15—Principles of Reactivity: Chemical Kinetics

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Hard-to-digest foods. Foods such as beans, cabbage, and broccoli are known to produce flatulence in some people due to incomplete digestion of complex sugars. However, an enzyme, when added to the food, can help break down these complex sugars and avoid "problem gas."

Faster and Faster

Certain foods such as beans, cabbage, and broccoli contain complex sugars known as oligosaccharides. Although these compounds are broken down to simple sugars during the digestive process, some people have a problem breaking them down completely. This failure can lead to a condition known politely as flatulence, because the undigested material is eventually fermented by anaerobic organisms in the colon to produce gases such as CO_2, H_2, CH_4, and small amounts of smelly compounds.

To help people who have this problem, a commercial product called Beano was developed. Its maker's advertising material states that Beano "is a food enzyme from a natural source that breaks down the complex sugars in gassy foods, making them more digestible."

As you will learn in this chapter, which describes the factors affecting the speed of chemical reactions, enzymes are biological catalysts. Their role is to speed up chemical reactions. One of the enzymes in Beano, galactosidase, accelerates the breakdown of the

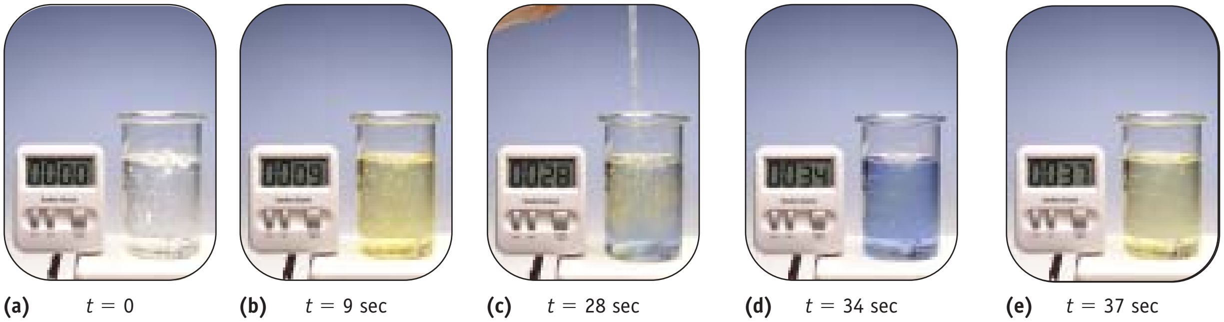

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Figure A CO_2 in water. (a) A cold solution of CO_2 in water. (b) A few drops of a dye (bromthymol blue) are added to the cold solution. The yellow color of the dye indicates an acidic solution. (c) A less than stoichiometric amount of sodium hydroxide is added, converting H_2CO_3 to HCO_3^- (and CO_3^{2-}). (d) The blue color of the dye indicates a basic solution. (e) The blue color begins to fade after some seconds as CO_2 slowly forms more H_2CO_3. The amount of H_2CO_3 formed is finally sufficient to consume the added NaOH and the solution is again acidic.

Chapter Goals

See Chapter Goals Revisited (page 741). Test your knowledge of these goals by taking the exam-prep quiz on the General ChemistryNow CD-ROM or website.

- Understand rates of reaction and the conditions affecting rates.
- Derive the rate equation, rate constant, and reaction order from experimental data.
- Use integrated rate laws.
- Understand the collision theory of reaction rates and the role of activation energy.
- Relate reaction mechanisms and rate laws.

Chapter Outline

oligosaccharides in certain foods to the simple sugars galactose and glucose.

$$\text{Oligosaccharide} + H_2O \xrightarrow{\text{galactosidase}} \text{galactose} + \text{glucose}$$

Carbonic anhydrase is one of the many enzymes that play important roles in biological processes (see page 732). Carbon dioxide dissolves in water to a small extent to produce carbonic acid, which ionizes to give H^+ and HCO_3^- ions.

$$CO_2(g) \longrightarrow CO_2(aq) \qquad (1)$$

$$CO_2(aq) + H_2O(\ell) \longrightarrow H_2CO_3(aq) \qquad (2)$$

$$H_2CO_3(aq) \longrightarrow H^+(aq) + HCO_3^-(aq) \qquad (3)$$

Carbonic anhydrase speeds up reactions 1 and 2. Many of the H^+ ions produced by ionization of H_2CO_3 (reaction 3) are picked up by hemoglobin in the blood as hemoglobin loses O_2. The resulting HCO_3^- ions are transported back to the lungs. When hemoglobin again takes on O_2, it releases H^+ ions. These ions and HCO_3^- re-form H_2CO_3, from which CO_2 is liberated and exhaled.

A simple experiment illustrates the effect of carbonic anhydrase. First, add a small amount of NaOH to a cold, aqueous solution of CO_2 (Figure A). The solution becomes basic immediately, because there is not enough H_2CO_3 in the solution to use up the NaOH. After some seconds, however, dissolved CO_2 slowly produces more H_2CO_3, which consumes NaOH, and the solution again becomes acidic.

Now try the experiment again, this time adding a few drops of blood to the solution (Figure B). Carbonic anhydrase in blood speeds up reactions 1 and 2 by a factor of about 10^7, as evidenced by the more rapid reaction that occurs under these conditions.

To learn more about Beano and enzymes, see J. R. Hardee, T. M. Montgomery, and W. H. Jones: *Journal of Chemical Education*, Vol. 77, p. 498, 2000. For a more detailed discussion of the rate of conversion of aqueous CO_2, see J. Bell: *Journal of Chemical Education*, Vol. 77, p. 1098, 2000.

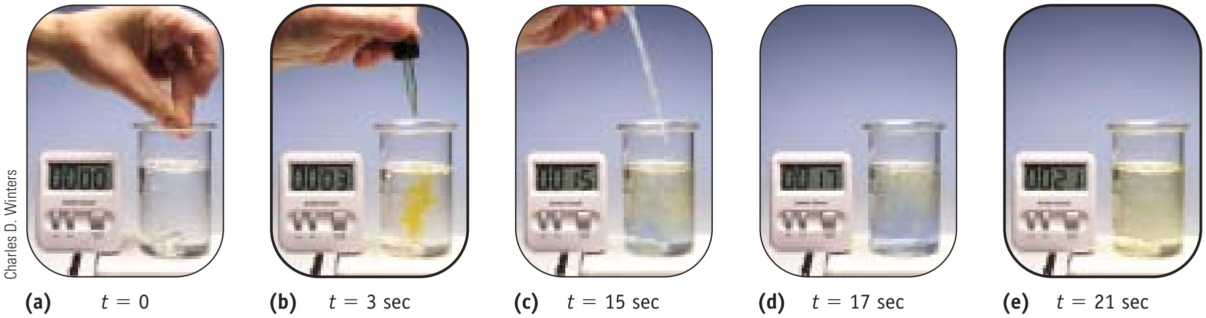

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Figure B Action of carbonic anhydrase. (a) A few drops of blood are added to a cold solution of CO_2 in water. (b) The dye indicates an acidic solution. (c, d) A less than stoichiometric amount of sodium hydroxide is added, converting H_2CO_3 to HCO_3^-(and CO_3^{2-}). The dye's blue color indicates a basic solution. (e) The blue color begins to fade after a few seconds as more H_2CO_3 forms, and the solution again becomes acidic. The formation of H_2CO_3 is more rapid in the presence of an enzyme.

To Review Before You Begin

- Review reaction stoichiometry (Chapters 4 and 5)
- Understand the distribution of molecular energies in a gas (Figure 12.14) and in a liquid (Figure 13.14)

When carrying out a chemical reaction, chemists are concerned with two issues: the *rate* at which the reaction proceeds and the *extent* to which the reaction is product-favored. Chapter 6 began to address the second question, and Chapters 16 and 19 will develop that topic further. In this chapter we turn to the other part of our question, **chemical kinetics**, the study of the rates of chemical reactions.

The study of kinetics is divided into two parts. The first part concerns the *macroscopic level*, which addresses rates of reactions: what the reaction rate means, how to determine a reaction rate experimentally, and how factors such as temperature and the concentrations of reactants influence rates. The second part considers chemical reactions at the *particulate level*. Here, the concern is with the **reaction mechanism,** the detailed pathway taken by atoms and molecules as a reaction proceeds. The goal is to reconcile data in the macroscopic world of chemistry with an understanding of how and why chemical reactions occur at the particulate level—and then to apply this information to control important reactions.

GENERAL Chemistry Now™

Throughout the chapter this icon introduces a list of resources on the General ChemistryNow CD-ROM or website (http://now.brookscole.com/kotz6e) that will:

- help you evaluate your knowledge of the material
- provide homework problems
- allow you to take an exam-prep quiz
- provide a personalized Learning Plan targeting resources that address areas you should study

15.1—Rates of Chemical Reactions

The concept of rate is encountered in many nonchemical circumstances. Common examples are the speed of an automobile given in terms of the distance traveled per unit time (e.g., kilometers per hour) and the rate of flow of water from a faucet given as volume per unit time (liters per minute). In each case a change is measured over an interval of time. The **rate of a chemical reaction** refers to the change in concentration of a substance per unit of time.

$$\text{Rate of reaction} = \frac{\text{change in concentration}}{\text{change in time}}$$

An easy way to gauge the speed of an automobile is to measure how far it travels during a specified time interval. Two measurements are made: distance traveled and time elapsed. The speed is the distance traveled divided by the time elapsed, or Δ(distance)/Δ(time). If an automobile travels 2.4 mi in 4.5 min (0.075 h), its average speed is (2.4 mi/0.075 h), or 32 mph.

Chemical reaction rates are determined in a similar manner. Two quantities, concentration and time, must be measured. The rate of the reaction can then be described as the change in the concentration of a reactant or a product per unit time—that is, Δ(concentration)/Δ(time).

For a rate study, the concentration of a substance undergoing reaction can be determined by a variety of methods. Concentrations can sometimes be measured directly, by using a pH meter, for example. Often, concentrations are obtained by measuring a property such as the absorbance of light that is related to concentration (Figure 15.1).

During a chemical reaction, amounts of reactants decrease with time, and amounts of products increase. It is possible to describe the rate of reaction based on either the increase in concentration of a product or the decrease in concentration of a reactant per unit of time. Consider the decomposition of N_2O_5 in a solvent. This reaction occurs according to the following equation:

$$2\ N_2O_5 \longrightarrow 4\ NO_2 + O_2$$

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(a) (b) (c)

Figure 15.1 An experiment to measure rate of reaction. (a) A few drops of blue food dye were added to water, followed by a solution of bleach. Initially, the concentration of dye was about 3.4×10^{-5} M, and the bleach (NaOCl) concentration was about 0.034 M. (b, c) The dye faded as it reacted with the bleach. The absorbance of the solution can be measured at various times using a spectrophotometer, and these values can be used to determine the concentration of the dye.

The progress of this reaction can be followed in a number of ways, including monitoring the increase in O_2 pressure. The amount of O_2 that is formed (calculated from measured values of *P*, *V*, and *T*) is related to the amount of N_2O_5 that has decomposed: For every 1 mol of O_2 formed, 2 mol of N_2O_5 decomposed. The amount of N_2O_5 in solution at a given time equals the initial amount of N_2O_5 minus the amount decomposed. (If the volume of the solution is known, the concentration can be determined from that amount.) Data for a typical experiment done at 30.0 °C are presented as a graph of concentration of N_2O_5 versus time in Figure 15.2.

The rate of this reaction for any interval of time can be expressed as the change in concentration of N_2O_5 divided by the change in time:

$$\text{Rate of reaction} = \frac{\text{change in } [N_2O_5]}{\text{change in time}} = -\frac{\Delta[N_2O_5]}{\Delta t}$$

Representing Concentration
Recall that square brackets around a formula indicate its concentration in mol/L (Section 5.8).

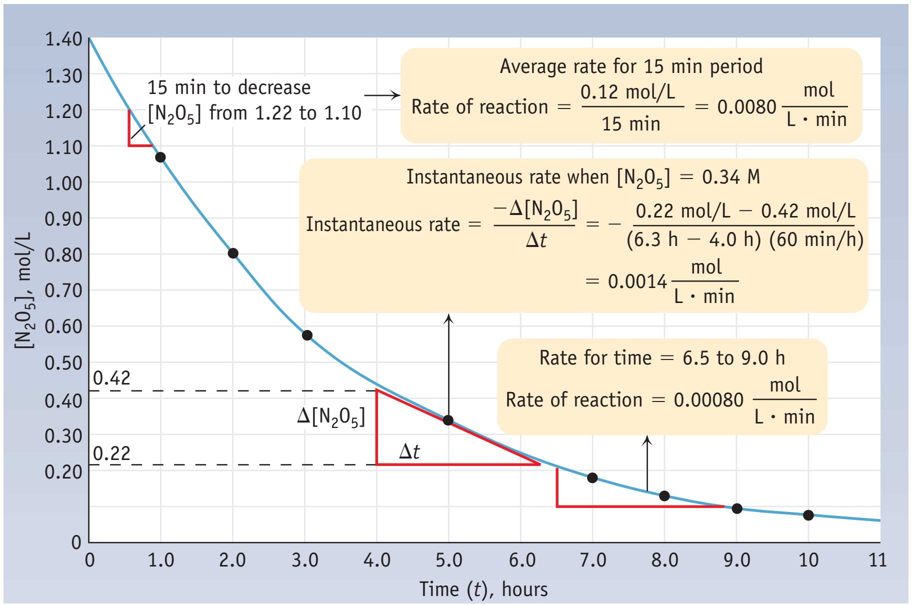
The minus sign is required because the concentration of N_2O_5 decreases with time, and the rate is always expressed as a positive quantity.

The rate could also be expressed in terms of the rate of formation of NO_2 or the rate of formation of O_2. Rates expressed in these ways will have a positive sign because the concentration is increasing. Furthermore, the rate of formation of NO_2 is twice the rate of decomposition of N_2O_5 because the balanced chemical equation tells us that 2 mol of NO_2 form when 1 mol of N_2O_5 decomposes. The rate of formation of O_2 is one half of the rate of decomposition of N_2O_5 because one mole of O_2 is formed per two moles of N_2O_5 decomposed. For example, the rate of disappearance of N_2O_5 between 40 min and 55 min (see Figure 15.2) is given by

$$-\frac{\Delta[N_2O_5]}{\Delta t} = -\frac{(1.10\ \text{mol/L}) - (1.22\ \text{mol/L})}{55\ \text{min} - 40\ \text{min}} = +\frac{0.12\ \text{mol/L}}{15\ \text{min}}$$

$$= 0.0080\ \frac{\text{mol } N_2O_5 \text{ consumed}}{\text{L} \cdot \text{min}}$$

Calculating Changes
Recall that when we calculate a change in a quantity, we always do so by subtracting the initial quantity from the final quantity: $\Delta X = X_{\text{final}} - X_{\text{initial}}$.



Active Figure 15.2 **A plot of reactant concentration versus time for the decomposition of N_2O_5.** The average rate for a 15-min interval from 40 min to 55 min is 0.0080 mol/L · min. The instantaneous rate calculated when $[N_2O_5] = 0.34$ M is 0.0014 mol/L · min.

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ChemistryNow™ **See the General ChemistryNow CD-ROM or website to explore an interactive version of this figure accompanied by an exercise.**

■ **Units of Reaction Rates**
Notice that the units used to describe reaction rates are mol/L · time.

Expressing the rate in terms of the rate of appearance of NO_2 produces a rate that is twice the rate of disappearance of N_2O_5.

$$\text{Rate} = \frac{\Delta[NO_2]}{\Delta t} = \frac{0.0080\ \text{mol}\ N_2O_5\ \text{consumed}}{\text{L}\cdot\text{min}} \times \frac{2\ \text{mol}\ NO_2\ \text{formed}}{1\ \text{mol}\ N_2O_5\ \text{consumed}}$$
$$= 0.016\ \frac{\text{mol}\ NO_2\ \text{formed}}{\text{L}\cdot\text{min}}$$

The rate of the reaction in terms of the rate at which O_2 is formed is

$$\text{Rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{0.0080\ \text{mol}\ N_2O_5\ \text{consumed}}{\text{L}\cdot\text{min}} \times \frac{1\ \text{mol}\ O_2\ \text{formed}}{2\ \text{mol}\ N_2O_5\ \text{consumed}}$$
$$= 0.0040\ \frac{\text{mol}\ O_2\ \text{formed}}{\text{L}\cdot\text{min}}$$

■ **Summarizing Rate Expressions**

$$-\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

for the reaction $2\ N_2O_5 \longrightarrow 4\ NO_2 + O_2$. To equate rates of disappearance or appearance, you should divide $\Delta[\text{reagent}]/\Delta t$ by the stoichiometric coefficient in the balanced equation.

Graphing concentration versus time on Figure 15.2 does not give a straight line because the rate of the reaction changes during the course of the reaction. The concentration of N_2O_5 decreases rapidly at the beginning of the reaction but more slowly near the end. We can verify this by comparing the rate of disappearance of N_2O_5 calculated previously (the concentration decreased by 0.12 mol/L in 15 min) with the rate of reaction calculated for the time interval from 6.5 h to 9.0 h (when the concentration drops by 0.12 mol/L in 150 min).

$$-\frac{\Delta[N_2O_5]}{\Delta t} = -\frac{(0.1\ \text{mol/L}) - (0.22\ \text{mol/L})}{540\ \text{min} - 390\ \text{min}} = +\frac{0.12\ \text{mol/L}}{150\ \text{min}}$$
$$= 0.00080\ \frac{\text{mol}}{\text{L}\cdot\text{min}}$$

The rate in this later stage of this reaction is only one tenth of the previous value.

The procedure we have used to calculate the reaction rate gives the **average rate** over the chosen time interval. We might also ask what the **instantaneous rate** is at a single point in time. The instantaneous rate is determined by drawing a line tangent to the concentration–time curve at a particular time (see Figure 15.2) and obtaining the rate from the slope of this line. For example, when $[N_2O_5] = 0.34$ mol/L and $t = 5.0$ h, the rate is

$$\text{Rate when } [N_2O_5] \text{ is } 0.34\text{ M} = -\frac{\Delta[N_2O_5]}{\Delta t} = +\frac{0.20 \text{ mol/L}}{140 \text{ min}} = 1.4 \times 10^{-3}\ \frac{\text{mol}}{\text{L} \cdot \text{min}}$$

At that particular moment in time ($t = 5.0$ h), N_2O_5 is being consumed at a rate of 0.0014 mol/L · min.

The difference between an average rate and an instantaneous rate has an analogy in the speed of an automobile. In the previous example, the car traveled 2.4 mi in 4.5 min for an average speed of 32 mph. At any instant in time, however, the car may be moving much slower or much faster. The instantaneous speed at any instant is indicated by the car's speedometer.

■ **The Slope of a Line**
The instantaneous rate in Figure 15.2 can be determined from an analysis of the slope of the line. See pages 35–36 for more on finding the slope of a line.

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See the General ChemistryNow CD-ROM or website:

- **Screen 15.2 Rates of Chemical Reactions,** for a visualization of ways to express reaction rates

Example 15.1—Relative Rates and Stoichiometry

Problem Give the relative rates for the disappearance of reactants and formation of products for the following reaction:

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

Strategy In this reaction PH_3 disappears and P_4 and H_2 are formed. Consequently, the value of $\Delta[PH_3]/\Delta t$ will be negative, whereas $\Delta[P_4]/\Delta t$ and $\Delta[H_2]/\Delta t$ will be positive. To equate rates, we divide $\Delta[\text{reagent}]/\Delta t$ by its stoichiometric coefficient in the balanced equation.

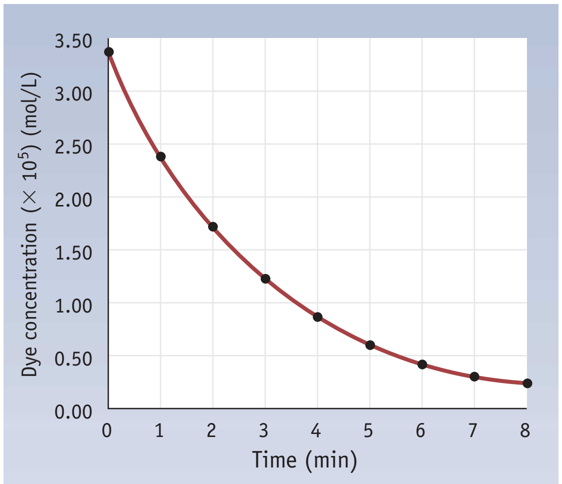
Solution Because four moles of PH_3 disappear for every one mole of P_4 formed, the numerical value of the rate of formation of P_4 can only be one fourth of the rate of disappearance of PH_3. Similarly, P_4 is formed at only one sixth of the rate that H_2 is formed.

$$-\frac{1}{4}\left(\frac{\Delta[PH_3]}{\Delta t}\right) = +\frac{\Delta[P_4]}{\Delta t} = +\frac{1}{6}\left(\frac{\Delta[H_2]}{\Delta t}\right)$$

Example 15.2—Rate of Reaction

Problem Data collected on the concentration of dye as a function of time (see Figure 15.1) are given in the graph below. What is the average rate of change of the dye concentration over the first 2 min? What is the average rate of change during the fifth minute (from $t = 4$ to $t = 5$)? Estimate the instantaneous rate at 4 min.

Strategy To find the average rate, calculate the difference in concentration at the beginning and end of a time period ($\Delta c = c_{\text{final}} - c_{\text{initial}}$) and divide by the elapsed time. To find the instan-



taneous rate, draw a line tangent to the graph at the given time. The slope of the line (page 35) is the instantaneous rate. (*See also General ChemistryNow CD-ROM or website Screen 15.2.*)

Solution The concentration of dye decreases from 3.4×10^{-5} M at $t = 0$ min to 1.7×10^{-5} M at $t = 2.0$ min. The average rate of the reaction in this interval of time is

$$-\frac{\Delta[\text{Dye}]}{\Delta t} = -\frac{(1.7 \times 10^{-5}\ \text{mol/L}) - (3.4 \times 10^{-5}\ \text{mol/L})}{2.0\ \text{min}} = \boxed{+\frac{8.5 \times 10^{-6}\ \text{mol}}{\text{L} \cdot \text{min}}}$$

The concentration of dye decreases from 0.90×10^{-5} M at $t = 4.0$ min to 0.60×10^{-5} M at $t = 5.0$ min. The average rate of the reaction in this interval of time is

$$-\frac{\Delta[\text{Dye}]}{\Delta t} = -\frac{(0.60 \times 10^{-5}\ \text{mol/L}) - (0.90 \times 10^{-5}\ \text{mol/L})}{1.0\ \text{min}} = \boxed{-\frac{3.0 \times 10^{-6}\ \text{mol}}{\text{L} \cdot \text{min}}}$$

Finally, from the slope of the line tangent to the curve, the instantaneous rate at 4 min is $\boxed{+3.5 \times 10^{-6}\ \text{mol/L} \cdot \text{min}}$.

Comment Notice that the average rate of reaction in the 4- to 5-min interval is less than half the value in the first minute.

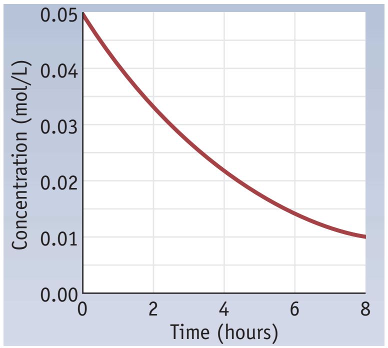
Exercise 15.1—Reaction Rates and Stoichiometry

What are the relative rates of appearance or disappearance of each product and reactant, respectively, in the decomposition of nitrosyl chloride, NOCl?

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

Exercise 15.2—Rate of Reaction

Sucrose decomposes to fructose and glucose in acid solution. A plot of the concentration of sucrose as a function of time is given here. What is the rate of change of the sucrose concentration over the first 2 h? What is the rate of change over the last 2 h? Estimate the instantaneous rate at 4 h.



Concentration versus time for the decomposition of sucrose. See Exercise 15.2.

