16

Chemical Kinetics

OUTLINE

OBJECTIVES

*After you have studied this chapter, you should be able to*

- *Express the rate of a chemical reaction in terms of changes in concentrations of reactants and products with time*

- *Describe the experimental factors that affect the rates of chemical reactions*

- *Use the rate-law expression for a reaction—the relationship between concentration and rate*

- *Use the concept of order of a reaction*

- *Apply the method of initial rates to find the rate-law expression for a reaction*

- *Use the integrated rate-law expression for a reaction—the relationship between concentration and time*

- *Analyze concentration-versus-time data to determine the order of a reaction*

- *Describe the collision theory of reaction rates*

- *Describe the main aspects of transition state theory and the role of activation energy in determining the rate of a reaction*

- *Explain how the mechanism of a reaction is related to its rate-law expression*

- *Predict the rate-law expression that would result from a proposed reaction mechanism*

- *Identify reactants, products, intermediates, and catalysts in a multistep reaction mechanism*

- *Explain how temperature affects rates of reactions*

- *Use the Arrhenius equation to relate the activation energy for a reaction to changes in its rate constant with changing temperature*

- *Explain how a catalyst changes the rate of a reaction*

- *Describe homogeneous catalysis and heterogeneous catalysis*

A burning building is an example of a rapid, highly exothermic reaction. Firefighters use basic principles of chemical kinetics to battle the fire. When water is sprayed onto a fire, its evaporation absorbs a large amount of energy; this lowers the temperature and slows the reaction. Other common methods for extinguishing fires include covering them with CO_2 (as with most household extinguishers), which decreases the supply of oxygen, and backburning (for grass and forest fires), which removes combustible material. In both cases, the removal of a reactant slows (or stops) the reaction.
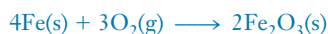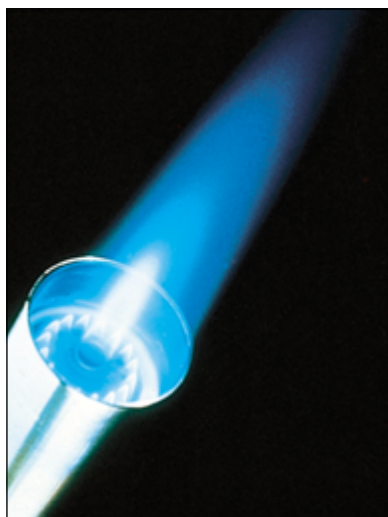
e are all familiar with processes in which some quantity changes with time— a car travels at 40 miles/hour, a faucet delivers water at 3 gallons/minute, or a factory produces 32,000 tires/day. Each of these ratios is called a rate. The **rate of a reaction** describes how fast reactants are used up and products are formed. **Chemical kinetics** is the study of *rates* of chemical reactions, the *factors* that affect reaction rates, and the *mechanisms* (the series of steps) by which reactions occur.

Our experience tells us that different chemical reactions occur at very different rates. For instance, combustion reactions—such as the burning of methane, CH_4, in natural gas and the combustion of isooctane, C_8H_{18}, in gasoline—proceed very rapidly, sometimes even explosively.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$
$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$
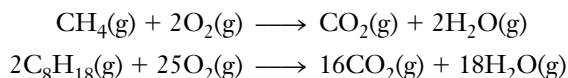
On the other hand, the rusting of iron occurs only very slowly.

In our study of thermodynamics, we learned to assess whether a particular reaction was favorable. The question of whether substantial reaction would occur in a certain time period is addressed by kinetics. If a reaction is not thermodynamically favored, it will not occur appreciably under the given conditions. Even though a reaction is thermodynamically favored, it might not occur at a measurable rate.

The reactions of strong acids with strong bases are thermodynamically favored *and* occur at very rapid rates. Consider, for example, the reaction of hydrochloric acid solution with solid magnesium hydroxide. It is thermodynamically spontaneous at standard state conditions, as indicated by the negative ΔG_{rxn}^0 value. It also occurs rapidly.

$$2HCl(aq) + Mg(OH)_2(s) \longrightarrow MgCl_2(aq) + 2H_2O(\ell) \qquad \Delta G_{rxn}^0 = -97 \text{ kJ/mol}$$
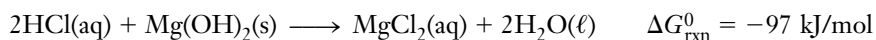
The reaction of diamond with oxygen is also thermodynamically spontaneous.

$$C(diamond) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta G_{rxn}^0 = -397 \text{ kJ/mol}$$
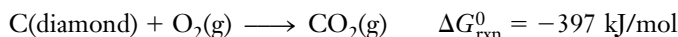
However, we know from experience that diamonds exposed to air, even over long periods, do not react to form carbon dioxide. The reaction does not occur at an observable rate near room temperature.

The reaction of graphite with oxygen is also spontaneous, with a similar value of ΔG_{rxn}^0, -394 kJ/mol. Once it is started, this reaction occurs rapidly. These observations of reaction speeds are explained by kinetics, not thermodynamics.

The rusting of iron is a complicated process. It can be represented in simplified form as

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

This is one of the reactions that occurs in a human digestive system when an antacid containing relatively insoluble magnesium hydroxide neutralizes excess stomach acid.

Recall that the units kJ/mol refer to the numbers of moles of reactants and products in the balanced equation.


A methane flame is a rapid reaction.

16-1 THE RATE OF A REACTION

Rates of reactions are usually expressed in units of moles per liter per unit time. If we know the chemical equation for a reaction, its rate can be determined by following the change in concentration of any product or reactant that can be detected quantitatively.

To describe the rate of a reaction, we must determine the concentration of a reactant or product at various times as the reaction proceeds. Devising effective methods for this is a continuing challenge for chemists who study chemical kinetics. If a reaction is slow enough, we can take samples from the reaction mixture after successive time intervals and then analyze them. For instance, if one reaction product is an acid, its concentration can be determined by titration (Section 11-2) after each time interval. The reaction of ethyl acetate with water in the presence of a small amount of strong acid produces acetic acid. The extent of the reaction at any time can be determined by titration of the acetic acid.

(a)

(b)

Figure 16-1 (a) Blue dye is reacting with bleach, which converts it into a colorless product. The color decreases and eventually disappears. The rate of the reaction could be determined by repeatedly measuring both the color intensity and the elapsed time. The concentration of dye could be calculated from the intensity of the blue color. (Solvent molecules and reaction product molecules have been omitted from the diagram for clarity).
(b) A spectroscopic method for determining reaction rates. Light of a wavelength that is absorbed by some substance whose concentration is changing is passed through a reaction chamber. Recording the change in light intensity gives a measure of the changing concentration of a reactant or product as the reaction progresses.

$$CH_3\overset{\displaystyle O}{\overset{\|}{C}}-OCH_2CH_3(aq) + H_2O(\ell) \xrightarrow{\ H^+\ } CH_3\overset{\displaystyle O}{\overset{\|}{C}}-OH(aq) + CH_3CH_2OH(aq)$$

ethyl acetate   acetic acid   ethanol

This approach is suitable only if the reaction is sufficiently slow that the time elapsed during withdrawal and analysis of the sample is negligible. Sometimes the sample is withdrawn and then quickly cooled ("quenched"). This slows the reaction (Section 16-8) so much that the desired concentration does not change significantly while the analysis is performed.

It is more convenient, especially when a reaction is rapid, to use a technique that continually monitors the change in some physical property of the system. If one of the reactants or products is colored, the increase (or decrease) in intensity of its color might be used to measure a decrease or increase in its concentration. Such an experiment is a special case of *spectroscopic* methods. These methods involve passing light (visible, infrared, or ultraviolet) through the sample. The light should have a wavelength that is absorbed by some substance whose concentration is changing (Figure 16-1). An appropriate light-sensing apparatus provides a signal that depends on the concentration of the absorbing substance. Modern techniques that use computer-controlled pulsing and sensing of lasers have enabled scientists to sample concentrations at intervals on the order of picoseconds

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 15.2, Rates of Chemical Reactions.

(1 picosecond $= 10^{-12}$ second) or even femtoseconds (1 femtosecond $= 10^{-15}$ second). Such studies have yielded information about very fast reactions, such as energy transfer resulting from absorption of light in photosynthesis.

If the progress of a reaction causes a change in the total number of moles of gas present, the change in pressure of the reaction mixture (held at constant temperature and constant volume) lets us measure how far the reaction has gone. For instance, the decomposition of dinitrogen pentoxide, $N_2O_5(g)$, has been studied by this method.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$
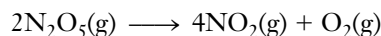
For every two moles of N_2O_5 gas that react, a total of five moles of gas is formed (four moles of NO_2 and one mole of O_2). The resulting increase in pressure can be related by the ideal gas equation to the total number of moles of gas present. This indicates the extent to which the reaction has occurred.

Once we have measured the changes in concentrations of reactants or products with time, how do we describe the rate of a reaction? Consider a hypothetical reaction.

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

In this generalized representation, a represents the coefficient of substance A in the balanced chemical equation, b is the coefficient of substance B, and so on. For example, in an earlier equation given for the decomposition of N_2O_5, $a = 2$, A represents N_2O_5, $c = 4$, C represents NO_2, and so on.

The amount of each substance present can be given by its concentration, usually expressed as molarity (mol/L) and designated by brackets. The rate at which the reaction proceeds can be described in terms of the rate at which one of the reactants disappears, $-\Delta[\text{A}]/\Delta t$ or $-\Delta[\text{B}]/\Delta t$, or the rate at which one of the products appears, $\Delta[\text{C}]/\Delta t$ or $\Delta[\text{D}]/\Delta t$. The reaction rate must be positive because it describes the forward (left-to-right) reaction, which consumes A and B. The concentrations of reactants A and B decrease in the time interval Δt. Thus, $\Delta[\text{A}]/\Delta t$ and $\Delta[\text{B}]/\Delta t$ would be *negative* quantities. The purpose of a negative sign in the definition of a rate of reaction is to make the rate a positive quantity.

If no other reaction takes place, the changes in concentration are related to one another. For every a mol/L that [A] decreases, [B] must decrease by b mol/L, [C] must increase by c mol/L, and so on. We wish to describe the rate of reaction on a basis that is the same regardless of which reactant or product we choose to measure. To do this, we can describe the number of *moles of reaction* that occur per liter in a given time. For instance, this is accomplished for reactant A as

$$\left(\frac{1 \text{ mol rxn}}{a \text{ mol A}}\right)\left(\begin{array}{c}\text{rate of decrease} \\ \text{in [A]}\end{array}\right) = -\left(\frac{1 \text{ mol rxn}}{a \text{ mol A}}\right)\left(\frac{\Delta[\text{A}]}{\Delta t}\right)$$

The units for rate of reaction are $\dfrac{\text{mol rxn}}{\text{L·time}}$, which we usually shorten to $\dfrac{\text{mol}}{\text{L·time}}$ or $\text{mol·L}^{-1}\text{·time}^{-1}$. The units $\dfrac{\text{mol}}{\text{L}}$ represent molarity, M, so the units for rate of reaction can also be written as $\dfrac{M}{\text{time}}$ or $M\text{·time}^{-1}$. Similarly, we can divide each concentration change by its coefficient in the balanced equation. Bringing signs to the beginning of each term, we write the rate of reaction based on the rate of change of concentration of each species.

In reactions involving gases, rates of reactions may be related to rates of change of partial pressures. Pressures of gases and concentrations of gases are directly proportional.

$PV = nRT$ or $P = \dfrac{n}{V}RT = MRT$

where M is molarity.

The Greek "delta," Δ, stands for "change in," just as it did in Chapter 15.

$$\text{rate of reaction} = \frac{1}{a}\begin{pmatrix}\text{rate of} \\ \text{decrease} \\ \text{in [A]}\end{pmatrix} = \frac{1}{b}\begin{pmatrix}\text{rate of} \\ \text{decrease} \\ \text{in [B]}\end{pmatrix} = \frac{1}{c}\begin{pmatrix}\text{rate of} \\ \text{increase} \\ \text{in [C]}\end{pmatrix} = \frac{1}{d}\begin{pmatrix}\text{rate of} \\ \text{increase} \\ \text{in [D]}\end{pmatrix}$$

$$\text{rate of reaction} = -\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right) = -\frac{1}{b}\left(\frac{\Delta[B]}{\Delta t}\right) = \frac{1}{c}\left(\frac{\Delta[C]}{\Delta t}\right) = \frac{1}{d}\left(\frac{\Delta[D]}{\Delta t}\right)$$

This representation gives several equalities, any one of which can be used to relate changes in observed concentrations to the rate of reaction.

The expressions just given describe the *average* rate over a time period Δt. The rigorous expressions for the rate at any instant involve the derivatives of concentrations with respect to time.

$$-\frac{1}{a}\left(\frac{d[A]}{dt}\right), \frac{1}{c}\left(\frac{d[C]}{dt}\right), \text{ and so on.}$$

The shorter the time period, the closer $\dfrac{\Delta(\text{concentration})}{\Delta t}$ is to the corresponding derivative.

✔ Problem-Solving Tip: *Signs and Divisors in Expressions for Rate*

As an analogy to these chemical reaction rate expressions, suppose we make sardine sandwiches by the following procedure:

$$2 \text{ bread slices} + 3 \text{ sardines} + 1 \text{ pickle} \longrightarrow 1 \text{ sandwich}$$
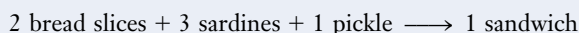
As time goes by, the number of sandwiches increases, so $\Delta(\text{sandwiches})$ is positive; the rate of the process is given by $\Delta(\text{sandwiches})/\Delta(\text{time})$. Alternatively, we would count the decreasing number of pickles at various times. Because $\Delta(\text{pickles})$ is negative, we must multiply by (-1) to make the rate positive; rate $= -\Delta(\text{pickles})/\Delta(\text{time})$. If we measure the rate by counting slices of bread, we must also take into account that bread slices are consumed *twice as fast* as sandwiches are produced, so rate $= -\frac{1}{2}(\Delta(\text{bread})/\Delta(\text{time}))$. Four different ways of describing the rate all have the same numerical value.

$$\text{rate} = \left(\frac{\Delta(\text{sandwiches})}{\Delta t}\right) = -\frac{1}{2}\left(\frac{\Delta(\text{bread})}{\Delta t}\right) = -\frac{1}{3}\left(\frac{\Delta(\text{sardines})}{\Delta t}\right) = -\left(\frac{\Delta(\text{pickles})}{\Delta t}\right)$$

Consider as a specific chemical example the gas-phase reaction that occurs when we mix 1.000 mole of hydrogen and 2.000 moles of iodine chloride at 230°C in a closed 1.000-liter container.

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

The coefficients tell us that one mole of H_2 disappears for every two moles of ICl that disappear and for every one mole of I_2 and two moles of HCl that are formed. In other terms, the rate of disappearance of moles of H_2 is one-half the rate of disappearance of moles of ICl, and so on. So we write the rate of reaction as

$$\text{rate of reaction} = \left(\begin{array}{c}\text{rate of}\\\text{decrease}\\\text{in }[H_2]\end{array}\right) = \frac{1}{2}\left(\begin{array}{c}\text{rate of}\\\text{decrease}\\\text{in }[ICl]\end{array}\right) = \left(\begin{array}{c}\text{rate of}\\\text{increase}\\\text{in }[I_2]\end{array}\right) = \frac{1}{2}\left(\begin{array}{c}\text{rate of}\\\text{increase}\\\text{in }[HCl]\end{array}\right)$$

$$\text{rate of reaction} = -\left(\frac{\Delta[H_2]}{\Delta t}\right) = -\frac{1}{2}\left(\frac{\Delta[ICl]}{\Delta t}\right) = \left(\frac{\Delta[I_2]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[HCl]}{\Delta t}\right)$$

Table 16-1 lists the concentrations of reactants remaining at 1-second intervals, beginning with the time of mixing ($t = 0$ seconds). The *average* rate of reaction over each 1-second interval is indicated in terms of the rate of decrease in concentration of hydrogen. Verify for yourself that the rate of loss of ICl is twice that of H_2. Therefore, the rate of reaction could also be expressed as rate $= -\frac{1}{2}(\Delta[ICl]/\Delta t)$. Increases in concentration of products could be used instead. Figure 16-2 shows graphically the rates of change of concentrations of all reactants and products.

TABLE 16-1 *Concentration and Rate Data for Reaction of 2.000 M ICl and 1.000 M H_2 at 230°C*

For example, the *average* rate over the interval from 1 to 2 seconds can be calculated as

$$-\frac{\Delta[H_2]}{\Delta t} =$$
$$-\frac{(0.526 - 0.674)\ mol\cdot L^{-1}}{(2-1)\ s}$$
$$= 0.148\ mol\cdot L^{-1}\cdot s^{-1}$$
$$= 0.148\ M\cdot s^{-1}$$

This does *not* mean that the reaction proceeds at this rate during the entire interval.

[ICl] (mol/L)	[H$_2$] (mol/L)	Average Rate During One Time Interval $= -\dfrac{\Delta[H_2]}{\Delta t}$ (M·s^{-1})	Time (t) (seconds)
2.000	1.000		0
		0.326	
1.348	0.674		1
		0.148	
1.052	0.526		2
		0.090	
0.872	0.436		3
		0.062	
0.748	0.374		4
		0.046	
0.656	0.328		5
		0.035	
0.586	0.293		6
		0.028	
0.530	0.265		7
		0.023	
0.484	0.242		8
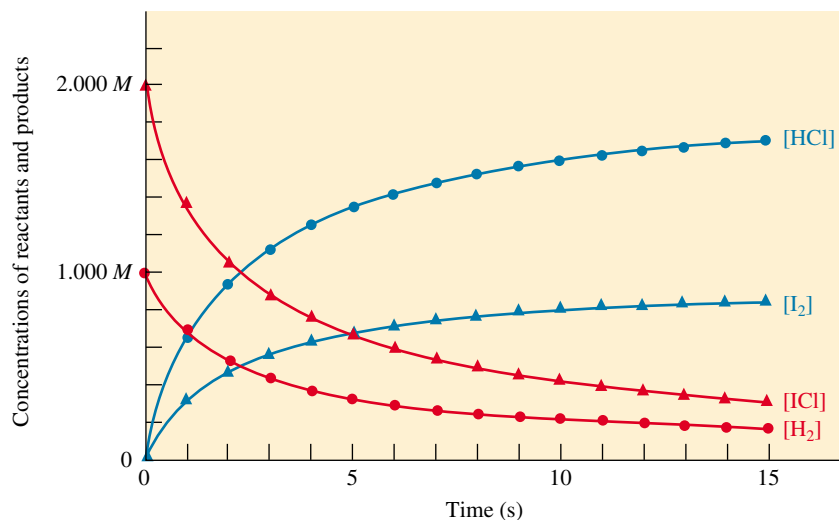
Figure 16-2 Plot of concentrations of all reactants and products versus time in the reaction of 1.000 M H$_2$ with 2.000 M ICl at 230°C, from data in Table 16-1 (and a few more points).
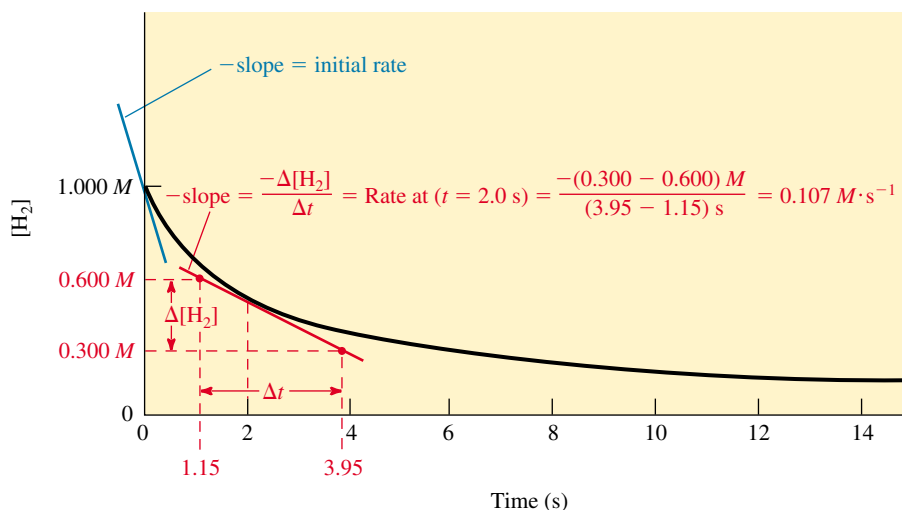
$-$slope = initial rate

$-$slope $= \dfrac{-\Delta[H_2]}{\Delta t} = $ Rate at (t = 2.0 s) $= \dfrac{-(0.300 - 0.600)\, M}{(3.95 - 1.15)\, \text{s}} = 0.107\ M\cdot\text{s}^{-1}$

1.000 M

0.600 M

$\Delta[H_2]$

0.300 M

Δt

0

0   2   4   6   8   10   12   14

1.15   3.95

Time (s)

Figure 16-3 Plot of H_2 concentration versus time for the reaction of 1.000 M H_2 with 2.000 M ICl. The instantaneous rate of reaction at any time, t, equals the negative of the slope of the tangent to this curve at time t. The initial rate of the reaction is equal to the negative of the initial slope (t = 0). The determination of the instantaneous rate at t = 2 seconds is illustrated. (If you do not recall how to find the slope of a straight line, refer to Figure 16-5.)

Figure 16-3 is a plot of the hydrogen concentration versus time, using data of Table 16-1. The initial rate, or the rate at the instant of mixing the reactants, is the negative of the slope at t = 0. The *instantaneous* rate of reaction at time t (2.0 seconds, for example) is the negative of the slope of the tangent to the curve at time t. We see that the rate decreases with time; lower concentrations of H_2 and ICl result in slower reaction. Had we plotted concentration of a product versus time, the rate would have been related to the *positive* slope of the tangent at time t.

Suppose a driver travels 40 miles in an hour; we describe his average speed (rate) as 40 mi/h. This does not necessarily mean that he drove at a steady speed. He might have stopped at a few traffic signals, made a fuel stop, driven sometimes faster, sometimes slower—his *instantaneous rate* (the rate at which he was traveling at any instant) was quite changeable.

EXAMPLE 16-1 *Rate of Reaction*

At some time, we observe that the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is forming NO_2 at the rate of 0.0072 $\dfrac{\text{mol}}{\text{L}\cdot\text{s}}$.

(a) What is the rate of change of $[O_2]$, $\dfrac{\Delta[O_2]}{\Delta t}$, in $\dfrac{\text{mol}}{\text{L}\cdot\text{s}}$, at this time?

(b) What is the rate of change of $[N_2O_5]$, $\dfrac{\Delta[N_2O_5]}{\Delta t}$, in $\dfrac{\text{mol}}{\text{L}\cdot\text{s}}$, at this time?

(c) What is the rate of reaction at this time?

Plan

We can use the mole ratios from the balanced equation to determine the rates of change of other products and reactants. The rate of reaction can then be derived from any one of these individual rates.

Solution

(a) The balanced equation gives the reaction ratio 1 mol $\dfrac{O_2}{4}$ mol NO_2.

$$\text{rate of change of } [O_2] = \dfrac{\Delta[O_2]}{\Delta t} = \dfrac{0.0072\ \text{mol } NO_2}{\text{L}\cdot\text{s}} \times \dfrac{1\ \text{mol } O_2}{4\ \text{mol } NO_2} = \boxed{0.0018\ \dfrac{\text{mol } O_2}{\text{L}\cdot\text{s}}}$$

(b) The balanced equation shows that 2 mol N_2O_5 is *consumed* for every 4 mol NO_2 that is *formed*. Because $[N_2O_5]$ is decreasing as $[NO_2]$ increases, we should write the reaction ratio as $\dfrac{-2 \text{ mol } N_2O_5}{4 \text{ mol } NO_2}$.

$$\text{rate of change of } [N_2O_5] = \frac{\Delta[N_2O_5]}{\Delta t} = \frac{0.0072 \text{ mol } NO_2}{\text{L} \cdot \text{s}} \times \frac{-2 \text{ mol } N_2O_5}{4 \text{ mol } NO_2}$$

$$= \boxed{-0.0036 \ \frac{\text{mol } N_2O_5}{\text{L} \cdot \text{s}}}$$

The rate of *change* of $[N_2O_5]$ with time, $\dfrac{\Delta[N_2O_5]}{\Delta t}$, is $-0.0036 \ \dfrac{\text{mol } N_2O_5}{\text{L} \cdot \text{s}}$, a *negative* number, because N_2O_5, a reactant, is being used up.

