

Reaction Rates

What You'll Learn

- ▶ You will investigate a model describing how chemical reactions occur as a result of collisions.
- ▶ You will compare the rates of chemical reactions under varying conditions.
- ▶ You will calculate the rates of chemical reactions.

Why It's Important

Perhaps someday you'll be involved with the space program. Rockets, along with their crews and cargo, are propelled into space by the result of a chemical reaction. An understanding of reaction rates is the tool that allows us to control chemical reactions and use them effectively.



Visit the Chemistry Web site at chemistrymc.com to find links about reaction rates.

This launch of the Mars Exploration Rover *Spirit* in June 2003 propelled the robot to its successful touchdown on Mars in January 2004.



DISCOVERY LAB



Materials

hydrogen peroxide
beaker or cup
baker's yeast
toothpicks

Speeding Reactions

Many chemical reactions occur so slowly that you don't even know they are happening. For some reactions, it is possible to alter the reaction speed using another substance.

Safety Precautions



Always use safety goggles and an apron in the lab.

Procedure

1. Create a "before and after" table and record your observations.
2. Pour about 10 mL of hydrogen peroxide into a small beaker or cup. Observe the hydrogen peroxide.
3. Add a "pinch" (1/8 tsp) of yeast to the hydrogen peroxide. Stir gently with a toothpick and observe the mixture again.

Analysis

Into what two products does hydrogen peroxide decompose? Why aren't bubbles produced in step 1? What is the function of the yeast?

Section

17.1

A Model for Reaction Rates

Objectives

- **Calculate** average rates of chemical reactions from experimental data.
- **Relate** rates of chemical reactions to collisions between reacting particles.

Vocabulary

reaction rate
collision theory
activated complex
transition state
activation energy

One of the most spectacular chemical reactions, the one between liquid hydrogen and liquid oxygen, provides the energy to launch rockets into space as shown on the opposite page. This reaction is fast and exothermic. Yet other reactions and processes you're familiar with, such as the hardening of concrete or the formation of fossil fuels, occur at considerably slower rates. The **DISCOVERY LAB** for this chapter emphasized that the speed at which a reaction occurs can vary if other substances are introduced into the reaction. In this section, you'll learn about a model that scientists use to describe and calculate the rates at which chemical reactions occur.

Expressing Reaction Rates

As you know, some chemical reactions are fast and others are slow; however, *fast* and *slow* are inexact, relative terms. Chemists, engineers, medical researchers, and others often need to be more specific.

Think about how you express speed or rate in the situations shown in **Figure 17-1** on the next page. The speed of the sprinter on the track team may be expressed as meters per second. The speed at which the hiker moves might be expressed differently, perhaps as meters per minute. We generally define the average rate of an action or process to be the change in a given quantity during a specific period of time. Recall from your study of math that the Greek letter delta (Δ) before a quantity indicates a change in the quantity. In equation form, average rate or speed is written as

$$\text{Average rate} = \frac{\Delta \text{quantity}}{\Delta t}$$



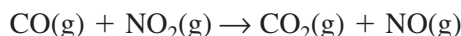
Figure 17-1

The average rate of travel for these activities is based on the change in distance over time. Similarly, the reaction rate is based on the change in concentration over time.

For chemical reactions, this equation defines the average rate at which reactants produce products, which is the amount of change of a reactant in a given period of time. Most often, chemists are concerned with changes in the molar concentration (mol/L, M) of a reactant or product during a reaction. Therefore, the **reaction rate** of a chemical reaction is stated as the change in concentration of a reactant or product per unit time, expressed as mol/(L·s). Brackets around the formula for a substance denote the molar concentration. For example, $[\text{NO}_2]$ represents the molar concentration of NO_2 .

It's important to understand that reaction rates are determined experimentally by measuring the concentrations of reactants and/or products in an actual chemical reaction. Reaction rates cannot be calculated from balanced equations as stoichiometric amounts can.

Suppose you wish to express the average rate of the reaction



during the time period beginning at time t_1 and ending at time t_2 . Calculating the rate at which the products of the reaction are produced results in a reaction rate having a positive value. The rate calculation based on the production of NO will have the form

$$\text{Average reaction rate} = \frac{[\text{NO}] \text{ at time } t_2 - [\text{NO}] \text{ at time } t_1}{t_2 - t_1} = \frac{\Delta[\text{NO}]}{\Delta t}$$

For example, if the concentration of NO is $0.00M$ at time $t_1 = 0.00 \text{ s}$ and $0.010M$ two seconds after the reaction begins, the following calculation gives the average rate of the reaction expressed as moles of NO produced per liter per second.

$$\begin{aligned} \text{Average reaction rate} &= \frac{0.010M - 0.000M}{2.00 \text{ s} - 0.00 \text{ s}} \\ &= \frac{0.010M}{2.00 \text{ s}} = 0.0050 \text{ mol/(L}\cdot\text{s)} \end{aligned}$$

Notice how the units calculate:

$$\frac{M}{s} = \frac{\text{mol/L}}{s} = \frac{\text{mol}}{L} \cdot \frac{1}{s} = \frac{\text{mol}}{(\text{L}\cdot\text{s})}$$

Although $\text{mol/L} = M$, chemists typically reserve M to express concentration and $\text{mol/(L}\cdot\text{s)}$ to express rate.