15.2—Reaction Conditions and Rate

For a chemical reaction to occur, molecules of the reactants must come together so that atoms can be exchanged or rearranged. Atoms and molecules are mobile in the gas phase or in solution, so reactions are often carried out using a mixture of gases or using solutions of reactants. Under these circumstances, several factors—reactant concentrations, temperature, and presence of catalysts—affect the speed of a reaction. If the reactant is a solid, the surface area available for reaction will also affect the rate of reaction.

The "iodine clock reaction" in Figure 15.3 illustrates the effect of concentration and temperature. The reaction mixture contains hydrogen peroxide (H_2O_2), iodide ion (I^-), vitamin C (ascorbic acid), and starch (which is an indicator of the presence of iodine, I_2). A sequence of reactions begins with the slow oxidation of iodide ion to I_2 by H_2O_2.

Effect of Temperature on Reaction Rate
Cooking involves chemical reactions, and a higher temperature results in foods cooking faster. In the laboratory, reaction mixtures are often heated to make reactions occur faster.

$$H_2O_2(aq) + 2\ I^-(aq) + 2\ H^+(aq) \longrightarrow 2\ H_2O(\ell) + I_2(aq)$$

As soon as I_2 is formed in the solution, vitamin C rapidly reduces it to I^-.

$$I_2(aq) + C_6H_8O_6(aq) \longrightarrow C_6H_6O_6(aq) + 2\ H^+(aq) + 2\ I^-(aq)$$

When all of the vitamin C has been consumed, I_2 remains in solution and forms a blue-black complex with starch. The time measured represents how long it has taken for the given amount of vitamin C to react. For the first experiment (A), the time required is 51 seconds. When the concentration of iodide ion is smaller (B), the time required for the vitamin C to be consumed is longer, 1 minute and 33 seconds. Finally, when the concentrations are again the same as in experiment B but the reaction mixture is heated, the reaction occurs more rapidly (56 seconds).

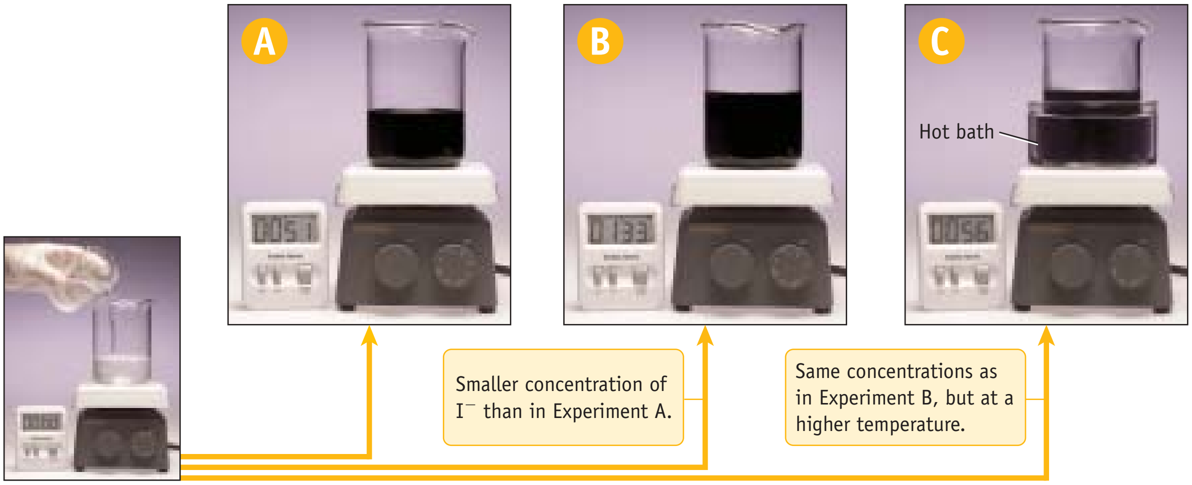
Catalysts are substances that accelerate chemical reactions but are not themselves transformed. For example, hydrogen peroxide, H_2O_2, decomposes to water and oxygen,

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

(a) Initial Experiment. The blue color of the starch-iodine complex develops in 51 seconds.

(b) Change Concentration. The blue color of starch-iodine complex develops in 1 minute, 33 seconds when the solution is less concentrated than A.

(c) Change Temperature. The blue color of the starch-iodine complex develops in 56 seconds when the solution is less concentrated than A but at a higher temperature.



Smaller concentration of I^- than in Experiment A.

Same concentrations as in Experiment B, but at a higher temperature.

Solutions containing vitamin C, H_2O_2, I^-, and starch are mixed.

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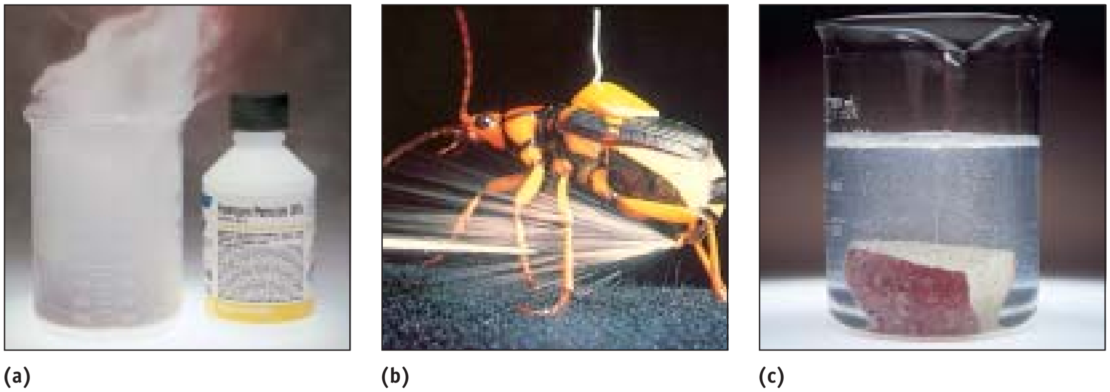
Figure 15.3 The iodine clock reaction. This reaction illustrates the effects of concentration and temperature on reaction rate. (You can do these experiments yourself with reagents available in the supermarket. For details see S. W. Wright: "The vitamin C clock reaction," *Journal of Chemical Education*, Vol. 79, p. 41, 2002.) (*See also General ChemistryNow CD-ROM or website Screen 15.11.*)



a and *c*, Charles D. Winters; *b*, Thomas Eisner with Daniel Aneshansley, Cornell University

Figure 15.4 **Catalyzed decomposition of H_2O_2.** (a) The rate of decomposition of hydrogen peroxide is increased by the catalyst MnO_2. Here a 30% solution of H_2O_2, poured onto the black solid MnO_2, rapidly decomposes to O_2 and H_2O. Steam forms because of the high heat of reaction. (b) A bombardier beetle uses the catalyzed decomposition of H_2O_2 as a defense mechanism. The heat of the reaction lets the insect eject hot water and other irritating chemicals with explosive force. (c) A naturally occurring catalyst, called an enzyme, decomposes hydrogen peroxide. Here the enzyme found in a potato is used to catalyze H_2O_2 decomposition, and bubbles of O_2 gas are seen rising in the solution.

but a solution of H_2O_2 can be stored for many months because the rate of the decomposition reaction is extremely slow. Adding a manganese salt, an iodide-containing salt, or a biological substance called an *enzyme* causes this reaction to occur rapidly, as shown by vigorous bubbling as gaseous oxygen escapes from the solution (Figure 15.4).

The surface area of a solid reactant can also affect the reaction rate. Only molecules at the surface of a solid can come in contact with other reactants. The smaller the particles of a solid, the more molecules found on the solid's surface. With very small particles, the effect of surface area on rate can be quite dramatic (Figure 15.5). Farmers know that explosions of fine dust particles (suspended in the air in an enclosed silo or at a feed mill) represent a major hazard.

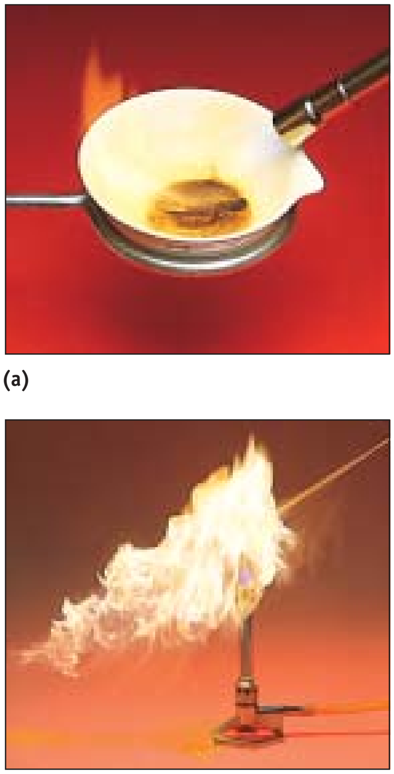


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Figure 15.5 **The combustion of lycopodium powder.** (a) The spores of this common fern burn only with difficulty when piled in a dish. (b) If the spores are ground to a fine powder and sprayed into a flame, combustion is rapid.

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See the General ChemistryNow CD-ROM or website:

- **Screens 15.3 and 15.4 Control of Reaction Rates,** for a visualization of the factors controlling rates and for a simulation of the effect of concentration on rate

15.3—Effect of Concentration on Reaction Rate

One important goal in studying kinetics is to determine how concentrations of reactants affect the reaction rate. The effects can be determined by evaluating the rate of a reaction using different concentrations of each reactant (with the temperature held constant). Consider, for example, the decomposition of N_2O_5 to NO_2 and O_2. Figure 15.2 presents data on the concentration of N_2O_5 as a function of time. We previously calculated that, when $[N_2O_5] = 0.34$ mol/L, the instantaneous rate of disappearance of N_2O_5 is 0.0014 mol/L · min. An evaluation of the instantaneous rate of the reaction when $[N_2O_5] = 0.68$ mol/L reveals a rate of 0.0028 mol/L · min. That is, doubling the concentration of N_2O_5 doubles the reaction rate. A similar exercise shows that if $[N_2O_5]$ is halved to 0.17 mol/L, the reaction rate is also halved.

These results tell us that the reaction rate is directly proportional to the reactant concentration for this reaction:

$$\text{Rate of reaction} \propto [N_2O_5]$$

where the symbol $\propto$ means "proportional to."

Different relationships between reaction rate and reactant concentration are encountered in other reactions. For example, the reaction rate could be independent of concentration, or it may depend on the reactant concentration raised to some power (that is, $[\text{reactant}]^n$). If the reaction involves several reactants, the reaction rate may depend on the concentrations of each of them or on only one of them. Finally, if a catalyst is involved, its concentration may also affect the rate.

Rate Equations

The relationship between reactant concentration and reaction rate is expressed by an equation called a **rate equation**, or **rate law**. For the decomposition of N_2O_5 the rate equation is

$$\text{Rate of reaction} = k[N_2O_5]$$

where the proportionality constant, k, is called the **rate constant**. This rate equation tells us that this reaction rate is proportional to the concentration of the reactant. That is, when $[N_2O_5]$ is doubled, the reaction doubles, for example.

In general, for a reaction such as

$$a\,A + b\,B \longrightarrow x\,X$$

the rate equation has the form

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

The rate equation expresses the fact that the rate of reaction is proportional to the reactant concentrations, each concentration being raised to some power. It is important to recognize that the exponents m and n are *not necessarily the stoichiometric coefficients* (a and b) for the balanced chemical equation. *The exponents must be determined by experiment.* They are often positive whole numbers, but they can also be negative numbers, fractions, or zero.

If a homogeneous catalyst is present, its concentration might also be included in the rate equation, even though the catalytic species does not appear in the balanced, overall equation for the reaction. Consider, for example, the decomposition of hydrogen peroxide in the presence of a catalyst such as iodide ion.

$$2\,H_2O_2(aq) \xrightarrow{I^-(aq)} 2\,H_2O(\ell) + O_2(g)$$

Experiments show that this reaction has the following rate equation:

$$\text{Reaction rate} = k[H_2O_2][I^-]$$

Here the exponent on each concentration term is 1, even though the stoichiometric coefficient of H_2O_2 is 2 and I^- does not appear in the balanced equation.

The Nature of Catalysts
A catalyst does not appear as a reactant in the balanced, overall equation for the peroxide decomposition reaction, but it may appear in the rate expression. It is common practice to indicate catalysts by placing them above the reaction arrow, as shown in the example. A homogeneous catalyst is one in the same phase as the reactants. For example, both H_2O_2 and I^- are dissolved in water.

The Order of a Reaction

The **order** of a reaction with respect to a particular reactant is the exponent of its concentration term in the rate expression, and the total reaction order is the sum

Overall Reaction Order
The overall reaction order is the sum of the reaction orders of the different reactants.

of the exponents on all concentration terms. For example, the rate equation for the decomposition of H_2O_2 in the presence of iodide ion,

$$\text{Reaction rate} = k[H_2O_2][I^-]$$

shows that the reaction is first order with respect to H_2O_2 and also with respect to I^-; it is second order overall. This tells us that the rate doubles if either $[H_2O_2]$ or $[I^-]$ is doubled and that the rate increases by a factor of 4 if both concentrations are doubled.

Consider another example, the reaction of NO and Cl_2:

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

The rate equation for this reaction is

$$\text{Rate} = k[NO]^2[Cl_2]$$

This reaction is second order in NO, first order in Cl_2, and third order overall. We can see how this rate equation is related to experimental data by examining some data for the rate of disappearance of NO.

Experiment	**[NO] mol/L**	**[Cl_2] mol/L**	**Rate mol/L · s**
1	0.250	0.250	1.43×10^{-6}
	↓ × 2	↓ no change	↓ × 4
2	0.500	0.250	5.72×10^{-6}
3	0.250	0.500	2.86×10^{-6}
4	0.500	0.500	11.4×10^{-6}

- *Experiments 1 and 2:* If $[Cl_2]$ is held constant and [NO] is doubled from 0.250 mol/L to 0.500 mol/L, the reaction rate increases by a factor of 4 (from 1.43×10^{-6} mol/L · s to 5.72×10^{-6} mol/L · s).

$$\frac{\text{Rate for experiment 2}}{\text{Rate for experiment 1}} = \frac{5.72 \times 10^{-6}\ \text{mol/L} \cdot \text{s}}{1.43 \times 10^{-6}\ \text{mol/L} \cdot \text{s}} = \frac{4}{1}$$

- *Experiments 1, 3, and 4*: Comparing experiments 1 and 3, we see that, when [NO] is held constant and $[Cl_2]$ is doubled from 0.250 mol/L to 0.500 mol/L, the rate is doubled. Comparing experiments 1 and 4, we see that if both [NO] and $[Cl_2]$ are doubled from 0.250 M to 0.500 M, then the rate (11.4×10^{-5} mol/L · s) is 8 times the original value.

The decomposition of ammonia on a platinum surface at 856 °C is interesting because it is zero order.

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

This means that the reaction rate is independent of NH_3 concentration.

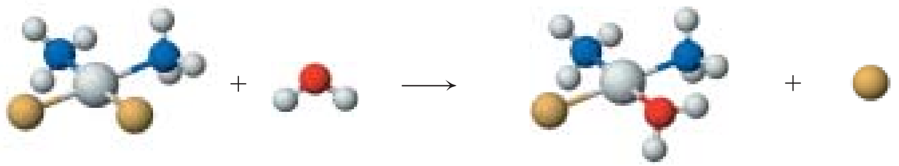
$$\text{Rate} = k[NH_3]^0 = k$$

The reaction order is important because it gives some insight into the most interesting question of all—how the reaction occurs. This is described further in Section 15.6.

The Rate Constant, *k*

The rate constant, k, is a proportionality constant that relates rate and concentration *at a given temperature*. It is an important quantity because it enables you to find the reaction rate for a new set of concentrations. To see how to use k, consider the substitution of Cl^- ion by water in the cancer chemotherapy agent cisplatin, $Pt(NH_3)_2Cl_2$.

$$Pt(NH_3)_2Cl_2(aq) + H_2O(\ell) \longrightarrow [Pt(NH_3)_2(H_2O)Cl]^+(aq) + Cl^-(aq)$$



Time and Rate Constants
The time in a rate constant can be seconds, minutes, hours, days, years, or whatever time unit is appropriate.

The rate expression for this reaction is

$$\text{Rate} = k[Pt(NH_3)_2Cl_2]$$

and the rate constant, k, is 0.090/h. Knowing k allows you to calculate the rate at a particular reactant concentration—for example, when $[Pt(NH_3)_2Cl_2] = 0.018$ mol/L:

$$\text{Rate} = (0.090/\text{h})(0.018 \text{ mol/L}) = 0.0016 \text{ mol/L} \cdot \text{h}$$

Reaction rates ($\Delta[R]/\Delta t$) have units of mol/L · time when concentrations are given as moles per liter. Rate constants must have units consistent with the units for the other terms in the rate equation.

- First-order reactions: the units of k are time^{-1}.
- Second-order reactions: the units of k are L/mol · time.
- Zero-order reaction: the units of k are mol/L · time.

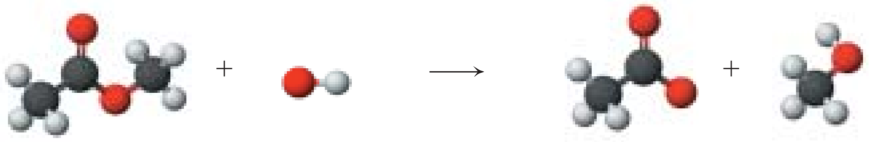
Expressing Time and Rate
The fraction 1/time can also be written as time^{-1}. For example, 1/y is equivalent to y^{-1}, and 1/s is equivalent to s^{-1}.

Determining a Rate Equation

A rate equation must be determined experimentally. One way to do so is by using the "method of initial rates." The **initial rate** is the instantaneous reaction rate at the start of the reaction (the rate at $t = 0$). An approximate value of the initial rate can be obtained by mixing the reactants and determining $\Delta[\text{product}]/\Delta t$ or $-\Delta[\text{reactant}]/\Delta t$ after 1% to 2% of the limiting reactant has been consumed. Measuring the rate during the initial stage of a reaction is convenient because initial concentrations are known, and this method avoids possible complications arising from interference by reaction products or the occurrence of side reactions.

As an example of the determination of a reaction rate by this method, let us look at the reaction of sodium hydroxide with methyl acetate to produce acetate ion and methanol.

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



Data in the table were collected for several experiments at 25 °C:

	Initial Concentrations		
Experiment	**[$CH_3CO_2CH_3$]**	**[OH^-]**	**Initial Reaction Rate (mol/L · s) at 25 °C**
1	0.050 M	0.050 M	0.00034
	↓ no change	↓ × 2	↓ × 2
2	0.050 M	0.10 M	0.00069
	↓ × 2	↓ no change	↓ × 2
3	0.10 M	0.10 M	0.00137

This table shows that when the initial concentration of one reactant (either $CH_3CO_2CH_3$ or OH^-) is doubled while the concentration of the other reactant is held constant, the initial reaction rate doubles. This rate doubling shows that the rate for the reaction is directly proportional to the concentrations of *both* $CH_3CO_2CH_3$ and OH^-; thus, the reaction is first order in each of these reactants. The rate equation that reflects these experimental observations is

$$\text{Rate} = k[\text{CH}_3\text{CO}_2\text{CH}_3][\text{OH}^-]$$

Using this equation we can predict that doubling *both* concentrations at the same time should cause the rate to go up by a factor of 4. What happens, however, if one concentration is doubled and the other is halved? The rate equation tells us the rate should not change!

If the rate equation is known, the value of k, the rate constant, can be found by substituting values for the rate and concentration into the rate equation. To find k for the methyl acetate/hydroxide ion reaction, for example, data from one of the experiments are substituted into the rate equation. Using the data from the first experiment, we have

$$\text{Rate} = 0.00034 \text{ mol/L} \cdot \text{s} = k(0.050 \text{ mol/L})(0.050 \text{ mol/L})$$

$$k = \frac{0.00034 \text{ mol/L} \cdot \text{s}}{(0.050 \text{ mol/L})(0.050 \text{ mol/L})} = 0.14 \text{ L/mol} \cdot \text{s}$$

GENERAL ChemistryNow™

See the General ChemistryNow CD-ROM or website:

- **Screen 15.4 Control of Reaction Rates (2) and Screen 15.5 Determination of the Rate Equation (1),** for a simulation, tutorial, and exercise on determining rate equations from a study of the effect of concentration on reaction rate

Example 15.3—Determining a Rate Equation

Problem The rate of the reaction between CO and NO_2

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

was studied at 540 K starting with various concentrations of CO and NO_2, and the data in the table were collected. Determine the rate equation and the value of the rate constant.

	Initial Concentrations		
Experiment	[CO], mol/L	$[NO_2]$, mol/L	Initial Rate (mol/L · h)
1	5.10×10^{-4}	0.350×10^{-4}	3.4×10^{-8}
2	5.10×10^{-4}	0.700×10^{-4}	6.8×10^{-8}
3	5.10×10^{-4}	0.175×10^{-4}	1.7×10^{-8}
4	1.02×10^{-3}	0.350×10^{-4}	6.8×10^{-8}
5	1.53×10^{-3}	0.350×10^{-4}	10.2×10^{-8}

Strategy For a reaction involving several reactants, the general approach is to keep the concentration of one reactant constant and then decide how the rate of reaction changes as the concentration of the other reagent is varied. Because the rate is proportional to the concentration of a reactant, say A, raised to some power *n* (the reaction order)

$$\text{Rate} \propto [\text{A}]^n$$

we can write the general equation

$$\frac{\text{Rate in experiment 2}}{\text{Rate in experiment 1}} = \frac{[\text{A}_2]^n}{[\text{A}_1]^n} = \left(\frac{[\text{A}_2]}{[\text{A}_1]}\right)^n$$

If [A] doubles ($[\text{A}_2] = 2[\text{A}_1]$), and the rate doubles from experiment 1 to experiment 2, then $n = 1$. If [A] doubles, and the rate goes up by 4, then $n = 2$.

Solution In the first three experiments, the concentration of CO remains constant. In the second experiment, the NO_2 concentration has been doubled relative to Experiment 1, leading to a twofold increase in the rate. Thus, $n = 1$ and the reaction is first order in NO_2.

$$\frac{6.8 \times 10^{-8}\ \text{mol/L} \cdot \text{h}}{3.4 \times 10^{-8}\ \text{mol/L} \cdot \text{h}} = \left(\frac{0.700 \times 10^{-4}}{0.350 \times 10^{-4}}\right)^n$$

$$2 = (2)^n$$

and so $n = 1$.

This finding is confirmed by experiment 3. Decreasing $[NO_2]$ to half its original value in experiment 3 causes the rate to decrease by half.

The data in experiments 1 and 4 (with constant $[NO_2]$) show that doubling [CO] doubles the rate, and the data from experiments 1 and 5 show that tripling the concentration of CO triples the rate. These results mean that the reaction is also first order in [CO]. We now know the rate equation is

$$\text{Rate} = k[\text{CO}][\text{NO}_2]$$

The rate constant, *k*, can be found by inserting data for one of the experiments into the rate equation. Using data from experiment 1, for example,

$$\text{Rate} = 3.4 \times 10^{-8}\ \text{mol/L} \cdot \text{h} = k(5.10 \times 10^{-4}\ \text{mol/L})(0.350 \times 10^{-4}\ \text{mol/L})$$

$$k = 1.9\ \text{L/mol} \cdot \text{h}$$

Example 15.4—Using a Rate Equation to Determine Rates

Problem Using the rate equation and rate constant determined for the reaction of CO and NO_2 at 540 K in Example 15.3, determine the initial rate of the reaction when $[\text{CO}] = 3.8 \times 10^{-4}$ and $[\text{NO}_2] = 0.650 \times 10^{-4}$.

Strategy A rate equation consists of three parts: a rate, a rate constant (*k*), and the concentration terms. If two of these parts are known (here *k* and the concentrations), the third can be calculated.