(c) The rate of reaction can be calculated from the rate of decrease of any reactant concentration or the rate of increase of any product concentration.

$$\text{rate of reaction} = -\frac{1}{2}\left(\frac{\Delta[N_2O_5]}{\Delta t}\right) = -\frac{1}{2}\left(-0.0036 \ \frac{\text{mol}}{\text{L} \cdot \text{s}}\right) = \boxed{0.0018 \ \frac{\text{mol}}{\text{L} \cdot \text{s}}}$$

$$\text{rate of reaction} = \frac{1}{4}\left(\frac{\Delta[NO_2]}{\Delta t}\right) = \frac{1}{4}\left(0.0072 \ \frac{\text{mol}}{\text{L} \cdot \text{s}}\right) = \boxed{0.0018 \ \frac{\text{mol}}{\text{L} \cdot \text{s}}}$$

$$\text{rate of reaction} = \frac{1}{1}\left(\frac{\Delta[O_2]}{\Delta t}\right) = \boxed{0.0018 \ \frac{\text{mol}}{\text{L} \cdot \text{s}}}$$

We see that the rate of reaction is the same, no matter which reactant or product we use to determine it. Remember that the mol in these units is interpreted as "moles of reaction."

You should now work Exercise 10.

FACTORS THAT AFFECT REACTION RATES

Often we want a reaction to take place rapidly enough to be practical but not so rapidly as to be dangerous. The controlled burning of fuel in an internal combustion engine is an example of such a process. On the other hand, we want some undesirable reactions, such as the spoiling of food, to take place more slowly.

Four factors have marked effects on the rates of chemical reactions. They are (1) nature of the reactants, (2) concentrations of the reactants, (3) temperature, and (4) the presence of a catalyst. Understanding their effects can help us control the rates of reactions in desirable ways. The study of these factors gives important insight into the details of the processes by which a reaction occurs. This kind of study is the basis for developing theories of chemical kinetics. Now we study these factors and the related theories—collision theory and transition state theory.

16-2 NATURE OF THE REACTANTS

The physical states of reacting substances are important in determining their reactivities. A puddle of liquid gasoline can burn smoothly, but gasoline vapors can burn explosively. Two immiscible liquids may react slowly at their interface, but if they are intimately mixed to provide better contact, the reaction speeds up. White phosphorus and red phosphorus are different solid forms (allotropes) of elemental phosphorus. White phosphorus ignites when exposed to oxygen in the air. By contrast, red phosphorus can be kept in open containers for long periods of time without noticeable reaction.

Samples of dry solid potassium sulfate, K_2SO_4, and dry solid barium nitrate, $Ba(NO_3)_2$, can be mixed with no appreciable reaction occurring for several years. But if aqueous solutions of the two are mixed, a reaction occurs rapidly, forming a white precipitate of barium sulfate.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) \qquad \text{(net ionic equation)}$$
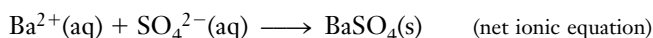
Chemical identities of elements and compounds affect reaction rates. Metallic sodium, with its low ionization energy, reacts rapidly with water at room temperature; metallic calcium has a higher ionization energy and reacts only slowly with water at room temperature. Solutions of a strong acid and a strong base react rapidly when they are mixed because the interactions involve mainly electrostatic attractions between ions in solution. Reactions that involve the breaking of covalent bonds are usually slower.

The extent of subdivision of solids or liquids can be crucial in determining reaction rates. Large chunks of most metals do not burn. But many powdered metals, with larger surface areas and hence more atoms exposed to the oxygen of the air, burn easily. One pound of fine iron wire rusts much more rapidly than a solid one-pound chunk of iron. Violent explosions sometimes occur in grain elevators, coal mines, and chemical plants in which large amounts of powdered substances are produced. These explosions are examples of the effect of large surface areas on rates of reaction. The rate of reaction depends on the surface area or degree of subdivision. The ultimate degree of subdivision would make all reactant molecules (or ions or atoms) accessible to react at any given time. This situation can be achieved when the reactants are in the gaseous state or in solution.

Two allotropes of phosphorus. White phosphorus (*above*) ignites and burns rapidly when exposed to oxygen in the air, so it is stored under water. Red phosphorus (*below*) reacts with air much more slowly, and can be stored in contact with air.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 15.3, Control of Reaction Rates (1): Surface Area.

Powdered chalk (mostly calcium carbonate, $CaCO_3$) reacts rapidly with dilute hydrochloric acid because it has a large total surface area. A stick of chalk has a much smaller surface area, so it reacts much more slowly.

16-3 CONCENTRATIONS OF REACTANTS: THE RATE-LAW EXPRESSION

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 15.4, Control of Reaction Rates (2): Concentration Dependence.

As the concentrations of reactants change at constant temperature, the rate of reaction changes. We write the **rate-law expression** (often called simply the **rate law**) for a reaction to describe how its rate depends on concentrations; this rate law is experimentally deduced for each reaction from a study of how its rate varies with concentration.

> The rate-law expression for a reaction in which A, B, . . . are reactants has the general form
>
> $$\text{rate} = k[\text{A}]^x[\text{B}]^y \ldots$$
>
> The constant k is called the **specific rate constant** (or just the **rate constant**) for the reaction at a particular temperature. The values of the exponents, x and y, and of the rate constant, k bear no necessary relationship to the coefficients in the *balanced chemical equation* for the overall reaction and must be determined *experimentally*.

The word *order* is used in kinetics in its mathematical meaning. This use is unrelated to the order–disorder discussion of entropy (Chapter 15).

The powers to which the concentrations are raised, x and y, are usually integers or zero but are occasionally fractional or even negative. A power of *one* means that the rate is directly proportional to the concentration of that reactant. A power of *two* means that the rate is directly proportional to the *square* of that concentration. A power of *zero* means that the rate does not depend on the concentration of that reactant, so long as some of the reactant is present. The value of x is said to be the **order** of the reaction with respect to A, and y is the order of the reaction with respect to B. The overall order of the reaction is $x + y$. Examples of observed rate laws for some reactions follow.

1. $3\text{NO}(g) \longrightarrow \text{N}_2\text{O}(g) + \text{NO}_2(g)$
$$\text{rate} = k[\text{NO}]^2 \qquad \text{second order in NO; second order overall}$$

2. $2\text{NO}_2(g) + \text{F}_2(g) \longrightarrow 2\text{NO}_2\text{F}(g)$
$$\text{rate} = k[\text{NO}_2][\text{F}_2] \qquad \text{first order in NO}_2 \text{ and first order in F}_2; \text{ second order overall}$$

3. $2\text{NO}_2(g) \longrightarrow 2\text{NO}(g) + \text{O}_2(g) \quad \text{rate} = k[\text{NO}_2]^2 \qquad \text{second order in NO}_2; \text{ second order overall}$

4. $\text{H}_2\text{O}_2(aq) + 3\text{I}^-(aq) + 2\text{H}^+(aq) \longrightarrow 2\text{H}_2\text{O}(\ell) + \text{I}_3^-(aq)$
$$\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^-] \qquad \text{first order in H}_2\text{O}_2 \text{ and first order in I}^-; \text{ zero order in H}^+; \text{ second order overall}$$

Any number raised to the zero power is one. Here $[\text{H}^+]^0 = 1$.

> We see that the orders (exponents) in the rate law expression *may* or *may not* match the coefficients in the balanced equation. There is *no* way to predict reaction orders from the balanced overall chemical equation. The orders must be determined experimentally.

More details about values and units of k will be discussed in later sections.

It is important to remember the following points about this specific rate constant, k.

1. Once the reaction orders are known, experimental data must be used to determine the value of k for the reaction at appropriate conditions.

2. The value we determine is for a *specific reaction*, represented by a balanced equation.

3. The units of k depend on the *overall order* of the reaction.

4. The value we determine does not change with concentrations of either reactants or products.

5. The value we determine does not change with time (Section 16-4).

6. The value we determine refers to the reaction *at a particular temperature* and changes if we change the temperature (Section 16-8).

7. The value we determine depends on whether a *catalyst* is present (Section 16-9).

EXAMPLE 16-2 *Interpretation of the Rate Law*

For a hypothetical reaction

$$A + B + C \longrightarrow products$$
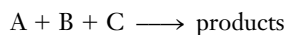
the rate law is determined to be

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

What happens to the reaction rate when we make each of the following concentration changes?

(a) We double the concentration of A without changing the concentration of B or C. (b) We double the concentration of B without changing the concentration of A or C. (c) We double the concentration of C without changing the concentration of A or B. (d) We double all three concentrations simultaneously.

Plan

We interpret the rate law to predict the changes in reaction rate. We remember that changing concentrations does not change the value of k.

Solution

(a) We see that rate is directly proportional to the *first power* of [A]. We do not change [B] or [C]. Doubling [A] (i.e., increasing [A] by a factor of 2) causes the reaction rate to increase by a factor of $2^1 = 2$ so the reaction rate doubles.

(b) We see that rate is directly proportional to the *second power* of [B]. We do not change [A] or [C]. Doubling [B] (i.e., increasing [B] by a factor of 2) causes the reaction rate to increase by a factor of $2^2 = 4$.

(c) The reaction rate is independent of [C], so changing [C] causes no change in reaction rate.

(d) Doubling all concentrations would cause the changes described in (a), (b), and (c) simultaneously. The rate would increase by a factor of 2 due to the change in [A], by a factor of 4 due to the change in [B], and be unaffected by the change in [C]. The result is that the reaction rate increases by a factor of $2^1 \times 2^2 = 8$.

You should now work Exercises 14 and 15.

We can use the **method of initial rates** to deduce the rate law from experimentally measured rate data. Usually we know the concentrations of all reactants at the start of the reaction. We can then measure the *initial rate* of the reaction, corresponding to these initial concentrations. The following tabulated data refer to the hypothetical reaction

$$A + 2B \longrightarrow C$$
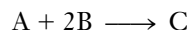
at a specific temperature. The brackets indicate the concentrations of the reacting species *at the beginning* of each experimental run listed in the first column—that is, the initial concentrations for each experiment.

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of C
1	1.0×10^{-2} M	1.0×10^{-2} M	1.5×10^{-6} $M \cdot s^{-1}$
2	1.0×10^{-2} M	2.0×10^{-2} M	3.0×10^{-6} $M \cdot s^{-1}$
3	2.0×10^{-2} M	1.0×10^{-2} M	6.0×10^{-6} $M \cdot s^{-1}$

In such an experiment we often keep some initial concentrations the same and vary others by simple factors, such as 2 or 3. This makes it easier to access the effect of each change on the rate.

Because we are describing the same reaction in each experiment, each is governed by the same rate-law expression. This expression has the form

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

Let's compare the initial rates of formation of product (reaction rates) for different experimental runs to see how changes in concentrations of reactants affect the rate of reaction. This lets us evaluate x and y, and then k.

We see that the initial concentration of A is the same in experiments 1 and 2; for these trials, any change in reaction rate would be due to different initial concentrations of B. Comparing these two experiments, we see that [B] has been changed by a factor of

$$\frac{2.0 \times 10^{-2}}{1.0 \times 10^{-2}} = 2.0 = \text{[B] ratio}$$

The rate changes by a factor of

$$\frac{3.0 \times 10^{-6}}{1.5 \times 10^{-6}} = 2.0 = \text{rate ratio}$$

The exponent y can be deduced from

$$\text{rate ratio} = (\text{[B] ratio})^y$$
$$2.0 = (2.0)^y \qquad \text{so} \qquad y = 1$$

The reaction is first order in [B]. Thus far we know that the rate expression is

$$\text{rate} = k[A]^x[B]^1$$

To evaluate x, we observe that the concentrations of [A] are different in experiments 1 and 3. For these two trials, the initial concentration of B is the same, so any change in reaction rate would be due to different initial concentrations of A. Comparing these two experiments, we see that [A] has been *multiplied* by a factor of

$$\frac{2.0 \times 10^{-2}}{1.0 \times 10^{-2}} = 2.0 = \text{[A] ratio}$$

Rate increases by a factor of

$$\frac{6.0 \times 10^{-6}}{1.5 \times 10^{-6}} = 4.0 = \text{rate ratio}$$

The exponent x can be deduced from

$$\text{rate ratio} = ([A] \text{ ratio})^x$$

$$4.0 = (2.0)^x \qquad \text{so} \qquad x = 2$$

The reaction is second order in [A]. We can now write its rate-law expression.

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

The specific rate constant, k, can be evaluated by substituting any of the three sets of data into the rate-law expression. Using the data from experiment 1 gives

$$\text{rate}_1 = k[A]_1^2[B]_1 \qquad \text{or} \qquad k = \frac{\text{rate}_1}{[A]_1^2[B]_1}$$

$$k = \frac{1.5 \times 10^{-6} \ M \cdot s^{-1}}{(1.0 \times 10^{-2} \ M)^2(1.0 \times 10^{-2} \ M)} = 1.5 \ M^{-2} \cdot s^{-1}$$

At the temperature at which the measurements were made, the rate-law expression for this reaction is

$$\text{rate} = k[A]^2[B] \qquad \text{or} \qquad \text{rate} = 1.5 \ M^{-2} \cdot s^{-1} \ [A]^2[B]$$

We can check our result by evaluating k from one of the other sets of data.

> Remember that the specific rate constant k does *not* change with concentration. Only a temperature change or the introduction of a catalyst can change the value of k.

> The units of k depend on the overall order of the reaction, consistent with converting the product of concentrations on the right to concentration/time on the left. For any reaction that is third order overall, the units of k are $M^{-2} \cdot \text{time}^{-1}$.

✓ **Problem-Solving Tip:** *Be Sure to Use the Rate of Reaction*

The rate-law expression should always give the dependence of the *rate of reaction* on concentrations. The data for the preceding calculation describe the rate of formation of the product C; the coefficient of C in the balanced equation is one, so the rate of reaction is equal to the rate of formation of C. If the coefficient of the measured substance had been 2, then before we began the analysis we should have divided each value of the "initial rate of formation" by 2 to obtain the initial rate of reaction. For instance, suppose we measure the rate of formation of AB in the reaction

$$A_2 + B_2 \longrightarrow 2AB$$
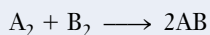
Then

$$\text{rate of increase} = \frac{1}{2}\left(\frac{\Delta[AB]}{\Delta t}\right) = \frac{1}{2} \ (\text{rate of formation of AB})$$

Then we would analyze how this reaction rate changes as we change the concentrations of reactants.

An Alternative Method

We can also use a simple algebraic approach to find the exponents in a rate-law expression. Consider the set of rate data given earlier for the hypothetical reaction

$$A + 2B \longrightarrow C$$
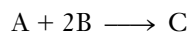
When heated in air, steel wool glows but does not burn rapidly, due to the low O_2 concentration in air (about 21%). When the glowing steel wool is put into pure oxygen, it burns vigorously because of the much greater accessibility of O_2 reactant molecules.

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of C $(M \cdot s^{-1})$
1	$1.0 \times 10^{-2}\ M$	$1.0 \times 10^{-2}\ M$	1.5×10^{-6}
2	$1.0 \times 10^{-2}\ M$	$2.0 \times 10^{-2}\ M$	3.0×10^{-6}
3	$2.0 \times 10^{-2}\ M$	$1.0 \times 10^{-2}\ M$	6.0×10^{-6}

Because we are describing the same reaction in each experiment, all the experiments are governed by the same rate-law expression,

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

The initial concentration of A is the same in experiments 1 and 2, so any change in the initial rates for these experiments would be due to different initial concentrations of B. To evaluate y, we solve the ratio of the rate-law expressions of these two experiments for y. We can divide the first rate-law expression by the corresponding terms in the second rate-law expression.

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[\text{A}]_1{}^x[\text{B}]_1{}^y}{k[\text{A}]_2{}^x[\text{B}]_2{}^y}$$

The value of k always cancels from such a ratio because it is constant at a particular temperature. The initial concentrations of A are equal, so they too cancel. Thus, the expression simplifies to

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

The only unknown in this equation is y. We substitute data from experiments 1 and 2 into the equation, which gives us

$$\frac{1.5 \times 10^{-6}\ M \cdot s^{-1}}{3.0 \times 10^{-6}\ M \cdot s^{-1}} = \left(\frac{1.0 \times 10^{-2}\ M}{2.0 \times 10^{-2}\ M}\right)^y$$

$$0.5 = (0.5)^y \qquad \text{so} \qquad y = 1$$

Thus far, we know that the rate-law expression is

$$\text{rate} = k[\text{A}]^x[\text{B}]^1$$

Next we evaluate x. In experiments 1 and 3, the initial concentration of B is the same, so any change in the initial rates for these experiments would be due to the different initial concentrations of A. We solve the ratio of the rate-law expressions of these two experiments for x. We divide the third rate-law expression by the corresponding terms in the first rate-law expression.

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[\text{A}]_3{}^x[\text{B}]_3{}^1}{k[\text{A}]_1{}^x[\text{B}]_1{}^1}$$

The value k cancels, and so do the concentrations of B because they are equal. Thus, the expression simplifies to

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{[\text{A}]_3{}^x}{[\text{A}]_1{}^x} = \left(\frac{[\text{A}]_3}{[\text{A}]_1}\right)^x$$

$$\frac{6.0 \times 10^{-6} \ M \cdot s^{-1}}{1.5 \times 10^{-6} \ M \cdot s^{-1}} = \left(\frac{2.0 \times 10^{-2} \ M}{1.0 \times 10^{-2} \ M}\right)^x$$

$$4.0 = (2.0)^x \quad \text{so} \quad x = 2$$

The power to which [A] is raised in the rate-law expression is 2, so the rate-law expression for this reaction is the same as that obtained earlier.

$$\text{rate} = k[A]^2[B]^1 \quad \text{or} \quad \text{rate} = k[A]^2[B]$$

EXAMPLE 16-3 *Method of Initial Rates*

Given the following data, determine the rate-law expression and the value of the rate constant for the reaction

$$2A + B + C \longrightarrow D + E$$
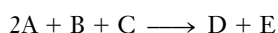
Experiment	Initial [A]	Initial [B]	Initial [C]	Initial Rate of Formation of E
1	0.20 M	0.20 M	0.20 M	$2.4 \times 10^{-6} \ M \cdot min^{-1}$
2	0.40 M	0.30 M	0.20 M	$9.6 \times 10^{-6} \ M \cdot min^{-1}$
3	0.20 M	0.30 M	0.20 M	$2.4 \times 10^{-6} \ M \cdot min^{-1}$
4	0.20 M	0.40 M	0.60 M	$7.2 \times 10^{-6} \ M \cdot min^{-1}$

The coefficient of E in the balanced equation is 1, so the rate of reaction is equal to the rate of formation of E.

Plan

The rate law is of the form Rate $= k[A]^x[B]^y[C]^z$. We must evaluate x, y, z, and k. We use the reasoning outlined earlier; in this presentation the first method is used.

The alternative algebraic method outlined above can also be used.

Solution

Dependence on [B]: In experiments 1 and 3, the initial concentrations of A and C are unchanged. Thus, any change in the rate would be due to the change in concentration of B. But we see that the rate is the same in experiments 1 and 3, even though the concentration of B is different. Thus, the reaction rate is independent of [B], so $y = 0$. We can neglect changes in [B] in the subsequent reasoning. The rate law must be

$[B]^0 = 1$

$$\text{rate} = k[A]^x[C]^z$$

Dependence on [C]: Experiments 1 and 4 involve the same initial concentration of A; thus the observed change in rate must be due entirely to the changed [C]. So we compare experiments 1 and 4 to find z.

$$[C] \text{ has been } multiplied \text{ by a factor of } \frac{0.60}{0.20} = 3.0 = [C] \text{ ratio}$$

The rate changes by a factor of

$$\frac{7.2 \times 10^{-6}}{2.4 \times 10^{-6}} = 3.0 = \text{rate ratio}$$

The exponent z can be deduced from

$$\text{rate ratio} = ([C] \text{ ratio})^z$$

$$3.0 = (3.0)^z \quad \text{so} \quad z = 1 \quad \text{The reaction is first order in [C].}$$

Now we know that the rate law is of the form

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

Dependence on [A]: We use experiments 1 and 2 to evaluate x, because [A] is changed, [B] does not matter, and [C] is unaltered. The observed rate change is due *only* to the changed [A].

$$[A] \text{ has been } \textit{multiplied} \text{ by a factor of } \frac{0.40}{0.20} = 2.0 = [A] \text{ ratio}$$

The rate changes by a factor of

$$\frac{9.6 \times 10^{-6}}{2.4 \times 10^{-6}} = 4.0 = \text{rate ratio}$$

The exponent x can be deduced from

$$\text{rate ratio} = ([A] \text{ ratio})^x$$

$$4.0 = (2.0)^x \quad \text{so} \quad \boxed{x = 2} \quad \text{The reaction is second order in [A].}$$

From these results we can write the complete rate-law expression.

$$\text{rate} = k[A]^2[B]^0[C]^1 \quad \text{or} \quad \boxed{\text{rate} = k[A]^2[C]}$$

We can evaluate the specific rate constant, k, by substituting any of the four sets of data into the rate-law expression we have just derived. Data from experiment 2 give

$$\text{rate}_2 = k[A]_2{}^2[C]_2$$

$$k = \frac{\text{rate}_2}{[A]_2{}^2[C]_2} = \frac{9.6 \times 10^{-6} \, M\cdot\text{min}^{-1}}{(0.40 \, M)^2(0.20 \, M)} = \boxed{3.0 \times 10^{-4} \, M^{-2}\cdot\text{min}^{-1}}$$

The rate-law expression can also be written with the value of k incorporated.

$$\boxed{\text{rate} = 3.0 \times 10^{-4} \, M^{-2}\cdot\text{min}^{-1} \, [A]^2[C]}$$

This expression allows us to calculate the rate at which this reaction occurs with any known concentrations of A and C (provided some B is present). As we shall see presently, changes in temperature change reaction rates. This value of k is valid *only* at the temperature at which the data were collected.

You should now work Exercises 17 and 18.

✓**Problem-Solving Tip:** *Check the Rate Law You Have Derived*

If the rate law that you deduce from initial rate data is correct, it will not matter which set of data you use to calculate k. As a check, you can calculate k several times, once from each set of experimental concentration and rate data. If the reaction orders in your derived rate law are correct, then all sets of experimental data will give the same value of k (within rounding error); but if the orders are wrong, then the k values will vary considerably.

EXAMPLE 16-4 *Method of Initial Rates*

Use the following initial rate data to determine the form of the rate-law expression for the reaction

$$3A + 2B \longrightarrow 2C + D$$
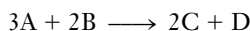
Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of D
1	$1.00 \times 10^{-2}\ M$	$1.00 \times 10^{-2}\ M$	$6.00 \times 10^{-3}\ M \cdot min^{-1}$
2	$2.00 \times 10^{-2}\ M$	$3.00 \times 10^{-2}\ M$	$1.44 \times 10^{-1}\ M \cdot min^{-1}$
3	$1.00 \times 10^{-2}\ M$	$2.00 \times 10^{-2}\ M$	$1.20 \times 10^{-2}\ M \cdot min^{-1}$

Plan

The rate law is of the form rate $= k[A]^x[B]^y$. No two experiments have the same initial [B], so let's use the alternative method presented earlier to evaluate x and y.

