**a**) If 10.0 g of the drug is stored at 25°C for one year, how many grams of the drug will remain at the end of the year?

(**b**) What is the half-life of the drug?

(**c**) How long will it take to decompose 65% of the drug?

41. In the first-order decomposition of acetone at 500°C

$$CH_3COCH_3(g) \longrightarrow \text{products}$$

It is found that it takes 12.7 h to decompose 0.0622 *M* acetone to 0.0133 *M*.

(**a**) Find *k* at 500°C.

(**b**) What is the rate of decomposition when $[CH_3COCH_3] = 0.0500\ M$?

(**c**) How many minutes will it take to decompose enough acetone so that 68% remains?

42. The decomposition of sulfuryl chloride, SO_2Cl_2, to sulfur dioxide and chlorine gases is a first-order reaction. It is found that at a certain temperature, it takes 1.43 hours to decompose 0.0714 *M* to 0.0681 *M*.

(**a**) What is the rate constant for the decomposition?

(**b**) What is the rate of decompostion when $[SO_2Cl_2] = 0.0462\ M$?

(**c**) How long will it take to decompose SO_2Cl_2 so that 45% remains?

43. Dinitrogen pentoxide gas decomposes to form nitrogen dioxide and oxygen. The reaction is first-order and has a rate constant of 0.247 h^{-1} at 25°C. If a 2.50-L flask originally contains N_2O_5 at a pressure of 756 mm Hg at 25°C, then how many moles of O_2 are formed after 135 minutes? (*Hint*: First write a balanced equation for the decomposition.)

44. Sucrose ($C_{12}H_{22}O_{11}$) hydrolyzes into glucose and fructose. The hydrolysis is a first-order reaction. The half-life for the hydrolysis of sucrose is 64.2 min at 25°C. How many grams of sucrose in 1.25 L of a 0.389 *M* solution are hydrolyzed in 1.73 hours?

45. Iodine-131 is used to treat tumors in the thyroid. Its decomposition is first-order with a half-life of 8.1 days. If a patient is given a sample containing 5.00 mg of I-131, how long will it take for 32% of the isotope to remain in her system?

46. Cesium-131 is the latest tool of nuclear medicine. It is used to treat malignant tumors by implanting Cs-131 directly into the tumor site. Its first-order half-life is 9.7 days. If a patient is implanted with 20.0 mg of Cs-131, how long will it take for 33% of the isotope to remain in his system?

47. Bromine-82 is used to study the flow and distribution of waste water. A sample contains 0.500 mg of Br-82. After 24 hours, 0.306 mg of Br-82 remains. What is the half-life of Br-82?

48. A sample of sodium-24 chloride contains 0.050 mg of Na-24 to study the sodium balance of an animal. After 24.9 h, 0.016 mg of Na-24 is left. What is the half-life of Na-24?

Zero- and Second-Order Reactions

49. The decomposition of A at 85°C is a zero-order reaction. It takes 35 minutes to decompose 37% of an inital mass of 282 mg.

(**a**) What is *k* at 85°C?

(**b**) What is the half-life of 282 mg at 85°C?

(**c**) What is the rate of decomposition for 282 mg at 85°C?

(**d**) If one starts with 464 mg, what is the rate of its decomposition at 85°C?

50. The decomposition of R at 33°C is a zero-order reaction. It takes 128 minutes to decompose 41.0% of an intial mass of 739 mg at 33°C. At 33°C,

(**a**) what is *k*?

(**b**) what is the half-life of 739 mg?

(**c**) what is the rate of decomposition for 739 mg?

(**d**) what is the rate of decomposition if one starts with an initial amount of 1.25 g?

51. For the zero-order decomposition of HI on a gold surface

$$HI(g) \xrightarrow{Au} \tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g)$$

it takes 16.0 s for the pressure of HI to drop from 1.00 atm to 0.200 atm.

(**a**) What is the rate constant for the reaction?

(**b**) How long will it take for the pressure to drop from 0.150 atm to 0.0432 atm?

(**c**) What is the half-life of HI at a pressure of 0.500 atm?