Solution Substitute k (= 1.9 L/mol · h) and the concentration of each reactant into the rate law determined in Example 15.3.

$$\text{Rate} = k[\text{CO}][\text{NO}_2] = (1.9\ \text{L/mol}\cdot\text{h})(3.8 \times 10^{-4}\ \text{mol/L})(0.650 \times 10^{-4}\ \text{mol/L})$$

$$\text{Rate} = 4.7 \times 10^{-8}\ \text{mol/L}\cdot\text{h}$$

Comment As a check on the calculated result, it is sometimes useful to make an educated guess at the answer before carrying out the mathematical solution. We know that the reaction here is first order in both reactants. Comparing the concentration values given in this problem with the concentration values in found experiment 1 in Example 15.3, we notice that [CO] is about three fourths of the concentration value, whereas $[\text{NO}_2]$ is almost twice the value. The effects do not precisely offset each other, but we might predict that the difference in rates between this experiment and experiment 1 will be fairly small, with the rate of this experiment being just a little greater. The calculated value bears this out.

Exercise 15.3—Determining a Rate Equation

The initial rate of the reaction of nitrogen monoxide and oxygen

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

was measured at 25 °C for various initial concentrations of NO and O_2. Data are collected in the table. Determine the rate equation from these data. What is the value of the rate constant, k, and what are its units?

	Initial Concentrations (mol/L)		Initial Rate
Experiment	[NO]	[O_2]	(mol/L · s)
1	0.020	0.010	0.028
2	0.020	0.020	0.057
3	0.020	0.040	0.114
4	0.040	0.020	0.227
5	0.010	0.020	0.014

Exercise 15.4—Using Rate Laws

The rate constant, k, is 0.090 h^{-1} for the reaction

$$\text{Pt(NH}_3)_2\text{Cl}_2\text{(aq)} + \text{H}_2\text{O}(\ell) \longrightarrow [\text{Pt(NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+\text{(aq)} + \text{Cl}^-\text{(aq)}$$

and the rate equation is

$$\text{Rate} = k[\text{Pt(NH}_3)_2\text{Cl}_2]$$

Calculate the rate of reaction when the concentration of $Pt(NH_3)_2Cl_2$ is 0.020 M. What is the rate of change in the concentration of Cl^- under these conditions?

15.4—Concentration–Time Relationships: Integrated Rate Laws

It is often useful or important to know how long a reaction must proceed to reach a predetermined concentration of some reactant or product, or what the reactant and product concentrations will be after some time has elapsed. One way to make this determination is to use a mathematical equation that relates time and concentration. That is, we would like to have an equation that will describe concentration–time curves like the one shown in Figure 15.2. With such an equation we could calculate a concentration at any given time or the length of time needed for a given amount of reactant to react.

First-Order Reactions

Suppose the reaction "R ⟶ products" is first order. This means the reaction rate is directly proportional to the concentration of R raised to the first power, or, mathematically,

$$-\frac{\Delta[\mathrm{R}]}{\Delta t} = k[\mathrm{R}]$$

Using calculus, this relationship can be transformed into a very useful equation called an **integrated rate equation** (because integral calculus is used in its derivation).

$$\ln \frac{[\mathrm{R}]_t}{[\mathrm{R}]_0} = -kt \qquad (15.1)$$

Initial and Final Time, *t*
The time $t = 0$ does not need to correspond to the actual beginning of the experiment. It can be the time when instrument readings were started, for example.

Here $[\mathrm{R}]_0$ and $[\mathrm{R}]_t$ are concentrations of the reactant at time $t = 0$ and at a later time, *t*, respectively. The *ratio* of concentrations, $[\mathrm{R}]_t/[\mathrm{R}]_0$, is the fraction of reactant that *remains* after a given time has elapsed. In words, the equation says

$$\text{Natural logarithm}\left(\frac{\text{concentration of R after some time}}{\text{concentration of R at start of experiment}}\right)$$
$$= \ln\,(\text{fraction remaining at time, } t)$$
$$= -(\text{rate constant})(\text{elapsed time})$$

Notice the negative sign in the equation. The ratio $[\mathrm{R}]_t/[\mathrm{R}]_0$ is less than 1 because $[\mathrm{R}]_t$ is always less than $[\mathrm{R}]_0$; the reactant R is consumed during the reaction. This means the logarithm of $[\mathrm{R}]_t/[\mathrm{R}]_0$ is negative, so the other side of the equation must also bear a negative sign.

Equation 15.1 is useful in three ways:

- If $[\mathrm{R}]_t/[\mathrm{R}]_0$ is measured in the laboratory after some amount of time has elapsed, then *k* can be calculated.
- If $[\mathrm{R}]_0$ and *k* are known, then the concentration of material expected to remain after a given amount of time ($[\mathrm{R}]_t$) can be calculated.
- If *k* is known, then the time elapsed until a specific fraction ($[\mathrm{R}]_t/[\mathrm{R}]_0$) remains can be calculated.

Finally, notice that *k* for a first-order reaction is independent of concentration; *k* has units of time^{-1} (y^{-1} or s^{-1}, for example). This means we can choose any convenient unit for $[\mathrm{R}]_t$ and $[\mathrm{R}]_0$: moles per liter, moles, grams, number of atoms, number of molecules, or pressure.

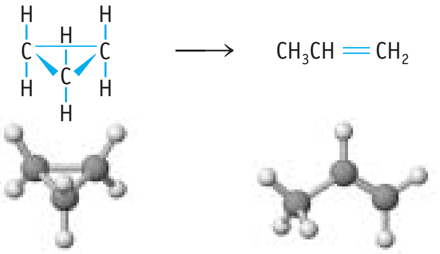
GENERAL Chemistry Now™

See the General ChemistryNow CD-ROM or website:

- **Screen 15.6 Concentration–Time Relationships,** for a tutorial on the use of the integrated first-order rate equation

Example 15.5—The First-Order Rate Equation

Problem In the past cyclopropane, C_3H_6, was used in a mixture with oxygen as an anesthetic. (This practice has almost ceased today, because the compound is very flammable.) When heated, cyclopropane rearranges to propene in a first-order process.



$$\text{Rate} = k[\text{cyclopropane}] \qquad k = 5.4 \times 10^{-2}\ \text{h}^{-1}$$

If the initial concentration of cyclopropane is 0.050 mol/L, how much time (in hours) must elapse for its concentration to drop to 0.010 mol/L?

Strategy The reaction is first order in cyclopropane. You know the rate constant, k, and the concentrations at $t = 0$ and after some time has elapsed. Use Equation 15.1 to calculate the time (t) elapsed to reach a concentration of 0.010 mol/L.

Solution The first-order rate equation applied to this reaction is

$$\ln \frac{[\text{cyclopropane}]_t}{[\text{cyclopropane}]_0} = -kt$$

Values for $[\text{cyclopropane}]_t$, $[\text{cyclopropane}]_0$, and k are given:

$$\ln \frac{[0.010]}{[0.050]} = -(5.4 \times 10^{-2}\ \text{h}^{-1})t$$

$$t = \frac{-\ln(0.20)}{5.4 \times 10^{-2}\ \text{h}^{-1}} = \frac{-(-1.61)}{5.4 \times 10^{-2}\ \text{h}^{-1}} = 30.\ \text{h}$$

Comment Cycloalkanes with fewer than five carbon atoms are strained because the C—C—C bond angles cannot match the preferred 109.5°. As a consequence of this ring strain, the ring opens readily to form propene.

Example 15.6—Using the First-Order Rate Equation

Problem Hydrogen peroxide decomposes in dilute sodium hydroxide at 20 °C in a first-order reaction:

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

$$\text{Rate} = k[H_2O_2] \qquad k = 1.06 \times 10^{-3}\ \text{min}^{-1}$$

What is the fraction remaining after exactly 100 min if the initial concentration of H_2O_2 is 0.020 mol/L? What is the concentration of the peroxide after exactly 100 min?

Strategy Because the reaction is first order in H_2O_2, we use Equation 15.1. Here $[H_2O_2]_0$, k, and t are known, and we are asked to find $[H_2O_2]_t$. Recall that

$$\frac{[R]_t}{[R]_0} = \text{fraction remaining}$$

Therefore, once this value is known, and knowing $[H_2O_2]_0$, we can calculate $[H_2O_2]_t$. *(See General ChemistryNow CD-ROM or website Screen 15.6.)*

Solution Substitute the known values into Equation 15.1.

$$\ln \frac{[H_2O_2]_t}{[H_2O_2]_0} = -kt = -(1.06 \times 10^{-3}\ \text{min}^{-1})(100\ \text{min})$$

$$\ln \frac{[H_2O_2]_t}{[H_2O_2]_0} = -0.106$$

Taking the antilogarithm of −0.106 [i.e., the inverse of ln (−0.106) or $e^{-0.106}$], we find the fraction remaining to be 0.90.

$$\text{Fraction remaining} = \frac{[H_2O_2]_t}{[H_2O_2]_0} = 0.90$$

Because $[H_2O_2]_0 = 0.020$ mol/L, this gives

$$[H_2O_2]_t = 0.018\ \text{mol/L}$$

Exercise 15.5—Using the First-Order Rate Equation

Sucrose, a sugar, decomposes in acid solution to give glucose and fructose. The reaction is first order in sucrose, and the rate constant at 25 °C is $k = 0.21\ \text{h}^{-1}$. If the initial concentration of sucrose is 0.010 mol/L, what is its concentration after 5.0 h?

Exercise 15.6—Using the First-Order Rate Equation

Gaseous NO_2 decomposes when heated:

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

The disappearance of NO_2 is a first-order reaction with $k = 3.6 \times 10^{-3}\ \text{s}^{-1}$ at 300 °C.

(a) A sample of gaseous NO_2 is placed in a flask and heated at 300 °C for 150 s. What fraction of the initial sample remains after this time?

(b) How long must a sample be heated so that 99% of the sample has decomposed?

Second-Order Reactions

Suppose the reaction "R ⟶ products" is second order. The rate equation is

$$-\frac{\Delta[R]}{\Delta t} = k[R]^2$$

Using the methods of calculus, this relationship can be transformed into the following equation that relates reactant concentration and time:

$$\frac{1}{[R]_t} - \frac{1}{[R]_0} = kt \qquad (15.2)$$

The same symbolism used with first-order reactions applies: $[R]_0$ is the concentration of reactant at the time $t = 0$, $[R]_t$ is the concentration at a later time, and k is the second-order rate constant (with units of L/mol · time).

Example 15.7—Using the Second-Order Integrated Rate Equation

Problem The gas-phase decomposition of HI

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

has the rate equation

$$-\frac{\Delta[HI]}{\Delta t} = k[HI]^2$$

where $k = 30.$ L/mol · min at 443 °C. How much time does it take for the concentration of HI to drop from 0.010 mol/L to 0.0050 mol/L at 443 °C?

Strategy Substitute the values of $[HI]_0$, $[HI]_t$, and k into Equation 15.2.

Solution Here $[HI]_0 = 0.010$ mol/L and $[HI]_t = 0.0050$ mol/L. Using Equation 15.2, we have

$$\frac{1}{0.0050 \text{ mol/L}} - \frac{1}{0.010 \text{ mol/L}} = (30. \text{ L/mol} \cdot \text{min})t$$

$$(2.0 \times 10^2 \text{ L/mol}) - (1.0 \times 10^2 \text{ L/mol}) = (30. \text{ L/mol} \cdot \text{min})t$$

$$t = 3.3 \text{ min}$$

Exercise 15.7—Using the Second-Order Concentration–Time Equation

Using the rate constant for HI decomposition given in Example 15.7, calculate the concentration of HI after 12 min if $[HI]_0 = 0.010$ mol/L.

Zero-Order Reactions

If a reaction (R ⟶ products) is zero order, the rate equation is

$$-\frac{\Delta[R]}{\Delta t} = k[R]^0$$

This equation leads to the integrated rate equation

$$\boxed{[R]_0 - [R]_t = kt} \qquad (15.3)$$

where the units of k are mol/L · s.

Graphical Methods for Determining Reaction Order and the Rate Constant

Equations 15.1, 15.2, and 15.3 relating concentration and time for first-, second-, and zero-order reactions, respectively, suggest a convenient way to determine the order of a reaction and its rate constant. Rearranged slightly, each of these equations has the form $y = mx + b$. This is the equation for a straight line, where m is the slope of the line and b is the y-intercept (the value of y when x is zero) (page 35). As illustrated here, $x = t$ in each case.

Zero order	**First order**	**Second order**
$\underset{\substack{\downarrow \\ y}}{[R]_t} = \underset{\substack{\downarrow \\ mx}}{-kt} + \underset{\substack{\downarrow \\ b}}{[R]_0}$	$\underset{\substack{\downarrow \\ y}}{\ln [R]_t} = \underset{\substack{\downarrow \\ mx}}{-kt} + \underset{\substack{\downarrow \\ b}}{\ln [R]_0}$	$\underset{\substack{\downarrow \\ y}}{\frac{1}{[R]_t}} = \underset{\substack{\downarrow \\ mx}}{+kt} + \underset{\substack{\downarrow \\ b}}{\frac{1}{[R]_0}}$

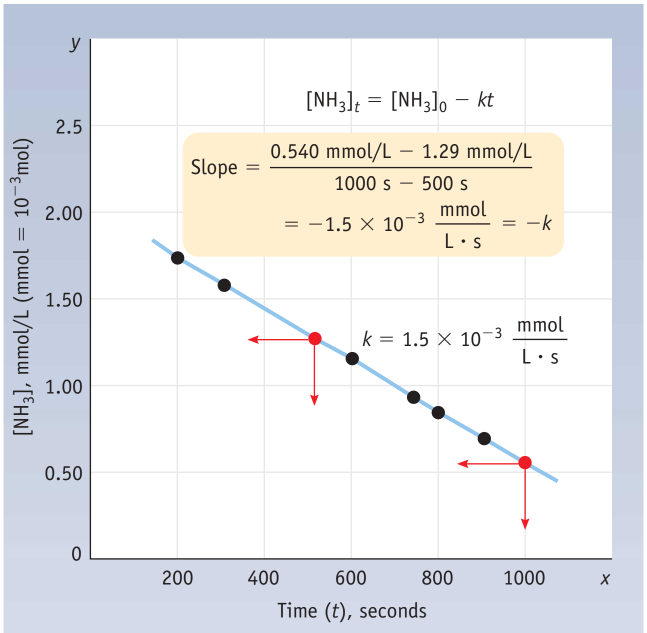


Figure 15.6 **Plot of a zero-order reaction.** A graph of the concentration of ammonia, $[NH_3]_t$, against time for the decomposition of NH_3

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

on a metal surface at 856 °C is a straight line, indicating that this is a zero-order reaction. The rate constant, k, for this reaction is found from the slope of the line; $k = -\text{slope}$. (The points chosen to calculate the slope are given in red.)

As an example of the use of a concentration/time equation, consider the zero-order decomposition of ammonia on a platinum surface.

$$2\ NH_3(g) \longrightarrow N_2(g) + 3\ H_2(g) \qquad \text{Rate} = k[NH_3]^0 = k$$

The rate here is proportional to the ammonia concentration to the zero power, which is 1. That is, the reaction rate is independent of NH_3 concentration. The straight line, obtained when the concentration at time t, $[R]_t$, is plotted against time (Figure 15.6), is proof that this reaction is zero order in NH_3 concentration. The rate constant, k, can be determined from the slope of the line. Here the slope $= -k$, so in this case

$$-k = -1.5 \times 10^{-3} \text{ mmol/L} \cdot \text{s}$$
$$k = 1.5 \times 10^{-3} \text{ mmol/L} \cdot \text{s}$$

The intercept of the line at $t = 0$ is equal to $[R]_0$.

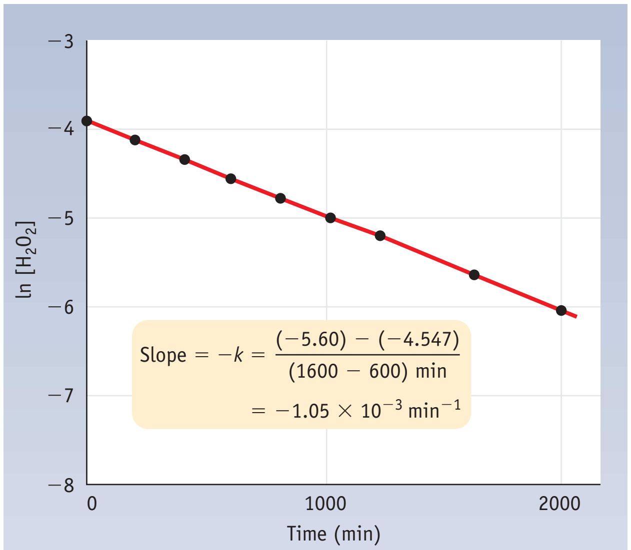
A plot of concentration versus time for a first-order reaction is always a curved line (see Figure 15.2). Plotting ln [reactant] versus time, however, produces a straight line with a negative slope when the reaction is first order in that reactant. Consider the decomposition of hydrogen peroxide, a first-order reaction referred to earlier in Example 15.6.

$$2\ H_2O_2(aq) \longrightarrow 2\ H_2O(\ell) + O_2(g)$$
$$\text{Rate} = k\,[H_2O_2]$$

Values of the concentration of H_2O_2 as a function of time for a typical experiment are given as the first two columns of numbers in Figure 15.7. The third column lists values of ln $[H_2O_2]$. A graph of ln $[H_2O_2]$ versus time produces a straight line, showing that the reaction is first order in H_2O_2. The negative of the slope of the line equals the rate constant for the reaction, $1.05 \times 10^{-3}\ \text{min}^{-1}$.

■ **Finding the Slope of a Line**
See Section 1.8 for a description of methods for finding the slope of a line. The graphing program on the General ChemistryNOW CD-ROM or website will also give the slope of a line from experimental data.

Time (min)	$[H_2O_2]$ mol/L	$\ln [H_2O_2]$
0	0.0200	−3.912
200	0.0160	−4.135
400	0.0131	−4.335
600	0.0106	−4.547
800	0.0086	−4.76
1000	0.0069	−4.98
1200	0.0056	−5.18
1600	0.0037	−5.60
2000	0.0024	−6.03



Active Figure 15.7 **The decomposition of H_2O_2.** If data for the decomposition of hydrogen peroxide,

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

are plotted as the natural logarithm of the H_2O_2 concentration versus time, the result is a straight line with a negative slope. This indicates a first-order reaction. The rate constant $k = -\text{slope}$.

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The decomposition of NO_2 is a second-order process.

$$NO_2(g) \longrightarrow NO(g) + \tfrac{1}{2}\ O_2(g)$$
$$\text{Rate} = k[NO_2]^2$$

This fact can be verified by showing that a plot of $1/[NO_2]$ versus time is a straight line (Figure 15.8). Here the slope of the line is equal to *k*.

To determine the reaction order, therefore, a chemist will plot the experimental concentration–time data in different ways until a straight-line plot is achieved. The mathematical relationships for zero-, first-, and second-order reactions are summarized in Table 15.1.

Figure 15.8 **A second-order reaction.** A plot of $1/[NO_2]$ versus time for the decomposition of NO_2,

$$NO_2(g) \longrightarrow NO(g) + \tfrac{1}{2}\ O_2(g)$$

results in a straight line. This confirms that this is a second-order reaction. The slope of the line equals the rate constant for this reaction.

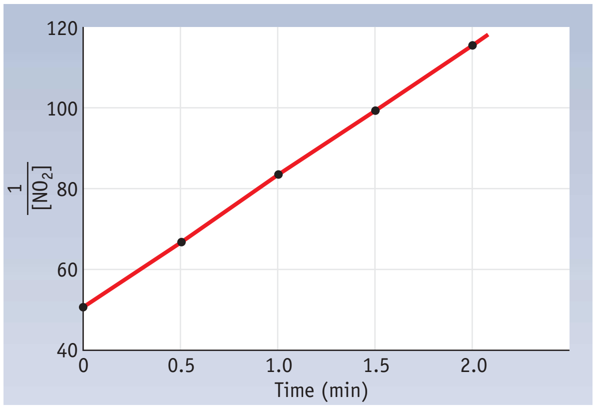

Table 15.1 Characteristic Properties of Reactions of the Type "R $\longrightarrow$ Products"

Order	Rate Equation	Integrated Rate Equation	Straight-Line Plot	Slope	*k* Units
0	$-\Delta[R]/\Delta T = k[R]^0$	$[R]_0 - [R]_t = kt$	$[R]_t$ vs. t	$-k$	mol/L · time
1	$-\Delta[R]/\Delta T = k[R]^1$	$\ln([R]_t/[R]_0) = -kt$	$\ln [R]_t$ vs. t	$-k$	time^{-1}
2	$-\Delta[R]/\Delta T = k[R]^2$	$(1/[R]_t) - (1/[R]_0) = kt$	$1/[R]_t$ vs. t	k	L/mol · time

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See the General ChemistryNow CD-ROM or website

- **Screen 15.7 Determination of Rate Equation (2),** for a tutorial on graphical methods

Exercise 15.8—Using Graphical Methods

Data for the decomposition of N_2O_5 in a particular solvent at 45 °C are as follows:

$[N_2O_5]$, mol/L	*t*, min
2.08	3.07
1.67	8.77
1.36	14.45
0.72	31.28

Plot $[N_2O_5]$, $\ln [N_2O_5]$, and $1/[N_2O_5]$ versus time, t. What is the order of the reaction? What is the rate constant for the reaction?

Half-Life and First-Order Reactions

The **half-life, $t_{1/2}$,** of a reaction is the time required for the concentration of a reactant to decrease to one-half its initial value. It indicates the rate at which a reactant is consumed in a chemical reaction: The longer the half-life, the slower the reaction. Half-life is used primarily when dealing with first-order processes.

The half-life, $t_{1/2}$, is the time when the fraction remaining of the reactant R is $\frac{1}{2}$.

$$[R]_t = \frac{1}{2}[R]_0 \quad \text{or} \quad \frac{[R]_t}{[R]_0} = \frac{1}{2}$$

Here $[R]_0$ is the initial concentration, and $[R]_t$ is the concentration after the reaction is half completed. To evaluate $t_{1/2}$ for a first-order reaction, we substitute $[R]_t/[R]_0 = \frac{1}{2}$ and $t = t_{1/2}$ into the integrated first-order rate equation (Equation 15.1),

$$\ln \frac{[R]_t}{[R]_0} = -kt$$

$$\ln\left(\tfrac{1}{2}\right) = -kt_{1/2}$$

Rearranging this equation (and knowing that $\ln 2 = 0.693$), we have a useful equation that relates half-life and the first-order rate constant:

$$\boxed{t_{1/2} = \frac{0.693}{k}} \qquad (15.4)$$

Half-Life and Radioactivity Half-life is a term often encountered when dealing with radioactive elements. Radioactive decay is a first-order process, and half-life is commonly used to describe how rapidly a radioactive element decays. See Chapter 23 and Example 15.9.

Half-Life Equations for Other Reaction Orders

For a zero-order reaction,

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

For a second-order reaction,

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

This equation identifies an important feature of first-order reactions: $t_{1/2}$ is *independent* of concentration.