Alternatively, you can choose to state the rate of the reaction as the rate at which CO is consumed, as shown below:

$$\text{Average reaction rate} = \frac{[\text{CO}] \text{ at time } t_2 - [\text{CO}] \text{ at time } t_1}{t_2 - t_1} = \frac{\Delta[\text{CO}]}{\Delta t}$$

Do you predict a positive or negative value for this reaction? In this case, a negative value indicates that the concentration of CO decreases as the reaction proceeds.

Actually, reaction rates must always be positive. When the rate is measured by the consumption of a reactant, scientists commonly apply a negative sign to the calculation to get a positive reaction rate. Therefore, the following form of the average rate equation is used to calculate the rate of consumption:

$$\text{Average reaction rate} = - \frac{\Delta \text{quantity}}{\Delta t}$$



EXAMPLE PROBLEM 17-1

Calculating Average Reaction Rates

Reaction data for the reaction between butyl chloride ($\text{C}_4\text{H}_9\text{Cl}$) and water (H_2O) is given in Table 17-1. Calculate the average reaction rate over this time period expressed as moles of $\text{C}_4\text{H}_9\text{Cl}$ consumed per liter per second.

1. Analyze the Problem

You are given the initial and final concentrations of $\text{C}_4\text{H}_9\text{Cl}$ and the initial and final times. You can calculate the average reaction rate of the chemical reaction using the change in concentration of butyl chloride in four seconds. In this problem, the reactant butyl chloride is consumed.

Known

$$t_1 = 0.00 \text{ s}$$

$$t_2 = 4.00 \text{ s}$$

$$[\text{C}_4\text{H}_9\text{Cl}] \text{ at } t_1 = 0.220M$$

$$[\text{C}_4\text{H}_9\text{Cl}] \text{ at } t_2 = 0.100M$$

Unknown

$$\text{Average reaction rate} = ? \text{ mol}/(\text{L}\cdot\text{s})$$

2. Solve for the Unknown

Write the equation for the average reaction rate, insert the known quantities, and perform the calculation.

$$\begin{aligned}\text{Average reaction rate} &= - \frac{[\text{C}_4\text{H}_9\text{Cl}] \text{ at time } t_2 - [\text{C}_4\text{H}_9\text{Cl}] \text{ at time } t_1}{t_2 - t_1} \\ &= - \frac{0.100M - 0.220M}{4.00 \text{ s} - 0.00 \text{ s}} \\ (\text{Substitute units}) &= - \frac{0.100 \text{ mol/L} - 0.220 \text{ mol/L}}{4.00 \text{ s} - 0.00 \text{ s}} \\ &= - \frac{-0.120 \text{ mol/L}}{4.00 \text{ s}} \\ &= 0.0300 \text{ mol}/(\text{L}\cdot\text{s})\end{aligned}$$

3. Evaluate the Answer

The average reaction rate of 0.0300 moles $\text{C}_4\text{H}_9\text{Cl}$ consumed per liter per second seems reasonable based on start and end amounts. The answer is correctly expressed in three significant figures.

Table 17-1

Molar Concentration of $\text{C}_4\text{H}_9\text{Cl}$	
$[\text{C}_4\text{H}_9\text{Cl}]$ at $t = 0.00 \text{ s}$	$[\text{C}_4\text{H}_9\text{Cl}]$ at $t = 4.00 \text{ s}$
0.220M	0.100M

PRACTICE PROBLEMS

Use the data in the following table to calculate the average reaction rates.

Experimental Data for $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$			
Time (s)	$[\text{H}_2]$ (M)	$[\text{Cl}_2]$ (M)	$[\text{HCl}]$ (M)
0.00	0.030	0.050	0.000
4.00	0.020	0.040	0.020

1. Calculate the average reaction rate expressed in moles H_2 consumed per liter per second.
2. Calculate the average reaction rate expressed in moles Cl_2 consumed per liter per second.
3. Calculate the average reaction rate expressed in moles HCl produced per liter per second.

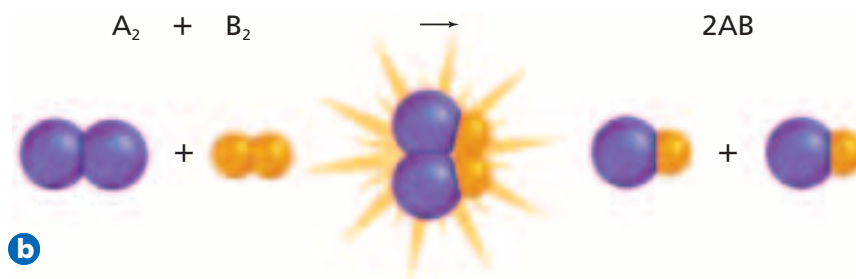


For more practice calculating average reaction rates, go to **Supplemental Practice Problems** in Appendix A.