52. For the zero-order decomposition of ammonia on tungsten

$$NH_3(g) \xrightarrow{W} \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g)$$

the rate constant is 2.08×10^{-4} mol/L·s.

(**a**) What is the half-life of a 0.250 *M* solution of ammonia?

(**b**) How long will it take for the concentration of ammonia to drop from 1.25 *M* to 0.388 *M*?

53. Ammonium cyanate, NH_4NCO, in water rearranges to produce urea, a common fertilizer, $(NH_2)_2CO$:

$$NH_4NCO(aq) \longrightarrow (NH_2)_2CO(aq)$$

The rearrangement is a seond-order reaction. It takes 11.6 h for the concentration of NH_4NCO to go from 0.250 *M* to 0.0841 *M*.

(**a**) What is *k* for the reaction?

(**b**) What is the half-life of the reaction when NH_4NCO is 0.100 *M*?

(c) How long will it take to rearrange 39% of a 0.450 *M* solution?

(d) How fast is a 0.839 *M* solution being changed to urea?

54. Butadiene, C_4H_6, dimerizes according to the following reaction:

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

The dimerization is a second-order reaction. It takes 145 s for the concentration of C_4H_6 to go from 0.350 *M* to 0.197 *M*.

(a) What is *k* for the dimerization?

(b) What is the half-life of the reaction when butadiene is 0.200 *M*?

(c) How long will it take to dimerize 28.9% of a 0.558 *M* sample?

(d) How fast is 0.128 *M* butadiene dimerizing?

55. The rate constant for the second-order reaction

$$NOBr(g) \longrightarrow NO(g) + \tfrac{1}{2}Br_2(g)$$

is 48 L/mol · min at a certain temperature. How long will it take to decompose 90.0% of a 0.0200 *M* solution of nitrosyl bromide?

56. The decomposition of nitrosyl chloride

$$NOCl(g) \longrightarrow NO(g) + \tfrac{1}{2}Cl_2(g)$$

is a second-order reaction. If it takes 0.20 min to decompose 15% of a 0.300 *M* solution of nitrosyl chloride, what is *k* for the reaction?

11-4 Models for Reaction Rate

11-5 Reaction Rate and Temperature

57. An increase in temperature from 23°C to 36°C increases the rate constant of a certain reaction by 50.0%. What is the activation energy of the reaction?

58. If the activation energy of a reaction is 9.13 kJ, then what is the percent increase in the rate constant when the temperature is increased from 27°C to 69°C?

59. The following data are obtained for the gas-phase decomposition of acetaldehyde:

k (L/mol·s)	0.0105	0.101	0.60	2.92
T (K)	700	750	800	850

Plot these data (ln *k* versus 1/*T*) and find the activation energy for the reaction.

60. The following data are obtained for the reaction

$$SiH_4(g) \longrightarrow Si(s) + 2H_2(g)$$

k (s^{-1})	0.048	2.3	49	590
t (°C)	500	600	700	800

Plot these data (ln *k* versus 1/*T*) and find the activation energy for the reaction.

61. Consider the following hypothetical reaction:

$$X + Y \longrightarrow \text{Products} \qquad \Delta H = -75 \text{ kJ}$$

Draw a reaction-energy diagram for the reaction if the activation energy is 32 kJ.

62. For the reaction

$$Q + R \longrightarrow Y + Z \qquad \Delta H = 128 \text{ kJ}$$

Draw a reaction-energy diagram for the reaction if its activation energy is 284 kJ.

63. The uncoiling of deoxyribonucleic acid (DNA) is a first-order reaction. Its activation energy is 420 kJ. At 37°C, the rate constant is 4.90×10^{-4} min^{-1}.

(a) What is the half-life of the uncoiling at 37°C (normal body temperature)?

(b) What is the half-life of the uncoiling if the organism has a temperature of 40°C (≈104°F)?

(c) By what factor does the rate of uncoiling increase (per °C) over this temperature interval?

64. The precipitation of egg albumin in water at 100°C has an activation energy of 52.0 kJ/mol. By what percent does the rate of precipitation decrease if the water is at 92°C?