To illustrate the concept of half-life, consider the first-order decomposition of H_2O_2:

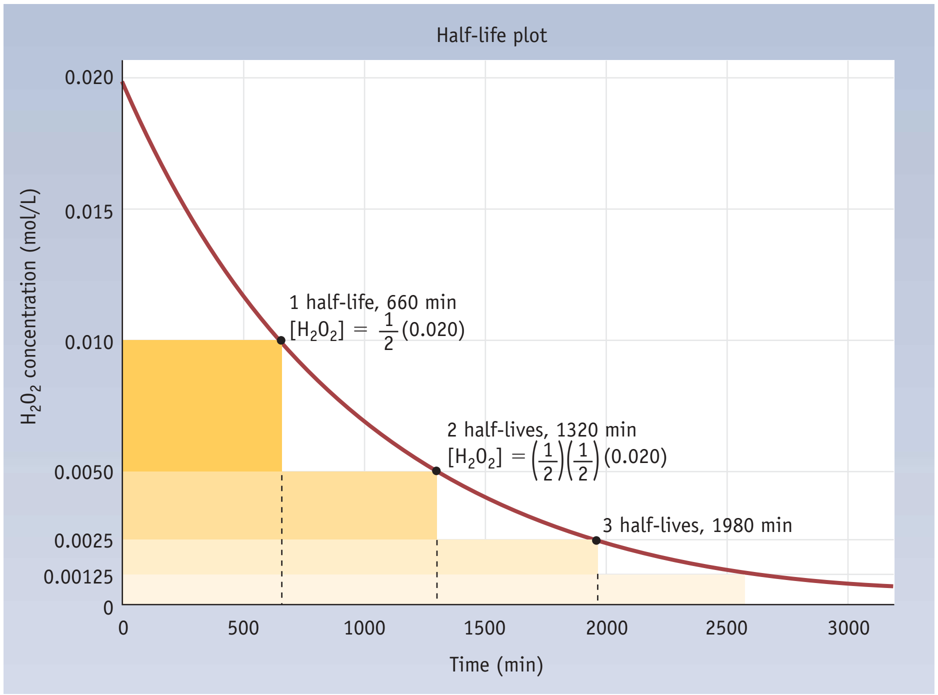
$$2\ \mathrm{H_2O_2(aq)} \longrightarrow 2\ \mathrm{H_2O}(\ell) + \mathrm{O_2(g)}$$

The data provided in Figure 15.7 allowed us to determine that the rate constant, k, for this reaction is $1.05 \times 10^{-3}\ \mathrm{min}^{-1}$. Using Equation 15.4, the half-life of H_2O_2 in this reaction can be calculated from the rate constant.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.05 \times 10^{-3}\ \mathrm{min}^{-1}} = 660.\ \mathrm{min}$$

In Figure 15.9, the concentration of H_2O_2 has been plotted as a function of time. This graph shows that $[H_2O_2]$ decreases by half within each 654-min period. The initial concentration of H_2O_2 is 0.020 M, but it drops to 0.010 M after 660 min. The concentration drops again by half (to 0.0050 M) after another 660 min. That is, after two half-lives (1320 min), the concentration is $(\frac{1}{2}) \times (\frac{1}{2}) = (\frac{1}{2})^2 = \frac{1}{4}$, or 25% of the initial concentration. After three half-lives (1980 min), the concentration has dropped to $(\frac{1}{2}) \times (\frac{1}{2}) \times (\frac{1}{2}) = (\frac{1}{2})^3 = \frac{1}{8}$, or 12.5% of the initial value; here $[H_2O_2] =$ 0.0025 M.

It is hard to visualize whether a reaction is fast or slow from the value of the rate constant. Can you tell from the value of the rate constant, $k = 1.05 \times 10^{-3}$ min,



Active Figure 15.9 **Half-life of a first-order reaction.** This concentration-versus-time curve shows the disappearance of H_2O_2 (where $k = 1.05 \times 10^{-3}\ \mathrm{min}^{-1}$). The concentration of H_2O_2 is halved every 660 min. (This plot of concentration versus time is similar in shape to those for all other first-order reactions.)

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whether the decomposition of H_2O_2 will require seconds, minutes, hours, or days to reach completion? Probably not, but this is easily assessed from the value of half-life for this reaction, 660 min. The half-life is just under 11 h, so you will have to wait several days for most of the H_2O_2 in a sample to decompose.

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See the General ChemistryNow CD-ROM or website:

- **Screen 15.8 Half-Life,** for tutorials on using half-life

Example 15.8—Half-Life and a First-Order Process

Problem Sucrose, $C_{12}H_{22}O_{11}$, decomposes to fructose and glucose in acid solution with the rate law

$$\text{Rate} = k[\text{sucrose}] \qquad k = 0.208\ \text{h}^{-1} \text{ at } 25\ °\text{C}$$

What amount of time is required for 87.5% of the initial concentration of sucrose to decompose?

Strategy After 87.5% of the sucrose has decomposed, 12.5% remains. That is, the fraction remaining is 0.125. To reach this point, three half-lives are required.

Half-Life	**Fraction Remaining**
1	0.5
2	0.25
3	0.125

Therefore, we calculate the half-life from Equation 15.4 and then multiply by 3.

Solution The half-life for the reaction is

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.208\ \text{h}^{-1}} = 3.33\ \text{h}$$

Three half-lives must elapse before the fraction remaining is 0.125, so

$$\text{Time elapsed} = 3 \times 3.33\ \text{h} = 9.99\ \text{h}$$

Example 15.9—Half-Life and First-Order Processes

Problem Radioactive radon-222 gas (^{222}Rn) from natural sources can seep into the basement of a home. The half-life of ^{222}Rn is 3.8 days. If a basement has 4.0×10^{13} atoms of ^{222}Rn per liter of air, and the radon gas is trapped in the basement, how many atoms of ^{222}Rn will remain after one month (30 days)?

Strategy Using Equation 15.1, and knowing the number of atoms at the beginning ($= [R]_0$), the elapsed time (30 days), and the rate constant, we can calculate the number of atoms remaining ($= [R]_t$). First, the rate constant, k, must be found from the half-life using Equation 15.4. (*See General ChemistryNow CD-ROM or website Screen 15.6.*)

Solution The rate constant, k, is

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.8\ \text{d}} = 0.18\ \text{d}^{-1}$$

Now use Equation 15.1 to calculate the number of atoms remaining after 30 days.

$$\ln \frac{[\mathrm{Rn}]_t}{4.0 \times 10^{13}\ \mathrm{atom/L}} = -(0.18\ \mathrm{d}^{-1})(30\ \mathrm{d}) = -5.5$$

$$\frac{[\mathrm{Rn}]_t}{4.0 \times 10^{13}\ \mathrm{atom/L}} = e^{-5.5} = 0.0042$$

$$[\mathrm{Rn}]_t = 1.7 \times 10^{11}\ \mathrm{atom/L}$$

Exercise 15.9—Half-Life and a First-Order Process

Americium is used in smoke detectors and in medicine for the treatment of certain malignancies. One isotope of americium, ^{241}Am, has a rate constant, k, for radioactive decay of 0.0016 y^{-1}. In contrast, radioactive iodine-125, which is used for studies of thyroid functioning, has a rate constant for decay of 0.011 d^{-1}.

(a) What are the half-lives of these isotopes?
(b) Which element decays faster?
(c) If you are given a dose of iodine-125, and have 1.6×10^{15} atoms, how many remain after 2.0 days?

15.5—A Microscopic View of Reaction Rates

Throughout this book we have turned to the particulate level of chemistry to understand chemical phenomena. The rate of a reaction is no exception. Looking at the way reactions occur at the atomic and molecular levels provides some insight into the various influences on rates of reactions.

Let us review the macroscopic observations we have made so far concerning reaction rates. We know the wide difference in rates of reaction relates to the specific compounds involved—from very fast reactions like the explosion that occurs when hydrogen and oxygen are exposed to a spark or flame (Figure 1.13), to slow reactions like the formation of rust that occur over days, weeks, or years. For a specific reaction, factors that influence reaction rate include the concentration of the reactants, the temperature of the reaction system, and the presence of catalysts. Let us next look at each of these influences in more depth.

Concentration, Reaction Rate, and Collision Theory

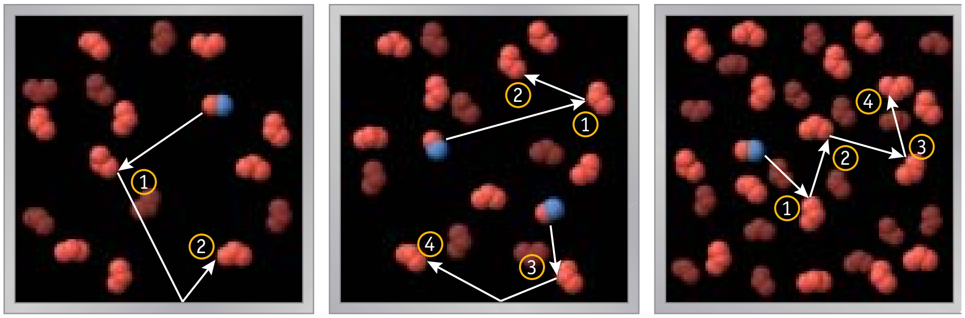
Consider the gas-phase reaction of nitric oxide and ozone:

$$\mathrm{NO(g)} + \mathrm{O_3(g)} \longrightarrow \mathrm{NO_2(g)} + \mathrm{O_2(g)}$$

The rate law for this product-favored reaction is first order in each reactant: Rate = $k[\mathrm{NO}][\mathrm{O_3}]$. How can this reaction have this rate law?

Let us consider the reaction at the particulate level and imagine a flask containing a mixture of NO and O_3 molecules in the gas phase. Both kinds of molecules are in rapid and random motion within the flask. They strike the walls of the vessel and collide with other molecules. For this or any other reaction to occur, the **collision theory** of reaction rates states that three conditions must be met:

1. The reacting molecules must collide with one another.
2. The reacting molecules must collide with sufficient energy to break bonds.



(a) 1 NO : 16 O_3 — *2 hits/second* **(b) 2 NO : 16 O_3** — *4 hits/second* **(c) 1 NO : 32 O_3** — *4 hits/second*

Figure 15.10 The effect of concentration on the frequency of molecular collisions. (a) A single NO molecule, moving among sixteen O_3 molecules, is shown colliding with two of them per second. (b) If two NO molecules move among four O_3 molecules, we would predict that four NO–O_3 collisions would occur per second. (c) If the number of O_3 molecules is doubled (to 32), the frequency of NO–O_3 collisions is also doubled, to four per second.

3. The molecules must collide in an orientation that can lead to rearrangement of the atoms.

We shall discuss each of these conditions within the context of the effects of concentration and temperature on reaction rate.

To react, molecules must collide with one another. The rate of their reaction is primarily related to the number of collisions, which is in turn related to their concentrations (Figure 15.10). Doubling the concentration of one reagent in the NO + O_3 reaction, say NO, will lead to twice the number of molecular collisions. Figure 15.10a shows a single molecule of one of the reactants (NO) moving randomly among sixteen O_3 molecules. In a given time period, it might collide with two O_3 molecules. The number of NO—O_3 collisions will double, however, if the concentration of NO molecules is doubled (to 2, as shown in Figure 15.10b) or if the number of O_3 molecules is doubled (to 32, as in Figure 15.10c). Thus we can explain the dependence of reaction rate on concentration: The number of collisions between the two reactant molecules is directly proportional to the concentration of each reactant, and the rate of the reaction shows a first-order dependence on each reactant.

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See the General ChemistryNow CD-ROM or website:

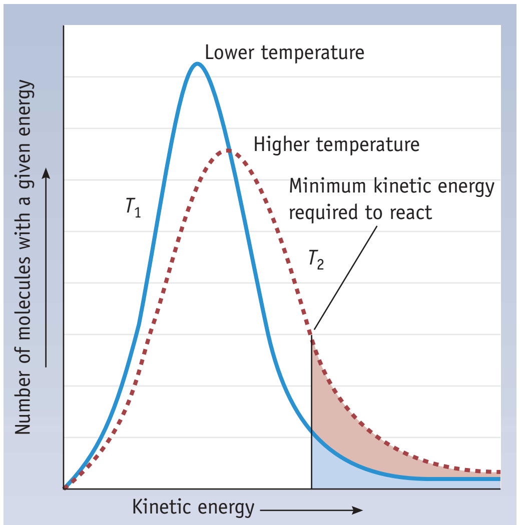
- **Screen 15.9 Microscopic View of Reactions (1),** for a visualization of collision theory

Temperature, Reaction Rate, and Activation Energy

In a laboratory or in the chemical industry, a chemical reaction is often carried out at elevated temperature because this allows the reaction to occur more rapidly. Conversely, it is sometimes desirable to lower the temperature to slow down a chemical reaction (to avoid an uncontrollable reaction or a potentially dangerous explosion). Chemists are very aware of the effect of temperature on the rate of a reaction. But how and why does temperature influence reaction rate?

A discussion of the effect of temperature on reaction rate goes back to the distribution of energies for molecules in a sample of a gas or liquid. Recall from studying gases and liquids that the molecules in a sample have a wide range of energies, described earlier as a Boltzmann distribution of energies [◀ Figure 12.14 and Figure 13.14]. That is, in any sample of a gas or liquid, some molecules have very low energies, others have very high energies, but most have some intermediate energy. As

Figure 15.11 Kinetic-energy distribution curve. The vertical axis gives the relative number of molecules possessing the energy indicated on the horizontal axis. The graph indicates the minimum energy required for an arbitrary reaction. At a higher temperature, a larger fraction of the molecules have sufficient energy to react. (Recall Figure 12.14, the Boltzmann distribution function, for a collection of gas molecules.)



the temperature increases, the average energy of the molecules in the sample increases, as does the fraction having higher energies (Figure 15.11).

Activation Energy

Molecules require some minimum energy to react. Chemists visualize this as an energy barrier that must be surmounted by the reactants for a reaction to occur (Figure 15.12). The energy required to surmount the barrier is called the **activation energy, E_a**. If the barrier is low, the energy required is low, and a high proportion of the molecules in a sample may have sufficient energy to react. In such a case, the reaction will be fast. If the barrier is high, the activation energy is high, and only a few reactant molecules in a sample may have sufficient energy. In this case, the reaction will be slow.

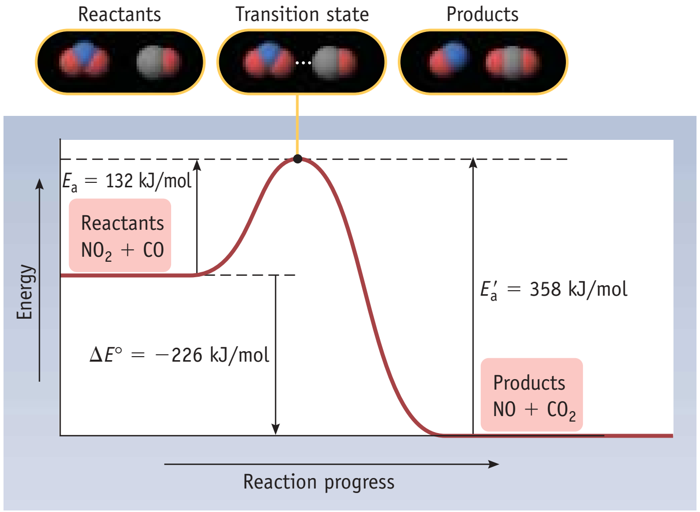
As an illustration of an activation energy barrier, consider the conversion of NO_2 and CO to NO and CO_2 or the reverse reaction (Figure 15.13). At the molecular level we imagine that the reaction involves the transfer of an O atom from an NO_2 molecule to a CO molecule (or, in the reverse reaction, the transfer of an O atom from CO_2 to NO).

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

These reactions cannot occur, however, without the initial input of energy, the activation energy. For example, for NO_2 to transfer an O atom to CO, the N—O bond must be broken. We show this process by using an energy diagram or *reaction coordinate diagram.* The horizontal axis represents the nature of the reactants and products as the reaction proceeds, and the vertical axis represents the potential energy of the system during the reaction. When NO_2 and CO approach and O atom transfer begins, an N—O bond is being broken and a C═O bond is forming. The energy of the system reaches a maximum at the **transition state**. At the transition state, sufficient energy has been concentrated in the appropriate bonds; bonds in the reactants can now break and new bonds can form to give products. The system is poised to go on to products, or it can return to the reactants. Because the transition state is at a maximum in potential energy, it cannot be isolated. However, chemists can


Charles D. Winters

Figure 15.12 An analogy to chemical activation energy. For the volleyball to go over the net, the player must give it sufficient energy.



Active Figure 15.13 **Activation energy.** The reaction of NO_2 and CO (to give NO and CO_2) has an activation energy barrier of 132 kJ/mol. The reverse reaction ($NO + CO_2 \longrightarrow NO_2 + CO$) requires 358 kJ/mol. The net energy change for the reaction of NO_2 and CO is −226 kJ/mol.

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sometimes get a notion of the transition state using computer molecular modeling techniques.

In the $NO_2 + CO$ reaction, 132 kJ/mol is required to reached the transition state at the top of the energy barrier. As the reaction "slides down" the other side of the barrier—as the N—O bond is finally broken and a C═O bond forms—the reaction evolves energy, 358 kJ/mol. The net energy involved in the reaction is

$$\text{Net energy} = +132 \text{ kJ/mol} + (-358 \text{ kJ/mol}) = -226 \text{ kJ/mol}$$

Overall, the reaction is exothermic by 226 kJ/mol.

What happens if NO and CO_2 are mixed to form NO_2 and CO? Now the reaction requires 358 kJ/mol to reach the transition state, and 132 kJ/mol is evolved on proceeding to the product, NO_2 and CO. The reaction in this direction is endothermic.

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- **Screen 15.10 Microscopic View of Reaction (2),** for a simulation of reaction coordinate diagrams

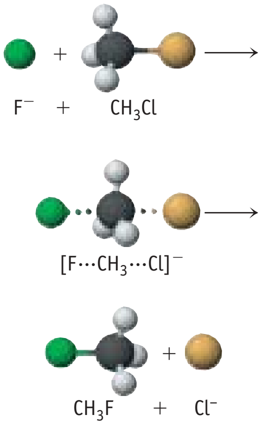
Effect of a Temperature Increase

The conversion of NO_2 and CO to products at room temperature is slow because only a few of the molecules have enough energy to undergo this reaction. The rate can be increased, by heating the sample, which has the effect of increasing the

A Closer Look

Reaction Coordinate Diagrams

Reaction coordinate diagrams (Figure 15.13) can convey a great deal of information. Another reaction that would have an energy diagram like that in Figure 15.13 is the substitution of a halogen atom of CH_3Cl by an ion such as F^-. Here the F^- ion attacks the molecule from the side opposite the Cl substituent. As F^- begins to form a bond to carbon, the C—Cl bond weakens and the CH_3 portion of the molecule changes shape. As time progresses, the products CH_3F and Cl^- are formed.



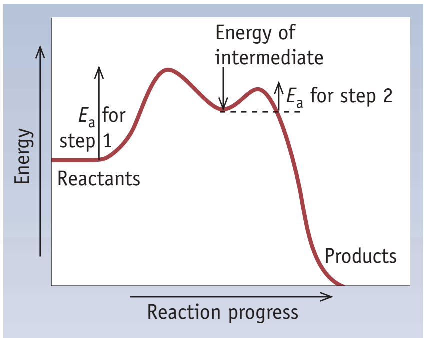
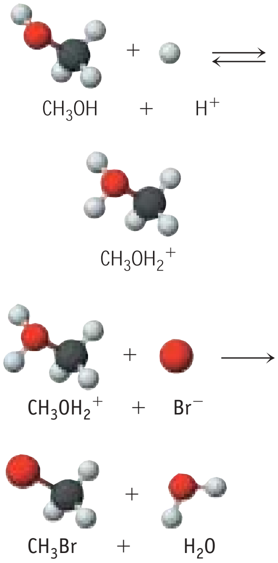


Figure A A reaction coordinate diagram for a two-step reaction, a process involving an intermediate.

The diagram in Figure A shows a different type of reaction, a two-step reaction that involves a reaction intermediate. An example would be the substitution of the —OH group on methanol by a halide ion in the presence of acid. In the first step, an H^+ ion attaches to the O of the C—O—H group in a rapid, reversible reaction. Activation energy is required to reach this state. The energy of this protonated species, $CH_3OH_2^+$, a reaction intermediate, is higher than the energies of the reactants and is represented by the dip in the curve shown in Figure A. In the second step, a halide ion, say Br^-, attacks the intermediate in a process that requires further activation energy. The final result is methyl bromide, CH_3Br, and water.



Notice in Figure A, as in Figure 15.13, that the energy of the products is lower than the energy of the reactants. The reaction is exothermic.

fraction of molecules having higher energies (Figure 15.11). Raising the temperature always increases the reaction rate by increasing the fraction of molecules with enough energy to surmount the activation energy barrier.

Effect of Molecular Orientation on Reaction Rate

Not only must the NO_2 and CO molecules collide with sufficient energy, but they must also come together in the correct orientation. Having a sufficiently high energy is necessary, but it is not sufficient to ensure that reactants will form products. For the reaction of NO_2 and CO, we can imagine that the transition state structure has one of the O atoms of NO_2 beginning to bind to the C atom of CO in preparation for O atom transfer (Figure 15.13). This “steric factor” is important in determining the rate of the reaction and affects the value of the rate constant, *k*. The lower the probability of achieving the proper alignment, the smaller the value of *k*, and the slower the reaction.

Imagine what happens when two or more complicated molecules collide. In only a small fraction of the collisions will the molecules come together in exactly the right orientation. Thus, only a tiny fraction of the collisions can be effective. No wonder some reactions are so slow. Conversely, it is amazing that so many are so fast!

The Arrhenius Equation

The observation that reaction rates depend on the energy and frequency of collisions between reacting molecules, on the temperature, and on whether the collisions have the correct geometry is summarized by the **Arrhenius equation**:

$$k = \text{rate constant} = \underset{\substack{\nearrow \\ \text{Frequency factor}}}{A}\,\underbrace{e^{-E_a/RT}}_{\text{Fraction of molecules with minimum energy for reaction}} \qquad (15.5)$$

where R is the gas constant with a value of 8.314510×10^{-3} kJ/K · mol. The parameter A is called the *frequency factor*, and it has units of L/mol · s. It is related to the number of collisions and to the fraction of collisions that have the correct geometry; A is specific to each reaction and is temperature-dependent. The factor $e^{-E_a/RT}$ is interpreted as the *fraction of molecules having the minimum energy required for reaction*; its value is always less than 1. As the table in the margin shows, this fraction changes significantly with temperature.

The Arrhenius equation is valuable because it can be used to (1) calculate the value of the activation energy from the temperature dependence of the rate constant and (2) calculate the rate constant for a given temperature if the activation energy and A are known. Taking the natural logarithm of each side of Equation 15.5, we have

$$\ln k = \ln A + \left(-\frac{E_a}{RT}\right)$$

If we rearrange this expression slightly, it becomes the equation for a straight line relating ln k to $(1/T)$:

$$\begin{array}{lcccl} \ln k & = & -\dfrac{E_a}{R}\left(\dfrac{1}{T}\right) & + \ln A & \longleftarrow \text{Arrhenius equation} \\ \downarrow & & \downarrow & \downarrow & \\ y & = & mx & + b & \longleftarrow \text{Equation for straight line} \end{array} \qquad (15.6)$$

This means that, if the natural logarithm of k (ln k) is plotted versus $1/T$, the result is a downward-sloping line with a slope of $(-E_a/R)$. Now we have a way to calculate E_a from experimental values of k at several temperatures, a calculation illustrated in Example 15.10 and in Figure 15.14.

Interpreting the Arrhenius Equation

(a) The exponential term gives the fraction of molecules having sufficient energy for reaction as a function of T.

Temperature (K)	**Value of $e^{-E_a/RT}$ for $E_a = 40$ kJ**
298	9.7×10^{-8}
400	5.9×10^{-6}
600	3.3×10^{-4}

(b) Significance of A. Although a complete understanding of A goes beyond the level of this text, it can be noted that A becomes smaller as the reactants become larger, a reflection of the "steric effect."

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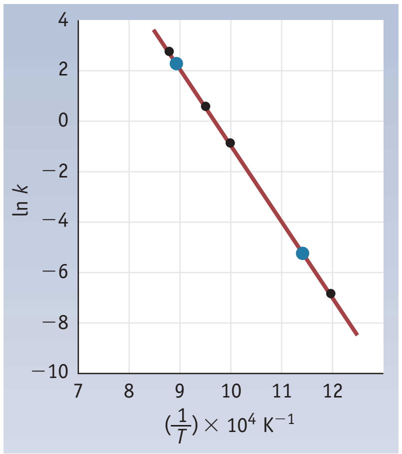
See the General ChemistryNow CD-ROM or website:

- **Screen 15.11 Control of Reaction Rates (3),** for a simulation and three tutorials on the temperature dependence of reaction rates and the Arrhenius equation



Active Figure 15.14 **Arrhenius plot.** A plot of ln k versus $1/T$ for the reaction $2\ N_2O(g) \longrightarrow 2\ N_2(g) + O_2(g)$. The slope of the line gives E_a. See Example 15.10.