Solution

The initial concentration of A is the same in experiments 1 and 3. We divide the third rate-law expression by the corresponding terms in the first one

$$\frac{rate_3}{rate_1} = \frac{k[A]_3{}^x[B]_3{}^y}{k[A]_1{}^x[B]_1{}^y}$$

The initial concentrations of A are equal, so they cancel, as does k. Simplifying and then substituting known values of rates and [B],

$$\frac{rate_3}{rate_1} = \frac{[B]_3{}^y}{[B]_1{}^y} \qquad \text{or} \qquad \frac{1.20 \times 10^{-2}\ M \cdot min}{6.00 \times 10^{-3}\ M \cdot min} = \left(\frac{2.00 \times 10^{-2}\ M}{1.00 \times 10^{-2}\ M}\right)^y$$

$$2.0 = (2.0)^y \qquad \text{or} \qquad \boxed{y = 1 \qquad \text{The reaction is first order in [B].}}$$

No two of the experimental runs have the same concentrations of B, so we must proceed somewhat differently. Let us compare experiments 1 and 2. The observed change in rate must be due to the *combination* of the changes in [A] and [B]. We can divide the second rate-law expression by the corresponding terms in the first one, cancel the equal k values, and collect terms.

$$\frac{rate_2}{rate_1} = \frac{k[A]_2{}^x[B]_2{}^y}{k[A]_1{}^x[B]_1{}^y} = \left(\frac{[A]_2}{[A]_1}\right)^x\left(\frac{[B]_2}{[B]_1}\right)^y$$

Now let's insert the known values for rates and concentrations and the known [B] exponent of 1.

$$\frac{1.44 \times 10^{-1}\ M \cdot min^{-1}}{6.00 \times 10^{-3}\ M \cdot min^{-1}} = \left(\frac{2.00 \times 10^{-2}\ M}{1.00 \times 10^{-2}\ M}\right)^x\left(\frac{3.00 \times 10^{-2}\ M}{1.00 \times 10^{-2}\ M}\right)^1$$

$$24.0 = (2.00)^x(3.00)$$

$$8.00 = (2.00)^x \qquad \text{or} \qquad \boxed{x = 3 \qquad \text{The reaction is third order in [A].}}$$

The rate-law expression has the form $\boxed{rate = k[A]^3[B].}$

You should now work Exercise 22.

16-4   CONCENTRATION VERSUS TIME: THE INTEGRATED RATE EQUATION

Often we want to know the concentration of a reactant that would remain after some specified time, or how long it would take for some amount of the reactants to be used up.

> The equation that relates *concentration* and *time* is the **integrated rate equation.** We can also use it to calculate the **half-life, $t_{1/2}$,** of a reactant—the time it takes for half of that reactant to be converted into product. The integrated rate equation and the half-life are different for reactions of different order.

See the Saunders Interactive General Chemistry CD-ROM, Screen 15.6, Concentration-Time Relationships.

We will look at relationships for some simple cases. If you know calculus, you may be interested in the derivation of the integrated rate equations. This development is presented in the Enrichments at the end of this section.

First-Order Reactions

a represents the coefficient of reactant A in the balanced overall equation.

For reactions involving $aA \rightarrow$ products that are *first order in* A and *first order overall*, the integrated rate equation is

$$\ln\left(\frac{[A]_0}{[A]}\right) = akt \qquad \text{(first order)}$$

$[A]_0$ is the initial concentration of reactant A, and $[A]$ is its concentration at some time, t, after the reaction begins. Solving this relationship for t gives

$$t = \frac{1}{ak} \ln\left(\frac{[A]_0}{[A]}\right)$$

When time $t_{1/2}$ has elapsed, half of the original $[A]_0$ has reacted, so half of it remains.

By definition, $[A] = \frac{1}{2}[A]_0$ at $t = t_{1/2}$. Thus

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

$$t_{1/2} = \frac{\ln 2}{ak} = \frac{0.693}{ak} \qquad \text{(first order)}$$

Nuclear decay (Chapter 26) is a very important first-order process. Exercises at the end of that chapter involve calculations of nuclear decay rates.

This relates the half-life of a reactant in a *first-order reaction* and its rate constant, k. In such reactions, the half-life *does not depend* on the initial concentration of A. This is not true for reactions having overall orders other than first order.

EXAMPLE 16-5   *Half-Life: First-Order Reaction*

Compound A decomposes to form B and C in a reaction that is first order with respect to A and first order overall. At 25°C, the specific rate constant for the reaction is 0.0450 s^{-1}. What is the half-life of A at 25°C?

$$A \longrightarrow B + C$$
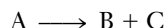
Plan

We use the equation given earlier for $t_{1/2}$ for a first-order reaction. The value of k is given in the problem; the coefficient of reactant A is $a = 1$.

Solution

$$t_{1/2} = \frac{\ln 2}{ak} = \frac{0.693}{1(0.0450 \text{ s}^{-1})} = \boxed{15.4 \text{ s}}$$

After 15.4 seconds of reaction, half of the original reactant remains, so that $[A] = \frac{1}{2}[A]_0$.

You should now work Exercise 39.

EXAMPLE 16-6   *Concentration Versus Time: First-Order Reaction*

The reaction $2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$ obeys the rate law Rate $= k[N_2O_5]$, in which the specific rate constant is 0.00840 s^{-1} at a certain temperature. (a) If 2.50 moles of N_2O_5 were placed in a 5.00-liter container at that temperature, how many moles of N_2O_5 would remain after 1.00 minute? (b) How long would it take for 90% of the original N_2O_5 to react?

Plan

We apply the integrated first-order rate equation.

$$\ln \left(\frac{[N_2O_5]_0}{[N_2O_5]} \right) = akt$$

(a) First, we must determine $[N_2O_5]_0$, the original molar concentration of N_2O_5. Then we solve for $[N_2O_5]$, the molar concentration after 1.00 minute. We must remember to express k and t using the same time units. Finally, we convert molar concentration of N_2O_5 to moles remaining. (b) We solve the integrated first-order equation for the required time.

Solution

The original concentration of N_2O_5 is

$$[N_2O_5]_0 = \frac{2.50 \text{ mol}}{5.00 \text{ L}} = 0.500 \text{ } M$$

The other quantities are

$$a = 2 \qquad k = 0.00840 \text{ s}^{-1} \qquad t = 1.00 \text{ min} = 60.0 \text{ s} \qquad [N_2O_5] = \underline{?}$$

The only unknown in the integrated rate equation is $[N_2O_5]$ after 1.00 minute. Let us solve for the unknown. Because $\ln x/y = \ln x - \ln y$,

$$\ln \frac{[N_2O_5]_0}{[N_2O_5]} = \ln [N_2O_5]_0 - \ln [N_2O_5] = akt$$

$$\ln [N_2O_5] = \ln [N_2O_5]_0 - akt$$

$$= \ln (0.500) - (2)(0.00840 \text{ s}^{-1})(60.0 \text{ s}) = -0.693 - 1.008$$

$$\ln [N_2O_5] = -1.701$$

Taking the inverse natural logarithm of both sides gives

inv $\ln x = e^{\ln x}$

$$[N_2O_5] = 1.82 \times 10^{-1} \text{ } M$$

Thus, after 1.00 minute of reaction, the concentration of N_2O_5 is 0.182 M. The number of moles of N_2O_5 left in the 5.00-L container is

$$\underline{?}\ mol\ N_2O_5 = 5.00\ L \times \frac{0.182\ mol}{L} = \boxed{0.910\ mol\ N_2O_5}$$

(b) Because the integrated *first-order* rate equation involves a *ratio* of concentrations, we do not need to obtain the numerical value of the required concentration. When 90.0% of the original N_2O_5 has reacted, 10.0% remains, or

$$[N_2O_5] = (0.100)[N_2O_5]_0$$

We make this substitution into the integrated rate equation and solve for the elapsed time, t.

$$\ln \frac{[N_2O_5]_0}{[N_2O_5]} = akt$$

$$\ln \frac{[N_2O_5]_0}{(0.100)[N_2O_5]_0} = (2)(0.00840\ s^{-1})t$$

$$\ln (10.0) = (0.0168\ s^{-1})t$$

$$2.302 = (0.0168\ s^{-1})t \qquad or \qquad t = \frac{2.302}{0.0168\ s^{-1}} = \boxed{137\ seconds}$$

You should now work Exercises 36 and 40.

✓ Problem-Solving Tip: *Does Your Answer Make Sense?*

We know that the amount of N_2O_5 in Example 16-6 must be decreasing. The calculated result, 0.910 mol N_2O_5 after 1.00 minute, is less than the initial amount, 2.50 mol N_2O_5, which is a reasonable result. If our solution had given a result that was *larger* than the original, we should recognize that we must have made some error. For example, if we had incorrectly written the equation as

$$\ln \frac{[N_2O_5]}{[N_2O_5]_0} = akt$$

we would have obtained $[N_2O_5] = 1.37\ M$, corresponding to 6.85 mol N_2O_5. This would be more N_2O_5 than was originally present, which we should immediately recognize as an impossible answer.

Second-Order Reactions

For reactions involving $aA \rightarrow$ products that are *second order with respect to* A *and second order overall*, the integrated rate equation is

$$\frac{1}{[A]} - \frac{1}{[A]_0} = akt \qquad \left(\begin{array}{l} \text{second order in A,} \\ \text{second order overall} \end{array} \right)$$

First-order reaction

$a = 1; [A]_0 = 1.0\,M$
$k = 0.40\,s^{-1}$

Second-order reaction

$a = 1; [A]_0 = 1.0\,M$
$k = 0.40\,M^{-1} \cdot s^{-1}$

[A] (M)

t (seconds)

(a)   (b)
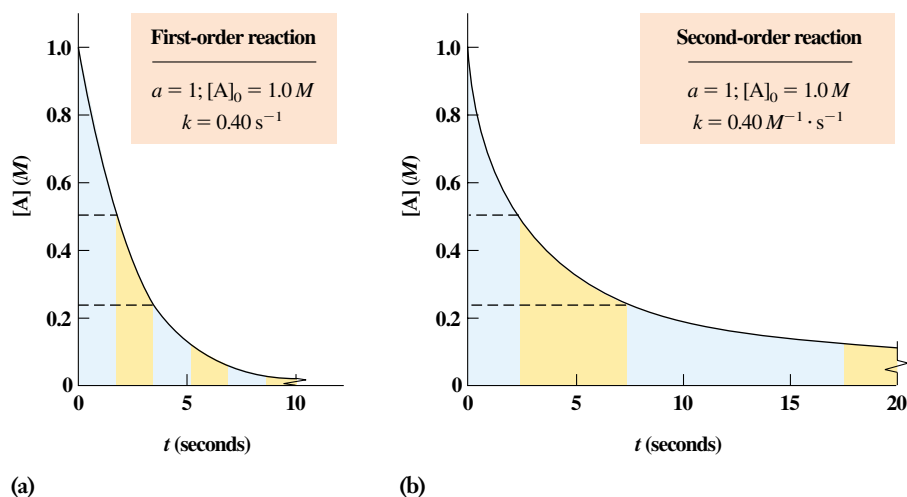
Figure 16-4 (a) Plot of concentration versus time for a first-order reaction. During the first half-life, 1.73 seconds, the concentration of A falls from $1.00\,M$ to $0.50\,M$. An additional 1.73 seconds is required for the concentration to fall by half again, from $0.50\,M$ to $0.25\,M$, and so on. For a first-order reaction, $t_{1/2} = \dfrac{\ln 2}{ak} = \dfrac{0.693}{ak}$; $t_{1/2}$ does not depend on the concentration at the beginning of that time period. (b) Plot of concentration versus time for a second-order reaction. The same values are used for a, $[A]_0$, and k as in part (a). During the first half-life, 2.50 seconds, the concentration of A falls from $1.00\,M$ to $0.50\,M$. The concentration falls by half again from 2.50 to 7.50 seconds, so the second half-life is 5.00 seconds. The half-life beginning at $0.25\,M$ is 10.00 seconds. For a second-order reaction, $t_{1/2} = \dfrac{1}{ak[A]_0}$; $t_{1/2}$ is inversely proportional to the concentration at the beginning of that time period.

For $t = t_{1/2}$, we have $[A] = \frac{1}{2}[A]_0$, so

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

Simplifying and solving for $t_{1/2}$, we obtain the relationship between the rate constant and $t_{1/2}$.

$$t_{1/2} = \frac{1}{ak[A]_0} \qquad \left(\begin{array}{l}\text{second order in A,}\\ \text{second order overall}\end{array}\right)$$

You should carry out the algebraic steps to solve for $t_{1/2}$.

In this case $t_{1/2}$ *depends on the initial concentration of* A. Figure 16-4 illustrates the different behavior of half-life for first- and second-order reactions.

EXAMPLE 16-7   *Half-Life: Second-Order Reaction*

Compounds A and B react to form C and D in a reaction that was found to be second order in A and second order overall. The rate constant at 30°C is 0.622 liter per mole per minute. What is the half-life of A when $4.10 \times 10^{-2}\,M$ A is mixed with excess B?

$$A + B \longrightarrow C + D \qquad \text{rate} = k[A]^2$$

Plan

As long as some B is present, only the concentration of A affects the rate. The reaction is second order in [A] and second order overall, so we use the appropriate equation for the half-life.

Solution

$$t_{1/2} = \frac{1}{ak[A]_0} = \frac{1}{(1)(0.622\ M^{-1} \cdot min^{-1})(4.10 \times 10^{-2}\ M)} = \boxed{39.2\ min}$$

EXAMPLE 16-8   *Concentration Versus Time: Second-Order Reaction*

The gas-phase decomposition of NOBr is second order in [NOBr], with $k = 0.810\ M^{-1} \cdot s^{-1}$ at 10°C. We start with $4.00 \times 10^{-3}\ M$ NOBr in a flask at 10°C. How many seconds does it take to use up $1.50 \times 10^{-3}\ M$ of this NOBr?

$$2NOBr(g) \longrightarrow 2NO(g) + Br_2(g) \qquad rate = k[NOBr]^2$$
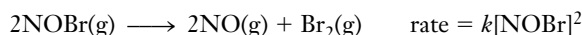
Plan

We first determine the concentration of NOBr that remains after $1.50 \times 10^{-3}\ M$ is used up. Then we use the second-order integrated rate equation to determine the time required to reach that concentration.

Solution

$$\underline{?}\ M\ NOBr\ remaining = (0.00400 - 0.00150)\ M = 0.00250\ M = [NOBr]$$

We solve the integrated rate equation $\dfrac{1}{[NOBr]} - \dfrac{1}{[NOBr]_0} = akt$ for t.

The coefficient of NOBr is $a = 2$.

$$t = \frac{1}{ak}\left(\frac{1}{[NOBr]} - \frac{1}{[NOBr]_0}\right) = \frac{1}{(2)(0.810\ M^{-1} \cdot s^{-1})}\left(\frac{1}{0.00250\ M} - \frac{1}{0.00400\ M}\right)$$

$$= \frac{1}{1.62\ M^{-1} \cdot s^{-1}}(400\ M^{-1} - 250\ M^{-1})$$

$$= \boxed{92.6\ s}$$

You should now work Exercise 34.

EXAMPLE 16-9   *Concentration Versus Time: Second-Order Reaction*

Consider the reaction of Example 16-8 at 10°C. If we start with $2.40 \times 10^{-3}\ M$ NOBr, what concentration of NOBr will remain after 5.00 minutes of reaction?

Plan

We use the integrated second-order rate equation to solve for the concentration of NOBr remaining at $t = 5.00$ minutes.

Solution

Again, we start with the expression $\dfrac{1}{[NOBr]} - \dfrac{1}{[NOBr]_0} = akt$. Then we put in the known values and solve for [NOBr].

$$\frac{1}{[NOBr]} - \frac{1}{2.40 \times 10^{-3}\ M} = (2)(0.810\ M^{-1} \cdot s^{-1})(5.00\ min)\left(\frac{60\ s}{1\ min}\right)$$

$$\frac{1}{[NOBr]} - 4.17 \times 10^2 \ M^{-1} = 486 \ M^{-1}$$

$$\frac{1}{[NOBr]} = 486 \ M^{-1} + 417 \ M^{-1} = 903 \ M^{-1}$$

$$[NOBr] = \frac{1}{903 \ M^{-1}} = \boxed{1.11 \times 10^{-3} \ M} \qquad \text{(46.2\% remains unreacted)}$$

Thus, 53.8% of the original concentration of NOBr reacts within the first 5 minutes. This is reasonable because, as you can easily verify, the reaction has an initial half-life of 257 seconds, or 4.29 minutes.

You should now work Exercises 35 and 38.

Zero-Order Reaction

For a reaction $aA \rightarrow$ products that is zero order, the reaction rate is independent of concentrations. We can write the rate-law expression as

$$\text{rate} = -\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right) = k$$

The corresponding integrated rate equation is

$$[A] = [A]_0 - akt \qquad \text{(zero order)}$$

and the half-life is

$$t_{1/2} = \frac{[A]_0}{2ak} \qquad \text{(zero order)}$$

Table 16-2 summarizes the relationships that we have presented in Sections 16-3 and 16-4.

TABLE 16-2	***Summary of Relationships for Various Orders of the Reaction*** ***aA → Products***		
		Order	
	Zero	*First*	*Second*
Rate-law expression	rate = k	rate = $k[A]$	rate = $k[A]^2$
Integrated rate equation	$[A] = [A]_0 - akt$	$\ln\dfrac{[A]_0}{[A]} = akt$ or $\log\dfrac{[A]_0}{[A]} = \dfrac{akt}{2.303}$	$\dfrac{1}{[A]} - \dfrac{1}{[A]_0} = akt$
Half-life, $t_{1/2}$	$\dfrac{[A]_0}{2ak}$	$\dfrac{\ln 2}{ak} = \dfrac{0.693}{ak}$	$\dfrac{1}{ak[A]_0}$

✔ **Problem-Solving Tip:** *Which Equation Should Be Used?*

How can you tell which equation to use to solve a particular problem?

1. You must decide whether to use the rate-law expression or the integrated rate equation. Remember that

  the *rate-law expression* relates *rate and concentration*

 whereas

  the *integrated rate equation* relates *time and concentration.*

 When you need to find the *rate* that corresponds to particular concentrations, or the concentrations needed to give a desired rate, you should use the rate-law expression. When *time* is involved in the problem, you should use the integrated rate equation.

2. You must choose the form of the rate-law expression or the integrated rate equation —zero, first, or second order—that is appropriate to the order of the reaction. These are summarized in Table 16-2. One of the following usually helps you decide.
 a. The statement of the problem may state explicitly what the order of the reaction is.
 b. The rate-law expression may be given, so that you can tell the order of the reaction from the exponents in that expression.
 c. The units of the specific rate constant, k, may be given; you can interpret these stated units to tell you the order of the reaction.

Order	Units of k
0	$M \cdot \text{time}^{-1}$
1	time^{-1}
2	$M^{-1} \cdot \text{time}^{-1}$

One method of assessing reaction order is based on comparing successive half-lives. As we have seen, $t_{1/2}$ for a first-order reaction does not depend on initial concentration. We can measure the time required for different concentrations of a reactant to fall to half of their original values. If this time remains constant, it is an indication that the reaction is first order for that reactant and first order overall (see Figure 16-4a). By contrast, for other orders of reaction, $t_{1/2}$ would change depending on initial concentration. For a second-order reaction, successively measured $t_{1/2}$ values would increase by a factor of 2 as $[A]_0$ decreases by a factor of 2 (see Figure 16-4b). $[A]_0$ is measured at the *beginning of each particular measurement period.*

◆ **E** n r i c h m e n t

Calculus Derivation of Integrated Rate Equations

The derivation of the integrated rate equation is an example of the use of calculus in chemistry. The following derivation is for a reaction that is assumed to be first order in a reactant A and first order overall. If you do not know calculus, you can still use the results of this derivation, as we have already shown in this section. For the reaction

$$aA \longrightarrow \text{products}$$
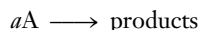
the rate is expressed as

$$\text{rate} = -\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right)$$

For a first-order reaction, the rate is proportional to the first power of [A].

$$-\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right) = k[A]$$

In calculus terms, we express the change during an infinitesimally short time dt as the derivative of [A] with respect to time.

$$-\frac{1}{a}\frac{d[A]}{dt} = k[A]$$

Separating variables, we obtain

$$-\frac{d[A]}{[A]} = (ak)dt$$

We integrate this equation with limits: As the reaction progresses from time = 0 (the start of the reaction) to time = t elapsed, the concentration of A goes from $[A]_0$, its starting value, to [A], the concentration remaining after time t:

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

The result of the integration is

$$-(\ln [A] - \ln [A]_0) = ak(t - 0) \qquad \text{or} \qquad \ln [A]_0 - \ln [A] = akt$$

Remembering that $\ln(x) - \ln(y) = \ln(x/y)$, we obtain

$$\ln\frac{[A]_0}{[A]} = akt \qquad \text{(first order)}$$

This is the integrated rate equation for a reaction that is first order in reactant A and first order overall.

Integrated rate equations can be derived similarly from other simple rate laws. For a reaction $aA \rightarrow$ products that is second order in reactant A and second order overall, we can write the rate equation as

$$-\frac{d[A]}{adt} = k[A]^2$$

Again, using the methods of calculus, we can separate variables, integrate, and rearrange to obtain the corresponding integrated second-order rate equation.

$$\frac{1}{[A]} - \frac{1}{[A]_0} = akt \qquad \text{(second order)}$$

$-\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right)$ represents the *average* rate over a finite time interval Δt. $-\frac{1}{a}\left(\frac{d[A]}{dt}\right)$ involves a change over an infinitesimally short time interval dt, so it represents the *instantaneous* rate.

(Enrichment, continued)

For a reaction $a\text{A} \rightarrow$ products that is zero order overall, we can write the rate equation as

$$-\frac{d[\text{A}]}{adt} = k$$

In this case, the calculus derivation already described leads to the integrated zero-order rate equation

$$[\text{A}] = [\text{A}]_0 - akt \qquad \text{(zero order)}$$

E n r i c h m e n t

Using Integrated Rate Equations to Determine Reaction Order

The integrated rate equation can help us to analyze concentration-versus-time data to determine reaction order. A graphical approach is often used. We can rearrange the integrated first-order rate equation

$$\ln \frac{[\text{A}]_0}{[\text{A}]} = akt$$

as follows. The logarithm of a quotient, $\ln (x/y)$, is equal to the difference of the logarithms, $\ln x - \ln y$, so we can write

$$\ln [\text{A}]_0 - \ln [\text{A}] = akt \qquad \text{or} \qquad \ln [\text{A}] = -akt + \ln [\text{A}]_0$$

Recall that the equation for a straight line may be written as

$$y = mx + b$$

where y is the variable plotted along the ordinate (vertical axis), x is the variable plotted along the abscissa (horizontal axis), m is the slope of the line, and b is the intercept of the line with the y axis (Figure 16-5). If we compare the last two equations, we find that $\ln [\text{A}]$ can be interpreted as y, and t as x.

$$\underbrace{\ln [\text{A}]}_{\displaystyle \downarrow \atop y} = \underbrace{-akt}_{\displaystyle \downarrow\downarrow \atop m\ x} + \underbrace{\ln [\text{A}]_0}_{\displaystyle \downarrow \atop b}$$

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 15.7, Determination of Rate Equations (2): Graphical Methods.
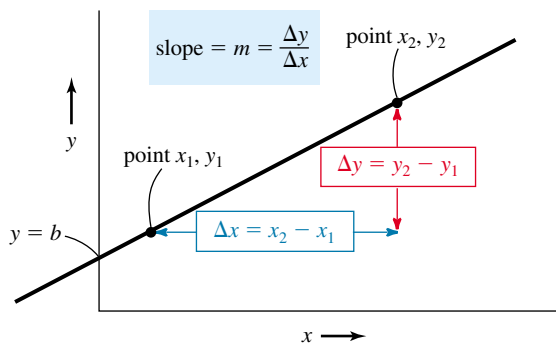
Figure 16-5 Plot of the equation $y = mx + b$, where m and b are constant. The slope of the line (positive in this case) is equal to m; the intercept on the y axis is equal to b.