65. Consider the hypothetical decomposition

$$Z \longrightarrow \text{products}$$

The rate of the reaction as a function of temperature in *M*/min is

$$\text{rate} = 2.7t - 19$$

where *t* is the temperature in °C.

(a) Calculate the rate of decomposition at 17°C and at 27°C.

(b) Estimate the activation energy of the reaction.

(c) What is the percent increase in rate for a 10°C increase in temperature?

66. The chirping rate of a cricket, X, in chirps per minute, near room temperature is

$$X = 7.2t - 32$$

where *t* is the temperature in °C.

(a) Calculate the chirping rates at 25°C and 35°C.

(b) Use your answers in (a) to estimate the activation energy for the chirping.

(c) What is the percentage increase for a 10°C rise in temperature?

67. For the reaction

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$$

the rate constant is 0.066 L/mol · min at 565°C and 22.8 L/mol · min at 728°C.

(a) What is the activation energy of the reaction?

(b) What is *k* at 485°C?

(c) At what temperature is *k*, the rate constant, equal to 11.6 L/mol · min?

68. For the decomposition of a peroxide, the activation energy is 17.4 kJ/mol. The rate constant at 25°C is 0.027 s^{-1}.

(a) What is the rate constant at 65°C?

(b) At what temperature will the rate constant be 25% greater than the rate constant at 25°C?

69. Consider a 5.000 *M* solution of the hypothetical compound R. Its decomposition is a second-order reaction and its activation energy is 57.6 kJ/mol. At 759°C, the half-life of the 5.000 *M* solution is 8.49 h. What is the half-life of the same solution at 700°C (3 significant figures)?

70. The decomposition of N_2O_5 to NO_2 and NO_3 is a first-order gas-phase reaction. At 25°C, the reaction has a half-life

of 2.81 s. At 45°C, the reaction has a half-life of 0.313 s. What is the activation energy of the reaction?

11-6 Catalysis

71. For a certain reaction, E_a is 135 kJ and $\Delta H = 45$ kJ. In the presence of a catalyst, the activation energy is 39% of that for the uncatalyzed reaction. Draw a diagram similar to Figure 11.14 but instead of showing two activated complexes (two humps) show only one activated complex (i.e., only one hump) for the reaction. What is the activation energy of the uncatalyzed reverse reaction?

72. Consider a reaction in which $E_a = 129$ kJ and $\Delta H = -29$ kJ. In the presence of a catalyst, the activation energy is 48% of the uncatalyzed reaction. Follow the directions in Question 71 in drawing an energy diagram.

73. A catalyst lowers the activation energy of a reaction from 215 kJ to 206 kJ. By what factor would you expect the reaction-rate constant to increase at 25°C? Assume that the frequency factors (A) are the same for both reactions. (*Hint:* Use the formula $\ln k = \ln A - E_a/RT$.)

74. A reaction has an activation energy of 363 kJ at 25°C. If the rate constant has to increase ten-fold, what should the activation energy of the catalyzed reaction be? (See Question 73 for assumptions and a hint.)

11-7 Reaction Mechanisms

75. Write the rate expression for each of the following elementary steps:

(a) $NO_3 + CO \longrightarrow NO_2 + CO_2$

(b) $I_2 \longrightarrow 2I$

(c) $NO + O_2 \longrightarrow NO_3$

76. Write the rate expression for each of the following elementary steps:

(a) $Cl_2 \longleftrightarrow 2Cl$

(b) $N_2O_2 + O_2 \longrightarrow 2NO_2$

(c) $I^- + HClO \longrightarrow HIO + Cl^-$

77. For the reaction between hydrogen and iodine,

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

the experimental rate expression is rate $= k[H_2][I_2]$. Show that this expression is consistent with the mechanism

$$I_2(g) \rightleftharpoons 2I(g) \qquad \text{(fast)}$$
$$H_2(g) + I(g) + I(g) \longrightarrow 2HI(g) \qquad \text{(slow)}$$

78. For the reaction

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

the experimental rate expression is rate $= k[NO]^2[H_2]$. The following mechanism is proposed:

$$2NO \rightleftharpoons N_2O_2 \qquad \text{(fast)}$$
$$N_2O_2 + H_2 \longrightarrow H_2O + N_2O \qquad \text{(slow)}$$
$$N_2O + H_2 \longrightarrow N_2 + H_2O \qquad \text{(fast)}$$

Is this mechanism consistent with the rate expression?