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Example 15.10—Determination of E_a from the Arrhenius Equation

Problem Using the experimental data shown in the table, calculate the activation energy E_a for the reaction

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

Experiment	Temperature (K)	k (L/mol · s)
1	1125	11.59
2	1053	1.67
3	1001	0.380
4	838	0.0011

Strategy To use the Arrhenius equation (Equation 15.6), we first need to calculate ln k and $1/T$ for each data point. These data are then plotted, and E_a is calculated from the resulting straight line (slope $= -E_a/R$).

Solution The data are expressed as $1/T$ and ln k.

Experiment	$1/T$ (K^{-1})	ln k
1	8.889×10^{-4}	2.4501
2	9.497×10^{-4}	0.513
3	9.990×10^{-4}	−0.968
4	11.9×10^{-4}	−6.81

Plotting these data gives the graph shown here. Choosing the large blue points on the graph in Figure 15.14, the slope is found to be

$$\text{Slope} = \frac{\Delta \ln k}{\Delta(1/T)} = \frac{2.0 - (-5.6)}{(9.0 - 11.5)(10^{-4})/\text{K}} = -3.0 \times 10^4\ \text{K}$$

The activation energy is evaluated from

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

$$-3.0 \times 10^4\ \text{K} = -\frac{E_a}{8.31 \times 10^{-3}\ \text{kJ/K} \cdot \text{mol}}$$

$$E_a = 250\ \text{kJ/mol}$$

In addition to the graphical method for evaluating E_a used in Example 15.10, E_a can be obtained algebraically. Knowing k at two different temperatures, we can write an equation for each of these conditions:

$$\ln k_1 = -\left(\frac{E_a}{RT_1}\right) + \ln A \quad \text{or} \quad \ln k_2 = -\left(\frac{E_a}{RT_2}\right) + \ln A$$

If one of these equations is subtracted from the other, we have

$$\ln k_2 - \ln k_1 = \ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad (15.7)$$

Example 15.11 demonstrates the use of this equation.

■ **E_a, Reaction Rates, and Temperature** A good rule of thumb is that reaction rates double for every 10 °C rise in temperature in the vicinity of room temperature.

Example 15.11—Calculating E_a from the Temperature Dependence of k

Problem Using values of k determined at two different temperatures, calculate the value of E_a for the decomposition of HI:

$$2\ HI(g) \longrightarrow H_2(g) + I_2(g)$$
$$k = 2.15 \times 10^{-8}\ L/(mol \cdot s)\ \text{at}\ 6.50 \times 10^{2}\ K$$
$$k = 2.39 \times 10^{-7}\ L/(mol \cdot s)\ \text{at}\ 7.00 \times 10^{2}\ K$$

Strategy Here we are given values of k_1, T_1, k_2, and T_2, so we use Equation 15.7.

Solution

$$\ln \frac{2.39 \times 10^{-7}\ L/(mol \cdot s)}{2.15 \times 10^{-8}\ L/(mol \cdot s)} = -\frac{E_a}{8.315 \times 10^{-3}\ kJ/K \cdot mol}\left[\frac{1}{7.00 \times 10^{2} K} - \frac{1}{6.50 \times 10^{2}\ K}\right]$$

Solving this equation for E_a, we find $E_a = 180\ kJ/mol$.

Comment When using Equation 15.7, be aware that another way to write the difference in fractions in brackets is

$$\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = \frac{T_1 - T_2}{T_1 T_2}$$

Also be very careful of significant figures.

Exercise 15.10—Calculating E_a from the Temperature Dependence of k

The colorless gas N_2O_4 decomposes to the brown gas NO_2 in a first-order reaction:

$$N_2O_4(g) \longrightarrow 2\ NO_2(g)$$

The rate constant $k = 4.5 \times 10^{3}\ s^{-1}$ at 274 K and $k = 1.00 \times 10^{4}\ s^{-1}$ at 283 K. What is the activation energy, E_a?

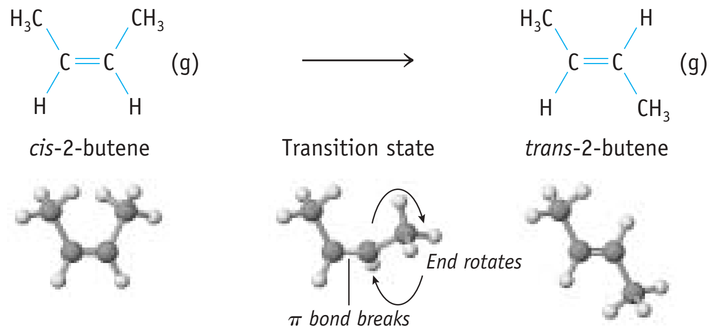
Effect of Catalysts on Reaction Rate

Catalysts are substances that speed up the rate of a chemical reaction, and we have seen several examples of catalysts in earlier discussions in this chapter: MnO_2 (Figure 15.4), iodide ion (page 705), an enzyme in a potato (page 706), and hydroxide ion (page 714) all catalyze the decomposition of hydrogen peroxide. In biological systems, catalysts called *enzymes* influence the rates of most reactions (page 699).

■ Enzymes: Biological Catalysts
Catalase is an enzyme whose function is to speed up the decomposition of hydrogen peroxide. This enzyme ensures that hydrogen peroxide, which is highly toxic, does not build up in the body.

Catalysts are not consumed in a chemical reaction. They are, however, intimately involved in the details of the reaction at the particulate level. Their function is to provide a different pathway with a lower activation energy for the reaction.

To illustrate how a catalyst participates in a reaction, let us consider the first-order interconversion of the butene isomer, *cis*-2-butene, to the slightly more stable isomer, *trans*-2-butene.



■ Butene Isomerization
Isomerization of *cis*-2-butene has the rate law "Rate = k[*cis*-2-butene]." In a large collection of *cis*-2-butene molecules, the probability that a molecule will isomerize is related to the fraction of molecules that have a high enough energy. The rate of such a reaction would have a first-order dependence on concentration. See Screen 10.8 of the General ChemistryNow CD-ROM or website to view an animation of the interconversion of butene isomers and the energy barrier to the process.

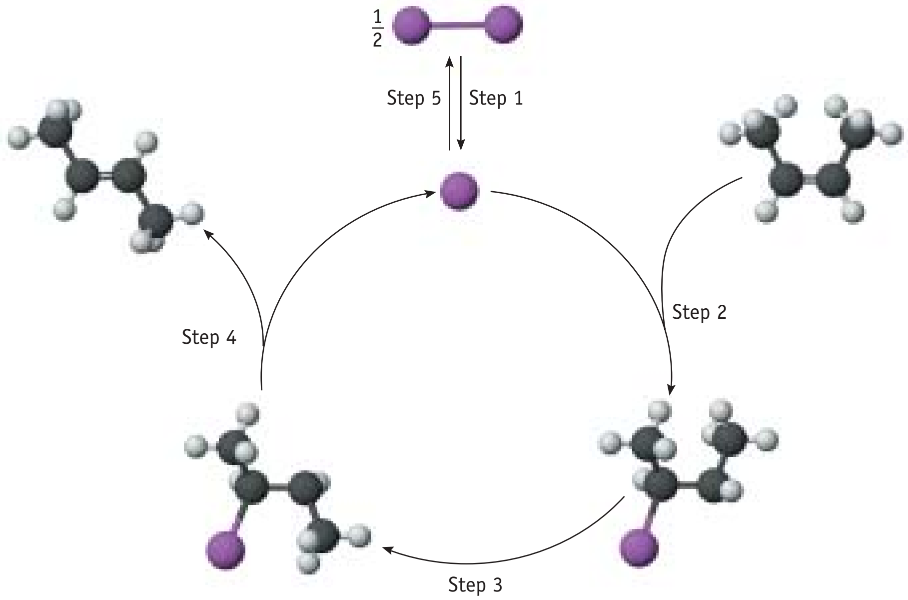


Figure 15.15 The mechanism of the iodine-catalyzed isomerization of *cis*-2-butene. *Cis*-2-butene is converted to *trans*-2-butene in the presence of a catalytic amount of iodine. Catalyzed reactions are often pictured in such diagrams to emphasize what chemists refer to as a "catalytic cycle."

The activation energy for the uncatalyzed conversion is relatively large—262 kJ/mol—because the π bond must be broken to allow one end of the molecule to rotate into a new position. Because of the high activation energy this is a slow reaction, and rather high temperatures are required for it to occur at a reasonable rate.

The *cis*- to *trans*-2-butene reaction is greatly accelerated by a catalyst, iodine. The presence of iodine allows the isomerization reaction to be carried out at a temperature several hundred degrees lower than the uncatalyzed reaction. Iodine is not consumed (nor is it a product), and it does not appear in the overall balanced equation. It does appear in the reaction rate law, however; the rate of the reaction depends on the square root of the iodine concentration:

$$\text{Rate} = k\,[\textit{cis}\text{-2-butene}]\,[I_2]^{1/2}$$

Catalysts and Activation Energy Barriers

An analogy to a catalyst is that the reaction "tunnels" through the activation energy barrier instead of moving over it.

The rate of the *cis–trans* conversion changes because the presence of I_2 changes the way the reaction occurs. That is, it changes the *mechanism* of the reaction (see Section 15.6 and Figure 15.15). The best hypothesis is that iodine molecules first dissociate to form iodine atoms (Step 1). An I atom then adds to one of the C atoms of the C═C double bond (Step 2). This converts the double bond between the carbon atoms to a single bond (the π bond is broken) and allows the ends of the molecule to twist freely relative to each other (Step 3). If the I atom then dissociates from the intermediate, the double bond can re-form in the *trans* configuration (Step 4).

The iodine atom catalyzing the rotation is now free to add to another molecule of *cis*-2-butene. The result is a kind of chain reaction, as one molecule of *cis*-2-butene after another is converted to the *trans* isomer. The chain is broken if the iodine atom recombines with another iodine atom to re-form molecular iodine.

An energy profile for the catalyzed reaction (Figure 15.16) shows that the overall energy barrier has been greatly lowered from the situation in the uncatalyzed reaction. In addition, the energy profile for the reaction includes several steps (a total of five), representing each step in the reaction. This proposed mechanism includes a series of chemical species called **reaction intermediates**, species formed in one step of the reaction and consumed in a later step. Iodine atoms are intermediates, as are the free radical species formed when an iodine atom adds to *cis*-2-butene.

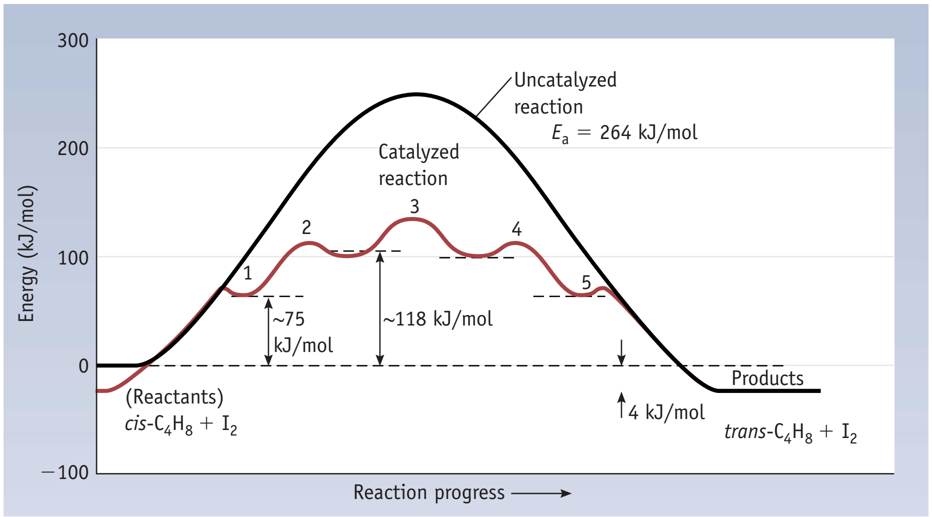


Figure 15.16 Energy profile for the iodine-catalyzed reaction of *cis*-2-butene. A catalyst accelerates a reaction by altering the mechanism so that the activation energy is lowered. With a smaller barrier to overcome, more reacting molecules have sufficient energy to surmount the barrier, and the reaction occurs more rapidly. The energy profile for the uncatalyzed conversion of *cis*-2-butene to *trans*-2-butene is shown by the black curve, and that for the iodine-catalyzed reaction is represented by the red curve. Notice that the shape of the barrier has changed because the mechanism has changed.

Five important points are associated with this mechanism:

- Iodine molecules, I_2, dissociate to atoms and then re-form. On the macroscopic level, the concentration of I_2 is unchanged. Iodine does not appear in the balanced, stoichiometric equation even though it appears in the rate equation. This is generally true of catalysts.
- Both the catalyst I_2 and the reactant *cis*-2-butene are in the gas phase. If a catalyst is present in the same phase as the reacting substance, it is called a **homogeneous catalyst**.
- Iodine atoms and the radical species formed by addition of an I atom to a 2-butene molecule are intermediates.
- The activation energy barrier to reaction is significantly lower because the mechanism changed. Dropping the activation energy from 264 kJ/mol for the uncatalyzed reaction to about 150 kJ/mol for the catalyzed process makes the catalyzed reaction 10^{15} times faster!
- The diagram of energy-versus-reaction progress has five energy barriers (five humps appear in the curve). This feature in the diagram means that the reaction occurs in a series of five steps.

What we have described here is a reaction mechanism. The uncatalyzed isomerization reaction of *cis*-2-butene is a one-step reaction mechanism, whereas the catalyzed mechanism involves a series of steps. We shall discuss reaction mechanisms in more detail in the next section.

GENERAL **Chemistry Now**™

See the General ChemistryNow CD-ROM or website:

- **Screen 15.14 Catalysis and Reaction Rate,** for a description of various catalysts, a visualization of the effect of a catalyst on activation energy, an interview of a scientist describing catalyst use in industry, two exercises on reaction mechanisms and the effect of catalysts, and a video exercise on catalysis

A Closer Look

Enzymes: Nature's Catalysts

Enzymes are powerful catalysts, typically producing a reaction rate that is 10^7 to 10^{14} times faster than the uncatalyzed rate. Metal ions are often part of an enzyme. Carboxypeptidase, for example, contains Zn^{2+} ions at the active site.

In 1913 Leonor Michaelis and Maud L. Menten proposed a general theory of enzyme action based on kinetic observations. They assumed that the substrate, S (the reactant), and the enzyme, E, form a complex, ES. This complex then breaks down, releasing the enzyme and the product, P.

$$E + S \rightleftharpoons ES \rightleftharpoons E + P$$

The table below lists a few important enzymes. One, carbonic anhydrase, was mentioned at the beginning of the chapter (page 699), where a simple experiment showed the rate-enhancing ability of this enzyme.

Here is another experiment you can do with carbonic anhydrase. Take a sip of very cold carbonated beverage. The tingling sensation you feel on your tongue and in your mouth is not from the CO_2 bubbles. Rather, it comes from the protons released when carbonic anhydrase accelerates the formation of H^+ ions from dissolved H_2CO_3 (see page 699). Acidification of nerve endings creates the tingling feeling.

The enzymes trypsin, chymotrypsin, and elastase are digestive enzymes, catalyzing the hydrolysis of peptide bonds [◀ page 532]. They are synthesized in the pancreas and secreted into the digestive tract.

Acetylcholinesterase is involved in transmission of nerve impulses. Many pesticides interfere with this enzyme, so farm workers are often tested to be sure they have not been overexposed to agricultural toxins.

The liver has the primary role in maintaining blood glucose levels. This organ produces glucose with phosphate groups attached (PO_4^{3-}). The enzyme glucose phosphatase in the liver has the function of removing the phosphate group before the glucose enters the blood.

See also "The Chemistry of Life: Biochemistry," page 530.

Charles D. Winters

Enzyme action. The tingling feeling you get when you drink a carbonated beverage comes from the H^+ ions released by H_2CO_3. The acid is formed rapidly from dissolved CO_2 in presence of the enzyme carbonic anhydrase.

Biologically Important Reactions Catalyzed by Enzymes

Enzyme	Enzyme Function or Reaction Catalyzed
Carbonic anhydrase	$CO_2 + H_2O \longrightarrow H_2CO_3$
Chymotrypsin	Cleavage of peptide linkages in proteins
Urease	$(H_2N)_2CO + 2\ H_2O + H^+ \longrightarrow 2\ NH_4^+ + HCO_3^-$
Catalase	$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$
Acetylcholinesterase	Regenerates acetylcholine, an important substance in the transmission of nerve impulses, from acetate and choline
Hexokinase and glucokinase	Both enzymes catalyze the formation of a phosphate ester linkage to a —OH group of a sugar. Glucokinase is a liver-specific enzyme, and the liver is the major organ for the storage of excess dietary sugar as glycogen.

15.6—Reaction Mechanisms

■ **Rate Laws and Mechanisms**
Rate laws are macroscopic observations. Mechanisms analyze how reactions occur at the particulate level.

One of the most important reasons to study reaction rates is the fact that rate laws help us to understand **reaction mechanisms**, the sequence of bond-making and bond-breaking steps that occurs during the conversion of reactants to products. The study of reaction mechanisms places us squarely within the realm of the particulate level of chemistry. We want to analyze the changes that atoms and molecules undergo when they react. We then want to relate this description back to the macroscopic world, to the experimental observations of reaction rates.

Based on the rate equation for a reaction, and by applying chemical intuition, chemists can often make an educated guess about the mechanism for the reaction. In some reactions, the conversion of reactants to products in a single step is envisioned. For example, nitrogen dioxide and carbon monoxide react in a single-step reaction, with the reaction occurring as a consequence of a collision between reac-

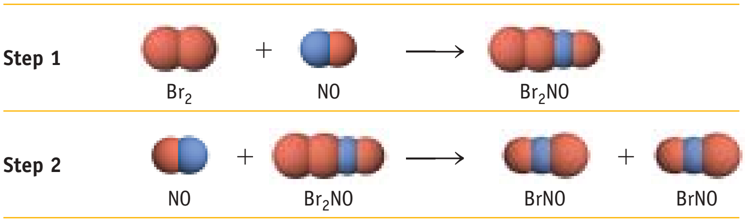


Figure 15.17 **A reaction mechanism.** A representation of the proposed two-step mechanism by which NO and Br_2 are converted to NOBr.

tant molecules (Figure 15.13). The uncatalyzed isomerization of *cis*-2-butene to *trans*-2-butene is also best described as a single-step reaction (Figure 15.16).

Most chemical reactions occur in a sequence of steps, however. We saw an example with the iodine-catalyzed 2-butene isomerization reaction. Another example of a reaction that occurs in several steps is the reaction of bromine and NO:

$$Br_2(g) + 2\ NO(g) \longrightarrow 2\ BrNO(g)$$

A single-step reaction would require that three reactant molecules collide simultaneously in just the right orientation to be productive. Clearly, such an event has a low probability of occurring. Thus, for this reaction it would be reasonable to look for a mechanism that occurs in a series of steps, with each step involving only one or two molecules. For example, in one possible mechanism Br_2 and NO might combine in an initial step to produce an intermediate species, Br_2NO (Figure 15.17). This intermediate would then react with another NO molecule to give the reaction products. The equation for the overall reaction is obtained by adding the equations for these two steps:

Step 1. $Br_2(g) + NO(g) \longrightarrow Br_2NO(g)$

Step 2. $Br_2NO(g) + NO(g) \longrightarrow 2\ BrNO(g)$

Overall Reaction: $Br_2(g) + 2\ NO(g) \longrightarrow 2\ BrNO(g)$

Each step in a multistep reaction sequence is an **elementary step**, which is defined as a chemical equation that describes a single molecular event such as the formation or rupture of a chemical bond or the displacement of atoms as a result of a molecular collision. Each step has its own activation energy barrier, E_a, and rate constant, k. The steps must add up to give the balanced equation for the overall reaction, and the time required to complete all of the steps defines the overall reaction rate. A series of steps that satisfactorily explain the kinetic properties of a chemical reaction constitutes a possible reaction mechanism.

Mechanisms of reactions are postulated starting with experimental data. To see how this is done, we first describe three types of elementary steps in terms of the concept of *molecularity*.

Molecularity of Elementary Steps

Elementary steps are classified by the number of reactant molecules (or ions, atoms, or free radicals) that come together. This whole, positive number is called the **molecularity** of the elementary step. When one molecule is the only reactant in an elementary step, the reaction is a **unimolecular** process. A **bimolecular** elementary process involves two molecules, which may be identical ($A + A \longrightarrow$ products) or different ($A + B \longrightarrow$ products). The mechanism proposed for the decomposition of ozone in the stratosphere is an example of the use of these terms.

Step 1. Unimolecular $O_3(g) \longrightarrow O_2(g) + O(g)$
Step 2. Bimolecular $O_3(g) + O(g) \longrightarrow 2\ O_2(g)$
Overall reaction: $2\ O_3(g) \longrightarrow 3\ O_2(g)$

Here an initial unimolecular step is followed by a bimolecular step.

A **termolecular** elementary step involves three molecules. It could involve three molecules of the same or a different type ($3\ A \longrightarrow$ products; $2\ A + B \longrightarrow$ products; or $A + B + C \longrightarrow$ products). As you might suspect, the simultaneous collision of three molecules is not likely, unless one of the molecules involved is in high concentration, such as a solvent molecule. In fact, most termolecular processes involve the collision of two reactant molecules and a third, inert molecule. The function of the inert molecule is to absorb the excess energy produced when a new chemical bond is formed by the first two molecules. For example, N_2 is unchanged in a termolecular reaction between oxygen molecules and oxygen atoms that produces ozone in the upper atmosphere:

$$O(g) + O_2(g) + N_2(g) \longrightarrow O_3(g) + \text{energetic } N_2(g)$$

The probability that four or more molecules will simultaneously collide with sufficient kinetic energy and proper orientation to react is so small that reaction molecularities greater than three are never proposed.

Rate Equations for Elementary Steps

As you have already seen, the experimentally determined rate equation for a reaction cannot be predicted from its overall stoichiometry. In contrast, *the rate equation for any elementary step is defined by the reaction stoichiometry. The rate equation of an elementary step is given by the product of the rate constant and the concentrations of the reactants in that step.* We can therefore write the rate equation for any elementary step, as shown by examples in the following table:

Elementary Step	Molecularity	Rate Equation
$A \longrightarrow$ product	unimolecular	Rate $= k[A]$
$A + B \longrightarrow$ product	bimolecular	Rate $= k[A][B]$
$A + A \longrightarrow$ product	bimolecular	Rate $= k[A]^2$
$2\ A + B \longrightarrow$ product	termolecular	Rate $= k[A]^2[B]$

For example, the rate laws for each of the two steps in the decomposition of ozone are

$$\text{Rate for (unimolecular) Step 1} = k[O_3]$$
$$\text{Rate for (bimolecular) Step 2} = k'[O_3][O]$$

When a reaction mechanism consists of two elementary steps, the two steps will likely occur at different rates. The two rate constants (k and k' in this example) are not expected to have the same value (nor the same units, if the two steps have different molecularities).

Molecularity and Reaction Order

The molecularity of an elementary step and its order are the same. A unimolecular elementary step must be first order, a bimolecular elementary step must be second order, and a termolecular elementary step must be third order. Such a direct relation between molecularity and order is emphatically *not* true for the *overall* reaction. If you discover experimentally that a reaction is first order, you cannot conclude that it occurs in a single, unimolecular elementary step. Similarly, a second-order rate equation does not imply that the reaction occurs in a single, bimolecular elementary step. An example illustrating this is the decomposition of N_2O_5:

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

Here the rate equation is “Rate = $k[N_2O_5]$,” but chemists are fairly certain that the mechanism involves a series of unimolecular and bimolecular steps.