Figure 17-2

a The product of a demolition derby, the crunch of metal, is the result of collisions between the cars. **b** The product of a chemical reaction is the result of collisions between atoms, ions, and molecules. Refer to **Table C-1** in Appendix C for a key to atom color conventions.

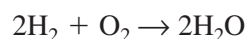


The Collision Theory

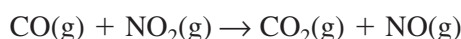
You have learned that reaction rates are calculated from experimental data. But what are we actually measuring with these calculations? Looking at chemical reactions from the molecular level will provide a clearer picture of exactly what reaction rates measure.

Have you ever seen a demolition derby in which the competing vehicles are constantly colliding? Each collision may result in the demolition of one or more vehicles as shown in **Figure 17-2a**. The reactants in a chemical reaction must also come together in order to form products, as shown in **Figure 17-2b**. The **collision theory** states that atoms, ions, and molecules must collide in order to react. The collision theory, summarized in **Table 17-2**, explains why reactions occur and how the rates of chemical reactions can be modified.

Consider the reaction between hydrogen gas (H_2) and oxygen gas (O_2).



According to the collision theory, H_2 and O_2 molecules must collide in order to react and produce H_2O . Now look at the reaction between carbon monoxide (CO) gas and nitrogen dioxide (NO_2) gas at a temperature above 500 K.



These molecules collide to produce carbon dioxide (CO_2) gas and nitrogen monoxide (NO) gas. However, detailed calculations of the number of molecular collisions per second yield a puzzling result—only a small fraction of collisions produce reactions. In this case, other factors must be considered.

Orientation and the activated complex Why don't the NO_2 and CO molecules shown in **Figure 17-3a** and **b** react when they collide? Analysis of this example indicates that in order for a collision to lead to a reaction, the carbon atom in a CO molecule must contact an oxygen atom in an NO_2 molecule at the instant of impact. Only in that way can a temporary bond between the carbon atom and an oxygen atom form. The collisions shown in **Figure 17-3a** and **b** do not lead to reactions because the molecules collide with unfavorable orientations. That is, because a carbon atom does not contact an oxygen atom at the instant of impact, the molecules simply rebound.

When the orientation of colliding molecules is correct, as **Figure 17-3c** illustrates, a reaction occurs as an oxygen atom is transferred from an NO_2 molecule to a CO molecule. A short-lived, intermediate substance is formed. The intermediate substance, in this case OCONO, is called an activated complex. An **activated complex** is a temporary, unstable arrangement of atoms that may form products or may break apart to re-form the reactants. Because the activated complex is as likely to form reactants as it is to form products, it is sometimes referred to as the **transition state**. An activated complex is the first step leading to the resulting chemical reaction.

Table 17-2

Collision Theory Summary

1. Reacting substances (atoms, ions, or molecules) must collide.
2. Reacting substances must collide with the correct orientation.
3. Reacting substances must collide with sufficient energy to form the activated complex.



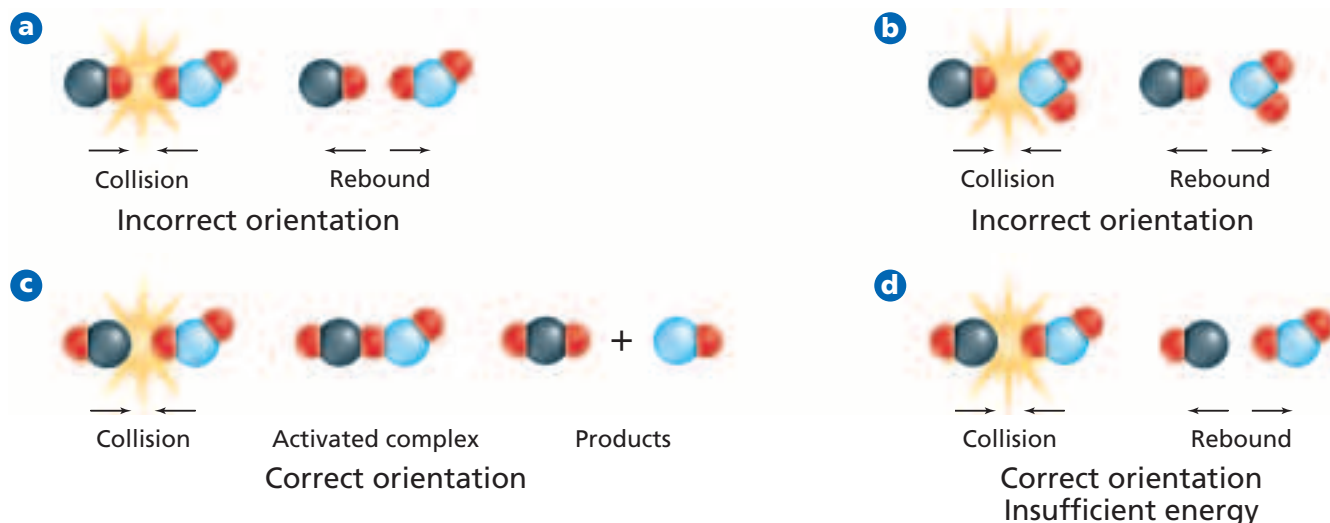


Figure 17-3

The collisions in **a** and **b** do not result in a reaction because the molecules are not in position to form bonds. The molecules in **c** are in the correct orientation when they collide, and a reaction occurs. The molecules in **d** are also in the correct positions on collision, but insufficient energy at the point of collision prevents a chemical reaction.