Figure 16-6 Plot of ln [A] versus time for a reaction $aA \rightarrow$ products that follows first-order kinetics. The observation that such a plot gives a straight line would confirm that the reaction is first order in [A] and first order overall, that is, rate = k[A]. The slope is equal to $-ak$. Because a and k are positive numbers, the slope of the line is always negative. Logarithms are dimensionless, so the slope has the units $(\text{time})^{-1}$. The logarithm of a quantity less than 1 is negative, so data points for concentrations less than 1 molar would appear below the time axis.

The quantity $-ak$ is a constant as the reaction proceeds, so it can be interpreted as m. The initial concentration of A is fixed, so ln $[A]_0$ is a constant for each experiment, and ln $[A]_0$ can be interpreted as b. Thus, a plot of ln [A] versus time for a first-order reaction would be expected to give a straight line (Figure 16-6) with the slope of the line equal to $-ak$ and the intercept equal to ln $[A]_0$.

We can proceed in a similar fashion with the integrated rate equation for a reaction that is second order in A and second order overall. We rearrange

$$\frac{1}{[A]} - \frac{1}{[A]_0} = akt \qquad \text{to read} \qquad \frac{1}{[A]} = akt + \frac{1}{[A]_0}$$

Again comparing this with the equation for a straight line, we see that a plot of 1/[A] versus time would be expected to give a straight line (Figure 16-7). The line would have a slope equal to ak and an intercept equal to $1/[A]_0$.

For a zero-order reaction, we can rearrange the integrated rate equation

$$[A]_0 - [A] = akt \qquad \text{to} \qquad [A] = -akt + [A]_0$$

Comparing this with the equation for a straight line, we see that a straight-line plot would be obtained by plotting concentration versus time, [A] versus t. The slope of this line is $-ak$, and the intercept is $[A]_0$.

This discussion suggests another way to deduce an unknown rate-law expression from experimental concentration data. The following approach is particularly useful for any decomposition reaction, one that involves only one reactant.

$$aA \longrightarrow \text{products}$$
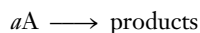
We plot the data in various ways as suggested above. *If* the reaction followed zero-order kinetics, *then* a plot of [A] versus t would give a straight line. But *if* the reaction followed first-order kinetics, *then* a plot of ln [A] versus t would give a straight line whose slope could be interpreted to derive a value of k. *If* the reaction were second order in A and second order overall, *then* neither of these plots would give a straight line, but a plot of 1/[A] versus t would. If none of these plots gave a straight line (within expected scatter due to experimental error), we would know that none of these is the correct order (rate law) for the reaction. Plots to test for other orders can be devised, as can graphical tests for rate-law expressions involving more than one reactant, but those are subjects for more advanced texts. The graphical approach that we have described is illustrated in the following example.

Figure 16-7 Plot of 1/[A] versus time for a reaction $aA \rightarrow$ products that follows a second-order kinetics. The observation that such a plot gives a straight line would confirm that the reaction is second order in [A] and second order overall, that is, rate = $k[A]^2$. The slope is equal to ak. Because a and k are positive numbers, the slope of the line is always positive. Because concentrations cannot be negative, 1/[A] is always positive, and the line is always above the time axis.

First order

ln $[A]_0$

slope = $-ak$

ln [A]
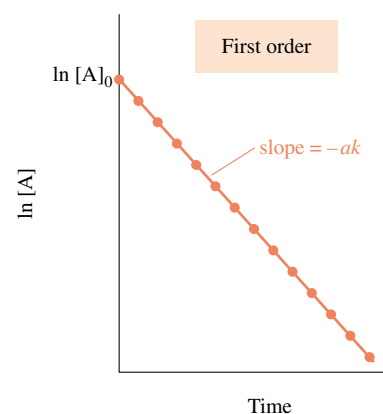
Time

It is not possible for *all* of the plots suggested here to yield straight lines for a given reaction. The nonlinearity of the plots may not become obvious, however, if the reaction times used are too short. In practice, all three lines might seem to be straight; we should then suspect that we need to observe the reaction for a longer time.

Second order

slope = ak

1/[A]

$1/[A]_0$

Time

Time (min)	[A] (mol/L)
0.00	2.000
2.00	1.107
4.00	0.612
6.00	0.338
8.00	0.187
10.00	0.103
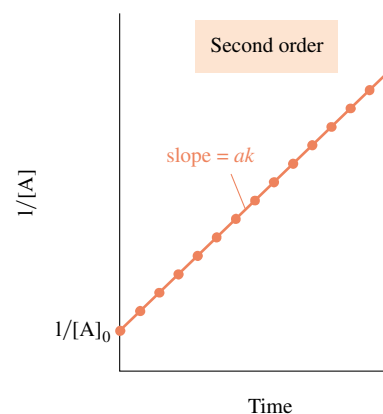
EXAMPLE 16-10 *Graphical Determination of Reaction Order*

We carry out the reaction $A \rightarrow B + C$ at a particular temperature. As the reaction proceeds, we measure the molarity of the reactant, [A], at various times. The observed data are tabulated in the margin. (a) Plot [A] versus time. (b) Plot ln [A] versus time. (c) Plot 1/[A] versus time. (d) What is the order of the reaction? (e) Write the rate-law expression for the reaction. (f) What is the value of k at this temperature?

Plan

For parts (a)–(c), we use the observed data to make the required plots, calculating related values as necessary. (d) We can determine the order of the reaction by observing which of these plots gives a straight line. (e) Knowing the order of the reaction, we can write the rate-law expression. (f) The value of k can be determined from the slope of the straight-line plot.

Solution

(a) The plot of [A] versus time is given in Figure 16-8b.

(b) We first use the given data to calculate the ln [A] column in Figure 16-8a. These data are then used to plot ln [A] versus time, as shown in Figure 16-8c.

(c) The given data are used to calculate the 1/[A] column in Figure 16-8a. Then we plot 1/[A] versus time, as shown in Figure 16-8d.

(d) It is clear from the answer to part (b) that the plot of ln [A] versus time gives a straight line. This tells us that the reaction is first order in [A].

(e) In the form of a rate-law expression, the answer to part (d) gives rate = k[A].

Time (min)	[A]	ln [A]	1/[A]
0.00	2.000	0.693	0.5000
2.00	1.107	0.102	0.9033
4.00	0.612	−0.491	1.63
6.00	0.338	−1.085	2.95
8.00	0.187	−1.677	5.35
10.00	0.103	−2.273	9.71

(a) Data for Example 16-10.

(b) Example 16-10(a).
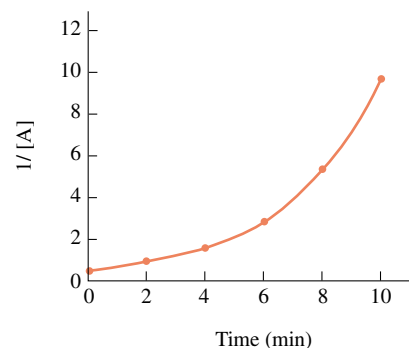
Figure 16-8 Data conversion and plots for Example 16-10. (a) The data are used to calculate the two columns ln [A] and 1/[A]. (b) Test for zero-order kinetics: a plot of [A] versus time. The nonlinearity of this plot shows that the reaction does not follow zero-order kinetics. (c) Test for first-order kinetics: a plot of ln [A] versus time. The observation that this plot gives a straight line indicates that the reaction follows first-order kinetics. (d) Test for second-order kinetics: a plot of 1/[A] versus time. If the reaction had followed second-order kinetics, this plot would have resulted in a straight line and the plot in part (c) would not.

(c) Example 16-10(b).

(d) Example 16-10(c).

(f) We use the straight-line plot in Figure 16-8c to find the value of the rate constant for this first-order reaction from the relationship

$$\text{slope} = -ak \qquad \text{or} \qquad k = -\frac{\text{slope}}{a}$$

To determine the slope of the straight line, we pick any two points, such as P and Q, on the line. From their coordinates, we calculate

$$\text{slope} = \frac{\text{change in ordinate}}{\text{change in abscissa}} = \frac{(-1.83) - (0.27)}{(8.50 - 1.50) \text{ min}} = -0.300 \text{ min}^{-1}$$

$$k = -\frac{\text{slope}}{a} = -\frac{-0.300 \text{ min}^{-1}}{1} = \boxed{0.300 \text{ min}^{-1}}$$

You should now work Exercises 44 and 45.

The graphical interpretations of concentration-versus-time data for some common reaction orders are summarized in Table 16-3.

✓ **Problem-Solving Tip:** *Some Warnings About the Graphical Method for Determining Reaction Order*

1. If we were dealing with real experimental data, there would be some error in each of the data points on the plot. For this reason, we should *not* use experimental data points to determine the slope. (Random experimental errors of only 10% can introduce errors of more than 100% in slopes based on only two points.) Rather we should draw the best straight line and then use points on that line to find its slope. Errors are further minimized by choosing points that are widely separated.

2. Remember that the ordinate is the vertical axis and the abscissa is the horizontal one. If you are not careful to keep the points in the same order in the numerator and denominator, you will get the wrong sign for the slope.

TABLE 16-3 *Graphical Interpretations for Various Orders of the Reaction $aA \rightarrow Products$*

	Order		
	Zero	*First*	*Second*
Plot that gives straight line	[A] vs. t	ln [A] vs. t	$\frac{1}{[A]}$ vs. t
Direction of straight-line slope	down with time	down with time	up with time
Interpretation of slope	$-ak$	$-ak$	ak
Interpretation of intercept	$[A]_0$	ln $[A]_0$	$\frac{1}{[A]_0}$

16-5 COLLISION THEORY OF REACTION RATES

The fundamental notion of the **collision theory of reaction rates** is that for a reaction to occur, molecules, atoms, or ions must first collide. Increased concentrations of reacting species result in greater numbers of collisions per unit time. However, not all collisions result in reaction; that is, not all collisions are **effective collisions.** For a collision to be effective, the reacting species must (1) possess at least a certain minimum energy necessary to rearrange outer electrons in breaking bonds and forming new ones and (2) have the proper orientations toward one another at the time of collision.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 15.9, Microscopic View of Reactions (1): Collision Theory.

> Collisions must occur in order for a chemical reaction to proceed, but they do not guarantee that a reaction will occur.

A collision between atoms, molecules, or ions is not like one between two hard billiard balls. Whether or not chemical species "collide" depends on the distance at which they can interact with one another. For instance, the gas-phase ion–molecule reaction $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$ can occur with a fairly long-range contact. This is because the interactions between ions and induced dipoles are effective over a relatively long distance. By contrast, the reacting species in the gas reaction $CH_3 + CH_3 \rightarrow C_2H_6$ are both neutral. They interact appreciably only through very short-range forces between induced dipoles, so they must approach one another very closely before we could say that they "collide."

Recall (Chapter 12) that the average kinetic energy of a collection of molecules is proportional to the absolute temperature. At higher temperatures, more of the molecules possess sufficient energy to react (Section 16-8).

The colliding molecules must have the proper orientation relative to one another *and* have sufficient energy to react. If colliding molecules have improper orientations, they do not react even though they may possess sufficient energy. Figure 16-9 depicts some possible collisions between molecules of NO and N_2O, which can react to form NO_2 and N_2.

$$NO + N_2O \longrightarrow NO_2 + N_2$$

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$
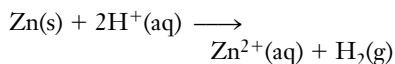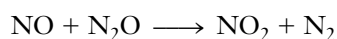
Dilute sulfuric acid reacts slowly with zinc metal (*left*), whereas more concentrated acid reacts rapidly (*right*). The $H^+(aq)$ concentration is higher in the more concentrated acid, and so more $H^+(aq)$ ions collide with Zn per unit time.

$$NO + N_2O \rightarrow NO_2 + N_2$$

(a) Effective orientation of collision

Reactants   Collision   Products

Reaction occurs

(b) Ineffective orientation of collision

Reactants   Collision   Reactants

No reaction

(c) Ineffective orientation of collision

Reactants   Collision   Reactants
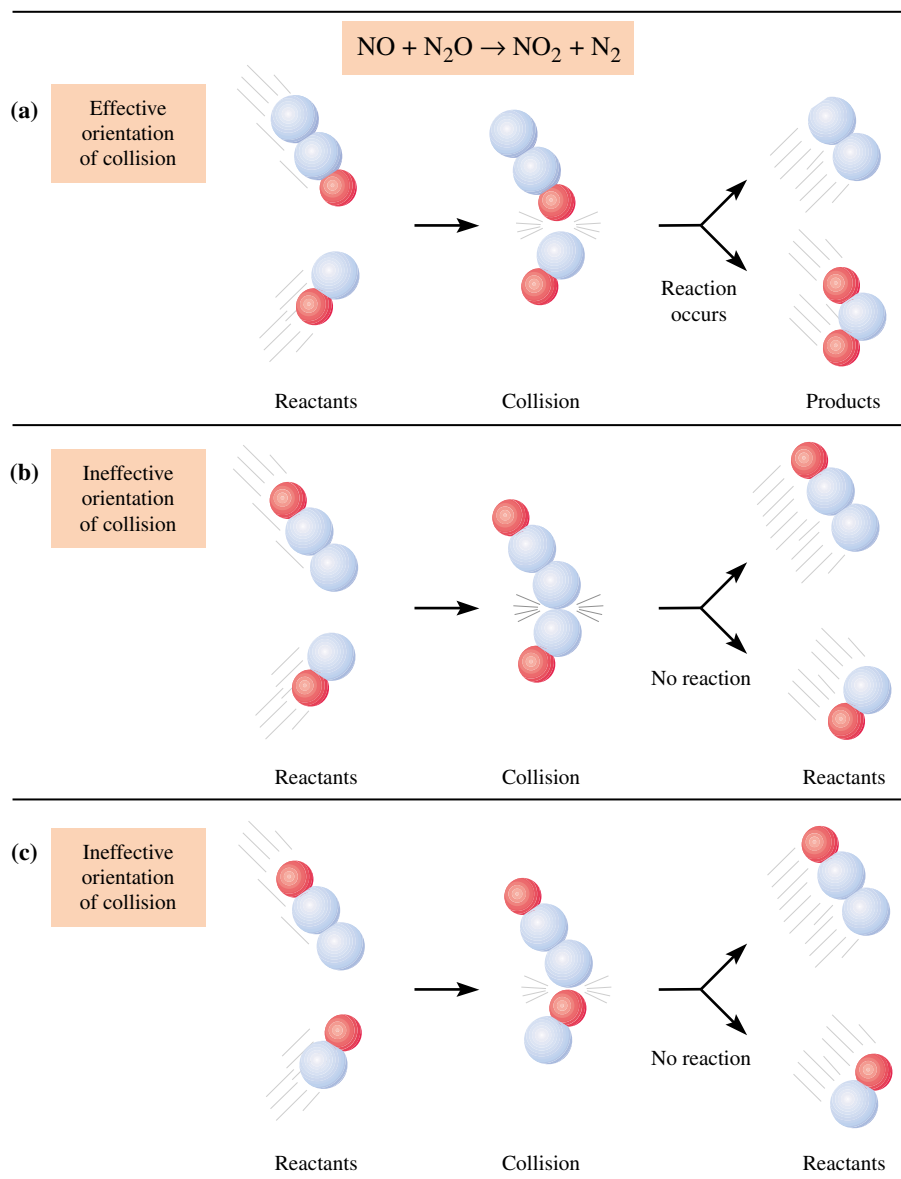
No reaction

Figure 16-9 Some possible collisions between N_2O and NO molecules in the gas phase. (a) A collision that could be effective in producing the reaction. (b, c) Collisions that would be ineffective. The molecules must have the proper orientations relative to one another *and* have sufficient energy to react.

Only the collision in Figure 16-9a is in the correct orientation to transfer an oxygen atom from the linear N_2O molecule to form the angular NO_2 molecule. For some reactions, the presence of a heterogeneous catalyst (Section 16-9) can increase the fraction of colliding molecules that have the proper orientations.

16-6 TRANSITION STATE THEORY

Chemical reactions involve the making and breaking of chemical bonds. The energy associated with a chemical bond is a form of potential energy. Reactions are accompanied by changes in potential energy. Consider the following hypothetical, one-step reaction at a certain temperature.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 15.10, Microscopic View of Reactions (2): Transition State Theory.

$$A + B_2 \longrightarrow AB + B$$

Figure 16-10 shows plots of potential energy versus the progress of the reaction. In Figure 16-10a the ground state energy of the reactants, A and B_2, is higher than the ground state energy of the products, AB and B. The energy released in the reaction is the difference between these two energies, ΔE. It is related to the change in enthalpy, ΔH^0_{rxn} (Section 15-11).

Quite often, for reaction to occur, some covalent bonds must be broken so that others can be formed. This can occur only if the molecules collide *with enough kinetic energy* to overcome the potential energy stabilization of the bonds. According to the **transition state theory,** the reactants pass through a short-lived, high-energy intermediate state, called a **transition state,** before the products are formed.

$$A + B{-}B \longrightarrow A{\text -}{\text -}{\text -}B{\text -}{\text -}{\text -}B \longrightarrow A{-}B + B$$
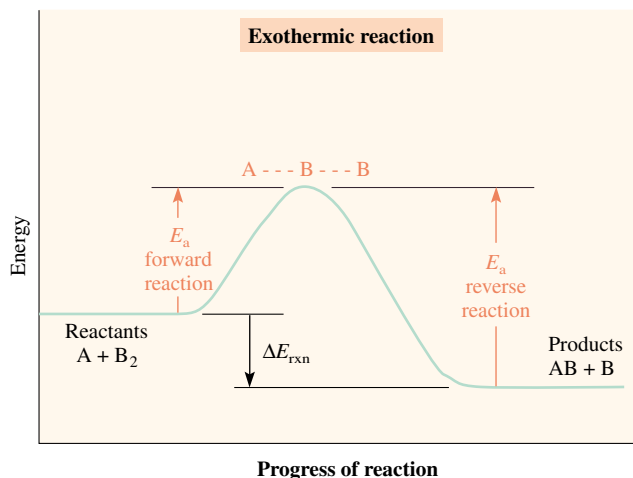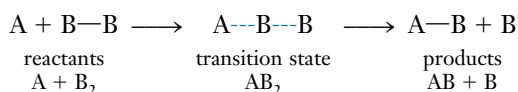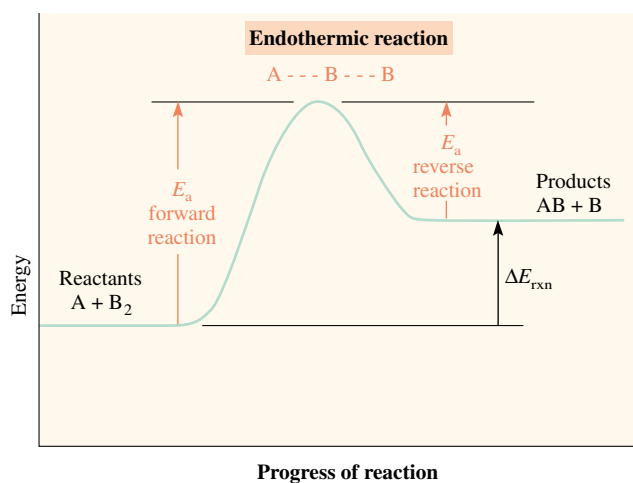
reactants	transition state	products
$A + B_2$	AB_2	$AB + B$

The "progress of reaction" represents how far the reaction has proceeded *along the pathway* leading from reactants to products. This coordinate is sometimes labeled the "reaction coordinate."

(a)

Figure 16-10 A potential energy diagram. (a) A reaction that releases energy (exothermic). An example of an exothermic gas-phase reaction is

$$H + I_2 \longrightarrow HI + I$$
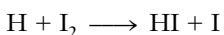
(b) A reaction that absorbs energy (endothermic). An example of an endothermic gas-phase reaction is

$$I + H_2 \longrightarrow HI + H$$

(b)
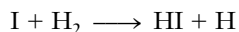
The **activation energy, E_a,** is the kinetic energy that reactant molecules must have to allow them to reach the transition state. If A and B_2 molecules do not possess the necessary amount of energy, E_a, when they collide, reaction cannot occur. If they do possess sufficient energy to "climb the energy barrier" to reach the transition state, the reaction can proceed. When the atoms go from the transition state arrangement to the product molecules, energy is *released*. If the reaction results in a net *release* of energy (see Figure 16-10a), *more* energy than the activation energy is returned to the surroundings and the reaction is exothermic. If the reaction results in a *net absorption* of energy (see Figure 16-10b), an amount less than E_a is given off when the transition state is converted to products and the reaction is endothermic. The *net* release of energy is ΔE_{rxn}.

For the reverse reaction to occur, some molecules on the right (AB) must have kinetic energy equal to the reverse activation energy, $E_{a\ reverse}$, to allow them to reach the transition state. As you can see from the potential energy diagrams in Figure 16-10,

$$E_{a\ forward} - E_{a\ reverse} = \Delta E_{reaction}$$

As we shall see, increasing the temperature changes the rate by altering the fraction of molecules that can get over a given energy barrier (Section 16-8). Introducing a catalyst increases the rate by providing a different pathway that has a lower activation energy (Section 16-9).

As a specific example that illustrates the ideas of collision theory and transition state theory, consider the reaction of iodide ions with methyl chloride.

$$I^- + CH_3Cl \longrightarrow CH_3I + Cl^-$$

Many studies have established that this reaction proceeds as shown in Figure 16-11a. The I^- ion must approach the CH_3Cl from the "back side" of the C—Cl bond, through the middle of the three hydrogen atoms. A collision of an I^- ion with a CH_3Cl molecule from any other direction would not lead to reaction. But a sufficiently energetic collision with

Remember that ΔE_{rxn} relates product energy to reactant energy, regardless of the pathway. ΔE_{rxn} is negative when energy is given off; ΔE_{rxn} is positive when energy is absorbed from the surroundings.

The CH_3Cl and CH_3I molecules each have tetrahedral molecular geometry.

(a) Before collision   Transition state   After reaction

(b)
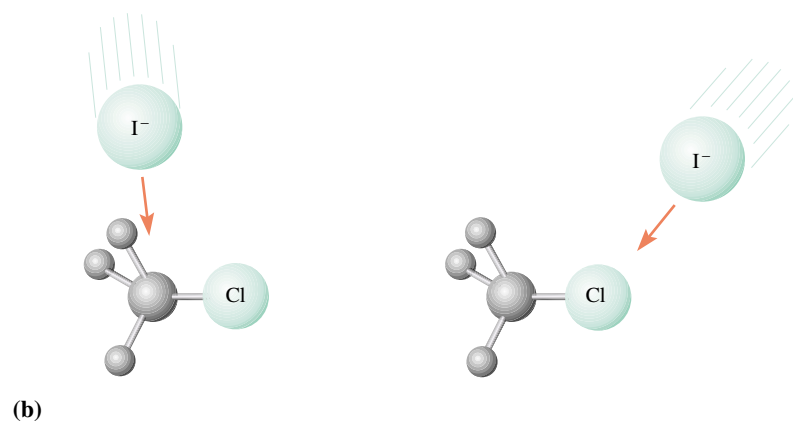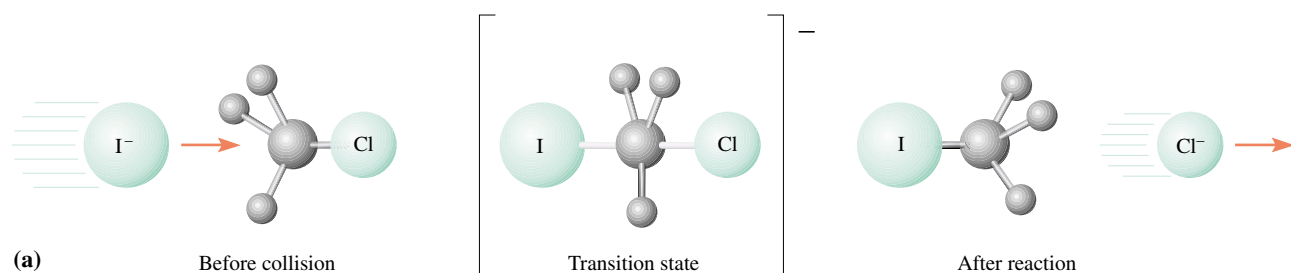
Figure 16-11 (a) A collision that could lead to reaction of I^- + CH_3Cl to give CH_3I + Cl^-. The I^- must approach along the "back side" of the C—Cl bond. (b) Two collisions that are not in the "correct" orientation to cause a reaction.

the appropriate orientation could allow the new I—C bond to form at the same time that the C—Cl bond is breaking. This collection of atoms, which we represent as

$$
\begin{array}{c}
\text{H} \quad \text{H} \\
\text{I}\cdots\text{C}\cdots\text{Cl} \\
| \\
\text{H}
\end{array}
$$
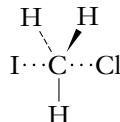
is what we call the transition state of this reaction (Figure 16-11a). From this state, either of two things could happen: (1) the I—C bond could finish forming and the C—Cl bond could finish breaking with Cl^- leaving, leading to products, or (2) the I—C bond could fall apart with I^- leaving and the C—Cl bond re-forming, leading back to reactants.