To see how the experimentally observed rate equation for the *overall reaction* is connected with a possible mechanism or sequence of elementary steps requires some chemical intuition. We will provide only a glimpse of the subject in the next section.

GENERAL ChemistryNow™

See the General ChemistryNow CD-ROM or website:

- **Screen 15.12 Reaction Mechanisms and Screen 15.13 Reaction Mechanisms and Rate Equations,** for exercises on reaction mechanisms

Example 15.12—Elementary Steps

Problem The hypochlorite ion undergoes self-oxidation–reduction to give chlorate, ClO_3^-, and chloride ions.

$$3\ ClO^-(aq) \longrightarrow ClO_3^-(aq) + 2\ Cl^-(aq)$$

This reaction is thought to occur in two steps:

Step 1. $ClO^-(aq) + ClO^-(aq) \longrightarrow ClO_2^-(aq) + Cl^-(aq)$

Step 2. $ClO_2^-(aq) + ClO^-(aq) \longrightarrow ClO_3^-(aq) + Cl^-(aq)$

What is the molecularity of each step? Write the rate equation for each reaction step. Show that the sum of these reactions gives the equation for the net reaction.

Strategy The molecularity is the number of ions or molecules involved in a reaction step. The rate equation involves the concentration of each ion or molecule in an elementary step, raised to the power of its stoichiometric coefficient.

Solution Because two ions are involved in each elementary step, each step is bimolecular. The rate equation for any elementary step involves the product of the concentrations of the reactants. Thus, in this case, the rate equations are

Step 1. Rate = $k[ClO^-]^2$

Step 2. Rate = $k[ClO^-][ClO_2^-]$

On adding the equations for the two elementary steps, we see that the ClO_2^- ion is an intermediate, a product of the first step and a reactant in the second step. It therefore cancels out, and we are left with the stoichiometric equation for the overall reaction:

Step 1. $ClO^-(aq) + ClO^-(aq) \longrightarrow \cancel{ClO_2^-}(aq) + Cl^-(aq)$

Step 2. $\cancel{ClO_2^-}(aq) + ClO^-(aq) \longrightarrow ClO_3^-(aq) + Cl^-(aq)$

Sum of steps: $3\ ClO^-(aq) \longrightarrow ClO_3^-(aq) + 2\ Cl^-(aq)$

Exercise 15.11—Elementary Steps

Nitric oxide is reduced by hydrogen to give nitrogen and water:

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

One possible mechanism for this reaction is

$$2\ \mathrm{NO(g)} \longrightarrow \mathrm{N_2O_2(g)}$$

$$\mathrm{N_2O_2(g)} + \mathrm{H_2(g)} \longrightarrow \mathrm{N_2O(g)} + \mathrm{H_2O(g)}$$

$$\mathrm{N_2O(g)} + \mathrm{H_2(g)} \longrightarrow \mathrm{N_2(g)} + \mathrm{H_2O(g)}$$

What is the molecularity of each of the three steps? What is the rate equation for the third step? Show that the sum of these elementary steps gives the net reaction.

Reaction Mechanisms and Rate Equations

The dependence of rate on concentration is an experimental fact. Mechanisms, by contrast, are constructs of our imagination, intuition, and good "chemical sense." To describe a mechanism, we need to make a guess (a *good* guess, we hope) about how the reaction occurs at the particulate level. Several mechanisms can often be proposed that correspond to the observed rate equation, and a postulated mechanism can be wrong. A good mechanism is a worthy goal because it allows us to understand the chemistry better. A practical consequence of a good mechanism is that it allows us to predict important things, such as how to control a reaction better and how to design new experiments.

One of the important guidelines of kinetics is that *products of a reaction can never be produced at a rate faster than the rate of the slowest step*. If one step in a multistep reaction is slower than the others, then the rate of the overall reaction is limited by the combined rates of all elementary steps up through the slowest step in the mechanism. Often the overall reaction rate and the rate of the slow step are nearly the same. If the slow step determines the rate of the reaction, it is called the **rate-determining step**, or rate-limiting step. You are already familiar with rate-determining steps. No matter how fast you shop in the supermarket, it always seems that the time it takes to finish is determined by the wait in the checkout line.

■ **Can You Derive a Mechanism?** At this introductory level you cannot be expected to derive reaction mechanisms. Given a mechanism, however, you can decide whether it agrees with experiment.

Imagine that a reaction takes place with a mechanism involving two sequential steps, and assume that we know the rates of both steps. The first step is slow and the second is fast:

Elementary Step 1 $\mathrm{A} + \mathrm{B} \xrightarrow[\text{Slow, } E_a \text{ large}]{k_1} \mathrm{X} + \mathrm{M}$

Elementary Step 2 $\mathrm{M} + \mathrm{A} \xrightarrow[\text{Fast, } E_a \text{ small}]{k_2} \mathrm{Y}$

Overall Reaction $2\ \mathrm{A} + \mathrm{B} \longrightarrow \mathrm{X} + \mathrm{Y}$

In the first step, A and B come together and slowly react to form one of the products (X) plus another reactive species, M. Almost as soon as M is formed, however, it is rapidly consumed by reaction with an additional molecule of A to form the second product Y. The products X and Y are the result of two elementary steps. The rate-determining elementary step is the first step. That is, the rate of the first step is equal to the rate of the overall reaction. This step is bimolecular and so has the rate equation

$$\text{Rate} = k_1[\text{A}][\text{B}]$$

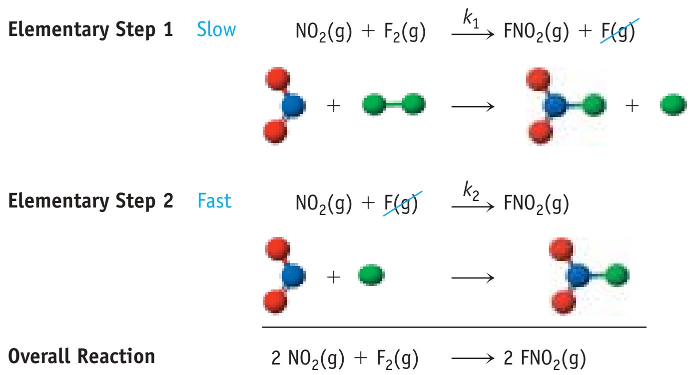
where k_1 is the rate constant for that step. The overall reaction is expected to follow this same second-order rate equation.

Let us apply these ideas to the mechanism of a real reaction. Experiment shows that the reaction of nitrogen dioxide with fluorine has a second-order rate equation:

Overall Reaction $2\ NO_2(g) + F_2(g) \longrightarrow 2\ FNO_2(g)$

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

The experimental rate equation immediately rules out the possibility that the reaction occurs in a single step. If the equation for the reaction represented an elementary step, the rate law would have a second-order dependence on $[NO_2]$. Because a single-step reaction is ruled out, it follows that the mechanism must include at least two steps. We can also conclude from the rate law that the rate-determining elementary step must involve NO_2 and F_2 in a 1 : 1 ratio. The simplest possible mechanism is as follows:



Elementary Step 1 Slow $NO_2(g) + F_2(g) \xrightarrow{k_1} FNO_2(g) + \cancel{F(g)}$

Elementary Step 2 Fast $NO_2(g) + \cancel{F(g)} \xrightarrow{k_2} FNO_2(g)$

Overall Reaction $2\ NO_2(g) + F_2(g) \longrightarrow 2\ FNO_2(g)$

This proposed mechanism suggests that molecules of NO_2 and F_2 first react to produce one molecule of the product (FNO_2) plus one F atom. In a second step, the F atom produced in the first step reacts with additional NO_2 to give a second molecule of product. If we assume that the first, bimolecular step is rate-determining, its rate equation would be "Rate = $k_1[NO_2][F_2]$," the same as the experimentally observed rate equation. The experimental rate constant is, therefore, the same as k_1.

The F atom formed in the first step of the NO_2/F_2 reaction is a reaction intermediate. It does not appear in the equation describing the overall reaction. Reaction intermediates usually have only a fleeting existence, but occasionally they have long enough lifetimes to be observed. One of the tests of a proposed mechanism is the detection of an intermediate.

Example 15.13—Elementary Steps and Reaction Mechanisms

Problem Oxygen atom transfer from nitrogen dioxide to carbon monoxide produces nitrogen monoxide and carbon dioxide (Figure 15.13):

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

This reaction has the following rate equation at temperatures less than 500 K:

$$\text{Rate} = k[\text{NO}_2]^2$$

Can this reaction occur in one bimolecular step whose stoichiometry is the same as the overall reaction?

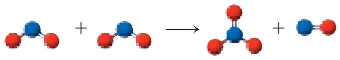
Strategy Write the rate law based on the equation for the $NO_2 + CO$ reaction occurring as an elementary step. If this rate law corresponds to the observed rate law, then the overall equation may reflect the way the reaction occurs.

Solution If the reaction occurs by the collision of one NO_2 molecule with one CO molecule, the rate equation would be

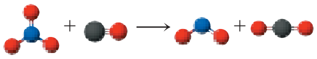
$$\text{Rate} = k[\text{NO}_2][\text{CO}]$$

This does not agree with experiment, so the mechanism must involve more than a single step. In one possible mechanism, the reaction occurs in two, bimolecular steps, the first one slow and the second one fast:

Elementary Step 1 Slow, rate-determining $2\ \text{NO}_2(g) \longrightarrow \cancel{\text{NO}_3}(g) + \text{NO}(g)$



Elementary Step 2 Fast $\cancel{\text{NO}_3}(g) + \text{CO}(g) \longrightarrow \text{NO}_2(g) + \text{CO}_2(g)$



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

The first (rate-determining) step has a rate equation that agrees with experiment, so this mechanism may be the way the reaction actually occurs.

Exercise 15.12—Elementary Steps and Reaction Mechanisms

The Raschig reaction produces hydrazine, N_2H_4, an industrially important reducing agent, from NH_3 and OCl^- in basic, aqueous solution. A proposed mechanism is

Step 1 Fast $\text{NH}_3(aq) + \text{OCl}^-(aq) \longrightarrow \text{NH}_2\text{Cl}(aq) + \text{OH}^-(aq)$

Step 2 Slow $\text{NH}_2\text{Cl}(aq) + \text{NH}_3(aq) \longrightarrow \text{N}_2\text{H}_5{}^+(aq) + \text{Cl}^-(aq)$

Step 3 Fast $\text{N}_2\text{H}_5{}^+(aq) + \text{OH}^-(aq) \longrightarrow \text{N}_2\text{H}_4(aq) + \text{H}_2\text{O}(\ell)$

(a) What is the overall stoichiometric equation?
(b) Which step of the three is rate-determining?
(c) Write the rate equation for the rate-determining elementary step.
(d) What reaction intermediates are involved?

Another common two-step reaction mechanism involves an initial fast reaction that produces an intermediate, followed by a slower second step in which the intermediate is converted to the final product. The rate of the reaction is determined by the second step, for which a rate law can be written. The rate of that step, however, depends on the concentration of the intermediate. An important thing to remember, though, is that *the rate law must be written with respect to the reactants only.* An intermediate, whose concentration will probably not be measurable, cannot appear as a term in the rate expression.

The reaction of nitrogen monoxide and oxygen is an example of a two-step reaction where the first step is fast and the second step is rate-determining.

$$\mathrm{2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)}$$
$$\mathrm{Rate} = k[\mathrm{NO}]^2[\mathrm{O_2}]$$

The experimentally determined rate law shows second-order dependence on NO_2 and first-order dependence on O_2. Although this rate law would be correct for a termolecular reaction, experimental evidence indicates that an intermediate is formed in this reaction. A possible two-step mechanism that proceeds through an intermediate is

Elementary Step 1. Fast, equilibrium $\mathrm{NO(g) + O_2(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{intermediate}}{\cancel{\mathrm{OONO(g)}}}$

Elementary Step 2. Slow, rate-determining $\mathrm{NO(g)} + \cancel{\mathrm{OONO(g)}} \xrightarrow{k_2} \mathrm{2\ NO_2(g)}$

Overall Reaction $\mathrm{NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)}$

The second step of this reaction is the slow step, and the overall rate depends on it. We can write a rate law for the second step:

$$\mathrm{Rate} = k_2[\mathrm{NO}][\mathrm{OONO}]$$

This rate law cannot be compared directly with the experimental rate law because it contains the concentration of an intermediate, OONO. Recall that the experimental rate law must be written only in terms of compounds appearing in the overall equation. We therefore need to express the postulated rate law in a way that eliminates the intermediate. To do so, we look at the rapid first step in this reaction sequence.

At the beginning of the reaction, NO and O_2 react rapidly and produce the intermediate OONO. The rate of formation can be defined by a rate law with a rate constant k_1:

$$\text{Rate of production of OONO} = k_1[\mathrm{NO}][\mathrm{O_2}]$$

Because the intermediate is consumed only very slowly in the second step, it is possible for the OONO to revert to NO and O_2 before it reacts further:

$$\text{Rate of reverse reaction (OONO to NO and O}_2\text{)} = k_{-1}[\mathrm{OONO}]$$

As NO and O_2 form OONO, their concentrations drop, so the rate of the forward reaction decreases. At the same time, the concentration of OONO builds up, so the rate of the reverse reaction increases. Eventually, the rates of the forward and reverse reactions become the same, and the first elementary step reaches a *state of equilibrium*. The forward and reverse reactions in the first elementary step are so much faster than the second elementary step that equilibrium is established before any significant amount of OONO is consumed by NO to give NO_2. The state of equilibrium for the first step remains throughout the lifetime of the overall reaction.

Because equilibrium is established when the rates of the forward and reverse reactions are the same, this means

$$\text{Rate of forward reaction} = \text{rate of reverse reaction}$$
$$k_1[\mathrm{NO}][\mathrm{O_2}] = k_{-1}[\mathrm{OONO}]$$

Rearranging this equation, we find

$$\frac{k_1}{k_{-1}} = \frac{[\mathrm{OONO}]}{[\mathrm{NO}][\mathrm{O_2}]} = K$$

Both k_1 and k_{-1} are constants (they will change only if the temperature changes). We can define a new constant K equal to the ratio of these two constants and called the *equilibrium constant*, which is equal to the quotient $[\mathrm{OONO}]/[\mathrm{NO}][\mathrm{O_2}]$. From this we can come up with an expression for the concentration of OONO:

$$[\mathrm{OONO}] = K[\mathrm{NO}][\mathrm{O_2}]$$

If $K[\mathrm{NO}][\mathrm{O_2}]$ is substituted for $[\mathrm{OONO}]$ in the rate law for the rate-determining elementary step, we have

$$\begin{aligned}\text{Rate} &= k_2[\mathrm{NO}][\mathrm{OONO}] = k_2[\mathrm{NO}]\{K[\mathrm{NO}][\mathrm{O_2}]\}\\ &= k_2K[\mathrm{NO}]^2[\mathrm{O_2}]\end{aligned}$$

Because both k_2 and K are constants, their product is another constant k', and we have

$$\text{Rate} = k'[\mathrm{NO}]^2[\mathrm{O_2}]$$

This is exactly the rate law derived from experiment. Thus, the sequence of reactions on which the rate law is based may be a reasonable mechanism for this reaction. It is *not* the only possible mechanism, however. This rate equation is also consistent with the reaction occurring in a single termolecular step. Another possible mechanism is illustrated in Example 15.14.

Example 15.14—Reaction Mechanism Involving an Equilibrium Step

Problem The $\mathrm{NO} + \mathrm{O_2}$ reaction described in the text could also occur by the following mechanism:

Elementary Step 1: Fast, equilibrium

$$\mathrm{NO(g)} + \mathrm{NO(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\text{intermediate}}{\mathrm{N_2O_2(g)}}$$

Elementary Step 2: Slow, rate-determining

$$\mathrm{N_2O_2(g)} + \mathrm{O_2(g)} \xrightarrow{k_2} \mathrm{NO_2(g)}$$

Overall Reaction: $2\ \mathrm{NO(g)} + \mathrm{O_2(g)} \longrightarrow 2\ \mathrm{NO_2(g)}$

Show that this mechanism leads to the following experimental rate law: Rate $= k[\mathrm{NO}]^2[\mathrm{O_2}]$.

Strategy The rate law for the rate-determining elementary step is

$$\text{Rate} = k_2[\mathrm{N_2O_2}][\mathrm{O_2}]$$

The compound $\mathrm{N_2O_2}$ is an intermediate and cannot appear in the final derived rate law. (A postulated rate law must not include an intermediate.) To obtain the rate law we use the equilibrium constant expression for the first step.

Solution $[\mathrm{N_2O_2}]$ and $[\mathrm{NO}]$ are related by the equilibrium constant.

$$\frac{k_1}{k_{-1}} = \frac{[\mathrm{N_2O_2}]}{[\mathrm{NO}]^2} = K$$

Problem-Solving Tip

Relating Rate Equations and Reaction Mechanisms

The connection between an experimental rate equation and the proposed reaction mechanism is important in chemistry.

1. Experiments must first be performed that define the effect of reactant concentrations on the rate of the reaction. This gives the experimental rate equation.
2. A mechanism for the reaction is proposed on the basis of the experimental rate equation, the principles of stoichiometry and molecular structure and bonding, general chemical experience, and intuition.
3. The *proposed* reaction mechanism is used to *derive* a rate equation. This rate equation must contain only those species present in the overall chemical reaction but not any reaction intermediates. If the derived and experimental rate equations are the same, the postulated mechanism *may* be a reasonable hypothesis of the reaction sequence.
4. If more than one mechanism can be proposed, and they all predict derived rate equations in agreement with experiment, then more experiments must be done.

If we solve this equation for $[N_2O_2]$, we have $[N_2O_2] = K[NO]^2$. When this is substituted into the derived rate law

$$\text{Rate} = k_2\{K[NO]^2\}[O_2]$$

the resulting equation is identical with the experimental rate law where $k_2K = k$.

Comment The $NO + O_2$ reaction has an experimental rate law for which at least three mechanisms can be proposed. The challenge is to decide which is correct. In this case further experimentation detected the species OONO as a short-lived intermediate, confirming the mechanism involving this intermediate.

Exercise 15.13—Reaction Mechanism Involving a Fast Initial Step

One possible mechanism for the decomposition of nitryl chloride, NO_2Cl, is

Elementary Step 1: Fast, Equilibrium $NO_2Cl(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2(g) + Cl(g)$

Elementary Step 2: Slow $NO_2Cl(g) + Cl(g) \xrightarrow{k_2} NO_2(g) + Cl_2(g)$

What is the overall reaction? What rate law would be derived from this mechanism? What effect does increasing the concentration of the product NO_2 have on the reaction rate?

Chapter Goals–Revisited

Now that you have studied this chapter, you should ask whether you have met the chapter goals. In particular you should be able to:

Understand rates of reaction and the conditions affecting rates

a. Explain the concept of reaction rate (Section 15.1).

b. Derive the average and instantaneous rates of a reaction from experimental information (Section 15.1). General ChemistryNow homework: Study Question(s) 5

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See the General ChemistryNow CD-ROM or website to:

- Assess your understanding with homework questions keyed to each goal
- Check your readiness for an exam by taking the exam-prep quiz and exploring the resources in the personalized Learning Plan it provides

- **c.** Describe factors that affect reaction rate (i.e., reactant concentrations, temperature, presence of a catalyst, and the state of the reactants) (Section 15.2). General ChemistryNow homework: SQ(s) 8, 10

Derive the rate equation, rate constant, and reaction order from experimental data

- **a.** Define the various parts of a rate equation (the rate constant and order of reaction) and understand their significance (Section 15.3). General ChemistryNow homework: SQ(s) 12, 14
- **b.** Derive a rate equation from experimental information (Section 15.3).

Use integrated rate laws

- **a.** Describe and use the relationships between reactant concentration and time for zero-order, first-order, and second-order reactions (Section 15.4 and Table 15.1). General ChemistryNow homework: SQ(s) 18, 20, 22, 23, 82
- **b.** Apply graphical methods for determining reaction order and the rate constant from experimental data (Section 15.4 and Table 15.1). General ChemistryNow homework: SQ(s) 36, 38
- **c.** Use the concept of half-life ($t_{1/2}$), especially for first-order reactions (Section 15.4). General ChemistryNow homework: SQ(s) 26, 30, 81

Understand the collision theory of reaction rates and the role of activation energy

- **a.** Describe the collision theory of reaction rates (Section 15.5).
- **b.** Relate activation energy (E_a) to the rate and thermodynamics of a reaction (Section 15.5). General ChemistryNow homework: SQ(s) 44, 79
- **c.** Use collision theory to describe the effect of reactant concentration on reaction rate (Section 15.5).
- **d.** Understand the effect of molecular orientation on reaction rate (Section 15.5).
- **e.** Describe the effect of temperature on reaction rate using the collision theory of reaction rates and the Arrhenius equation (Equation 15.7 and Section 15.5).
- **f.** Use Equations 15.5, 15.6, and 15.7 to calculate the activation energy from experimental data (Section 15.5).

Relate reaction mechanisms and rate laws

- **a.** Describe the functioning of a catalyst and its effect on the activation energy and mechanism of a reaction (Section 15.5).
- **b.** Define homogeneous and heterogeneous catalysts (Section 15.5).
- **c.** Understand the concept of a reaction mechanism (the sequence of bond-making and bond-breaking steps that occurs during the conversion of reactants to products) and the relation of the mechanism to the overall, stoichiometric equation for a reaction (Section 15.6).
- **d.** Describe the elementary steps of a mechanism and give their molecularity (Section 15.6). General ChemistryNow homework: SQ(s) 48, 50
- **e.** Define the rate-determining step in a mechanism and identify any reaction intermediates (Section 15.6). General ChemistryNow homework: SQ(s) 52

Key Equations

Equation 15.1 (page 713)
Integrated rate equation for a first-order reaction (in which $-\Delta[\text{R}]/\Delta t = k[\text{R}]$).

$$\ln \frac{[\text{R}]_t}{[\text{R}]_0} = -kt$$

Here $[\text{R}]_0$ and $[\text{R}]_t$ are concentrations of the reactant at time $t = 0$ and at a later time, t. The *ratio* of concentrations, $[\text{R}]_t/[\text{R}]_0$, is the fraction of reactant that *remains* after a given time has elapsed.

Equation 15.2 (page 715)
Integrated rate equation for a second-order reaction (in which $-\Delta[\text{R}]/\Delta t = k[\text{R}]^2$).

$$\frac{1}{[\text{R}]_t} - \frac{1}{[\text{R}]_0} = kt$$

Equation 15.3 (page 716)
Integrated rate equation for a zero-order reaction (in which $-\Delta[\text{R}]/\Delta t = k[\text{R}]^0$).

$$[\text{R}]_0 - [\text{R}]_t = kt$$

Equation 15.4 (page 719)
The relation between the half-life ($t_{1/2}$) and the rate constant (k) for a first-order reaction.

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

Equation 15.5 (page 727)
Arrhenius equation in exponential form

$$k = \text{rate constant} = \underset{\text{Frequency factor}}{A}\,\underbrace{e^{-E_a/RT}}_{\text{Fraction of molecules with minimum energy for reaction}}$$

A is the frequency factor, E_a is the activation energy, T is the temperature (in kelvins), and R is the gas constant ($= 8.314510 \times 10^{-3}\ \text{kJ}/K \cdot \text{mol}$).

Equation 15.6 (page 727)
Expanded Arrhenius equation in logarithmic form.

$$\begin{array}{ccccl} \ln k & = & -\dfrac{E_a}{R}\left(\dfrac{1}{T}\right) & + \ln A & \longleftarrow \text{Arrhenius equation} \\ \downarrow & & \downarrow & \downarrow & \\ y & = & mx & + b & \longleftarrow \text{Equation for straight line} \end{array}$$

Equation 15.7 (page 728)
A version of the Arrhenius equation used to calculate the activation energy for a reaction when you know the values of the rate constant at two temperatures (in kelvins).

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

Study Questions

▲ denotes more challenging questions.

■ denotes questions available in the Homework and Goals section of the General ChemistryNow CD-ROM or website.