Activation energy and reaction The collision depicted in **Figure 17-3d** does not lead to a reaction for a different reason. Although the CO and NO₂ molecules collide with a favorable orientation, no reaction occurs because they collide with insufficient energy to form the activated complex. The minimum amount of energy that reacting particles must have to form the activated complex and lead to a reaction is called the **activation energy**, E_a .

Activation energy has a direct influence on the rate of a reaction. A high E_a means that relatively few collisions will have the required energy to produce the activated complex and the reaction rate will be low. On the other hand, a low E_a means that more collisions will have sufficient energy to react, and the reaction rate will be higher. The **problem-solving LAB** below emphasizes this fact. It might be helpful to think of this relationship in terms of a person pushing a heavy cart up a hill. If the hill is high, a substantial amount of energy and effort will be required to move the cart and it will take a long time to get it to the top. If the hill is low, less energy will be required and the task will be accomplished faster.

problem-solving LAB

Speed and Energy of Collision

Designing an Experiment Controlling the rate of a reaction is common in your everyday experience. Consider two of the major appliances in your kitchen: a refrigerator slows down chemical processes that cause food to spoil and an oven speeds up chemical processes that cause foods to cook. Petroleum and natural gases require a spark to run your car's engine and heat your home.

Analysis

According to collision theory, reactants must collide with enough energy in order to react. Recall from the kinetic-molecular theory that mass and velocity determine the kinetic energy of a parti-

cle. In addition, temperature is a measure of the average kinetic energy of the particles in a sample of matter. According to kinetic-molecular theory, how are the frequency and energy of collisions between gas particles related to temperature?

Thinking Critically

How would you design an experiment with a handful of marbles and a shoe box lid to simulate the range of speeds among a group of particles at a given temperature? How would you model an increase in temperature? Describe how your marble model would demonstrate the relationship between temperature and the frequency and energy of the collisions among a group of particles.

Figure 17-4

In an exothermic reaction, molecules collide with enough energy to overcome the activation energy barrier, form an activated complex, then release energy and form products at a lower energy level.

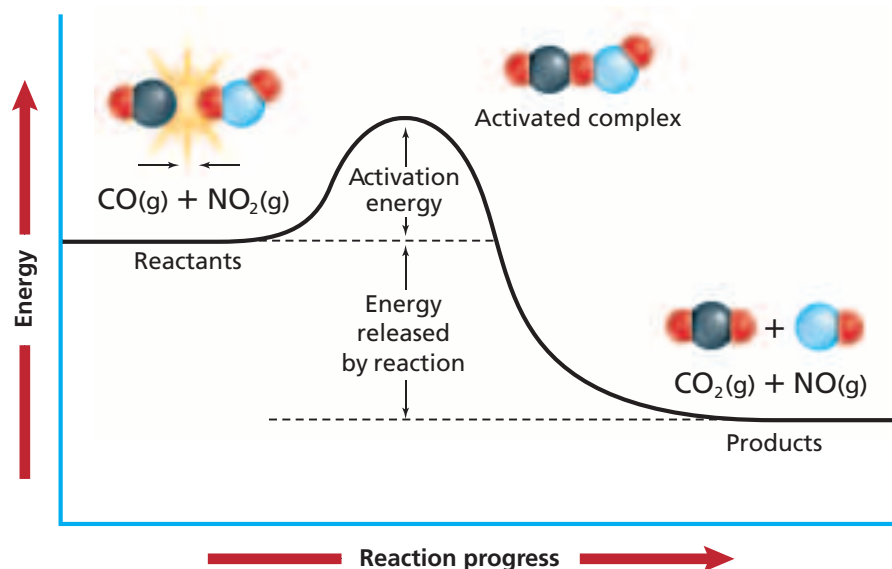
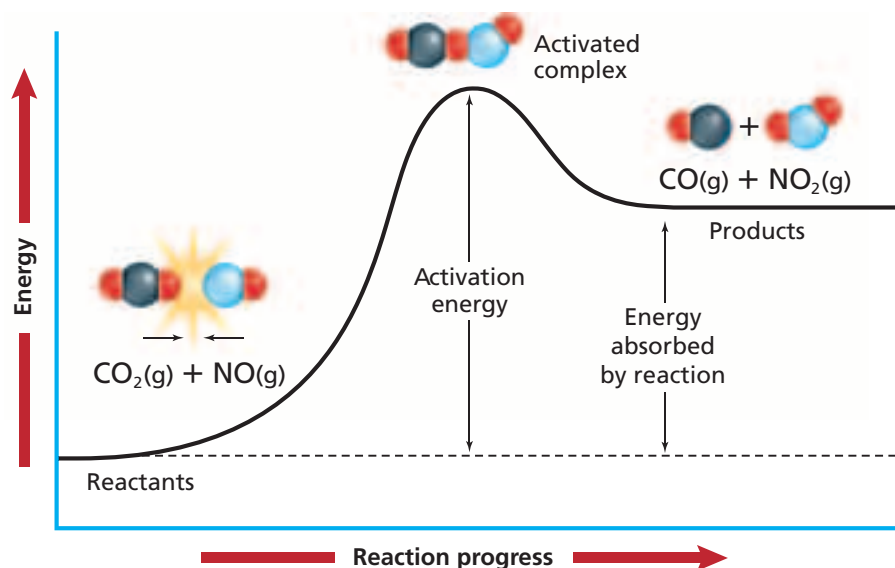