16-7 REACTION MECHANISMS AND THE RATE-LAW EXPRESSION

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 15.12, Reaction Mechanisms.

The step-by-step pathway by which a reaction occurs is called its **mechanism.** Some reactions take place in a single step, but most reactions occur in a series of **elementary steps.**

> The reaction orders *for any single elementary step* are equal to the coefficients for that step.

In many mechanisms, however, one step is much slower than the others.

> A reaction can never occur faster than its slowest step.

This slow step is called the **rate-determining step.** The speed at which the slow step occurs limits the rate at which the overall reaction occurs.

As an analogy, suppose you often drive a distance of 120 miles at the speed limit of 60 mi/h, requiring 2 hours. But one day there is an accident along the route, causing a slow-down for several hours. After passing the accident scene, you resume the posted speed of 60 mi/h. If the total time for this trip was 4 hours, then the *average* speed would be only 120 miles/4 hours, or 30 mi/h. Even though you drove for many miles at the same high speed, 60 mi/h, the overall rate was limited by the slow step, passing the accident scene.

The balanced equation for the overall reaction is equal to the sum of *all* the individual steps, including any steps that might follow the rate-determining step. We emphasize again that the rate-law exponents *do not necessarily match* the coefficients of the *overall* balanced equation.

> For the general overall reaction
>
> $$aA + bB \longrightarrow cC + dD$$
>
> the experimentally determined rate-law expression has the form
>
> $$\text{rate} = k[A]^x[B]^y$$
>
> The values of x and y are related to the coefficients of the reactants in the slowest step, influenced in some cases by earlier steps.
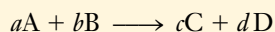
Using a combination of experimental data and chemical intuition, we can *postulate* a mechanism by which a reaction could occur. We can never prove absolutely that a proposed mechanism is correct. All we can do is postulate a mechanism that is *consistent* with experimental data. We might later detect reaction-intermediate species that are not explained by the proposed mechanism. We must then modify the mechanism or discard it and propose a new one.

As an example, the reaction of nitrogen dioxide and carbon monoxide has been found to be second order with respect to NO_2 and zero order with respect to CO below 225°C.

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) \qquad rate = k[NO_2]^2$$

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 15.13, Reaction Mechanisms and Rate Equations.
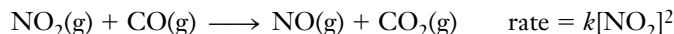
The balanced equation for the overall reaction shows the stoichiometry but *does not necessarily mean* that the reaction simply occurs by one molecule of NO_2 colliding with one molecule of CO. If the reaction really took place in *that* one step, then the rate would be first order in NO_2 and first order in CO, or rate = $k[NO_2][CO]$. The fact that the experimentally determined orders do not match the coefficients in the overall balanced equation tells us that *the reaction does not take place in one step.*

The following proposed two-step mechanism is consistent with the observed rate-law expression.

(1) $NO_2 + NO_2 \longrightarrow N_2O_4$ (slow)

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

        $NO_2 + CO \longrightarrow NO + CO_2$ (overall)
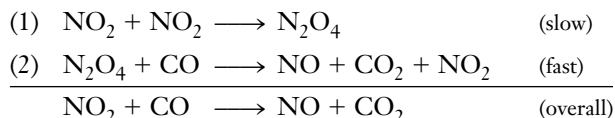
The rate-determining step of this mechanism involves a *bimolecular* collision between two NO_2 molecules. This is consistent with the rate expression involving $[NO_2]^2$. Because the CO is involved only after the slow step has occurred, the reaction rate would not depend on [CO] (i.e., the reaction would be zero order in CO) if this were the actual mechanism. In this proposed mechanism, N_2O_4 is formed in one step and is completely consumed in a later step. Such a species is called a **reaction intermediate.**

In other studies of this reaction, however, nitrogen trioxide, NO_3, has been detected as a transient (short-lived) intermediate. The mechanism now thought to be correct is
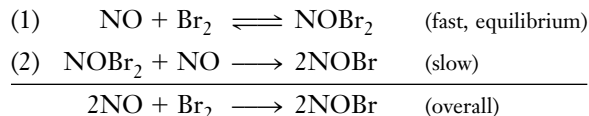
Some reaction intermediates are so unstable that it is very difficult to prove experimentally that they exist.

(1) $NO_2 + NO_2 \longrightarrow NO_3 + NO$ (slow)

(2) $NO_3 + CO \longrightarrow NO_2 + CO_2$ (fast)

       $NO_2 + CO \longrightarrow NO + CO_2$ (overall)
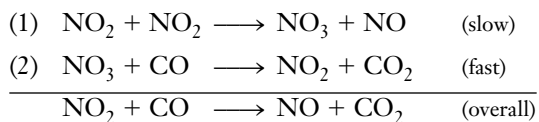
In this proposed mechanism two molecules of NO_2 collide to produce one molecule each of NO_3 and NO. The reaction intermediate NO_3 then collides with one molecule of CO and reacts very rapidly to produce one molecule each of NO_2 and CO_2. Even though two NO_2 molecules are consumed in the first step, one is produced in the second step. The net result is that only one NO_2 molecule is consumed in the overall reaction.

Each of these proposed mechanisms meets both criteria for a plausible mechanism: (1) The steps add to give the equation for the overall reaction, and (2) the mechanism is consistent with the experimentally determined rate-law expression (in that two NO_2 molecules and no CO molecules are reactants in the slow step). The NO_3 that has been detected is evidence in favor of the second mechanism, but this does not unequivocally *prove* that mechanism; it may be possible to think of other mechanisms that would involve NO_3 as an intermediate and would also be consistent with the observed rate law.

You should be able to distinguish among various species that can appear in a reaction mechanism. So far, we have seen three such species:

1. *Reactant:* More is consumed than is formed.

2. *Product:* More is formed than is consumed.

3. *Reaction intermediate:* Formed in earlier steps, then consumed in an equal amount in later steps.

The gas-phase reaction of nitrogen oxide and bromine is known to be second order in NO and first order in Br_2.

$$2NO(g) + B_2(g) \longrightarrow 2NOBr(g) \qquad rate = k[NO]^2[Br_2]$$

A one-step collision involving two NO molecules and one Br_2 molecule would be consistent with the experimentally determined rate-law expression. However, the likelihood of all *three* molecules colliding simultaneously is far less than the likelihood of two colliding. *Routes involving only bimolecular collisions or unimolecular decompositions are thought to be more favorable in reaction mechanisms.* The mechanism is believed to be

$$
\begin{array}{lll}
(1) & NO + Br_2 \rightleftharpoons NOBr_2 & \text{(fast, equilibrium)} \\
(2) & NOBr_2 + NO \longrightarrow 2NOBr & \text{(slow)} \\
\hline
& 2NO + Br_2 \longrightarrow 2NOBr & \text{(overall)}
\end{array}
$$

The first step involves the collision of one NO molecule (reactant) and one Br_2 molecule (reactant) to produce the intermediate species $NOBr_2$. The $NOBr_2$ can react rapidly, however, to re-form NO and Br_2. We say that this is an *equilibrium step*. Eventually another NO molecule (reactant) can collide with a short-lived $NOBr_2$ molecule and react to produce two NOBr molecules (product).

To analyze the rate law that would be consistent with this proposed mechanism, we again start with the slow (rate-determining) step, step 2. Denoting the rate constant for this step as k_2, we could express the rate of this step as

$$rate = k_2[NOBr_2][NO]$$

However, $NOBr_2$ is a reaction intermediate, so its concentration at the beginning of the second step may not be easy to measure directly. Because $NOBr_2$ is formed in a fast equilibrium step, we can relate its concentration to the concentrations of the original reactants. When a reaction or reaction step is at *equilibrium*, its forward (f) and reverse (r) rates are equal.

$$rate_{1f} = rate_{1r}$$

Because this is an elementary step, we can write the rate expression for both directions from the equation for the elementary step

$$k_{1f}[NO][Br_2] = k_{1r}[NOBr_2]$$

and then rearrange for $[NOBr_2]$.

$$[NOBr_2] = \frac{k_{1f}}{k_{1r}}[NO][Br_2]$$

When we substitute the right side of this equation for $[NOBr_2]$ in the rate expression for the rate-determining step, rate = $k_2[NOBr_2][NO]$, we arrive at the experimentally determined rate-law expression.

$$rate = k_2\left(\frac{k_{1f}}{k_{1r}}[NO][Br_2]\right)[NO] \qquad or \qquad rate = k[NO]^2[Br_2]$$

Think how unlikely it is for three moving billiard balls to collide *simultaneously.*

Any fast step that precedes a slow step reaches equilibrium.

The rate-law expression of step 2 (the rate-determining step) determines the rate law for the overall reaction.

The product and quotient of constants k_2, k_{1f}, and k_{1r} is another constant, k.
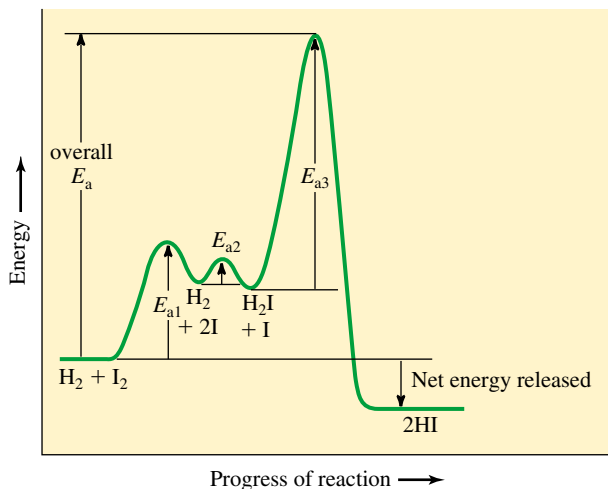
Figure 16-12 A graphical representation of the relative energies of activation for a postulated mechanism for the gas-phase reaction

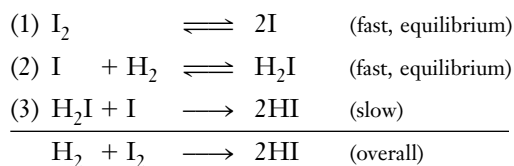$$H_2 + I_2 \longrightarrow 2HI$$
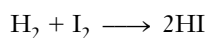
Similar interpretations apply to most other overall third- or higher-order reactions, as well as many lower-order reactions. When several steps are about equally slow, however, the analysis of experimental data is more complex. Fractional or negative reaction orders result from complex multistep mechanisms.

One of the earliest kinetic studies involved the gas-phase reaction of hydrogen and iodine to form hydrogen iodide. The reaction was found to be first order in both hydrogen and iodine.

$$H_2(g) + I_2(g) \longrightarrow 2HI(g) \qquad rate = k[H_2][I_2]$$

The mechanism that was accepted for many years involved collision of single molecules of H_2 and I_2 in a simple one-step reaction. Current evidence indicates a more complex process, however. Most kineticists now accept the following mechanism.

(1) I_2	$\rightleftharpoons$	$2I$	(fast, equilibrium)
(2) $I + H_2$	$\rightleftharpoons$	H_2I	(fast, equilibrium)
(3) $H_2I + I$	$\longrightarrow$	$2HI$	(slow)
$H_2 + I_2$	$\longrightarrow$	$2HI$	(overall)

Apply the algebraic approach described earlier to show that this mechanism is consistent with the observed rate-law expression.

In this case neither original reactant appears in the rate-determining step, but both appear in the rate-law expression. Each step is a reaction in itself. Transition state theory tells us that each step has its own activation energy. Because step 3 is the slowest, we know that its activation energy is the highest, as shown in Figure 16-12.

In summary

The experimentally determined reaction orders of reactants indicate the number of molecules of those reactants involved in (1) the slow step only, if it occurs first, or (2) the slow step *and* any fast equilibrium steps preceding the slow step.

16-8 TEMPERATURE: THE ARRHENIUS EQUATION

The average kinetic energy of a collection of molecules is proportional to the absolute temperature. At a particular temperature, T_1, a definite fraction of the reactant molecules have sufficient kinetic energy, $\mathrm{KE} > E_a$, to react to form product molecules on collision. At a higher temperature, T_2, a greater fraction of the molecules possess the necessary activation energy, and the reaction proceeds at a faster rate. This is depicted in Figure 16-13a.

From experimental observations, Svante Arrhenius developed the mathematical relationship among activation energy, absolute temperature, and the specific rate constant of a reaction, k, at that temperature. The relationship, called the Arrhenius equation, is

e = 2.718 is the base of *natural* logarithms (ln).

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

or, in logarithmic form,

$$\ln k = \ln A - \frac{E_a}{RT}$$

In this expression, A is a constant having the same units as the rate constant. It is equal to the fraction of collisions with the proper orientations when all reactant concentrations are one molar. R is the universal gas constant, expressed with the same energy units in its numerator as are used for E_a. For instance, when E_a is known in J/mol, the value $R = 8.314$ J/mol·K is appropriate. Here the unit "mol" is interpreted as "mole of reaction," as described in Chapter 15. One important point is the following: The greater the value of E_a, the smaller the value of k and the slower the reaction rate (other factors being equal).

Figure 16-13 *(Left)* The effect of temperature on the number of molecules that have kinetic energies greater than E_a. At T_2, a higher fraction of molecules possess at least E_a, the activation energy. The area between the distribution curve and the horizontal axis is proportional to the total number of molecules present. The total area is the same at T_1 and T_2. The shaded areas represent the number of particles that exceed the energy of activation, E_a. *(Right)* Consider two hypothetical reactions 1 and 2, where the activation energy of reaction 1 is less than that of reaction 2—that is, $E_{a1} < E_{a2}$. At any given temperature, a larger fraction of the molecules have energies that exceed E_{a1} than that exceed E_{a2}, so reaction 1 would have a higher specific rate constant, k, than reaction 2 at the same reactant concentrations.
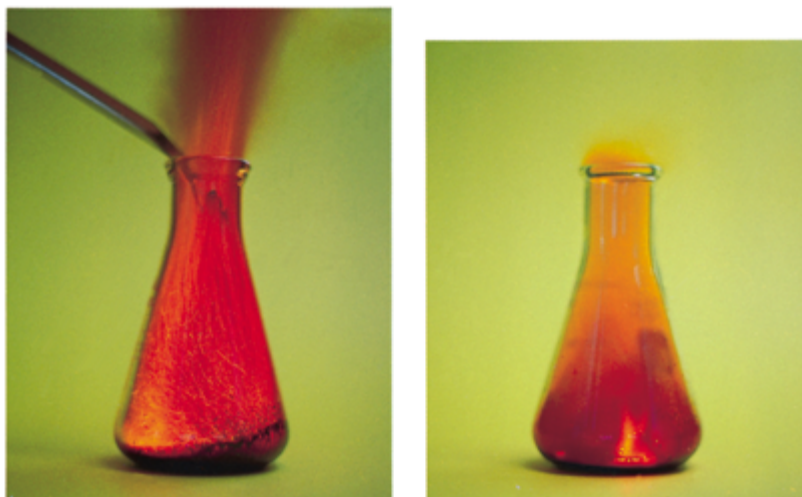
Antimony powder reacts with bromine more rapidly at 75°C (*left*) than at 25°C (*right*).

This is because fewer collisions take place with sufficient energy to get over a high-energy barrier (see Figure 16-13b).

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 15.11, Control of Reaction Rates (3): Temperature Dependence.

The Arrhenius equation predicts that increasing T results in a faster reaction for the same E_a and concentrations.

| If T increases | $\Rightarrow$ | E_a/RT decreases | $\Rightarrow$ | $-E_a/RT$ increases | $\Rightarrow$ | $e^{-E_a/RT}$ increases | $\Rightarrow$ | k increases | $\Rightarrow$ | Reaction speeds up |
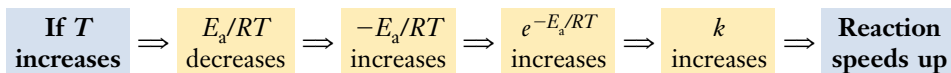
Let's look at how the rate constant varies with temperature for a given single reaction. Assume that the activation energy and the factor A do not vary with temperature. We can write the Arrhenius equation for two different temperatures. Then we subtract one equation from the other and rearrange the result to obtain

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

Let's substitute some typical values into this equation. The activation energy for many reactions that occur near room temperature is about 50 kJ/mol. For such a reaction, a temperature increase from 300 K to 310 K would result in

$$\ln \frac{k_2}{k_1} = \frac{50,000 \text{ J/mol}}{(8.314 \text{ J/mol·K})}\left(\frac{1}{300 \text{ K}} - \frac{1}{310 \text{ K}}\right) = 0.647$$

$$\frac{k_2}{k_1} = 1.91 \approx 2$$

Chemists sometimes use the rule of thumb that near room temperature the rate of a reaction approximately doubles with a 10°C rise in temperature. Such a "rule" must be used with care, however, because it obviously depends on the activation energy.

Which egg will cook faster—the one in ice water (*left*) or the one in boiling water (*right*)? Why—in terms of what you have learned in this chapter?

EXAMPLE 16-11   *Arrhenius Equation*

The specific rate constant, k, for the following first-order reaction is 9.16×10^{-3} s^{-1} at 0.0°C. The activation energy of this reaction is 88.0 kJ/mol. Determine the value of k at 2.0°C.

$$N_2O_5 \longrightarrow NO_2 + NO_3$$
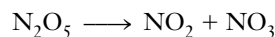
Plan

First we tabulate the values, remembering to convert temperature to the Kelvin scale.

$$E_a = 88{,}000 \text{ J/mol} \qquad\qquad R = 8.314 \text{ J/mol·K}$$
$$k_1 = 9.16 \times 10^{-3} \text{ s}^{-1} \qquad \text{at} \qquad T_1 = 0.0°C + 273 = 273 \text{ K}$$
$$k_2 = \underline{\ ?\ } \qquad\qquad \text{at} \qquad T_2 = 2.0°C + 273 = 275 \text{ K}$$

We use these values in the "two-temperature" form of the Arrhenius equation.

Solution

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

$$\ln\left(\frac{k_2}{9.16 \times 10^{-3} \text{ s}^{-1}}\right) = \frac{88{,}000 \text{ J/mol}}{8.314 \dfrac{\text{J}}{\text{mol·K}}} \left(\frac{1}{273 \text{ K}} - \frac{1}{275 \text{ K}} \right) = 0.282$$

Taking inverse (natural) logarithms of both sides,

$$\frac{k_2}{9.16 \times 10^{-3} \text{ s}^{-1}} = 1.32$$

$$k_2 = 1.32(9.16 \times 10^{-3} \text{ s}^{-1}) = \boxed{1.21 \times 10^{-2} \text{ s}^{-1}}$$

We see that a very small temperature difference, only 2°C, causes an increase in the rate constant (and hence in the reaction rate for the same concentrations) of about 32%. Such sensitivity of rate to temperature change makes the control and measurement of temperature extremely important in chemical reactions.

You should now work Exercise 53.

EXAMPLE 16-12   *Activation Energy*

The gas-phase decomposition of ethyl iodide to give ethylene and hydrogen iodide is a first-order reaction.

$$C_2H_5I \longrightarrow C_2H_4 + HI$$
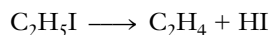
At 600. K, the value of k is 1.60×10^{-5} s^{-1}. When the temperature is raised to 700. K, the value of k increases to 6.36×10^{-3} s^{-1}. What is the activation energy for this reaction?

Plan

We know k at two different temperatures. We solve the two-temperature forms of the Arrhenius equation for E_a and evaluate.

Solution

$$k_1 = 1.60 \times 10^{-5} \text{ s}^{-1} \text{ at } T_1 = 600. \text{ K} \qquad k_2 = 6.36 \times 10^{-3} \text{ s}^{-1} \text{ at } T_2 = 700. \text{ K}$$
$$R = 8.314 \text{ J/mol·K} \qquad\qquad\qquad E_a = \underline{\ ?\ }$$

We arrange the Arrhenius equation for E_a.

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

Substituting,

$$E_a = \frac{\left(8.314 \dfrac{J}{mol \cdot K}\right) \ln\left(\dfrac{6.36 \times 10^{-3} \ s^{-1}}{1.60 \times 10^{-5} \ s^{-1}}\right)}{\left(\dfrac{1}{600.K} - \dfrac{1}{700}.K\right)} = \frac{\left(8.314 \dfrac{J}{mol \cdot K}\right)(5.98)}{2.38 \times 10^{-4} \ K^{-1}} = \boxed{\begin{array}{l}2.09 \times 10^5 \ J/mol \\ or \quad 209 \ kJ/mol\end{array}}$$

You should now work Exercise 54.

The determination of E_a in the manner illustrated in Example 16-12 may be subject to considerable error because it depends on the measurement of k at only two temperatures. Any error in either of these k values would greatly affect the resulting value of E_a. A more reliable method that uses many measured values for the same reaction is based on a graphical approach. Let us rearrange the single-temperature logarithmic form of the Arrhenius equation and compare it with the equation for a straight line.

Compare this approach to that described in the earlier Enrichment section for determining k.

$$\underbrace{\ln k}_{\downarrow \atop y} = \underbrace{-\left(\frac{E_a}{R}\right)}_{\downarrow \atop m}\underbrace{\left(\frac{1}{T}\right)}_{\downarrow \atop x} + \underbrace{\ln A}_{\downarrow \atop b}$$

The value of the collision frequency factor, A, is very nearly constant over moderate temperature changes. Thus, $\ln A$ can be interpreted as the constant term in the equation (the intercept). The slope of the straight line obtained by plotting $\ln k$ versus $1/T$ equals $-E_a/R$. This allows us to determine the value of the activation energy from the slope (Figure 16-14). Exercises 57 and 58 use this method.
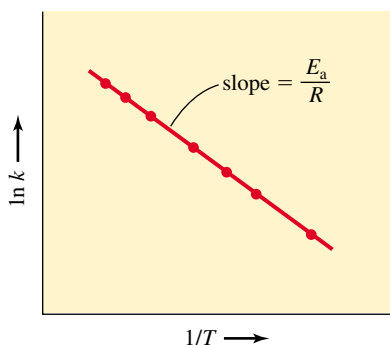
Figure 16-14 A graphical method for determining activation energy, E_a. At each of several different temperatures, the rate constant, k, is determined by methods such as those in Sections 16-3 and 16-4. A plot of $\ln k$ versus $1/T$ gives a straight line with negative slope. The slope of this straight line is $-E_a/R$. Use of this graphical method is often desirable, because it partially compensates for experimental errors in individual k and T values.