Blue numbered questions have answers in Appendix O and fully worked solutions in the *Student Solutions Manual.*

Structures of many of the compounds used in these questions are found on the General ChemistryNow CD-ROM or website in the Models folder.

GENERAL ChemistryNow™ Assess your understanding of this chapter's topics with additional quizzing and conceptual questions at **http://now.brookscole.com/kotz6e**

Practicing Skills

Reaction Rates

(See Examples 15.1–15.2, Exercises 15.1–15.2, and General ChemistryNow CD-ROM or website Screen 15.2.)

1. Give the relative rates of disappearance of reactants and formation of products for each of the following reactions.
   (a) $2\ O_3(g) \longrightarrow 3\ O_2(g)$
   (b) $2\ HOF(g) \longrightarrow 2\ HF(g) + O_2(g)$

2. Give the relative rates of disappearance of reactants and formation of products for each of the following reactions.
   (a) $2\ NO(g) + Br_2(g) \longrightarrow 2\ NOBr(g)$
   (b) $N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$

3. In the reaction $2\ O_3(g) \longrightarrow 3\ O_2(g)$, the rate of formation of O_2 is 1.5×10^{-3} mol/L · s. What is the rate of decomposition of O_3?

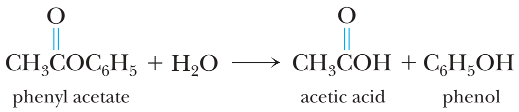
4. In the synthesis of ammonia, if $-\Delta[H_2]/\Delta t = 4.5 \times 10^{-4}$ mol/ L · min, what is $\Delta[NH_3]/\Delta t$?
   $N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$

5. ■ Experimental data are listed here for the reaction $A \longrightarrow 2\ B$.

Time (s)	[B] (mol/L)
0.00	0.000
10.0	0.326
20.0	0.572
30.0	0.750
40.0	0.890

   (a) Prepare a graph from these data, connect the points with a smooth line, and calculate the rate of change of [B] for each 10-s interval from 0.0 to 40.0 s. Does the rate of change decrease from one time interval to the next? Suggest a reason for this result.
   (b) How is the rate of change of [A] related to the rate of change of [B] in each time interval? Calculate the rate of change of [A] for the time interval from 10.0 to 20.0 s.
   (c) What is the instantaneous rate when [B] = 0.750 mol/L?

6. Phenyl acetate, an ester, reacts with water according to the equation



$$CH_3\overset{\overset{O}{\|}}{C}OC_6H_5 + H_2O \longrightarrow CH_3\overset{\overset{O}{\|}}{C}OH + C_6H_5OH$$

The data in the table were collected for this reaction at 5 °C.

Time (s)	[Phenyl acetate] (mol/L)
0	0.55
15.0	0.42
30.0	0.31
45.0	0.23
60.0	0.17
75.0	0.12
90.0	0.085

   (a) Plot the phenyl acetate concentration versus time, and describe the shape of the curve observed.
   (b) Calculate the rate of change of the phenyl acetate concentration during the period 15.0 s to 30.0 s and also during the period 75.0 s to 90.0 s. Compare the values, and suggest a reason why one value is smaller than the other.
   (c) What is the rate of change of the phenol concentration during the time period 60.0 s to 75.0 s?
   (d) What is the instantaneous rate at 15.0 s?

Concentration and Rate Equations

(See Examples 15.3–15.4, Exercises 15.3–15.4, and General ChemistryNow CD-ROM or website Screens 15.4 and 15.5.)

7. Using the rate equation "Rate = $k[A]^2[B]$," define the order of the reaction with respect to A and B. What is the total order of the reaction?

8. ■ A reaction has the experimental rate equation "Rate = $k[A]^2$." How will the rate change if the concentration of A is tripled? If the concentration of A is halved?

9. The reaction between ozone and nitrogen dioxide at 231 K is first order in both $[NO_2]$ and $[O_3]$.

$$2\ NO_2(g) + O_3(g) \longrightarrow N_2O_5(s) + O_2(g)$$

   (a) Write the rate equation for the reaction.

(b) If the concentration of NO_2 is tripled, what is the change in the reaction rate?

(c) What is the effect on reaction rate if the concentration of O_3 is halved?

10. ■ Nitrosyl bromide, NOBr, is formed from NO and Br_2:

$$2\ NO(g) + Br_2(g) \longrightarrow 2\ NOBr(g)$$

Experiments show that this reaction is second order in NO and first order in Br_2.

(a) Write the rate equation for the reaction.

(b) How does the initial reaction rate change if the concentration of Br_2 is changed from 0.0022 mol/L to 0.0066 mol/L?

(c) What is the change in the initial rate if the concentration of NO is changed from 0.0024 mol/L to 0.0012 mol/L?

11. The data in the table are for the reaction of NO and O_2 at 660 K.

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

Reactant Concentration (mol/L)		**Rate of Disappearance of NO (mol/L · s)**
[NO]	**[O_2]**	
0.010	0.010	2.5×10^{-5}
0.020	0.010	1.0×10^{-4}
0.010	0.020	5.0×10^{-5}

(a) Determine the order of the reaction for each reactant.

(b) Write the rate equation for the reaction.

(c) Calculate the rate constant.

(d) Calculate the rate (in mol/L · s) at the instant when $[NO] = 0.015$ mol/L and $[O_2] = 0.0050$ mol/L.

(e) At the instant when NO is reacting at the rate 1.0×10^{-4} mol/L · s, what is the rate at which O_2 is reacting and NO_2 is forming?

12. ■ The reaction

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

was studied at 904 °C, and the data in the table were collected.

Reactant Concentration (mol/L)		**Rate of Appearance of N_2 (mol/L · s)**
[NO]	**[H_2]**	
0.420	0.122	0.136
0.210	0.122	0.0339
0.210	0.244	0.0678
0.105	0.488	0.0339

(a) Determine the order of the reaction for each reactant.

(b) Write the rate equation for the reaction.

(c) Calculate the rate constant for the reaction.

(d) Find the rate of appearance of N_2 at the instant when $[NO] = 0.350$ mol/L and $[H_2] = 0.205$ mol/L.

13. Data for the reaction $2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)$ are given in the table.

	Concentration (mol/L)		**Initial Rate**
Experiment	**[NO]**	**[O_2]**	**(mol/L · h)**
1	3.6×10^{-4}	5.2×10^{-3}	3.4×10^{-8}
2	3.6×10^{-4}	1.04×10^{-2}	6.8×10^{-8}
3	1.8×10^{-4}	1.04×10^{-2}	1.7×10^{-8}
4	1.8×10^{-4}	5.2×10^{-3}	?

(a) What is the rate law for this reaction?

(b) What is the rate constant for the reaction?

(c) What is the initial rate of the reaction in experiment 4?

14. ■ Data for the following reaction are given in the table below.

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

	Concentration (mol/L)		**Initial Rate**
Experiment	**[CO]**	**[NO_2]**	**(mol/L · h)**
1	5.0×10^{-4}	0.36×10^{-4}	3.4×10^{-8}
2	5.0×10^{-4}	0.18×10^{-4}	1.7×10^{-8}
3	1.0×10^{-3}	0.36×10^{-4}	6.8×10^{-8}
4	1.5×10^{-3}	0.72×10^{-4}	?

(a) What is the rate law for this reaction?

(b) What is the rate constant for the reaction?

(c) What is the initial rate of the reaction in experiment 4?

15. Carbon monoxide reacts with O_2 to form CO_2:

$$2\ CO(g) + O_2(g) \longrightarrow 2\ CO_2(g)$$

Information on this reaction is given in the table below.

[CO] (mol/L)	**[O_2] (mol/L)**	**Rate (mol/L · min)**
0.02	0.02	3.68×10^{-5}
0.04	0.02	1.47×10^{-4}
0.02	0.04	7.36×10^{-5}

(a) What is the rate law for this reaction?

(b) What is the order of the reaction with respect to CO? What is the order with respect O_2? What is the overall order of the reaction?

(c) What is the value for the rate constant, *k*?

16. Data for the reaction

$$H_2PO_4^-(aq) + OH^-(aq) \longrightarrow HPO_4^{2-}(aq) + H_2O(\ell)$$

are provided in the table.

Experiment	**[$H_2PO_4^-$] (M)**	**[OH^-] (M)**	**Initial Rate (mol/L · min)**
1	0.0030	0.00040	0.0020
2	0.0030	0.00080	0.0080
3	0.0090	0.00040	0.0060
4	?	0.00033	0.0020

(a) What is the rate law for this reaction?
(b) What is the value of k?
(c) What is the concentration of $H_2PO_4^-$ in experiment 4?

Concentration–Time Relationships

(See Examples 15.5–15.7, Exercises 15.5–15.7, and General ChemistryNow CD-ROM or website Screen 15.6.)

17. The rate equation for the hydrolysis of sucrose to fructose and glucose

$$C_{12}H_{22}O_{11}(aq) + H_2O(\ell) \longrightarrow 2\ C_6H_{12}O_6(aq)$$

is "$-\Delta[\text{sucrose}]/\Delta t = k[C_{12}H_{22}O_{11}]$." After 2.57 h at 27 °C, the sucrose concentration decreased from 0.0146 M to 0.0132 M. Find the rate constant, k.

18. ■ The decomposition of N_2O_5 in CCl_4 is a first-order reaction. If 2.56 mg of N_2O_5 is present initially, and 2.50 mg is present after 4.26 min at 55 °C, what is the value of the rate constant, k?

19. The decomposition of SO_2Cl_2 is a first-order reaction:

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

The rate constant for the reaction is $2.8 \times 10^{-3}\ \text{min}^{-1}$ at 600 K. If the initial concentration of SO_2Cl_2 is 1.24×10^{-3} mol/L, how long will it take for the concentration to drop to 0.31×10^{-3} mol/L?

20. ■ The conversion of cyclopropane to propene, described in Example 15.5, occurs with a first-order rate constant of $5.4 \times 10^{-2}\ \text{h}^{-1}$. How long will it take for the concentration of cyclopropane to decrease from an initial concentration 0.080 mol/L to 0.020 mol/L?

21. Ammonium cyanate, NH_4NCO, rearranges in water to give urea, $(NH_2)_2CO$:

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

The rate equation for this process is "Rate = $k[NH_4NCO]^2$," where $k = 0.0113$ L/mol · min. If the original concentration of NH_4NCO in solution is 0.229 mol/L, how long will it take for the concentration to decrease to 0.180 mol/L?

22. ■ The decomposition of nitrogen dioxide at a high temperature

$$NO_2(g) \longrightarrow NO(g) + \tfrac{1}{2}\ O_2(g)$$

is second order in this reactant. The rate constant for this reaction is 3.40 L/mol · min. Determine the time needed for the concentration of NO_2 to decrease from 2.00 mol/L to 1.50 mol/L.

23. ■ Hydrogen peroxide, $H_2O_2(aq)$, decomposes to $H_2O(\ell)$ and $O_2(g)$ in a reaction that is first order in H_2O_2 and has a rate constant $k = 1.06 \times 10^{-3}\ \text{min}^{-1}$.
(a) How long will it take for 15% of a sample of H_2O_2 to decompose?
(b) How long will it take for 85% of the sample to decompose?

24. The thermal decomposition of HCO_2H is a first-order reaction with a rate constant of $2.4 \times 10^{-3}\ \text{s}^{-1}$ at a given temperature. How long will it take for three fourths of a sample of HCO_2H to decompose?

Half-Life

(See Examples 15.8 and 15.9, Exercise 15.9, and General ChemistryNow CD-ROM or website Screen 15.8.)

25. The rate equation for the decomposition of N_2O_5 (giving NO_2 and O_2) is "$-\Delta[N_2O_5]/\Delta t = k[N_2O_5]$." The value of k is $5.0 \times 10^{-4}\ \text{s}^{-1}$ for the reaction at a particular temperature.
(a) Calculate the half-life of N_2O_5.
(b) How long does it take for the N_2O_5 concentration to drop to one tenth of its original value?

26. ■ The decomposition of SO_2Cl_2

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

is first order in SO_2Cl_2, and the reaction has a half-life of 245 min at 600 K. If you begin with 3.6×10^{-3} mol of SO_2Cl_2 in a 1.0-L flask, how long will it take for the quantity of SO_2Cl_2 to decrease to 2.00×10^{-4} mol?

27. Gaseous azomethane, $CH_3N{=}NCH_3$, decomposes in a first-order reaction when heated:

$$CH_3N{=}NCH_3(g) \longrightarrow N_2(g) + C_2H_6(g)$$

The rate constant for this reaction at 425 °C is $40.8\ \text{min}^{-1}$. If the initial quantity of azomethane in the flask is 2.00 g, how much remains after 0.0500 min? What quantity of N_2 is formed in this time?

28. The compound $Xe(CF_3)_2$ decomposes in a first-order reaction to elemental Xe with a half-life of 30. min. If you place 7.50 mg of $Xe(CF_3)_2$ in a flask, how long must you wait until only 0.25 mg of $Xe(CF_3)_2$ remains?

29. The radioactive isotope ^{64}Cu is used in the form of copper(II) acetate to study Wilson's disease. The isotope has a half-life of 12.70 h. What fraction of radioactive copper(II) acetate remains after 64 h?

30. ■ Radioactive gold-198 is used in the diagnosis of liver problems. The half-life of this isotope is 2.7 days. If you begin with a 5.6-mg sample of the isotope, how much of this sample remains after 1.0 day?

31. Formic acid decomposes at 550 °C according to the equation

$$HCO_2H(g) \longrightarrow CO_2(g) + H_2(g)$$

The reaction follows first-order kinetics. In an experiment, it is determined that 75% of a sample of HCO_2H has decomposed in 72 seconds. Determine $t_{1/2}$ for this reaction.

32. The decomposition of SO_2Cl_2 to SO_2 and Cl_2 at high temperature is a first-order reaction with a half-life of 2.5×10^3 min. What fraction of SO_2Cl_2 will remain after 750 min?

Graphical Analysis: Rate Equations and *k*

(See Exercise 15.8 and General ChemistryNow CD-ROM or website Screen 15.7.)

33. Common sugar, sucrose, breaks down in dilute acid solution to form glucose and fructose. Both products have the same formula, $C_6H_{12}O_6$.

$$C_{12}H_{22}O_{11}(aq) + H_2O(\ell) \longrightarrow 2\ C_6H_{12}O_6(aq)$$

The rate of this reaction has been studied in acid solution, and the data in the table were obtained.

Time (min)	$[C_{12}H_{22}O_{11}]$ (mol/L)
0	0.316
39	0.274
80	0.238
140	0.190
210	0.146

(a) Plot ln [sucrose] versus time and 1/[sucrose] versus time. What is the order of the reaction?

(b) Write the rate equation for the reaction, and calculate the rate constant, *k*.

(c) Estimate the concentration of sucrose after 175 min.

34. Data for the reaction of phenyl acetate with water are given in Study Question 6. Plot these data as ln [phenyl acetate] and 1/[phenyl acetate] versus time. Based on the appearance of the two graphs, what can you conclude about the order of the reaction with respect to phenyl acetate? Working from the data and the rate law, determine the rate constant for the reaction.

35. Data for the decomposition of dinitrogen oxide

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

on a gold surface at 900 °C are given below. Verify that the reaction is first order by preparing a graph of ln $[N_2O]$ versus time. Derive the rate constant from the slope of the line in this graph. Using the rate law and value of *k*, determine the decomposition rate at 900 °C when $[N_2O]$ = 0.035 mol/L.

Time (min)	$[N_2O]$ (mol/L)
15.0	0.0835
30.0	0.0680
80.0	0.0350
120.0	0.0220

36. ■ Ammonia decomposes when heated according to the equation

$$NH_3(g) \longrightarrow NH_2(g) + H(g)$$

The data in the table for this reaction were collected at a high temperature.

Time (h)	$[NH_3]$ (mol/L)
0	8.00×10^{-7}
25	6.75×10^{-7}
50	5.84×10^{-7}
75	5.15×10^{-7}

Plot ln $[NH_3]$ versus time and $1/[NH_3]$ versus time. What is the order of this reaction with respect to NH_3? Find the rate constant for the reaction from the slope.

37. Gaseous $[NO_2]$ decomposes at 573 K.

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

The concentration of NO_2 was measured as a function of time. A graph of $1/[NO_2]$ versus time gives a straight line with a slope of 1.1 L/mol · s. What is the rate law for this reaction? What is the rate constant?

38. ■ The decomposition of HOF occurs at 25 °C.

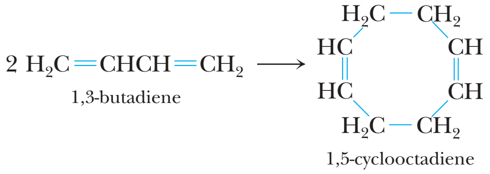
$$2\ HOF(g) \longrightarrow 2\ HF(g) + O_2(g)$$

Using the data in the table below, determine the rate law and then calculate the rate constant.

[HOF] (mol/L)	Time (min)
0.850	0
0.810	2.00
0.754	5.00
0.526	20.0
0.243	50.0

39. For the reaction $2\ C_2F_4 \longrightarrow C_4F_8$, a graph of $1/[C_2F_4]$ versus time gives a straight line with a slope of +0.04 L/mol · s. What is the rate law for this reaction?

40. Butadiene, $C_4H_6(g)$, dimerizes when heated, forming 1,5-cyclooctadiene, C_8H_{12}. The data in the table were collected.



$[C_4H_6]$ (mol/L)	Time (s)
1.0×10^{-2}	0
8.7×10^{-3}	200.
7.7×10^{-3}	500.
6.9×10^{-3}	800.
5.8×10^{-3}	1200.

(a) Use a graphical method to verify that this is a second-order reaction.
(b) Calculate the rate constant for this reaction.

Kinetics and Energy

(See Examples 15.10 and 15.11, Exercise 15.10, and General ChemistryNow CD-ROM or website Screens 15.9 and 15.10.)

41. Calculate the activation energy, E_a, for the reaction

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

from the observed rate constants: k at 25 °C $= 3.46 \times 10^{-5}\ s^{-1}$ and k at 55 °C $= 1.5 \times 10^{-3}\ s^{-1}$.

42. If the rate constant for a reaction triples when the temperature rises from 3.00×10^2 K to 3.10×10^2 K, what is the activation energy of the reaction?

43. When heated to a high temperature, cyclobutane, C_4H_8, decomposes to ethylene:

$$C_4H_8(g) \longrightarrow 2\ C_2H_4(g)$$

The activation energy, E_a, for this reaction is 260 kJ/mol. At 800 K, the rate constant $k = 0.0315\ s^{-1}$. Determine the value of k at 850 K.

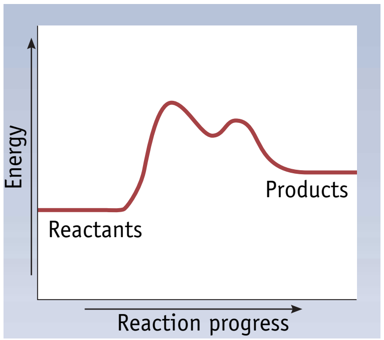
44. ■ When heated, cyclopropane is converted to propene (see Example 15.5). Rate constants for this reaction at 470 °C and 510 °C are $k = 1.10 \times 10^{-4}\ s^{-1}$ and $k = 1.02 \times 10^{-3}\ s^{-1}$, respectively. Determine the activation energy, E_a, from these data.

45. The reaction of H_2 molecules with F atoms

$$H_2(g) + F(g) \longrightarrow HF(g) + H(g)$$

has an activation energy of 8 kJ/mol and an energy change of −133 kJ/mol. Draw a diagram similar to Figure 15.13 for this process. Indicate the activation energy and enthalpy of reaction on this diagram.

46. Answer questions (a) and (b) based on the accompanying reaction coordinate diagram.
(a) Is the reaction exothermic or endothermic?
(b) Does the reaction occur in more than one step? If so, how many?



Reaction Mechanisms

(See Examples 15.12–15.14, Exercises 15.11–15.13, and General ChemistryNow CD-ROM or website, Screens 15.12 and 15.13.)

47. What is the rate law for each of the following *elementary* reactions?
(a) $NO(g) + NO_3(g) \longrightarrow 2\ NO_2(g)$
(b) $Cl(g) + H_2(g) \longrightarrow HCl(g) + H(g)$
(c) $(CH_3)_3CBr(aq) \longrightarrow (CH_3)_3C^+(aq) + Br^-(aq)$

48. ■ What is the rate law for each of the following *elementary* reactions?
(a) $Cl(g) + ICl(g) \longrightarrow I(g) + Cl_2(g)$
(b) $O(g) + O_3(g) \longrightarrow 2\ O_2(g)$
(c) $2\ NO_2(g) \longrightarrow N_2O_4(g)$

49. Ozone, O_3, in the earth's upper atmosphere decomposes according to the equation

$$2\ O_3(g) \longrightarrow 3\ O_2(g)$$

The mechanism of the reaction is thought to proceed through an initial fast, reversible step followed by a slow, second step.

Step 1 Fast, reversible $O_3(g) \rightleftharpoons O_2(g) + O(g)$
Step 2 Slow $O_3(g) + O(g) \longrightarrow 2\ O_2(g)$

(a) Which of the steps is rate-determining?
(b) Write the rate equation for the rate-determining step.

50. ■ The reaction of $NO_2(g)$ and $CO(g)$ is thought to occur in two steps:

Step 1 Slow $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$
Step 2 Fast $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$

(a) Show that the elementary steps add up to give the overall, stoichiometric equation.
(b) What is the molecularity of each step?
(c) For this mechanism to be consistent with kinetic data, what must be the experimental rate equation?
(d) Identify any intermediates in this reaction.

51. Iodide ion is oxidized in acid solution by hydrogen peroxide (Figure 15.3).

$$H_2O_2(aq) + 2\ H^+(aq) + 2\ I^-(aq) \longrightarrow I_2(aq) + 2\ H_2O(\ell)$$

A proposed mechanism is

Step 1 Slow $H_2O_2(aq) + I^-(aq) \longrightarrow H_2O(\ell) + OI^-(aq)$
Step 2 Fast $H^+(aq) + OI^-(aq) \longrightarrow HOI(aq)$
Step 3 Fast $HOI(aq) + H^+(aq) + I^-(aq) \longrightarrow I_2(aq) + H_2O(\ell)$

(a) Show that the three elementary steps add up to give the overall, stoichiometric equation.
(b) What is the molecularity of each step?
(c) For this mechanism to be consistent with kinetic data, what must be the experimental rate equation?
(d) Identify any intermediates in the elementary steps in this reaction.

52. ■ The mechanism for the reaction of CH_3OH and HBr is believed to involve two steps. The overall reaction is exothermic.

Step 1 Fast, endothermic

$$CH_3OH + H^+ \rightleftharpoons CH_3OH_2^+$$

Step 2 Slow

$$CH_3OH_2^+ + Br^- \longrightarrow CH_3Br + H_2O$$

(a) Write an equation for the overall reaction.
(b) Draw a reaction coordinate diagram for this reaction.
(c) Show that the rate law for this reaction is $-\Delta[CH_3OH]/\Delta t = k[CH_3OH][H^+][Br^-]$.

53. A proposed mechanism for the reaction of NO_2 and CO is

Step 1 Slow, endothermic

$$2\ NO_2(g) \longrightarrow NO(g) + NO_3(g)$$

Step 2 Fast, exothermic

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

Overall Reaction Exothermic

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

(a) Identify each of the following as a reactant, product, or intermediate: $NO_2(g)$, $CO(g)$, $NO_3(g)$, $CO_2(g)$, $NO(g)$.
(b) Draw a reaction coordinate diagram for this reaction. Indicate on this drawing the activation energy for each step and the overall reaction enthalpy.

54. A three-step mechanism for the reaction of $(CH_3)_3CBr$ and H_2O is proposed:

Step 1 Slow

$$(CH_3)_3CBr \longrightarrow (CH_3)_3C^+ + Br^-$$

Step 2 Fast

$$(CH_3)_3C^+ + H_2O \longrightarrow (CH_3)_3COH_2^+$$

Step 3 Fast

$$(CH_3)_3COH_2^+ + Br^- \longrightarrow (CH_3)_3COH + HBr$$

(a) Write an equation for the overall reaction.
(b) Which step is rate-determining?
(c) What rate law is expected for this reaction?