Figure 17-4 shows the energy diagram for the progress of the reaction between carbon monoxide and nitrogen dioxide. Does this energy diagram look somewhat different from those you studied in Chapter 16? Why? In addition to the energies of the reactants and products, this diagram shows the activation energy of the reaction. Activation energy can be thought of as a barrier the reactants must overcome in order to form the products. In this case, the CO and NO_2 molecules collide with enough energy to overcome the barrier, and the products formed lie at a lower energy level. Do you recall that reactions that lose energy, such as this example, are called exothermic reactions?

For many reactions, the process from reactants to products is reversible. **Figure 17-5** shows the reverse endothermic reaction between CO_2 and NO to reform CO and NO_2 . In this reverse reaction, the reactants, which are the molecules that were formed in the exothermic forward reaction, lie at a low energy level and must overcome a significant activation energy to reform CO and NO_2 . This requires an input of energy. If this reverse reaction is achieved, CO and NO_2 again lie at a high energy level.

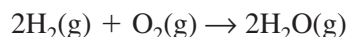
Figure 17-5

In the reverse endothermic reaction, the reactant molecules lying at a low energy level must absorb energy to overcome the activation energy barrier and form high-energy products.



The influence of spontaneity Recall from Chapter 16 that reaction spontaneity is related to change in free energy, ΔG . If ΔG is negative, the reaction is spontaneous under the conditions specified. If ΔG is positive, the reaction is not spontaneous. Let's now consider whether spontaneity has any effect on reaction rates. Are more spontaneous reactions faster than less spontaneous ones?

To investigate the relationship between spontaneity and reaction rate, consider the following gas-phase reaction between hydrogen and oxygen.



Here, $\Delta G = -458 \text{ kJ}$ at 298 K (25°C) and 1 atm pressure. Because ΔG is negative, the reaction is spontaneous. For the same reaction, $\Delta H = -484 \text{ kJ}$, which means that the reaction is highly exothermic. You can examine the speed of this reaction by filling a tape-wrapped soda bottle with stoichiometric quantities of the two gases—two volumes hydrogen and one volume oxygen. A thermometer in the stopper allows you to monitor the temperature inside the bottle. As you watch for evidence of a reaction, the temperature remains constant for hours. Have the gases escaped? Or have they simply failed to react? If you remove the stopper and hold a burning splint to the mouth of the bottle, a reaction occurs explosively. Clearly, the hydrogen and oxygen gases have not escaped from the bottle. Yet they did not react noticeably until you supplied additional energy in the form of a lighted splint. The example shown in **Figure 17-6** illustrates this same phenomenon. The soap bubbles you see billowing from the bowl are filled with hydrogen. When the lighted splint introduces additional energy, an explosive reaction occurs between the hydrogen that was contained in the bubbles and oxygen in the air.

As these examples show, reaction spontaneity in the form of ΔG implies *absolutely nothing* about the speed of the reaction; ΔG merely indicates the natural tendency for a reaction or process to proceed. Factors other than spontaneity, however, do affect the rate of a chemical reaction. These factors are keys in controlling and using the power of chemistry.

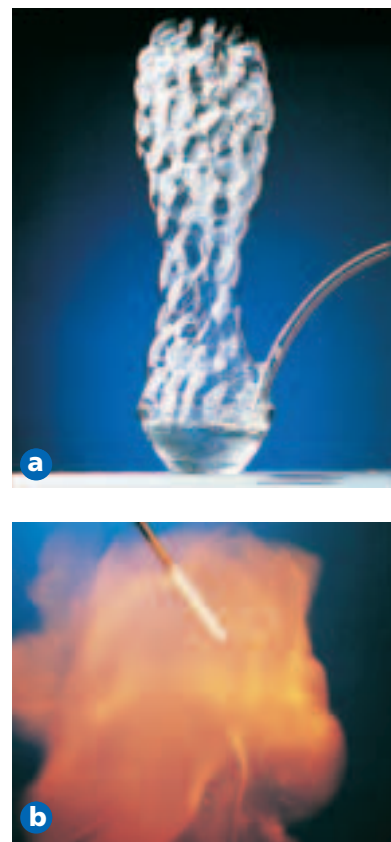


Figure 17-6

- a** Although the reaction of hydrogen and oxygen is spontaneous, the combination does not produce an obvious reaction when mixed.
- b** If an additional form of energy is introduced to the same spontaneous reaction, the reaction rate increases significantly.