79. At low temperatures, the rate law for the reaction

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

is as follows: rate = (constant) $[NO_2]^2$. Which of the following mechanisms is consistent with the rate law?

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

(b) $2NO_2 \rightleftharpoons N_2O_4$ (fast)
$N_2O_4 + 2CO \longrightarrow 2CO_2 + 2NO$ (slow)

(c) $2NO_2 \longrightarrow NO_3 + NO$ (slow)
$NO_3 + CO \longrightarrow NO_2 + CO_2$ (fast)

(d) $2NO_2 \longrightarrow 2NO + O_2$ (slow)
$O_2 + 2CO \longrightarrow 2CO_2$ (fast)

80. Two mechanisms are proposed for the reaction

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

Mechanism 1:
$$NO + O_2 \rightleftharpoons NO_3 \qquad \text{(fast)}$$
$$NO_3 + NO \longrightarrow 2NO_2 \qquad \text{(slow)}$$

Mechanism 2:
$$NO + NO \rightleftharpoons N_2O_2 \qquad \text{(fast)}$$
$$N_2O_2 + O_2 \longrightarrow 2NO_2 \qquad \text{(slow)}$$

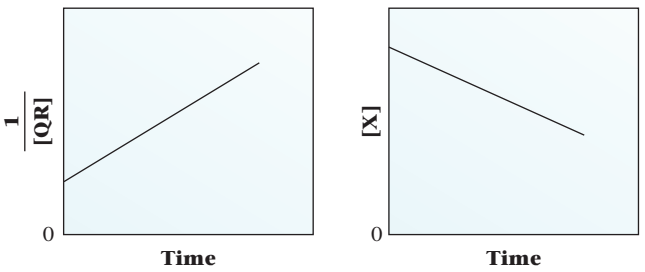
Show that each of these mechanisms is consistent with the observed rate law: rate $= k[NO]^2[O_2]$.

Unclassified

81. The hypothetical reaction

$$QR + X \longrightarrow \text{products}$$

was monitored at 27°C as a function of time. The following plots are obtained:



(a) Write the rate expression for the reaction.

(b) What is the rate constant if the rate of the reaction is 0.29 mol/L · min when [QR] = [X] = 1.000 *M*?

(c) What is the half-life for the consumption of QR when [QR] = 0.0866 *M*?

(d) If the initial concentration of [X] = 5.00 *M*, what is [X] after 4.7 min?

82. When a base is added to an aqueous solution of chlorine dioxide gas, the following reaction occurs:

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

The reaction is first-order in OH^- and second-order for ClO_2. Initially, when $[ClO_2] = 0.010\ M$ and $[OH^-] = 0.030\ M$, the rate of the reaction is 6.00×10^{-4} mol/L · s. What is the rate of the reaction when 50.0 mL of 0.200 *M* ClO_2 and 95.0 mL of 0.155 *M* NaOH are added?

83. The decomposition of sulfuryl chloride, SO_2Cl_2, to sulfur dioxide and chlorine gases is a first-order reaction.

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

At a certain temperature, the half-life of SO_2Cl_2 is 7.5×10^2 min. Consider a sealed flask with 122.0 g of SO_2Cl_2.

(a) How long will it take to reduce the amount of SO_2Cl_2 in the sealed flask to 45.0 g?

(b) If the decomposition is stopped after 29.0 h, what volume of Cl_2 at 27°C and 1.00 atm is produced?

84. How much faster would a reaction proceed at 46°C than at 28°C if the activation energy of the reaction is 121 kJ/mol?