Figure 16-15 Potential energy diagrams showing the effect of a catalyst. The catalyst provides a different mechanism, corresponding to a lower-energy pathway, for the formation of the products. A catalyzed reaction typically occurs in several steps, each with its own barrier, but the overall energy barrier for the net reaction, E_a', is lower than that for the uncatalyzed reaction, E_a. The value of ΔE_{rxn} depends only on the states of the reactants and products, so it is the same for either path.
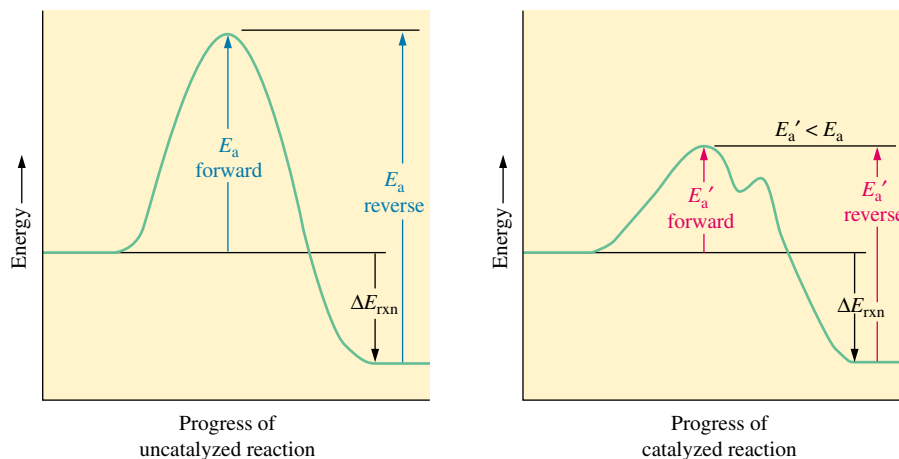
Progress of uncatalyzed reaction

Progress of catalyzed reaction
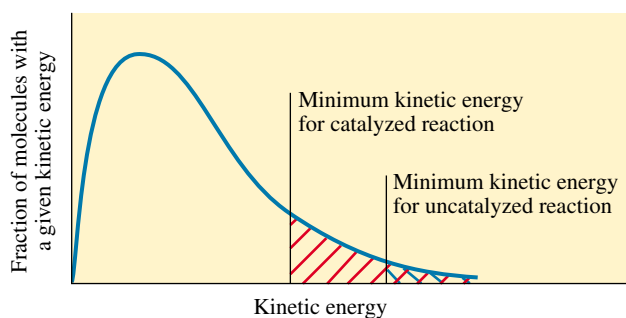
Figure 16-16 When a catalyst is present, the energy barrier is lowered. Thus, more molecules possess the minimum kinetic energy necessary for reaction. This is analogous to allowing more students to pass a course by lowering the requirements.

16-9 CATALYSTS

Catalysts are substances that can be added to reacting systems to increase the rate of reaction. They allow reactions to occur via alternative pathways that increase reaction rates by lowering activation energies.

The activation energy is lowered in all catalyzed reactions, as depicted in Figures 16-15 and 16-16. A catalyst does take part in the reaction, but all of it is re-formed in later steps. Thus, a catalyst does not appear in the balanced equation for the reaction.

For constant T and the same concentrations,

| If E_a decreases | $\Rightarrow$ | E_a/RT decreases | $\Rightarrow$ | $-E_a/RT$ increases | $\Rightarrow$ | $e^{-E_a/RT}$ increases | $\Rightarrow$ | k increases | $\Rightarrow$ | **Reaction speeds up** |
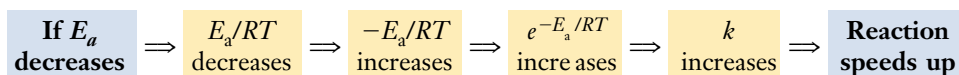
We can describe two categories of catalysts: (1) homogeneous catalysts and (2) hetero-geneous catalysts.

Homogeneous Catalysis

A **homogeneous catalyst** exists in the same phase as the reactants. Ceric ion, Ce^{4+}, at one time was an important laboratory oxidizing agent that was used in many redox titrations (Section 11-8). For example, Ce^{4+} oxidizes thallium(I) ions in solution; this reaction is catalyzed by the addition of a very small amount of a soluble salt containing manganese(II) ions, Mn^{2+}. The Mn^{2+} acts as a homogeneous catalyst.

$$2Ce^{4+} + Tl^+ \xrightarrow{\ Mn^{2+}\ } 2Ce^{3+} + Tl^{3+}$$
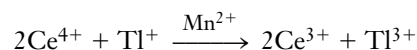
This reaction is thought to proceed by the following sequence of elementary steps.

$$
\begin{array}{ll}
Ce^{4+} + Mn^{2+} \longrightarrow Ce^{3+} + Mn^{3+} & \text{step 1} \\
Ce^{4+} + Mn^{3+} \longrightarrow Ce^{3+} + Mn^{4+} & \text{step 2} \\
\underline{Mn^{4+} + Tl^+ \ \longrightarrow Mn^{2+} + Tl^{3+}} & \text{step 3} \\
2Ce^{4+} + Tl^+ \ \longrightarrow 2Ce^{3+} + Tl^{3+} & \text{overall}
\end{array}
$$
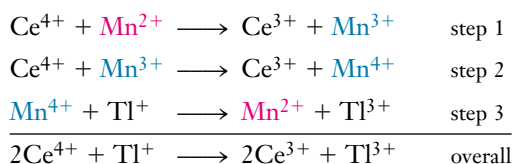
Some of the Mn^{2+} catalyst reacts in step 1, but an equal amount is regenerated in step 3 and is thus available to react again. The two ions shown in blue, Mn^{3+} and Mn^{4+}, are *reaction intermediates*. Mn^{3+} ions are formed in step 1 and consumed in an equal amount in step 2; similarly, Mn^{4+} ions are formed in step 2 and consumed in an equal amount in step 3.

We can now summarize the species that can appear in a reaction mechanism.

1. *Reactant:* More is consumed than is formed.
2. *Product:* More is formed than is consumed.
3. *Reaction intermediate:* Formed in earlier steps, then consumed in an equal amount in later steps.
4. *Catalyst:* Consumed in earlier steps, then regenerated in an equal amount in later steps.

Strong acids function as homogeneous catalysts in the acid-catalyzed hydrolysis of esters (a class of organic compounds—Section 27-14). Using ethyl acetate (a component of nail polish removers) as an example of an ester, we can write the overall reaction as follows.

"Hydrolysis" means reaction with water.

$$\underset{\text{ethyl acetate}}{CH_3\overset{O}{\overset{\|}{C}}-OCH_2CH_3(aq)} + H_2O \xrightarrow{\ H^+\ } \underset{\text{acetic acid}}{CH_3\overset{O}{\overset{\|}{C}}-OH(aq)} + \underset{\text{ethanol}}{CH_3CH_2OH(aq)}$$
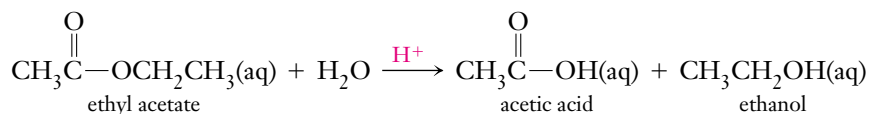
This is a thermodynamically favored reaction, but because of its high energy of activation, it occurs only very, very slowly when no catalyst is present. In the presence of strong acids, however, the reaction occurs more rapidly. In this acid-catalyzed hydrolysis, different intermediates with lower activation energies are formed. The sequence of steps in the *postulated* mechanism follows.

Groups of atoms that are involved in the change in each step are shown in blue. The catalyst, H^+, is shown in red.

$$CH_3-\overset{\overset{O}{\|}}{C}-OCH_2CH_3 + H^+ \longrightarrow \left[CH_3-\overset{\overset{\overset{+}{O}H}{\|}}{C}-OCH_2CH_3 \right] \quad \text{step 1}$$

$$CH_3-\overset{\overset{\overset{+}{O}H}{\|}}{C}-OCH_2CH_3 + H_2O \longrightarrow \left[CH_3-\underset{\underset{\underset{H \quad H}{}}{\overset{+}{O}}}{\overset{\overset{OH}{|}}{C}}-OCH_2CH_3 \right] \quad \text{step 2}$$

$$CH_3-\underset{\underset{\underset{H \quad H}{}}{\overset{+}{O}}}{\overset{\overset{OH}{|}}{C}}-OCH_2CH_3 \longrightarrow \left[CH_3-\underset{\underset{HO \quad H}{}}{\overset{\overset{OH}{|}}{C}}-\overset{+}{O}-CH_2CH_3 \right] \quad \text{step 3}$$

$$CH_3-\underset{\underset{HO \quad H}{}}{\overset{\overset{OH}{|}}{C}}-\overset{+}{O}-CH_2CH_3 \longrightarrow \left[CH_3-\overset{\overset{\overset{+}{O}H}{\|}}{C}-OH \right] + HOCH_2CH_3 \quad \text{step 4}$$

$$\text{ethanol}$$

$$CH_3-\overset{\overset{\overset{+}{O}H}{\|}}{C}-OH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH + H^+ \quad \text{step 5}$$

$$\text{acetic acid}$$

$$CH_3-\overset{\overset{O}{\|}}{C}-OCH_2CH_3 + H_2O \xrightarrow{H^+} CH_3-\overset{\overset{O}{\|}}{C}-OH + CH_3CH_2OH \quad \text{overall}$$

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

We see that H^+ is a reactant in step 1, but it is completely regenerated in step 5. H^+ is therefore a catalyst. The species shown in brackets in steps 1 through 4 are *reaction intermediates*. Ethyl acetate and water are the reactants, and acetic acid and ethanol are the products of the overall catalyzed reaction.

All intermediates in this sequence of elementary steps are charged species, but this is not always the case.

Heterogeneous Catalysis

A **heterogeneous catalyst** (also known as a **contact catalyst**) is present in a different phase from the reactants. Such catalysts are usually solids, and they lower activation energies by providing surfaces on which reactions can occur. The first step in the catalytic process is usually *adsorption*, in which one or more of the reactants become attached to the solid surface. Some reactant molecules may be held in particular orientations, or some bonds may be weakened; in other molecules, some bonds may be broken to form atoms or smaller molecular fragments. This causes *activation* of the reactants. As a result, *reac-*

The petroleum industry uses numerous heterogeneous catalysts. Many of them contain highly colored compounds of transition metal ions. Several are shown here.

tion occurs more readily than would otherwise be possible. In a final step, *desorption*, the product molecules leave the surface, freeing reaction sites to be used again. Most contact catalysts are more effective as small particles, because they have relatively large surface areas.

Transition metals and their compounds function as effective catalysts in many homogeneous and heterogeneous reactions. Vacant *d* orbitals in many transition metal ions can accept electrons from reactants to form intermediates. These subsequently decompose to form products. Three transition metals, Pt, Pd, and Ni, are often used as finely divided solids to provide surfaces on which heterogeneous reactions can occur.

The catalytic converters (Figure 16-17) built into automobile exhaust systems contain two types of heterogeneous catalysts, powdered noble metals and powdered transition metal oxides. They catalyze the oxidation of unburned hydrocarbon fuel (reaction 1) and of partial combustion products such as carbon monoxide (reaction 2, shown in Figure 16-18).

1.
$$2C_8H_{18}(g) + 25O_2(g) \xrightarrow[\text{NiO}]{\text{Pt}} 16CO_2(g) + 18H_2O(g)$$
$\uparrow$
isooctane (a component of gasoline)

2.
$$2CO(g) + O_2(g) \xrightarrow[\text{NiO}]{\text{Pt}} 2CO_2(g)$$
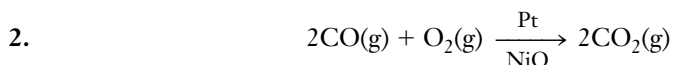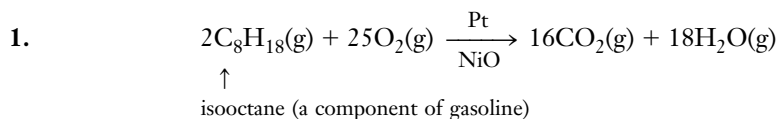
It is desirable to carry out these reactions in automobile exhaust systems. Carbon monoxide is very poisonous. The latter reaction is so slow that a mixture of CO and O_2 gas at the exhaust temperature would remain unreacted for thousands of years in the absence of a catalyst! Yet the addition of only a small amount of a solid, finely divided transition metal catalyst promotes the production of up to a mole of CO_2 per minute. Because this reaction is a very simple but important one, it has been studied extensively by surface chemists. It is one of the best understood heterogeneously catalyzed reactions. The major features of the catalytic process are shown in Figure 16-18.

The same catalysts also catalyze another reaction, the decomposition of nitrogen oxide, NO, into harmless N_2 and O_2.

$$2NO(g) \xrightarrow[\text{NiO}]{\text{Pt}} N_2(g) + O_2(g)$$
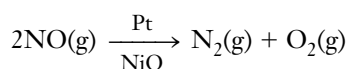
At the high temperatures of the combustion of any fuel in air, nitrogen and oxygen combine to form nitrogen oxide.

(a)

(b)
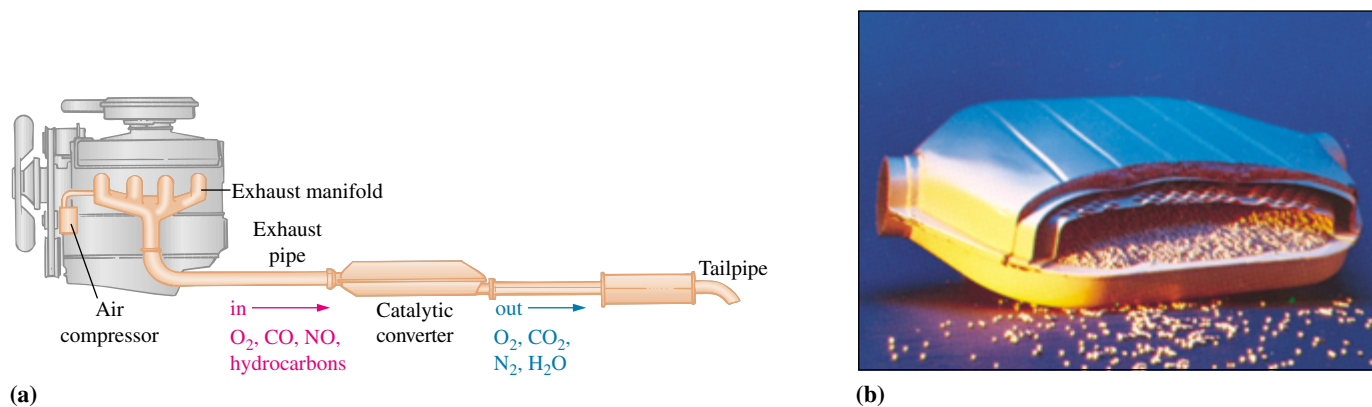
Figure 16-17 (a) The arrangement of a catalytic converter in an automobile. (b) A cutaway view of a catalytic converter, showing the pellets of catalyst.

(a) *Adsorption*: CO and O_2 reactant molecules become bound to the surface:

$$CO(g) \longrightarrow CO(surface) \quad \text{and} \quad O_2(g) \longrightarrow O_2(surface)$$

The CO molecules are linked through their C atoms to one or more metal atoms on the surface. The O_2 molecules are more weakly bound.

Catalyst surface

(b) *Activation*: The O_2 molecules dissociate into O atoms, which are held in place more tightly:

$$O_2(surface) \longrightarrow 2O(surface)$$

The CO molecules stick to the surface, but they migrate easily across the surface.

(d) *Desorption*: The weakly bound CO_2 product molecules leave the surface:

$$CO_2(surface) \longrightarrow CO_2(g)$$

Fresh reactant molecules can then replace them to start the cycle again [back to step (a)].

(c) *Reaction*: O atoms react with bound CO molecules, to form CO_2 molecules:

$$CO(surface) + O(surface) \longrightarrow CO_2(surface)$$

The resulting CO_2 molecules bind to the surface *very poorly*.

Figure 16-18   A schematic representation of the catalysis of the reaction
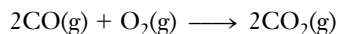
$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

on a metallic surface.

Nitrogen oxide is a serious air pollutant because it is oxidized to nitrogen dioxide, NO_2, which reacts with water to form nitric acid and with other products of the incomplete combustion of hydrocarbons to form nitrates. The latter are eye irritants in photochemical smog.

These three reactions, catalyzed in catalytic converters, are all exothermic and thermodynamically favored. Unfortunately, other energetically favored reactions are also accelerated by the mixed catalysts. All fossil fuels contain sulfur compounds, which are oxidized to sulfur dioxide during combustion. Sulfur dioxide, itself an air pollutant, undergoes further oxidation to form sulfur trioxide as it passes through the catalytic bed.
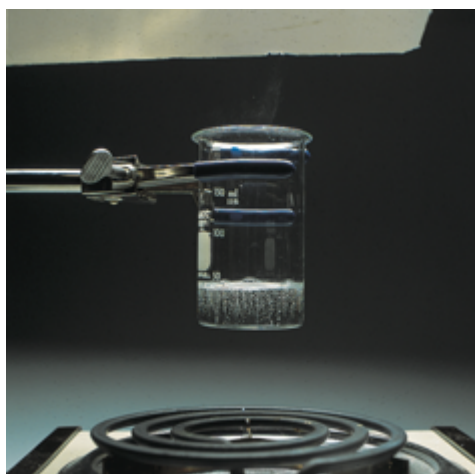
(a)

(b)

(c)

A 30% hydrogen peroxide, H_2O_2, solution at room temperature decomposes very slowly to form O_2 and H_2O. (a) This reaction takes place more rapidly if the solution is heated. (b) A very small amount of a transition metal oxide is added. (c) This oxide catalyzes the decomposition reaction. The catalyzed reaction is rapid, so the exothermic reaction quickly heats the solution to the boiling point of water, forming steam. The temperature increase further accelerates the decomposition. Never use a syringe with a metal tip to withdraw a sample from a 30% hydrogen peroxide solution. (d) The bombardier beetle uses a catalyzed decomposition of hydrogen peroxide as a means of defense. An enzyme produced by the beetle catalyzes the rapid exothermic reaction. The resulting steam, along with other irritating chemicals, is ejected.

(d)

$$2SO_2(g) + O_2(g) \xrightarrow[\text{NiO}]{\text{Pt}} 2SO_3(g)$$
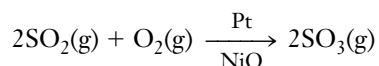
Sulfur trioxide is probably a worse pollutant than sulfur dioxide, because SO_3 is the acid anhydride of strong, corrosive sulfuric acid. Sulfur trioxide reacts with water vapor in the air, as well as in auto exhausts, to form sulfuric acid droplets. This problem must be overcome if the current type of catalytic converter is to see continued use. These same catalysts also suffer from the problem of being "poisoned"—that is, made inactive—by lead. Leaded fuels contain tetraethyl lead, $Pb(C_2H_5)_4$, and tetramethyl lead, $Pb(CH_3)_4$. Such fuels are not suitable for automobiles equipped with catalytic converters and are excluded by U. S. law from use in such cars.

Reactions that occur in the presence of a solid catalyst, as on a metal surface (heterogeneous catalysis) often follow zero-order kinetics. For instance, the rate of decomposition of $NO_2(g)$ at high pressures on a platinum metal surface does not change if we add more NO_2. This is because only the NO_2 molecules on the surface can react. If the metal surface is completely covered with NO_2 molecules, no additional molecules can be *adsorbed* until the ones already there have reacted and the products have *desorbed*. Thus, the rate of the

Maintaining the continued efficiency of all three reactions in a "three-way" catalytic converter is a delicate matter. It requires control of such factors as the O_2 supply pressure and the order in which the reactants reach the catalyst. Modern automobile engines use microcomputer chips, based on an O_2 sensor in the exhaust stream, to control air valves.

The Environment

Ozone

Ozone, O_3, is such a powerful oxidizing agent that in significant concentrations it destroys many plastics, metals, and rubber, as well as both plant and animal tissues. We therefore try to minimize exposure to ozone in our immediate environment. In the upper atmosphere, however, ozone plays a very important role in the absorption of harmful radiation from the sun. Maintaining appropriate concentrations of ozone—minimizing its production where ozone is harmful and preventing its destruction where ozone is helpful—is an important challenge in environmental chemistry.

Ozone is formed in the upper atmosphere as some O_2 molecules absorb high-energy electromagnetic radiation from the sun and dissociate into oxygen atoms; these then combine with other O_2 molecules to form ozone.

$$O_2(g) + \text{UV radiation} \longrightarrow 2O(g) \quad \text{(step 1—occurs once)}$$
$$\underline{O_2(g) + O(g) \longrightarrow O_3(g) \quad \text{(step 2—occurs twice)}}$$
$$3O_2(g) + \text{UV radiation} \longrightarrow 2O_3(g) \quad \text{(net reaction)}$$
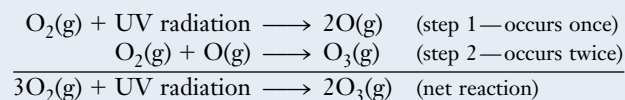
Although it decomposes in the upper atmosphere, the ozone supply is continuously replenished by this process. Its concentration in the stratosphere (≈ 7–31 miles above the earth's surface) is about 10 ppm (parts per million), whereas it is only about 0.04 ppm near the earth's surface.

The high-altitude ozone layer is responsible for absorbing much of the dangerous ultraviolet light from the sun in the 20–30 Å wavelength range.

$$O_3(g) + \text{UV radiation} \longrightarrow O_2(g) + O(g)$$
$$\text{(step 1—occurs once)}$$
$$\underline{O_2(g) + O(g) \longrightarrow O_3(g) \quad \text{(step 2—occurs once)}}$$
$$\text{No net reaction}$$
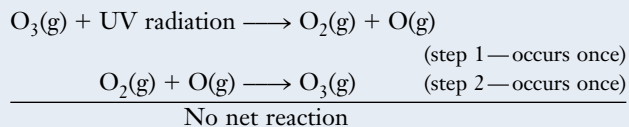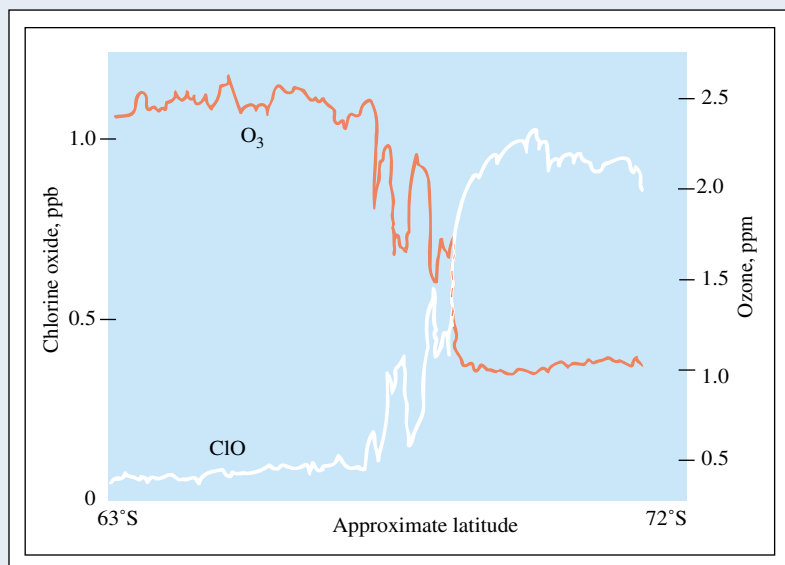
We see that each time this sequence takes place, it absorbs one photon of ultraviolet light; however, the process regenerates as much ozone as it uses up. Each stratospheric ozone molecule can thus absorb a significant amount of ultraviolet light. If this high-energy radiation reached the surface of the earth in higher intensity, it would be very harmful to plants and animals (including humans). It has been estimated that the incidence of skin cancer would increase by 2% for every 1% decrease in the concentration of ozone in the stratosphere.

Chlorofluorocarbons (CFCs) are chemically inert, non-flammable, nontoxic compounds that are superb solvents and have been used in many industrial processes; they are excellent coolants for air conditioners and refrigerators. Two CFCs that have been widely used are Freon-11 and Freon-12 (Freon is a DuPont trade name).