Section 17.1 Assessment

4. What does the reaction rate indicate about a particular chemical reaction?
5. How is the rate of a chemical reaction usually expressed?
6. What is the collision theory, and how does it relate to reaction rates?
7. According to the collision theory, what must happen in order for two molecules to react?
8. How is the speed of a chemical reaction related to the spontaneity of the reaction?
9. **Thinking Critically** How would the rate of the reaction $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$ stated as the consumption of hydrogen compare with the rate stated as the consumption of oxygen?
10. **Interpreting Scientific Illustrations** Based on your analysis of **Figures 17-4** and **5**, how does E_a for the reaction $\text{CO} + \text{NO}_2 \leftarrow \text{CO}_2 + \text{NO}$ (the reverse reaction) compare with that of the reaction $\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$ (the forward reaction)?



Factors Affecting Reaction Rates

Objectives

- **Identify** factors that affect the rates of chemical reactions.
- **Explain** the role of a catalyst.

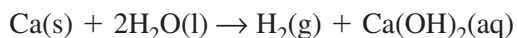
Vocabulary

catalyst
inhibitor
heterogeneous catalyst
homogeneous catalyst

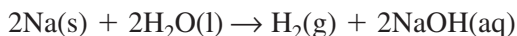
According to the collision theory, chemical reactions occur when molecules collide in a particular orientation and with sufficient energy to achieve activation energy. You can probably identify chemical reactions that occur fast, such as gasoline combustion, and others that occur more slowly, such as iron rusting. But can the reaction rate of any single reaction vary, or is the reaction rate constant regardless of the conditions? In this section you will learn that the reaction rate for almost any chemical reaction can be modified by varying the conditions of the reaction.

The Nature of Reactants

An important factor that affects the rate of a chemical reaction is the reactive nature of the reactants. As you know, some substances react more readily than others. For example, calcium and sodium are both reactive metals; however, what happens when each metal is added to water is distinctly different. When a small piece of calcium is placed in cold water, as shown in **Figure 17-7a**, the calcium and water react slowly to form hydrogen gas and aqueous calcium hydroxide.



When a small piece of sodium is placed in cold water, the sodium and water react quickly to form hydrogen gas and aqueous sodium hydroxide, as shown in **Figure 17-7b**.



Comparing the two equations, it's evident that the reactions are similar. However, the reaction between sodium and water occurs much faster because sodium is more reactive with water than calcium is. In fact, the reaction releases so much heat so quickly that the hydrogen gas ignites as it is formed.

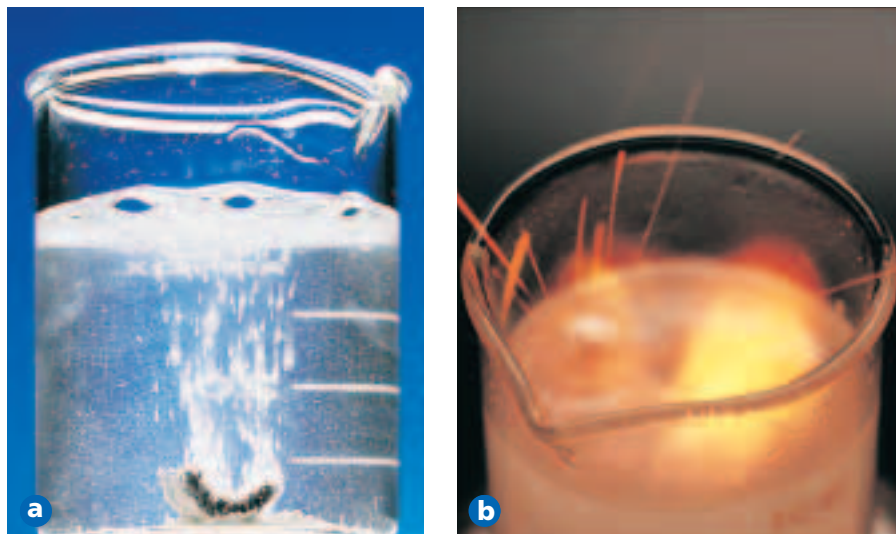


Figure 17-7

The tendency of a substance to react influences the rate of a reaction involving the substance. The more reactive a substance is, the faster the reaction rate.



Figure 17-8

- a** The concentration of oxygen in the air surrounding the steel wool is much less than that of the pure oxygen in the flask.
- b** The higher oxygen concentration accounts for the faster reaction.

Concentration

Reactions speed up when the concentrations of reacting particles are increased. One of the fundamental principles of the collision theory is that particles must collide to react. The number of particles in a reaction makes a difference in the rate at which the reaction takes place. Think about a reaction where reactant A combines with reactant B. At a given concentration of A and B, the molecules of A collide with B to produce AB at a particular rate. What happens if the amount of B is increased? Increasing the concentration of B makes more molecules available with which A can collide. Reactant A “finds” reactant B more easily because there are more B molecules in the area, which increases probability of collision, and ultimately increases the rate of reaction between A and B.