85. A reaction has an activation energy of 85 kJ. What percentage increase would one get for k for every 5°C increase in temperature around room temperature, 25°C?

86. For the first-order thermal decomposition of ozone

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

$k = 3 \times 10^{-26}\ s^{-1}$ at 25°C. What is the half-life for this reaction in years? Comment on the likelihood that this reaction contributes to the depletion of the ozone layer.

87. A drug decomposes in the blood by a first-order process. A pill containing 0.500 g of the active ingredient reaches its maximum concentration of 2.5 mg/100 mL of blood. If the half-life of the active ingredient is 75 min, what is its concentration in the blood 2.0 h after the maximum concentration has been reached?

88. Page 295 has a two-point equation relating k (the rate constant) and T (temperature). Derive a two-point equation relating k and activation energy for a catalyzed and an uncatalyzed reaction at the same temperature. Assume that A is the same for both reactions.

Conceptual Problems

89. The greatest increase in the reaction rate for the reaction between A and C, where rate = $k[A]^{1/2}$ [C], is caused by

(**a**) doubling [A] (**b**) halving [C]
(**c**) halving [A] (**d**) doubling [A] and [C]

90. Consider the reaction between methyl acetate and water:

$$CH_3COOCH_3\,(aq) + H_2O \longrightarrow CH_3COOH(aq) + CH_3OH(aq)$$

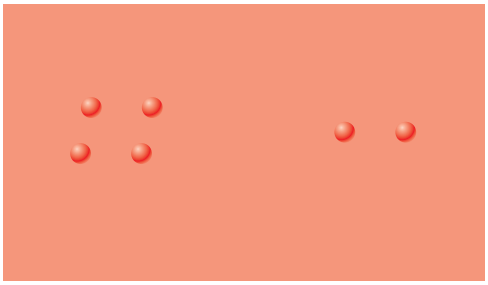
The rate law for the reaction at 25°C is:

$$\text{rate} = k[CH_3COOCH_3][H^+]$$

The reaction is carried out in one liter of a solution that is 0.48 M CH_3COOCH_3 and 0.122 M H^+. Fill in the blanks with increases, decreases, or remains the same.

(**a**) The rate of the reaction _____ when 125 mL of water is added.
(**b**) The value of k _____ when the temperature is increased to 38°C.
(**c**) The value of E_a _____ when HCl is added.
(**d**) The rate of the reaction _____ when NaOH is added.
(**e**) The value of k _____ when a catalyst is added.

91. Consider the decomposition of A represented by circles, where each circle represents a molecule of A.

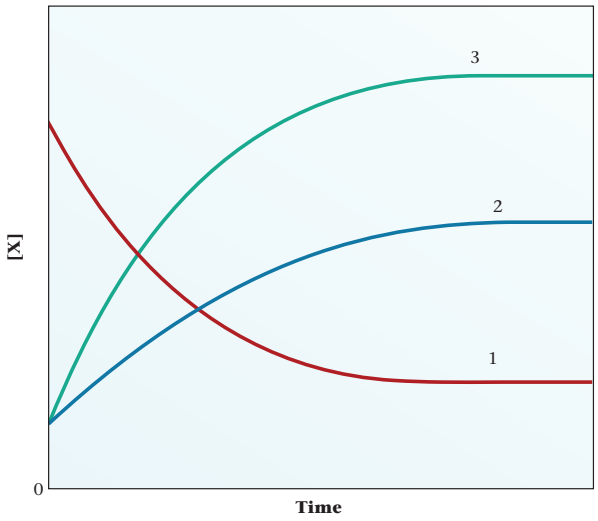


Is the reaction zero-order, first-order, or second-order?

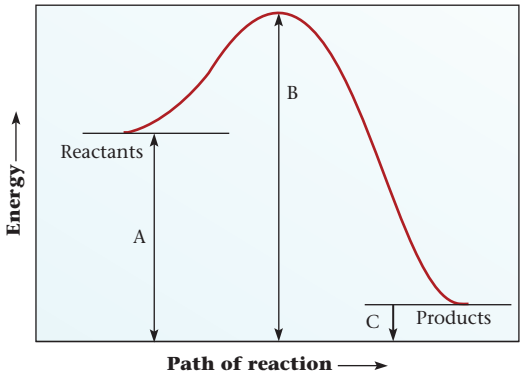
92. Consider the decomposition reaction

$$2X \longrightarrow 2Y + Z$$

The following graph shows the change in concentration with respect to time for the reaction. What does each of the curves labeled 1, 2, and 3 represent?