Freon-11 is CCl_3F Freon-12 is CCl_2F_2
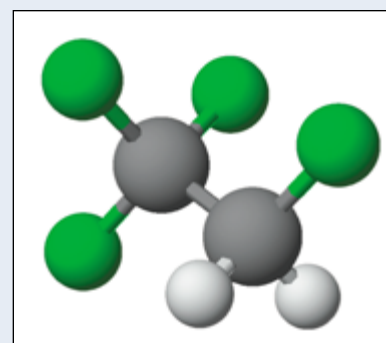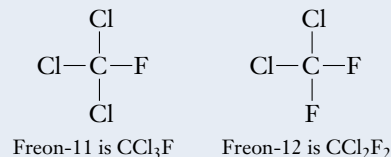
The compound known as HCFC-134, a fluorocarbon currently used in home and automobile air conditioners.

A plot that shows the decrease in $[O_3]$ as $[ClO]$ increases over Antarctica.

The CFCs are so unreactive that they do not readily decompose, that is, break down into simpler compounds, when they are released into the atmosphere. Over time the CFCs are carried into the stratosphere by air currents, where they are exposed to large amounts of ultraviolet radiation.

In 1974, Mario Molina and Sherwood Rowland of the University of California–Irvine demonstrated in their laboratory that when CFCs are exposed to ultraviolet radiation they break down to form chlorine *radicals* ($:\ddot{C}l\cdot$).

$$F-\overset{\displaystyle F}{\underset{\displaystyle Cl}{C}}-Cl \xrightarrow[\text{radiation}]{\text{UV}} F-\overset{\displaystyle F}{\underset{\displaystyle Cl}{C}}\cdot \; + \; :\ddot{\ddot{C}}l\cdot \qquad \text{(a chlorine radical)}$$
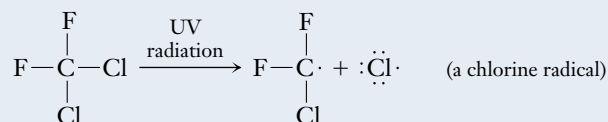
Molina and Rowland predicted that these very reactive radicals could cause problems by catalyzing the destruction of ozone in the stratosphere.

Each spring since 1979, researchers have observed a thinning of the ozone layer over Antarctica. Each spring (autumn in the Northern Hemisphere) beginning in 1983, satellite images have shown a "hole" in the ozone layer over the South Pole. During August and September 1987, a NASA research team flew a plane equipped with sophisticated analytical instruments into the ozone hole 25 times. Their measurements demonstrated that as the concentration of the chlorine oxide radicals, Cl—O increased, the concentration of ozone decreased.

By September 1992, this **ozone hole** was nearly three times the area of the United States. In December 1994, three years of data from NASA's Upper Atmosphere Research Satellite (UARS) provided conclusive evidence that CFCs are primarily responsible for this destruction of the ozone layer. Considerable thinning of the ozone layer in the Northern Hemisphere has also been observed.

The following is a simplified representation of the **chain reaction** that is now believed to account for most of the ozone destruction in the stratosphere.

$$:\ddot{\ddot{C}}l\cdot \; + \; O_3 \longrightarrow Cl-\ddot{\ddot{O}}\cdot \; + \; O_2 \qquad \text{(step 1)}$$

$$Cl-\ddot{\ddot{O}}\cdot \; + \; O \longrightarrow :\ddot{\ddot{C}}l\cdot \; + \; O_2 \qquad \text{(step 2)}$$

$$\overline{O_3(g) \; + \; O \longrightarrow 2O_2(g)} \qquad \text{(net reaction)}$$
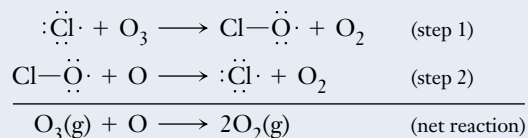
A sufficient supply of oxygen atoms, O, is available in the upper atmosphere for the second step to occur. The net reaction results in the destruction of a molecule of ozone. The chlorine radical that initiates the first step of this reaction sequence is regenerated in the second step, however, and so a single chlorine radical can act as a catalyst to destroy many
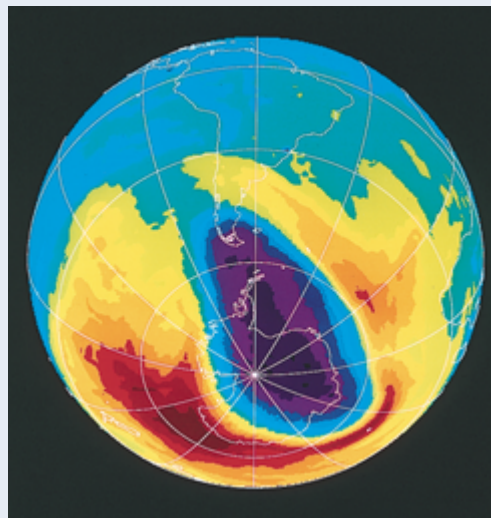
A computer-generated image of part of the Southern Hemisphere on October 17, 1994, reveals the ozone "hole" (black and purple areas) *over Antarctica and the tip of South America. Relatively low ozone levels* (blue and green areas) *extend into much of South America as well as Central America. Normal ozone levels are shown in yellow, orange, and red. The ozone hole is not stationary but moves about as a result of air currents. (Courtesy NASA)*

thousands of O_3 molecules. Other well-known reactions also destroy ozone in the stratosphere, but the evidence shows conclusively that the CFCs are the principal culprits.

Since January 1978, the use of CFCs in aerosol cans in the United States has been banned; increasingly strict laws prohibit the release into the atmosphere of CFCs from sources such as automobile air conditioners and discarded refrigerators. The Montreal Protocol, signed by 24 countries in 1989, called for reductions in production and use of many CFCs. International agreements have since called for a complete ban on CFC production. Efforts to develop suitable replacement substances and controls for existing CFCs continue. The good news is that scientists expect the ozone hole to decrease and possibly disappear during the twenty-first century *if* current international treaties remain in effect and *if* they are implemented throughout the world. These are two very large *ifs*.

Additional information on stratospheric ozone can be found at the EPA Web site, http://www.epa.gov/docs/ozone. The Web site for this textbook will direct you to additional information about ozone.
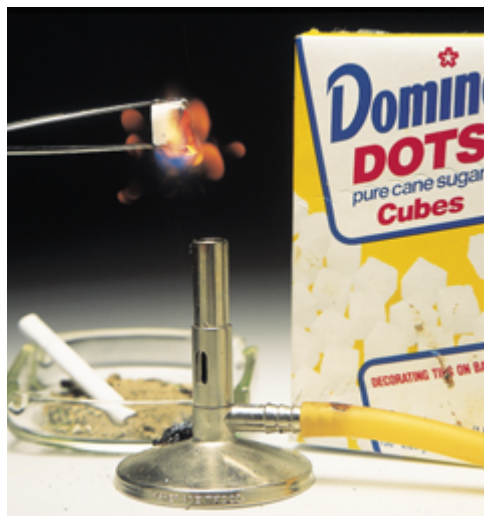
reaction is controlled only by the availability of reaction sites on the Pt surface, and not by the total number of NO_2 molecules available.

Some other important reactions that are catalyzed by transition metals and their oxides follow.

1. The Haber process for the production of ammonia (Section 17-7).

$$N_2 + 3H_2 \xrightarrow[\text{high T, P}]{\text{Fe, Fe oxides}} 2NH_3$$
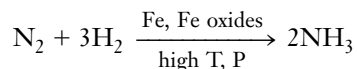
2. The contact process for the production of sulfur trioxide in the manufacture of sulfuric acid (Section 24-11).

$$2SO_2 + O_2 \xrightarrow[400°C]{V_2O_5} 2SO_3$$
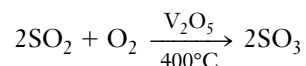
3. The chlorination of benzene (Section 27-16).

$$\underset{\text{benzene}}{C_6H_6} + Cl_2 \xrightarrow{FeBr_3} \underset{\text{chlorobenzene}}{C_6H_5Cl} + HCl$$
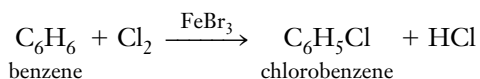
4. The hydrogenation of unsaturated hydrocarbons (Section 27-17).

$$RCH{=}CH_2 + H_2 \xrightarrow{Pt} RCH_2CH_3 \qquad R = \text{organic groups}$$

Enzymes as Biological Catalysts

Enzymes are proteins that act as catalysts for specific biochemical reactions in living systems. The reactants in enzyme-catalyzed reactions are called **substrates.** Thousands of vital processes in our bodies are catalyzed by many distinct enzymes. For instance, the enzyme carbonic anhydrase catalyzes the combination of CO_2 and water (the substrates), facilitating most of the transport of carbon dioxide in the blood. This combination reaction, ordinarily uselessly slow, proceeds rapidly in the presence of carbonic anhydrase; a single molecule of this enzyme can promote the conversion of more than 1 million molecules of carbon dioxide each second. Each enzyme is extremely specific, catalyzing only a few closely related reactions—or, in many cases, only one particular reaction—for only certain substrates. Modern theories of enzyme action attribute this to the requirement of very specific matching of shapes (molecular geometries) for a particular substrate to bind to a particular enzyme (Figure 16-19).

When heated, a sugar cube (sucrose, melting point 185°C) melts but does not burn. A sugar cube rubbed in cigarette ash burns before it melts. The cigarette ash contains trace amounts of metal compounds that catalyze the combustion of sugar.
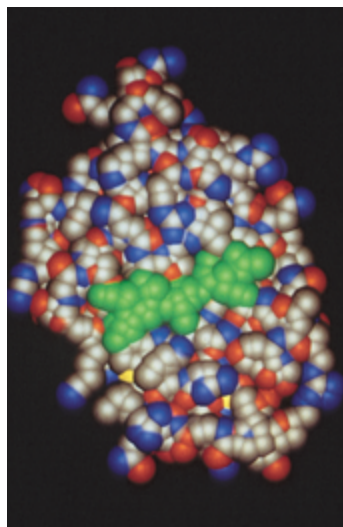
A space-filling model of the enzyme lysozyme. This enzyme catalyzes the hydrolysis of polysaccharides (complex carbohydrates) found in bacterial cell walls, that is, it breaks the link between two adjacent sugar units in the polysaccharide. The intact polysaccharide, shown here in green, fits into the active site, which is a cleft in the surface of the lysozyme molecule. The arrangement of hydrogen-bonding groups in the active site of the enzyme surface matches that on the polysaccharide, but other molecules with different hydrogen-bonding groups do not fit as well, so the enzyme exhibits very specific bonding for polysaccharides. After the hydrolysis reaction has taken place, the product molecules do not fit the active site as well, so they are released, making way for another polysaccharide to be bound to the enzyme active site.
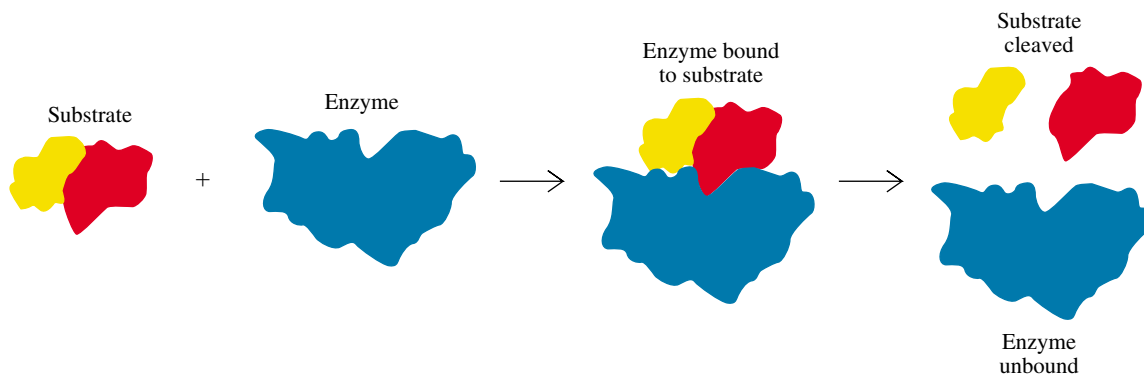
Figure 16-19   A schematic representation of a simplified mechanism (lock-and-key) for enzyme reaction. The substrates (reactants) fit the active sites of the enzyme molecule much as keys fit locks. When the reaction is complete, the products do not fit the active sites as well as the reactants did. They separate from the enzyme, leaving it free to catalyze the reaction of additional reactant molecules. The enzyme is not permanently changed by the process. The illustration here is for a process in which a complex reactant molecule is split to form two simpler product molecules. The formation of simple sugars from complex carbohydrates is a similar reaction. Some enzymes catalyze the combination of simple molecules to form more complex ones.

Enzyme-catalyzed reactions are important examples of zero-order reactions; that is, the rate of such a reaction is independent of the concentration of the substrate (provided *some* substrate is present).

$$\text{rate} = k$$

The active site on an enzyme can bind to only one substrate molecule at a time (or one pair, if the reaction links two reactant molecules), no matter how many other substrate molecules are available in the vicinity.

Transition metal ions are present in the active sites of some enzymes.

Ammonia is a very important industrial chemical that is used as a fertilizer and in the manufacture of many other chemicals. The reaction of nitrogen with hydrogen is a thermodynamically spontaneous reaction (product-favored), but without a catalyst it is very slow, even at high temperatures. The Haber process for its preparation involves the use of iron as a catalyst at 450°C to 500°C and high pressures.

$$N_2(g) + 3H_2(g) \xrightarrow{\text{Fe}} 2NH_3(g) \qquad \Delta G^0 = -194.7 \text{ kJ/mol (at 500°C)}$$

Even so, iron is not a very effective catalyst.

In contrast, the reaction between N_2 and H_2 to form NH_3 is catalyzed at room temperature and atmospheric pressure by a class of enzymes, called nitrogenases, that are present in some bacteria. Legumes are plants that support these bacteria; they are able to obtain nitrogen as N_2 from the atmosphere and convert it to ammonia.

The process is called nitrogen fixation. The ammonia can be used in the synthesis of many nitrogen-containing biological compounds such as proteins and nucleic acids.

In comparison with manufactured catalysts, most enzymes are tremendously efficient under very mild conditions. If chemists and biochemists could develop catalysts with a small fraction of the efficiency of enzymes, such catalysts could be a great boon to the world's health and economy. One of the most active areas of current chemical research involves attempts to discover or synthesize catalysts that can mimic the efficiency of naturally occurring enzymes such as nitrogenases. Such a development would be important in industry. It would eliminate the costs of the high temperature and high pressure that are necessary in the Haber process. This could decrease the cost of food grown with the aid of ammonia-based fertilizers. Ultimately this would help greatly to feed the world's growing population.

Key Terms

Activation energy   The kinetic energy that reactant molecules must have to allow them to reach the transition state so that a reaction can occur.

Arrhenius equation   An equation that relates the specific rate constant to activation energy and temperature.

Catalyst   A substance that increases the rate at which a reaction occurs. It remains unchanged when the reaction is complete.

Chemical kinetics   The study of rates and mechanisms of chemical reactions and of the factors on which they depend.

Collision theory   A theory of reaction rates that states that effective collisions between reactant molecules must take place for reaction to occur.

Contact catalyst   See *Heterogeneous catalyst*.

Effective collision   A collision between molecules that results in reaction; one in which molecules collide with proper orientations and with sufficient energy to react.

Elementary step   An individual step in the mechanism by which a reaction occurs. For each elementary step, the reaction orders *do* match the reactant coefficients in that step.

Enzyme   A protein that acts as a catalyst in a biological system.

Half-life of a reactant   The time required for half of that reactant to be converted into product(s).

Heterogeneous catalyst   A catalyst that exists in a different phase (solid, liquid, or gas) from the reactants; a contact catalyst.

Homogeneous catalyst   A catalyst that exists in the same phase (liquid or gas) as the reactants.

Integrated rate equation   An equation that relates the concentration of a reactant remaining to the time elapsed; has different mathematical forms for different orders of reaction.

Method of initial rates   A method of determining the rate-law expression by carrying out a reaction with different initial concentrations and analyzing the resulting changes in initial rates.

Order of a reactant   The power to which the reactant's concentration is raised to the rate-law expression.

Order of a reaction   The sum of the powers to which all concentrations are raised in the rate-law expression; also called overall order of a reaction.

Rate constant (also called **specific rate constant**)   An experimentally determined proportionality constant that is different for different reactions and that, for a given reaction, changes only with temperature or the presence of a catalyst; k in the rate-law expression, Rate $= k[A]^x[B]^y$.

Rate-determining step   The slowest step in a reaction mechanism; the step that limits the overall rate of reaction.

Rate-law expression (also called **rate law**)   An equation that relates the rate of a reaction to the concentrations of the reactants and the specific rate constant; rate $= k[A]^x[B]^y$. The exponents of reactant concentrations *do not necessarily* match the coefficients in the overall balanced chemical equation. The rate-law expression must be determined from experimental data.

Rate of reaction   The change in concentration of a reactant or product per unit time.

Reaction coordinate   The progress along the pathway from reactants to products; sometimes called "progress of reaction".

Reaction intermediate   A species that is produced and then entirely consumed during a multistep reaction; usually short-lived.

Reaction mechanism   The sequence of steps by which reactants are converted into products.

Substrate   A reactant in an enzyme-catalyzed reaction.

Thermodynamically favorable (spontaneous) reaction   A reaction that occurs with a net release of free energy, G; a reaction for which ΔG is negative (see Section 15-15).

Transition state   A relatively high-energy state in which bonds in reactant molecules are partially broken and new ones are partially formed.

Transition state theory   A theory of reaction rates that states that reactants pass through high-energy transition states before forming products.

Exercises

General Concepts

1. Briefly summarize the effects of each of the four factors that affect rates of reactions.
2. Describe the basic features of collision theory and transition state theory.
3. What is a rate-law expression? Describe how it is determined for a particular reaction.
4. Distinguish between reactions that are thermodynamically favorable and reactions that are kinetically favorable. What can be said about relationships between the two?
5. What is meant by the order of a reaction?
6. What, if anything, can be said about the relationship between the coefficients of the balanced *overall* equation for a reaction and the powers to which concentrations are raised in the rate-law expression? To what are these powers related?
7. Express the rate of reaction in terms of the rate of change of each reactant and product in the following reactions.
   (a) $H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow$
   $$I_2(aq) + 2H_2O(\ell)$$
   (b) $2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$
   (c) $CH_3COOH(aq) + OH^-(aq) \longrightarrow$
   $$CH_3COO^-(aq) + H_2O(\ell)$$

8. Express the rate of reaction in terms of the rate of change of each reactant and each product in the following.
   (a) $3ClO^-(aq) \longrightarrow ClO_3^-(aq) + 2Cl^-(aq)$
   (b) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
   (c) $C_2H_4(g) + Br_2(g) \longrightarrow C_2H_4Br_2(g)$
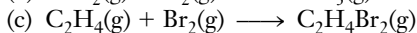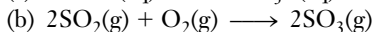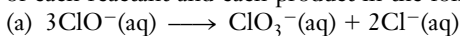
9. At a given time, N_2 is reacting with H_2 at a rate of 0.25 M/min to produce NH_3. At that same time, what is the rate at which the other reactant is changing and the rate at which the product is changing?

$$N_2 + 3H_2 \longrightarrow 2NH_3$$
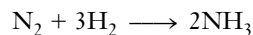
10. The following equation shows the production of NO and H_2O by oxidation of ammonia. At a given time, NH_3 is reacting at a rate of 1.10 M/min. At that same time, which is the rate at which the other reactant is changing and the rate at which each product is changing?

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$
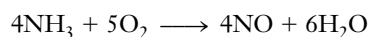
11. Why do large crystals of sugar burn more slowly than finely ground sugar?

12. Some fireworks are bright because of the burning of magnesium. Speculate on how fireworks might be constructed using magnesium. How might the sizes of the pieces of magnesium be important? What would you expect to occur if pieces that were too large were used? Too small?

Rate-Law Expression

13. If doubling the initial concentration of a reactant doubles the initial rate of reaction, what is the order of the reaction with respect to the reactant? If this concentration change causes the rate to increase by a factor of 8, what is the order? If the concentration changes and the rate remains the same, what is the order?

14. The rate expression for the following reaction at a certain temperature is rate $= k[NO]^2[O_2]$. Two experiments involving this reaction are carried out at the same temperature. In the second experiment the initial concentration of NO is halved while the initial concentra-

tion of O_2 is doubled. The initial rate in the second experiment will be _____ times that of the first.

$$2NO + O_2 \longrightarrow 2NO_2$$
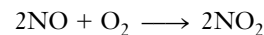
15. The rate-law expression for the following reaction is found to be rate $= k [N_2O_5]$. What is the overall reaction order?

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$
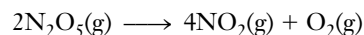
16. Use times expressed in seconds to give the units of the rate constant for reactions that are overall (a) first order; (b) second order; (c) third order; (d) of order $1\frac{1}{2}$.

17. Rate data were obtained at 25°C for the following reaction. What is the rate-law expression for this reaction?

$$A + 2B \longrightarrow C + 2D$$
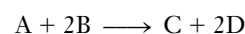
Expt.	[A] [mol/L]	[B] [mol/L]	Initial Rate of Formation of C
1	0.10	0.10	3.0×10^{-4} M·min^{-1}
2	0.30	0.30	9.0×10^{-4} M·min^{-1}
3	0.30	0.10	3.0×10^{-4} M·min^{-1}
4	0.40	0.20	6.0×10^{-4} M·min^{-1}

18. Rate data were obtained for the following reaction at 25°C. What is the rate-law expression for the reaction?

$$2A + B + 2C \longrightarrow D + 2E$$
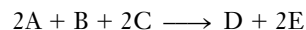
Expt.	Initial [A]	Initial [B]	Initial [C]	Initial Rate of Formation of D
1	0.10 M	0.20 M	0.10 M	5.0×10^{-4} M·min^{-1}
2	0.20 M	0.20 M	0.30 M	1.5×10^{-3} M·min^{-1}
3	0.30 M	0.20 M	0.10 M	5.0×10^{-4} M·min^{-1}
4	0.40 M	0.60 M	0.30 M	4.5×10^{-3} M·min^{-1}

19. (a) A certain reaction is zero order in reactant A and second order in reactant B. If the concentrations of both reactants are doubled, what happens to the reaction rate? (b) What would happen to the reaction rate if the reaction in part (a) were first order in A and first order in B?

20. The rate expression for the following reaction is shown to be rate $= k[A]^2[B_2]$. If, during a reaction, the concentrations of both A and B_2 were suddenly halved, the rate of the reaction would _____ by a factor of _____.

$$A + B_2 \longrightarrow products$$
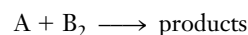
21. Rate data were collected for the following reaction at a particular temperature.

$$A + B \longrightarrow products$$
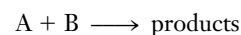
Expt.	$[A]_0$ (mol/L)	$[B]_0$ (mol/L)	Initial Rate of Reaction
1	0.10	0.10	$0.0090\ M \cdot s^{-1}$
2	0.20	0.10	$0.036\ \ M \cdot s^{-1}$
3	0.10	0.20	$0.018\ \ M \cdot s^{-1}$
4	0.10	0.30	$0.027\ \ M \cdot s^{-1}$

(a) What is the rate-law expression for this reaction? (b) Describe the order of the reaction with respect to each reactant and to the overall order.

22. Rate data were collected for the following reaction at a particular temperature.

$$2ClO_2(aq) + 2OH^-(aq) \longrightarrow$$
$$ClO_3^-(aq) + ClO_2^-(aq) + H_2O(\ell)$$
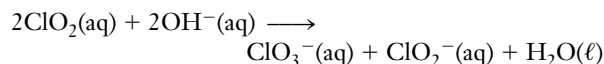
Expt.	$[ClO_2]_0$ (mol/L)	$[OH^-]_0$ (mol/L)	Initial Rate of Reaction
1	0.012	0.012	$2.07 \times 10^{-4}\ M \cdot s^{-1}$
2	0.024	0.012	$8.28 \times 10^{-4}\ M \cdot s^{-1}$
3	0.012	0.024	$4.14 \times 10^{-4}\ M \cdot s^{-1}$
4	0.024	0.024	$1.66 \times 10^{-3}\ M \cdot s^{-1}$

(a) What is the rate-law expression for this reaction? (b) Describe the order of the reaction with respect to each reactant and to the overall order.