Look at the two reactions shown in **Figure 17-8**. Steel wool is first heated over a burner until it is red hot. In **Figure 17-8a**, the hot steel wool reacts with oxygen in the air. How does this reaction compare with the one in **Figure 17-8b**, in which the hot steel wool is lowered immediately into a flask containing nearly 100 percent oxygen—approximately five times the concentration of oxygen in air? Applying the collision theory to this reaction, the higher concentration of oxygen increases the collision frequency between iron atoms and oxygen molecules, which increases the rate of the reaction.

If you have ever been near a person using bottled oxygen or seen an oxygen generator, you may have noticed a sign cautioning against smoking or using open flames. Can you now explain the reason for the caution notice? The high concentration of oxygen could cause a combustion reaction to occur at an explosive rate. The **CHEMLAB** at the end of this chapter gives you an opportunity to further investigate the effect of concentration on reaction rates.

Surface Area

Now suppose you were to lower a red-hot chunk of steel instead of steel wool into a flask of oxygen gas. The oxygen would react with the steel much more slowly than it would with the steel wool. Using what you know about the collision theory, can you explain why? You are correct if you said that, for the same mass of iron, steel wool has much more surface area than the chunk of steel. The greater surface area of the steel wool allows the oxygen molecules to collide with many more iron atoms per unit of time.

Try at Home

LAB

See page 960 in Appendix E for
Surface Area and Cooking Eggs



Figure 17-9

Increasing the surface area of reactants provides more opportunity for collisions with other reactants, thereby increasing the reaction rate.

Pulverizing (or grinding) a substance is one way to increase its rate of reaction. This is because, for the same mass, many small particles possess more total surface area than one large particle. So, a spoonful of granulated sugar placed in a cup of water dissolves faster than the same mass of sugar in a single chunk, which has less surface area, as shown in **Figure 17-9**. This example illustrates that increasing the surface area of a reactant does not change its concentration, but it does increase the rate of reaction by increasing the collision rate between reacting particles.

Temperature

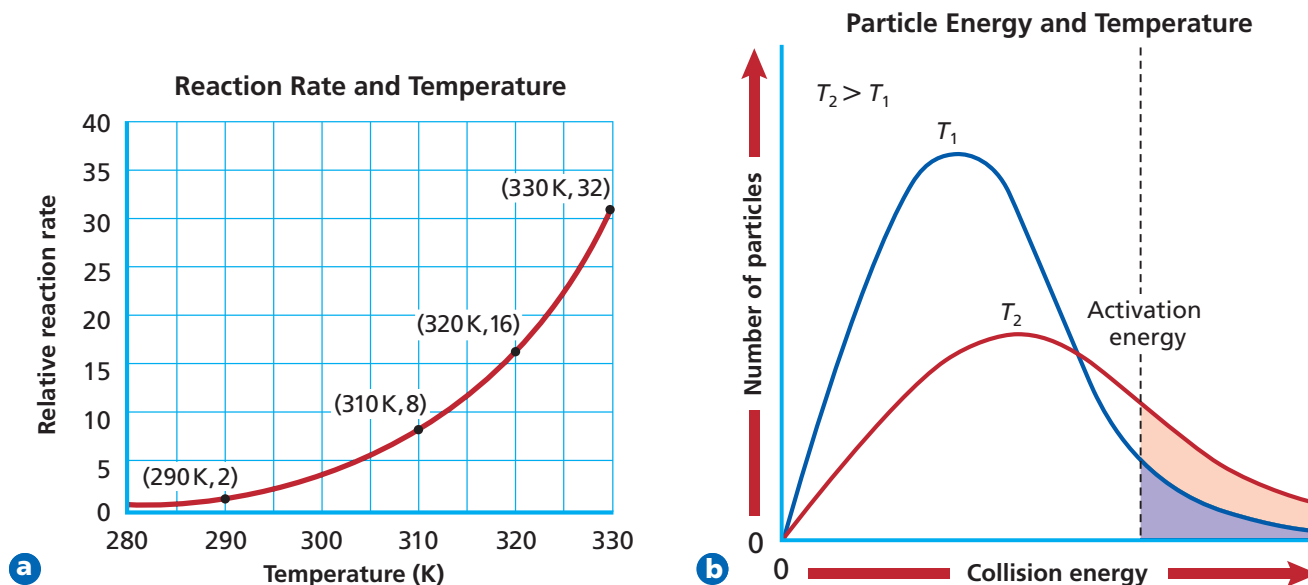
Generally, increasing the temperature at which a reaction occurs increases the reaction rate. For example, you know that the reactions that cause foods to spoil occur much faster at room temperature than when the foods are refrigerated. The graph in **Figure 17-10a** illustrates that increasing the temperature by 10 K can approximately double the rate of a reaction. How can a small increase in temperature have such a significant effect?

As you learned in Chapter 13, increasing the temperature of a substance increases the average kinetic energy of the particles that make up the substance. For that reason, reacting particles collide more frequently at higher temperatures than at lower temperatures. However, that fact alone doesn't account for the increase in reaction rate with increasing temperature. To better understand how reaction rate varies with temperature, examine the graph shown in **Figure 17-10b**. This graph compares the numbers of particles having sufficient energy to react at temperatures T_1 and T_2 , where T_2 is greater than T_1 . The shaded area under each curve represents the number of collisions having energy equal to or greater than the activation energy. The dotted line indicates the activation energy (E_a) for the reaction. How do the shaded areas compare? The number of high-energy collisions at the higher temperature, T_2 , is much greater than at the lower temperature, T_1 . Therefore, as the temperature increases more collisions result in a reaction.