93. Consider the following activation energy diagram.



Which of the following statements about the diagram are true?

(**a**) E_a (forward) < E_a (reverse)
(**b**) B represents the activation energy of the forward reaction.
(**c**) Energy (ΔH) for the reaction is A − C.
(**d**) E_a (forward) = B − A
(**e**) E_a (forward) = E_a (reverse) − C

94. Three first-order reactions have the following activation energies:

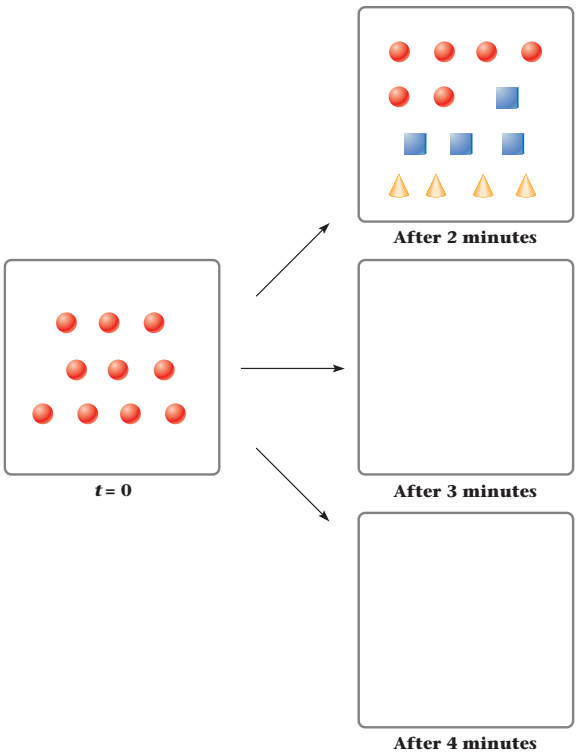
Reaction	A	B	C
E_a(kJ)	75	136	292

(**a**) Which reaction is the fastest?
(**b**) Which reaction has the largest half-life?
(**c**) Which reaction has the largest rate?

95. Consider the first-order decomposition reaction

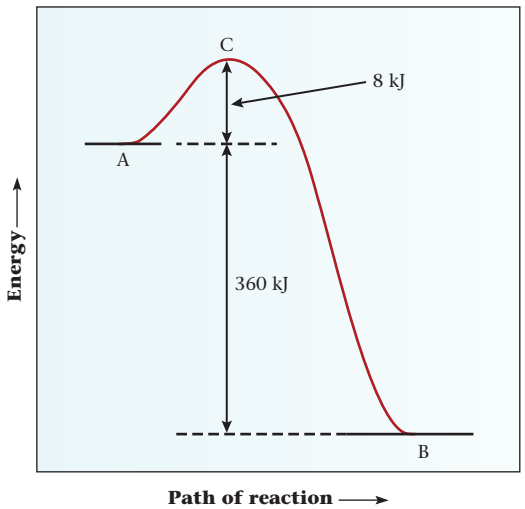
$$A \longrightarrow B + C$$

where A (circles) decomposes to B (triangles) and C (squares). Given the following boxes representing the reaction at $t = 2$ minutes, fill in the boxes with products at the indicated time. Estimate the half-life of the reaction.



96. Consider the following energy diagram (not to scale) for the reaction.

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



(**a**) What is the activation energy of the forward reaction?
(**b**) At what point would $2CH_3$ (g) appear?
(**c**) What is ΔH for the reaction?
(**d**) What is the activation energy of the reverse reaction?
(**e**) At what point would C_2H_6 certainly be found?
(**f**) What is any species at point C called?