General Questions

These questions are not designated as to type or location in the chapter. They may contain several concepts.

55. A reaction has the following experimental rate equation: Rate $= k[A]^2[B]$. If the concentration of A is doubled and the concentration of B is halved, what happens to the reaction rate?

56. After five half-life periods for a first-order reaction, what fraction of reactant remains?

57. To determine the concentration dependence of the rate of the reaction

$$H_2PO_3^-(aq) + OH^-(aq) \longrightarrow HPO_3^{2-}(aq) + H_2O(\ell)$$

you might measure $[OH^-]$ as a function of time using a pH meter. (To do so, you would set up conditions under which $[H_2PO_3^-]$ remains constant, by using a large excess of this reactant.) How would you prove a second-order rate dependence for $[OH^-]$?

58. Gaseous ammonia is made by the reaction

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

Use the information on the formation of NH_3 given in the table to answer the questions that follow.

$[N_2]$(M)	**$[H_2]$ (M)**	**Rate (mol/L · min)**
0.030	0.010	4.21×10^{-5}
0.060	0.010	1.68×10^{-4}
0.030	0.020	3.37×10^{-4}

(a) Determine n and m in the rate equation: Rate $= k[N_2]^n[H_2]^m$.
(b) Calculate the value of the rate constant.
(c) What is the order of the reaction with respect to $[H_2]$?
(d) What is the overall order of the reaction?

59. The decomposition of ammonia is first order with respect to NH_3. (Compare with Study Question 58.)

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

(a) What is the rate equation for this reaction?
(b) Calculate the rate constant, k, given the following data:

$[NH_3]$ (mol/L)	**Time (s)**
0.67	0
0.26	19

(c) Determine the half-life of NH_3.

60. Data for the following reaction are given in the table.

$$2\ NO(g) + Br_2(g) \longrightarrow 2\ NOBr(g)$$

Experiment	**[NO] (M)**	**$[Br_2]$ (M)**	**Initial Rate (mol/L · s)**
1	1.0×10^{-2}	2.0×10^{-2}	2.4×10^{-2}
2	4.0×10^{-2}	2.0×10^{-2}	0.384
3	1.0×10^{-2}	5.0×10^{-2}	6.0×10^{-2}

(a) What is the order of the reaction with respect to [NO]?
(b) What is the order with respect to $[Br_2]$?
(c) What is the overall order of the reaction?

61. The decomposition of CO_2 is first order with respect to the concentration of CO_2.

$$2\ CO_2(g) \longrightarrow 2\ CO(g) + O_2(g)$$

Data on this reaction are provided in the table below.

$[CO_2]$ (mol/L)	Time (s)
0.38	0
0.27	12

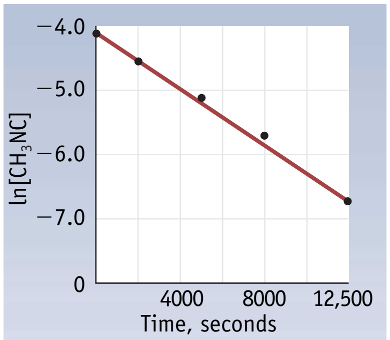
(a) Write the rate equation for this reaction.
(b) Use the data to determine the value of *k*.
(c) What is the half-life of CO_2 under these conditions?

62. The isomerization of CH_3NC occurs slowly when CH_3NC is heated.

$$CH_3NC(g) \longrightarrow CH_3CN(g)$$

To study the rate of this reaction at 488 K, data on $[CH_3NC]$ were collected at various times. Analysis led to the graph below.

(a) What is the rate law for this reaction?
(b) What is the equation for the straight line in this graph?
(c) Calculate the rate constant for this reaction, giving the correct units.
(d) How long does it takes for half of the sample to isomerize?
(e) What is the concentration of CH_3NC after 10,000 s?



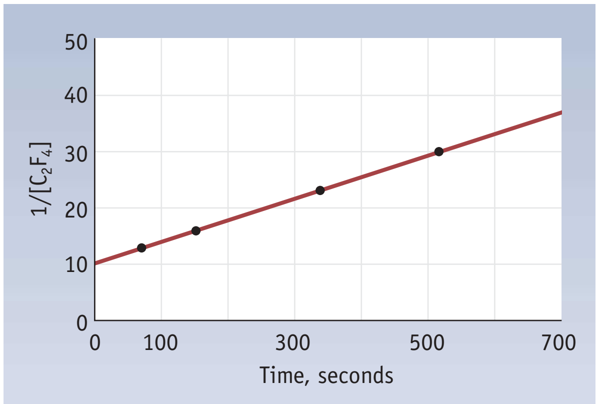
63. When heated, tetrafluoroethylene dimerizes to form octafluorocyclobutane.

$$2\ C_2F_4(g) \longrightarrow C_4F_8(g)$$

To determine the rate of this reaction at 488 K, the data in the table were collected. Analysis was done graphically, as shown below:

$[C_2F_4]$ (M)	Time (s)
0.100	0
0.080	56
0.060	150.
0.040	335
0.030	520.

(a) What is the rate law for this reaction?
(b) What is the value of the rate constant?
(c) What is the concentration of C_2F_4 after 600 s?
(d) How long will it take until the reaction is 90% complete?



64. Data in the table were collected at 540 K for the following reaction:

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

(a) Derive the rate equation.
(b) Determine the reaction order with respect to each reactant.
(c) Calculate the rate constant, giving the correct units for *k*.

Initial Concentration (mol/L)		Initial Rate (mol/L · h)
[CO]	$[NO_2]$	
5.1×10^{-4}	0.35×10^{-4}	3.4×10^{-8}
5.1×10^{-4}	0.70×10^{-4}	6.8×10^{-8}
5.1×10^{-4}	0.18×10^{-4}	1.7×10^{-8}
1.0×10^{-3}	0.35×10^{-4}	6.8×10^{-8}
1.5×10^{-3}	0.35×10^{-4}	10.2×10^{-8}

65. Ammonium cyanate, NH_4NCO, rearranges in water to give urea, $(NH_2)_2CO$:

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

Time (min)	$[NH_4NCO]$ (mol/L)
0	0.458
4.50×10^1	0.370
1.07×10^2	0.292
2.30×10^2	0.212
6.00×10^2	0.114

Using the data in the table:

(a) Decide whether the reaction is first order or second order.

(b) Calculate k for this reaction.

(c) Calculate the half-life of ammonium cyanate under these conditions.

(d) Calculate the concentration of NH_4NCO after 12.0 h.

66. Nitrogen oxides, NO_x (a mixture of NO and NO_2 collectively designated as NO_x), play an essential role in the production of pollutants found in photochemical smog. The NO_x in the atmosphere is slowly broken down to N_2 and O_2 in a first-order reaction. The average half-life of NO_x in the smokestack emissions in a large city during daylight is 3.9 h.

(a) Starting with 1.50 mg in an experiment, what quantity of NO_x remains after 5.25 h?

(b) How many hours of daylight must have elapsed to decrease 1.50 mg of NO_x to 2.50×10^{-6} mg?

67. At temperatures below 500 K, the reaction between carbon monoxide and nitrogen dioxide

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

has the following rate equation: Rate = $k[NO_2]^2$. Which of the three mechanisms suggested here best agrees with the experimentally observed rate equation?

Mechanism 1 *Single, elementary step*

$$NO_2 + CO \longrightarrow CO_2 + NO$$

Mechanism 2 *Two steps*

Slow $NO_2 + NO_2 \longrightarrow NO_3 + NO$

Fast $NO_3 + CO \longrightarrow NO_2 + CO_2$

Mechanism 3 *Two steps*

Slow $NO_2 \longrightarrow NO + O$

Fast $CO + O \longrightarrow CO_2$

68. Nitryl fluoride can be made by treating nitrogen dioxide with fluorine:

$$2\ NO_2(g) + F_2(g) \longrightarrow 2\ NO_2F(g)$$

Use the rate data in the table to do the following:

(a) Write the rate equation for the reaction.

(b) Indicate the order of reaction with respect to each component of the reaction.

(c) Find the numerical value of the rate constant, k.

	Initial Concentrations (mol/L)			**Initial Rate**
Experiment	**$[NO_2]$**	**$[F_2]$**	**$[NO_2F]$**	**(mol/L · s)**
1	0.001	0.005	0.001	2×10^{-4}
2	0.002	0.005	0.001	4×10^{-4}
3	0.006	0.002	0.001	4.8×10^{-4}
4	0.006	0.004	0.001	9.6×10^{-4}
5	0.001	0.001	0.001	4×10^{-5}
6	0.001	0.001	0.002	4×10^{-5}

69. ▲ The decomposition of dinitrogen pentaoxide

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

has the following rate equation: $-\Delta[N_2O_5]/\Delta t = k[N_2O_5]$. It has been found experimentally that the decomposition is 20% complete in 6.0 h at 300 K. Calculate the rate constant and the half-life at 300 K.

70. The data in the table give the temperature dependence of the rate constant for the reaction $N_2O_5(g) \longrightarrow 2\ NO_2(g) + \frac{1}{2}\ O_2(g)$. Plot these data in the appropriate way to derive the activation energy for the reaction.

T(K)	**k(s^{-1})**
338	4.87×10^{-3}
328	1.50×10^{-3}
318	4.98×10^{-4}
308	1.35×10^{-4}
298	3.46×10^{-5}
273	7.87×10^{-7}

71. The decomposition of gaseous dimethyl ether at ordinary pressures is first order. Its half-life is 25.0 min at 500 °C:

$$CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g)$$

(a) Starting with 8.00 g of dimethyl ether, what mass remains (in grams) after 125 min and after 145 min?

(b) Calculate the time in minutes required to decrease 7.60 ng (nanograms) to 2.25 ng.

(c) What fraction of the original dimethyl ether remains after 150 min?

72. The decomposition of phosphine, PH_3, proceeds according to the equation

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

It is found that the reaction has the following rate equation: Rate = $k[PH_3]$. The half-life of PH_3 is 37.9 s at 120 °C.

(a) How much time is required for three fourths of the PH_3 to decompose?

(b) What fraction of the original sample of PH_3 remains after 1 min?

73. Three mechanisms are proposed for the gas-phase reaction of NO with Br_2 to give BrNO:

Mechanism 1

$$NO(g) + NO(g) + Br_2(g) \longrightarrow 2\ BrNO(g)$$

Mechanism 2

Step 1 Slow $NO(g) + Br_2(g) \longrightarrow Br_2NO(g)$

Step 2 Fast $Br_2NO(g) + NO(g) \longrightarrow 2\ BrNO(g)$

Mechanism 3

Step 1 Slow $NO(g) + NO(g) \longrightarrow N_2O_2(g)$

Step 2 Fast $N_2O_2(g) + Br_2(g) \longrightarrow 2\ BrNO(g)$

(a) Write the balanced equation for the net reaction.

(b) What is the molecularity for each step in each mechanism?

(c) What are the intermediates formed in mechanisms 2 and 3?

(d) Compare the rate laws that are derived from these three mechanisms. How could you differentiate them experimentally?

74. Radioactive iodine-131, which has a half-life of 8.04 days, is used in the form of sodium iodide to treat cancer of the thyroid. If you begin with 25.0 mg of $Na^{131}I$, what quantity of the material remains after 31 days?

75. The ozone in the earth's ozone layer decomposes according to the equation

$$2\ O_3(g) \longrightarrow 3\ O_2(g)$$

The mechanism of the reaction is thought to proceed through an initial fast equilibrium and a slow step:

Step 1 Fast, Reversible $O_3(g) \rightleftarrows O_2(g) + O(g)$

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

Show that the mechanism agrees with this experimental rate law: $-\Delta[O_3]/\Delta t = k[O_3]^2/[O_2]$.

76. Hundreds of different reactions can occur in the stratosphere, among them reactions that destroy the earth's ozone layer. The table below lists several (second-order) reactions of Cl atoms with ozone and organic compounds; each is given with its rate constant.

Reaction	Rate Constant (298 K, cm^3/molecule · s)
(a) $Cl + O_3 \longrightarrow ClO + O_2$	1.2×10^{-11}
(b) $Cl + CH_4 \longrightarrow HCl + CH_3$	1.0×10^{-13}
(c) $Cl + C_3H_8 \longrightarrow HCl + C_3H_7$	1.4×10^{-10}
(d) $Cl + CH_2FCl \longrightarrow HCl + CHFCl$	3.0×10^{-18}

For equal concentrations of Cl and the other reactant, which is the slowest reaction? Which is the fastest reaction?

77. Data for the reaction

$$[Mn(CO)_5(CH_3CN)]^+ + NC_5H_5 \longrightarrow [Mn(CO)_5(NC_5H_5)]^+ + CH_3CN$$

are given in the table. Calculate E_a from a plot of ln k versus $1/T$.

T(K)	k(min^{-1})
298	0.0409
308	0.0818
318	0.157

78. The gas-phase reaction

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

has an activation energy of 103 kJ, and the rate constant is 0.0900 min^{-1} at 328.0 K. Find the rate constant at 318.0 K.

79. ■ ▲ Egg protein albumin is precipitated when an egg is cooked in boiling (100 °C) water. E_a for this first-order reaction is 52.0 kJ/mol. Estimate the time to prepare a 3-min egg at an altitude at which water boils at 90 °C.

80. ▲ Two molecules of the unsaturated hydrocarbon 1,3-butadiene (C_4H_6) form the "dimer" C_8H_{12} at higher temperatures.

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

Use the following data to determine the order of the reaction and the rate constant, k. (Note that the total pressure is the pressure of the unreacted C_4H_6 at any time and the pressure of the C_8H_{12}.)

Time (min)	Total Pressure (mm Hg)
0	436
3.5	421
11.5	390
18.3	367
25.0	346
32.0	328
41.2	306

81. ■ ▲ Hypofluorous acid, HOF, is very unstable, decomposing in a first-order reaction to give HF and O_2, with a half-life of only 30 min at room temperature:

$$HOF(g) \longrightarrow HF(g) + \tfrac{1}{2}\ O_2(g)$$

If the partial pressure of HOF in a 1.00-L flask is initially 1.00×10^2 mm Hg at 25 °C, what is the total pressure in the flask and the partial pressure of HOF after exactly 30 min? After 45 min?

82. ■ ▲ We know that the decomposition of SO_2Cl_2 is first order in SO_2Cl_2,

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

with a half-life of 245 min at 600 K. If you begin with a partial pressure of SO_2Cl_2 of 25 mm Hg in a 1.0-L flask, what is the partial pressure of each reactant and product after 245 min? What is the partial pressure of each reactant after 12 h?

83. The substitution of CO in $Ni(CO)_4$ by another group L [where L is an electron-pair donor such as $P(CH_3)_3$] was studied some years ago and led to an understanding of some of the general principles that govern the chemistry of compounds having metal–CO bonds. (See J. P. Day, F. Basolo, and R. G. Pearson: *Journal of the American Chemical Society,* Vol. 90, p. 6927, 1968.) A detailed study of the kinetics of the reaction led to the following mechanism:

Slow $Ni(CO)_4 \longrightarrow Ni(CO)_3 + CO$

Fast $Ni(CO)_3 + L \longrightarrow Ni(CO)_3L$

(a) What is the molecularity of each of the elementary reactions?

(b) Doubling the concentration of $Ni(CO)_4$ increased the reaction rate by a factor of 2. Doubling the concentration of L had no effect on the reaction rate. Based on this information, write the rate equation for the reaction. Does this agree with the mechanism described?

(c) The experimental rate constant for the reaction, when $L = P(C_6H_5)_3$, is $9.3 \times 10^{-3}\ s^{-1}$ at 20 °C. If the initial concentration of $Ni(CO)_4$ is 0.025 M, what is the concentration of the product after 5.0 min?

84. Screen 15.5 of the General ChemistryNow CD-ROM or website describes how to determine experimentally a rate law using the method of initial rates.

(a) Why is it best to measure the rate of reaction at the beginning of the process for this method to be valid?

(b) The first experiment shows that the initial rate of NH_4NCO degradation is 2.2×10^{-4} mol/L · s when $[NH_4NCO] = 0.14$ M. Using the rate law determined on this screen, predict what the rate would be if $[NH_4NCO] = 0.18$ M.

Summary and Conceptual Questions

The following questions may use concepts from the preceding chapters.

85. Hydrogenation reactions, processes wherein H_2 is added to a molecule, are usually catalyzed. An excellent catalyst is a very finely divided metal suspended in the reaction solvent. Tell why finely divided rhodium, for example, is a much more efficient catalyst than a small block of the metal.

86. ▲ It is instructive to use a mathematical model in connection with Study Question 85. Suppose you have 1000 blocks, each of which is 1.0 cm on a side. If all 1000 of these blocks are stacked to give a cube that is 10. cm on a side, what fraction of the 1000 blocks have at least one surface on the outside surface of the cube? Next divide the 1000 blocks into eight equal piles of blocks and form them into eight cubes, 5.0 cm on a side. What fraction of the blocks now have at least one surface on the outside of the cubes? How does this mathematical model pertain to Study Question 85?

87. The following statements relate to the reaction with the following rate law: Rate $= k[H_2][I_2]$.

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

Determine which of the following statements are true. If a statement is false, indicate why it is incorrect.

(a) The reaction must occur in a single step.

(b) This is a second-order reaction overall.

(c) Raising the temperature will cause the value of k to decrease.

(d) Raising the temperature lowers the activation energy for this reaction.

(e) If the concentrations of both reactants are doubled, the rate will double.

(f) Adding a catalyst in the reaction will cause the initial rate to increase.

88. Chlorine atoms contribute to the destruction of the earth's ozone layer by the following sequence of reactions:

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

where the O atoms in the second step come from the decomposition of ozone by sunlight:

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

What is the net equation on summing these three equations? Why does this lead to ozone loss in the stratosphere? What is the role played by Cl in this sequence of reactions? What name is given to species such as ClO?

89. Describe each of the following statements as true or false. If false, rewrite the sentence to make it correct.

(a) The rate-determining elementary step in a reaction is the slowest step in a mechanism.

(b) It is possible to change the rate constant by changing the temperature.

(c) As a reaction proceeds at constant temperature, the rate remains constant.

(d) A reaction that is third order overall must involve more than one step.

90. Identify which of the following statements are incorrect. If the statement is incorrect, rewrite it to be correct.

(a) Reactions are faster at a higher temperature because activation energies are lower.

(b) Rates increase with increasing concentration of reactants because there are more collisions between reactant molecules.

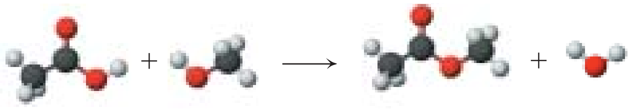
(c) At higher temperatures a larger fraction of molecules have enough energy to get over the activation energy barrier.

(d) Catalyzed and uncatalyzed reactions have identical mechanisms.

91. The reaction cyclopropane ⟶ propene occurs on a platinum metal surface at 200 °C. (The platinum is a catalyst.) The reaction is first order in cyclopropane. Indicate how the following quantities change (increase, decrease, or no change) as this reaction progresses, assuming constant temperature.

(a) [cyclopropane]
(b) [propene]
(c) [catalyst]
(d) the rate constant, *k*
(e) the order of the reaction
(f) the half-life of cyclopropane

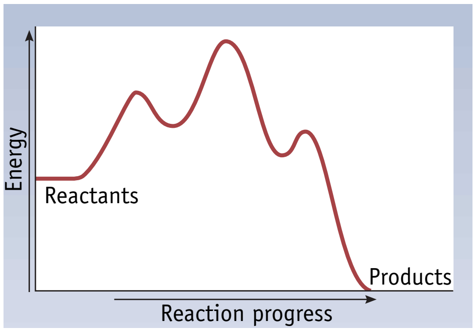
92. Isotopes are often used as "tracers" to follow an atom through a chemical reaction, and the following is an example. Acetic acid reacts with methanol by eliminating a molecule of water and forming methyl acetate (see Chapter 11).



$$CH_3CO_2H + CH_3OH \longrightarrow CH_3CO_2CH_3 + H_2O$$

Explain how you could use the isotope ^{18}O to show whether the oxygen atom in the water comes from the —OH of the acid or the —OH of the alcohol.

93. Examine the reaction coordinate diagram given here.



(a) How many steps are in the mechanism for the reaction described by this diagram?
(b) Is the reaction overall exothermic or endothermic?

94. Draw a reaction energy diagram for an exothermic reaction that occurs in a single step. Mark the activation energy, and identify the net energy change for the reaction on this diagram. Draw a second diagram that represents the same reaction in the presence of a catalyst. Identify the activation energy of this reaction and the energy change. Is the activation energy in the two drawings different? Does the energy evolved in the two reactions differ?

95. Screen 15.2 of the General ChemistryNow CD-ROM or website (Rates of Chemical Reactions) illustrates the rate at which a blue dye is bleached.

(a) What is the difference between an instantaneous rate and an average rate?
(b) Observe the graph of food dye versus time on this screen. (Click the "tool" icon on this screen.) The plot shows the concentration of dye as the reaction progresses. What does the steepness of the plot at any particular time tell you about the rate of the reaction at that time?
(c) As the reaction progresses, the concentration of dye decreases as it is consumed. What happens to the reaction rate as this occurs? What is the relationship between reaction rate and dye concentration?

96. Watch the video on Screen 15.4 of the General ChemistryNow CD-ROM or website (Control of Reaction Rates—Concentration Dependence).

(a) How does an increase in HCl concentration affect the rate of the reaction of the acid with magnesium metal?
(b) On the second portion of this screen are data for the rate of decomposition of N_2O_5 (click "More"). The initial reaction rate is given for three separate experiments, each beginning with a different concentration of N_2O_5. How is the initial reaction rate related to $[N_2O_5]$?

97. The "Microscopic View of Reactions" is described on Screen 15.9 of the General ChemistryNow CD-ROM or website.

(a) According to collision theory, what three conditions must be met for two molecules to react?
(b) Examine the animations that play when numbers 1 and 2 are selected. One of these occurs at a higher temperature than the other. Which one? Explain briefly.
(c) Examine the animations that play when numbers 2 and 3 are selected. Would you expect the reaction of O_3 with N_2,

$$O_3(g) + N_2(g) \longrightarrow O_2(g) + ONN(g)$$

to be more or less sensitive to requiring a proper orientation for reaction than the reaction displayed on this screen? Explain briefly.

98. "Reaction Mechanisms and Rate Equations" are described on Screen 15.13 of the General ChemistryNow CD-ROM or website.

(a) What is the relationship between the stoichiometric coefficients of the reactants in an elementary step and the rate law for that step?
(b) What is the rate law for Step 2 of mechanism 2?
(d) Examine the "Isotopic Labeling" sidebar to this screen. If the transfer of an oxygen atom from NO_2 to CO, occurred in a single-step would any $N^{16}O^{18}O$ be found if the reaction is started using a mixture of $N^{16}O_2$ and $N^{18}O_2$? Why or why not?

99. The mechanism for the iodide ion–catalyzed decomposition of H_2O_2 is described on Screen 15.14 (Catalysis and Reaction Rate) of the General ChemistryNow CD-ROM or website.

(a) Examine the mechanism for the iodide ion–catalyzed decomposition of H_2O_2. Explain how the mechanism shows that I^- is a catalyst.

(b) How does the reaction coordinate diagram show that the catalyzed reaction is expected to be faster than the uncatalyzed reaction?

100. Many biochemical reactions are catalyzed by acids. A typical mechanism consistent with the experimental results (in which HA is the acid and X is the reactant) is

Step 1 Fast, reversible $HA \rightleftharpoons H^+ + A^-$
Step 2 Fast, reversible $X + H^+ \rightleftharpoons XH^+$
Step 3 Slow $XH^+ \longrightarrow \text{products}$

What rate law is derived from this mechanism? What is the order of the reaction with respect to HA? How would doubling the concentration of HA affect the reaction?

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