23. The reaction $(C_2H_5)_2(NH)_2 + I_2 \rightarrow (C_2H_5)_2N_2 + 2HI$ gives the following initial rates.

Expt.	$[(C_2H_5)_2(NH)_2]_0$ (mol/L)	$[I_2]_0$ (mol/L)	Initial Rate of Formation of $(C_2H_5)_2N_2$
1	0.015	0.015	$3.15\ M \cdot s^{-1}$
2	0.015	0.045	$9.45\ M \cdot s^{-1}$
3	0.030	0.045	$18.9\ \ M \cdot s^{-1}$

Write the rate-law expression.

24. Given the following data for the reaction $A + B \rightarrow C$, write the rate-law expression.

Expt.	Initial [A]	Initial [B]	Initial Rate of Formation of C
1	0.20 M	0.10 M	$5.0 \times 10^{-6}\ M \cdot s^{-1}$
2	0.30 M	0.10 M	$7.5 \times 10^{-6}\ M \cdot s^{-1}$
3	0.40 M	0.20 M	$4.0 \times 10^{-5}\ M \cdot s^{-1}$

*25. Given the following data for the reaction $A + B \rightarrow C$, write the rate-law expression.

Expt.	Initial [A]	Initial [B]	Initial Rate of Formation of C
1	0.25	0.15	$8.0\ \times 10^{-5}\ M/s$
2	0.25	0.30	$3.2\ \times 10^{-4}\ M/s$
3	0.50	0.60	$5.12 \times 10^{-3}\ M/s$

*26. Given the following data for the reaction $A + B \rightarrow C$, write the rate-law expression.

Expt.	Initial [A]	Initial [B]	Initial Rate of Formation of C
1	0.10 M	0.10 M	$2.0\ \times 10^{-4}\ M/s$
2	0.20 M	0.10 M	$8.0\ \times 10^{-4}\ M/s$
3	0.40 M	0.20 M	$2.56 \times 10^{-2}\ M/s$

*27. Consider a chemical reaction between compounds A and B that is first order in A and first order in B. From the information shown here, fill in the blanks.

Expt.	Rate $(M \cdot s^{-1})$	[A]	[B]
1	0.24	0.20 M	0.050 M
2	0.20	_____ M	0.030 M
3	0.80	0.40 M	_____ M

*28. Consider a chemical reaction of compounds A and B that was found to be first order in A and second order in B. From the following information, fill in the blanks.

Expt.	Rate $(M \cdot s^{-1})$	[A]	[B]
1	0.150	1.00 M	0.200 M
2	_____	2.00 M	0.200 M
3	_____	2.00 M	0.400 M

29. The following rearrangement reaction is first order:

$$CH_3NC \longrightarrow CH_3CN$$
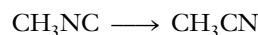
In a table of kinetics data we find the following values listed for this reaction: $A = 3.98 \times 10^{13}\ s^{-1}$, $E_a = 160$ kJ/mol. (a) Calculate the value of the specific rate constant at room temperature, 25°C. (b) Calculate the value of the specific rate constant at 115°C.

30. The following gas-phase decomposition reaction is first order:

$$C_2H_5Cl \longrightarrow C_2H_4 + HCl$$
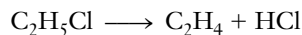
In a table of kinetics data we find the following values listed for this reaction: $A = 1.58 \times 10^{13}$ s^{-1}, $E_a = 237$ kJ/mol. (a) Calculate the value of the specific rate constant at room temperature, 25°C. (b) Calculate the value of the specific rate constant at 275°C.

*31. The rate of decomposition of NO$_2$ by the following reaction at some temperature is 5.4×10^{-5} mol NO$_2$/L·s when [NO$_2$] = 0.0110 mol/L.

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$
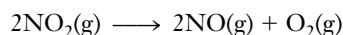
(a) Assume that the rate law is rate = k[NO$_2$]. What rate of disappearance of NO$_2$ would be predicted when [NO$_2$] = 0.00550 mol/L? (b) Now assume that the rate law is rate = k[NO$_2$]^2. What rate of disappearance of NO$_2$ would be predicted when [NO$_2$] = 0.00550 mol/L? (c) The rate when [NO$_2$] = 0.00550 mol/L is observed to be 1.4×10^{-5} mol NO$_2$/L·s. Which rate law is correct? (d) Calculate the rate constant. (*Reminder:* Express the rate of reaction in terms of rate of disappearance of NO$_2$.)

Integrated Rate Equations and Half-Life

32. What is meant by the half-life of a reactant?

33. The rate law for the reaction of sucrose in water,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 2C_6H_{12}O_6$$
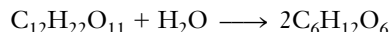
is rate = k[C$_{12}$H$_{22}$O$_{11}$]. After 2.57 hours at 25°C, 6.00 g/L of C$_{12}$H$_{22}$O$_{11}$ has decreased to 5.40 g/L. Evaluate k for this reaction at 25°C.

34. The rate constant for the decomposition of nitrogen dioxide

$$2NO_2 \longrightarrow 2NO + O_2$$
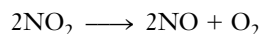
with a laser beam is 1.70 M^{-1}·min^{-1}. Find the time, in seconds, needed to decrease 2.00 mol/L of NO$_2$ to 1.25 mol/L.

35. The second-order rate constant for the following gas-phase reaction is 0.0442 M^{-1}·s^{-1}. We start with 0.135 mol C$_2$F$_4$ in a 2.00-liter container, with no C$_4$F$_8$ initially present.

$$2C_2F_4 \longrightarrow C_4F_8$$
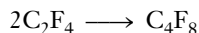
(a) What will be the concentration of C$_2$F$_4$ after 1.00 hour? (b) What will be the concentration of C$_4$F$_8$ after 1.00 hour? (c) What is the half-life of the reaction for the initial C$_2$F$_4$ concentration given in part (a)? (d) How long will it take for half of the C$_2$F$_4$ that remains after 1.00 hour to disappear?

36. The decomposition reaction of carbon disulfide, CS$_2$, to carbon monosulfide, CS, and sulfur is first order with $k = 2.8 \times 10^{-7}$ s^{-1} at 1000°C.

$$CS_2 \longrightarrow CS + S$$
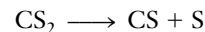
(a) What is the half-life of this reaction at 1000°C? (b) How many days would pass before a 2.00-gram sample of CS$_2$ had decomposed to the extent that 0.75 gram of CS$_2$ remained? (c) Refer to part (b). How many grams of CS would be present after this length of time? (d) How much of a 2.00-gram sample of CS$_2$ would remain after 45.0 days?

*37. The first-order rate constant for the conversion of cyclobutane to ethylene at 1000°C is 87 s^{-1}.

cyclobutane   ethylene
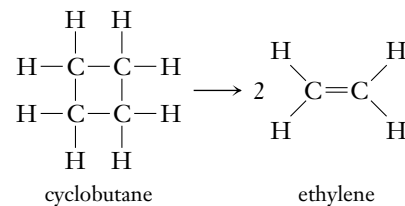
(a) What is the half-life of this reaction at 1000°C? (b) If you started with 2.00 g of cyclobutane, how long would it take to consume 1.50 g of it? (*Hint:* Write the ratio of concentrations, [A]$_0$/[A], in terms of mass, molecular weight, and volume.) (c) How much of an initial 1.00-g sample of cyclobutane would remain after 1.00 s?

*38. For the reaction

$$2NO_2 \longrightarrow 2NO + O_2$$
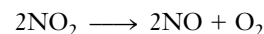
the rate equation is

$$\text{rate} = 1.4 \times 10^{-10} \ M^{-1}\cdot\text{s}^{-1}[NO_2]^2 \quad \text{at } 25°C$$

(a) If 3.00 mol of NO$_2$ is initially present in a sealed 2.00-L vessel at 25°C, what is the half-life of the reaction? (b) Refer to part (a). What concentration and how many grams of NO$_2$ remain after 115 years? (c) Refer to part (b). What concentration of NO would have been produced during the same period of time?

39. The first-order rate constant for the radioactive decay of radium-223 is 0.0606 day^{-1}. What is the half-life of radium-223?

40. Cyclopropane rearranges to form propene

cyclopropane   propene
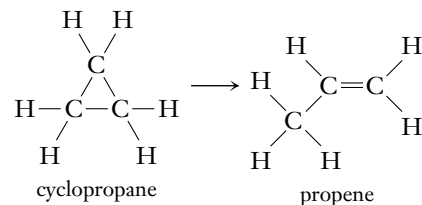
in a reaction that follows first-order kinetics. At 800 K, the specific rate constant for this reaction is 2.74×10^{-3} s^{-1}. Suppose we start with a cyclopropane concentration of 0.290 M. How long will it take for 99.0% of the cyclopropane to disappear according to this reaction?

41. The rate constant for the first-order reaction

$$N_2O_5 \longrightarrow 2NO_2 + \tfrac{1}{2}O_2$$
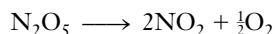
is 1.20×10^{-2} s^{-1} at 45°C, and the initial concentration of N_2O_5 is 0.00500 M. (a) How long will it take for the concentration to decrease to 0.00110 M? (b) How much longer will it take for a further decrease to 0.000900 M?

42. It is found that 47.0 minutes is required for the concentration of substance A to decrease from 0.75 M to 0.20 M. What is the rate constant for this first-order decomposition?

$$A \longrightarrow B + C$$
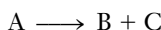
43. The thermal decomposition of ammonia at high temperatures was studied in the presence of inert gases. Data at 2000 K are given for a single experiment.

$$NH_3 \longrightarrow NH_2 + H$$
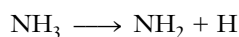
t (hours)	$[NH_3]$ (mol/L)
0	8.000×10^{-7}
25	$6.75\ \times 10^{-7}$
50	$5.84\ \times 10^{-7}$
75	$5.15\ \times 10^{-7}$

Plot the appropriate concentration expressions against time to find the order of the reaction. Find the rate constant of the reaction from the slope of the line. Use the given data and the appropriate integrated rate equation to check your answer.

44. The following data were obtained from a study of the decomposition of a sample of HI on the surface of a gold wire. (a) Plot the data to find the order of the reaction, the rate constant, and the rate equation. (b) Calculate the HI concentration in mmol/L at 600. s.

t (seconds)	$[HI]$ (mmol/L)
0.	5.46
250.	4.10
500.	2.73
750.	1.37

45. The decomposition of SO_2Cl_2 in the gas phase,
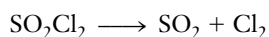
$$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

can be studied by measuring the concentration of Cl_2 as the reaction proceeds. We begin with $[SO_2Cl_2]_0 = 0.250$ M. Holding the temperature constant at 320°C, we monitor the Cl_2 concentration, with the following results.

t (hours)	$[Cl_2]$ (mol/L)
0.00	0.000
2.00	0.037
4.00	0.068
6.00	0.095
8.00	0.117
10.00	0.137
12.00	0.153
14.00	0.168
16.00	0.180
18.00	0.190
20.00	0.199

(a) Plot $[Cl_2]$ versus t. (b) Plot $[SO_2Cl_2]$ versus t. (c) Determine the rate law for this reaction. (d) What is the value, with units, for the specific rate constant at 320°C? (e) How long would it take for 95% of the original SO_2Cl_2 to react?

***46.** At some temperature, the rate constant for the decomposition of HI on a gold surface is 0.080 $M \cdot$s^{-1}.

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$
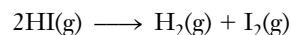
(a) What is the order of the reaction? (b) How long will it take for the concentration of HI to drop from 1.50 M to 0.30 M?

Activation Energy, Temperature, and Catalysts

47. Draw typical reaction energy diagrams for one-step reactions that release energy and that absorb energy. Distinguish between the net energy change, ΔE, for each kind of reaction and the activation energy. Indicate potential energies of products and reactants for both kinds of reactions.

48. Use graphs to illustrate how the presence of a catalyst can affect the rate of a reaction.

49. How do homogeneous catalysts and heterogeneous catalysts differ?

50. (a) Why should one expect an increase in temperature to increase the initial rate of reaction? (b) Why should one expect a reaction in the gaseous state to be faster than the same reaction in the solid state?

51. What is the activation energy for a reaction if its rate constant is found to triple when the temperature is raised from 300 K to 310 K?

52. What is the activation energy for a reaction if its rate constant is found to triple when the temperature is raised from 600 K to 610 K?

53. For a gas-phase reaction, $E_a = 103$ kJ/mol, and the rate constant is 0.0850 min^{-1} at 273 K. Find the rate constant at 323 K.

54. The rate constant of a reaction is tripled when the temperature is increased from 298 K to 308 K. Find E_a.

55. The rate constant for the decomposition of N_2O

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$$
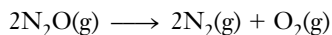
is 2.6×10^{-11} s^{-1} at 300°C and 2.1×10^{-10} s^{-1} at 330°C. Calculate the activation energy for this reaction. Prepare a reaction coordinate diagram like Figure 16-10 using -164.1 kJ/mol as the ΔE_{rxn}.

56. For a particular reaction, $\Delta E^0 = 51.51$ kJ/mol, $k = 8.0 \times 10^{-7}$ s^{-1} at 0.0°C, and $k = 8.9 \times 10^{-4}$ s^{-1} at 50.0°C. Prepare a reaction coordinate diagram like Figure 16-10 for this reaction.

*57. You are given the rate constant as a function of temperature for the exchange reaction

$$Mn(CO)_5(CH_3CN)^+ + NC_5H_5 \longrightarrow$$
$$Mn(CO)_5(NC_5H_5)^+ + CH_3CN$$
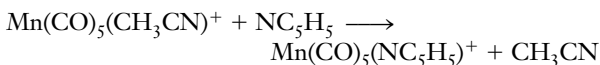
T (K)	k (min^{-1})
298	0.0409
308	0.0818
318	0.157

(a) Calculate E_a from a plot of log k versus $1/T$. (b) Use the graph to predict the value of k at 311 K. (c) What is the numerical value of the collision frequency factor, A, in the Arrhenius equation?

*58. The rearrangement of cyclopropane to propene described in Exercise 40 has been studied at various temperatures. The following values for the specific rate constant have been determined experimentally.

T (K)	k (s^{-1})
600.	3.30×10^{-9}
650.	2.19×10^{-7}
700.	7.96×10^{-6}
750.	1.80×10^{-4}
800.	2.74×10^{-3}
850.	3.04×10^{-2}
900.	2.58×10^{-1}

(a) From the appropriate plot of these data, determine the value of the activation energy for this reaction. (b) Use the graph to estimate the value of k at 500 K. (c) Use the graph to estimate the temperature at which the value of k would be equal to 5.00×10^{-5} s^{-1}.

59. Biological reactions nearly always occur in the presence of enzymes as catalysts. The enzyme catalase, which acts on peroxides, reduces the E_a for the reaction from 72 kJ/mol (uncatalyzed) to 28 kJ/mol (catalyzed). By what factor does the reaction rate increase at normal body temperature, 37.0°C, for the same reactant (peroxide) concentration? Assume that the collision factor, A, remains constant.

*60. The enzyme carbonic anhydrase catalyzes the hydration of carbon dioxide.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
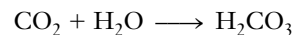
This reaction is involved in the transfer of CO_2 from tissues to the lungs via the bloodstream. One enzyme molecule hydrates 10^6 molecules of CO_2 per second. How many kilograms of CO_2 are hydrated in one hour in 1 L by 1.0×10^{-6} M enzyme?

61. The following gas-phase reaction follows first-order kinetics.

$$ClO_2F \longrightarrow ClOF + O$$
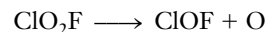
The activation energy of this reaction is 186 kJ/mol. The value of k at 322°C is 6.76×10^{-4} s^{-1}. (a) What would be the value of k for this reaction at 25°C? (b) At what temperature would this reaction have a k value of 3.00×10^{-2} s^{-1}?

62. The following gas-phase reaction is first order.

$$N_2O_5 \longrightarrow NO_2 + NO_3$$
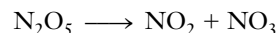
The activation energy of this reaction is 88 kJ/mol. The value of k at 0°C is 9.16×10^{-3} s^{-1}. (a) What would be the value of k for this reaction at room temperature, 25°C? (b) At what temperature would this reaction have a k value of 3.00×10^{-2} s^{-1}?

Reaction Mechanisms

63. Define *reaction mechanism*. Why do we believe that only bimolecular collisions and unimolecular decompositions are important in most reaction mechanisms?

64. The rate equation for the reaction

$$Cl_2(aq) + H_2S(aq) \longrightarrow S(s) + 2HCl(aq)$$
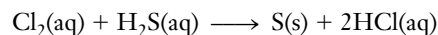
is found to be rate $= k[Cl_2][H_2S]$. Which of the following mechanisms are consistent with the rate law?

(a)
$Cl_2 \longrightarrow Cl^+ + Cl^-$	(slow)	
$Cl^- + H_2S \longrightarrow HCl + HS^-$	(fast)	
$Cl^+ + HS^- \longrightarrow HCl + S$	(fast)	
$Cl_2 + H_2S \longrightarrow S + 2HCl$	(overall)	

(b)
$Cl_2 + H_2S \longrightarrow HCl + Cl^+ + HS^-$	(slow)
$Cl^+ + HS^- \longrightarrow HCl + S$	(fast)
$Cl_2 + H_2S \longrightarrow S + 2HCl$	(overall)

segmentsegmentsegmentmentgmentment

consistent with the given kinetic data? Show how you arrived at your answer.

(a) $NO_2 + NO_2 \rightleftharpoons N_2O_4$ (fast, equilibrium)
   $N_2O_4 + O_3 \longrightarrow N_2O_5 + O_2$ (slow)

(b) $NO_2 + O_3 \longrightarrow NO_3 + O_2$ (slow)
 $NO_3 + NO_2 \longrightarrow N_2O_5$ (fast)
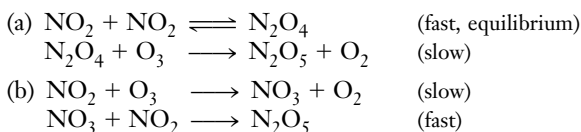
Mixed Exercises

74. Some reactions occur faster than others due to differences in the shapes of the reactants. Use the collision theory to explain these observations.

75. How it is possible for two reactant molecules to collide with the correct orientation and still not react?

76. (a) What is the transition state in a reactant mechanism? (b) Are the energy of activation and the transition state related concepts? Explain. (c) How does the activation energy affect the rate of reaction?

77. Refer to the reaction and data in Exercise 61. We begin with 3.60 mol of ClO_2F in a 3.00-L container. (a) How many moles of ClO_2F would remain after 1.00 min at 25°C? (b) How much time would be required for 99.0% of the ClO_2F to decompose at 25°C?

78. Refer to the reaction and data in Exercise 62. We begin with 3.60 mol of N_2O_5 in a 3.00-L container. (a) How many moles of N_2O_5 would remain after 1.00 min at 25°C? (b) How much time would be required for 99.0% of the N_2O_5 to decompose at 25°C?

79. The decomposition of gaseous dimethyl ether

$$CH_3OCH_3 \longrightarrow CH_4 + CO + H_2$$
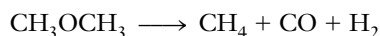
follows first-order kinetics. Its half-life is 25.0 min at 500°C. (a) Starting with 10.00 g of dimethyl ether at 500°C, how many grams would remain after 150 min? (b) In part (a), how many grams would remain after 180 min? (c) In part (b), what fraction remains and what fraction reacts? (d) Calculate the time, in minutes, required to decrease 9.20 mg of dimethyl ether to 2.40 mg.

80. The rate of the hemoglobin (Hb)–carbon monoxide reaction,

$$4Hb + 3CO \longrightarrow Hb_4(CO)_3$$
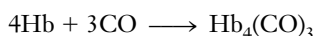
has been studied at 20°C. Concentrations are expressed in micromoles per liter (μmol/L).

Concentration (μmol/L)		Rate of Disappearance of Hb (μmol·L^{-1}·s^{-1})
[Hb]	[CO]	
3.36	1.00	0.941
6.72	1.00	1.88
6.72	3.00	5.64

(a) Write the rate equation for the reaction. (b) Calculate the rate constant for the reaction. (c) Calculate the rate, at the instant when [Hb] = 1.50 and [CO] = 0.600 μmol/L.

81. How does an enzyme change the speed with which a reaction reaches equilibrium? Can an enzyme change the final equilibrium concentrations? Explain.

CONCEPTUAL EXERCISES

82. Write the net ionic equation for the following reaction. Construct a potential energy diagram, like Figure 16-10, for this reaction.

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(\ell)$$
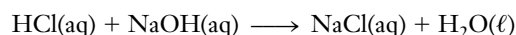
83. Starting with only two molecules of each reactant in a reaction that is first order in each reactant, show how the collision theory predicts that the rate of reaction will double if the amount of either reactant is doubled.

84. A sentence in an introductory chemistry textbook reads, "Dioxygen reacts with itself to form trioxygen, ozone, according to the following equation, $3O_2 \rightarrow 2O_3$." As a student of chemistry, what would you write to criticize this sentence?

85. A stream of gaseous H_2 is directed onto finely divided platinum powder in the open air. The metal immediately glows white-hot and continues to do so as long as the stream continues. Explain.

86. Is the activation energy of a reaction expected to be higher or lower when the same reactants are in the gaseous state rather than the liquid or solid state? Explain.

BUILDING YOUR KNOWLEDGE

87. The following explanation of the operation of a pressure cooker appears in a cookbook: "Boiling water in the presence of air can never produce a temperature higher than 212°F, no matter how high the heat source. But in a pressure cooker, the air is withdrawn first, so the boiling water can be maintained at higher temperatures." Support or criticize this explanation.

*88. A cookbook gives the following general guideline for use of a pressure cooker. "For steaming vegetables, cooking time at a gauge pressure of 15 pounds per square inch (psi) is $\frac{1}{3}$ that at atmospheric pressure." Remember that gauge pressure is measured relative to the external atmospheric pressure, which is 15 psi at sea level. From this information, estimate the activation energy for the process of steaming vegetables. (*Hint:* Clausius and Clapeyron may be able to help you.)

89. For most reactions that involve an enzyme, the rate of product formation versus reactant concentration increases as reactant concentration increases until a maximum value is obtained, after which further increases do not yield increased rates. Using a description like that in Figure 16-19, describe how the reaction may be first order with respect to substrate but the amount of enzyme can also be a determining factor.

90. Using the mechanism and energy values shown in Figure 16-12, prepare Lewis formulas that illustrate the species that are likely to be present at each of the peaks and troughs in the graphical representation given in Figure 16-12. (*Hint:* You may need to label some bonds as being weaker, stretched, in the process of being formed, and so on.)

91. The activation energy for the reaction

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$
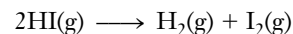
is 179 kJ/mol. Construct a diagram similar to Figure 16-10 for this reaction. (*Hint:* Calculate ΔH^0 from values in Appendix K. How does ΔH^0 compare with ΔE^0 for this reaction?)

*92. The activation energy for the reaction between O_3 and NO is 9.6 kJ/mol.

$$O_3(g) + NO(g) \longrightarrow NO_2(g) + O_2(g)$$
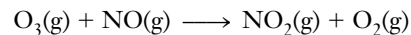
(a) Use the thermodynamic quantities in Appendix K to calculate ΔH^0 for this reaction. (b) Prepare an activation energy plot similar to Figure 16-10 for this reaction. (*Hint:* How does ΔH^0 compare with ΔE^0 for this reaction?)