97. For the reaction

$$A + B \longrightarrow C$$

the rate expression is rate $= k$[A][B]

(**a**) Given three test tubes, with different concentrations of A and B, which test tube has the smallest rate?
(**1**) 0.10 *M* A; 0.10 *M* B
(**2**) 0.15 *M* A; 0.15 *M* B
(**3**) 0.06 *M* A; 1.0 *M* B

(**b**) If the temperature is increased, describe (using the words *increases*, *decreases*, or *remains the same*) what happens to the rate, the value of k, and E_a.

98. The following experiments are performed for the first-order reaction:

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

Fill in the blanks. If the answer cannot be calculated with the given information, write NC on the blank(s) provided.

	Expt. 1	Expt. 2	Expt. 3	Expt. 4
[A]	0.100	0.200	0.100	0.100
Catalyst	No	No	Yes	No
Temperature	25°C	25°C	25°C	30°C
k (min^{-1})	0.5	_____	1	0.6
Rate (mol/L · min)	_____	_____	_____	_____
E_a (kJ)	32	_____	_____	_____

Challenge Problems

99. The gas-phase reaction between hydrogen and iodine

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

proceeds with a rate constant for the forward reaction at 700°C of 138 L/mol · s and an activation energy of 165 kJ/mol.

(**a**) Calculate the activation energy of the reverse reaction given that $\Delta H_f°$ for HI is 26.48 kJ/mol and $\Delta H_f°$ for I_2(g) is 62.44 kJ/mol.

(**b**) Calculate the rate constant for the reverse reaction at 700°C. (Assume A in the equation $k = Ae^{-E_a/RT}$ is the same for both forward and reverse reactions.)

(**c**) Calculate the rate of the reverse reaction if the concentration of HI is 0.200 *M*. The reverse reaction is second-order in HI.

100. Consider the coagulation of a protein at 100°C. The first-order reaction has an activation energy of 69 kJ/mol. If the protein takes 5.4 minutes to coagulate in boiling water at 100°C, then how long will it take to coagulate the protein at an altitude where water boils at 87°C?

101. For a first-order reaction aA $\longrightarrow$ products, where $a \neq 1$, the rate is $-\Delta[A]/a\ \Delta t$, or in derivative notation, $-\frac{1}{a}\frac{d[A]}{dt}$. Derive the integrated rate law for the first-order decomposition of a moles of reactant.

102. The following data apply to the reaction

$$A(g) + 3B(g) + 2C(g) \longrightarrow \text{products}$$

[A]	[B]	[C]	Rate
0.20	0.40	0.10	X
0.40	0.40	0.20	$8X$
0.20	0.20	0.20	X
0.40	0.40	0.10	$4X$

Determine the rate law for the reaction.

103. Using calculus, derive the equation for

(**a**) the concentration-time relation for a second-order reaction (see Table 11.2).

(**b**) the concentration-time relation for a third-order reaction, A ⟶ product.

104. In a first-order reaction, suppose that a quantity X of a reactant is added at regular intervals of time, Δt. At first the amount of reactant in the system builds up; eventually, however, it levels off at a saturation value given by the expression

$$\text{saturation value} = \frac{X}{1 - 10^{-a}} \qquad \text{where } a = 0.30\,\frac{\Delta t}{t_{1/2}}$$

This analysis applies to prescription drugs, of which you take a certain amount each day. Suppose that you take 0.100 g of a drug three times a day and that the half-life for elimination is 2.0 days. Using this equation, calculate the mass of the drug in the body at saturation. Suppose further that side effects show up when 0.500 g of the drug accumulates in the body. As a pharmacist, what is the maximum dosage you could assign to a patient for an 8-h period without causing side effects?

105. Consider the hypothetical first-order reaction

$$2A(g) \rightarrow X(g) + \tfrac{1}{2}Y(g)$$

At a certain temperature, the half-life of the reaction is 19.0 min. A 1.00-L flask contains A with a partial pressure of 622 mm Hg. If the temperature is kept constant, what are the partial pressures of A, X, and Y after 42 minutes?