As you can see, increasing the temperature of the reactants increases the reaction rate because raising the kinetic energy of the reacting particles raises both the collision frequency and the collision energy. You can investigate the relationship between reaction rate and temperature by performing the **miniLAB** for this chapter.

Figure 17-10

- a** Increasing the temperature of a reaction increases the frequency of collisions and therefore the rate of reaction.
- b** Increasing the temperature also raises the kinetic energy of the particles, thus more of the collisions at high temperatures have enough energy to overcome the activation energy barrier and react.



Examining Reaction Rate and Temperature

Recognizing Cause and Effect Several factors affect the rate of a chemical reaction. This lab allows you to examine the effect of temperature on a common chemical reaction.

Materials small beaker, thermometer, hot plate, 250-mL beaker, balance, water, effervescent (bicarbonate) tablet, stopwatch or clock with second hand

Procedure



1. Take a single effervescent tablet and break it into four roughly equal pieces.
2. Measure the mass of one piece of the tablet. Measure 50 mL of room-temperature water (approximately 20°C) into a small cup or beaker. Measure the temperature of the water.
3. With a stopwatch ready, add the piece of tablet to the water. Record the amount of time elapsed between when the tablet hits the water and when you see that all of the piece of tablet has dissolved in the water.
4. Repeat steps 2 and 3 twice more, except use water temperatures of about 50°C and 65°C. Be sure to raise the temperature gradually and maintain the desired temperature (equilibrate) throughout the run.



Analysis

1. Calculate the reaction rate by finding the mass/time for each run.
2. Graph the reaction rate (mass/time) versus temperature for the runs.
3. What is the relationship between reaction rate and temperature for this reaction?
4. Using your graphed data, predict the reaction rate for the reaction carried out at 40°C. Heat and equilibrate the water to 40°C and use the last piece of tablet to test your prediction.
5. How did your prediction for the reaction rate at 40°C compare to the actual reaction rate?

Catalysts

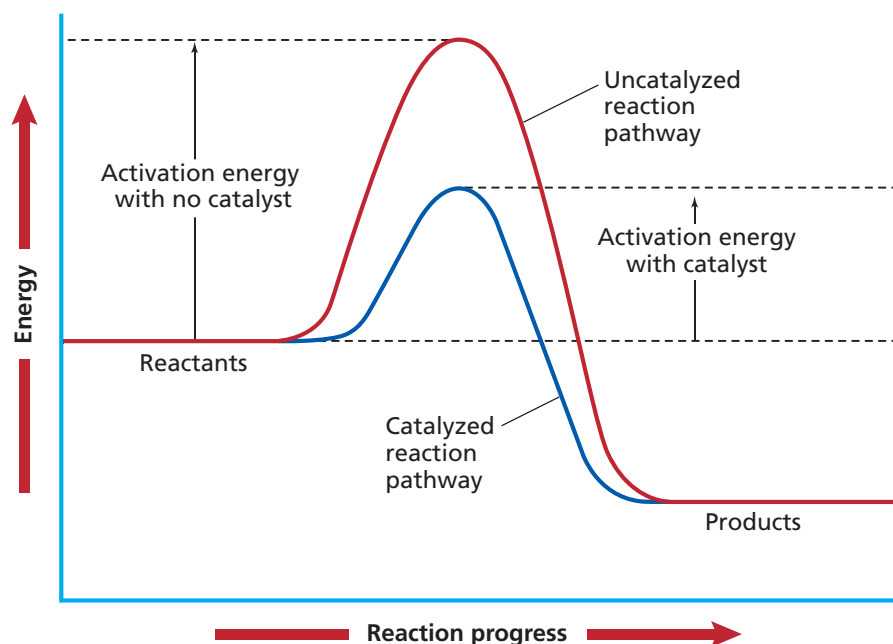
You've seen that increasing the temperature and/or the concentration of reactants can dramatically increase the rate of a reaction. However, an increase in temperature is not always the best (or most practical) thing to do. For example, suppose that you want to increase the rate of a reaction such as the decomposition of glucose in a living cell. Increasing the temperature and/or the concentration of reactants is not a viable alternative because it might harm or kill the cell.

It is a fact that many chemical reactions in living organisms would not occur quickly enough to sustain life at normal living temperatures if it were not for the presence of enzymes. An enzyme is a type of **catalyst**, a substance that increases the rate of a chemical reaction without itself being consumed in the reaction. Although catalysts are important substances in a chemical reaction, a catalyst does not yield more product and is not included in the product(s) of the reaction. In fact, catalysts are not included in the chemical equation.

How does a catalyst increase the reaction rate? **Figure 17-11** on the next page shows the energy diagram for an exothermic chemical reaction. The red line represents the uncatalyzed reaction pathway—the reaction pathway with no catalyst present. The blue line represents the catalyzed reaction pathway.

Figure 17-11

This energy diagram shows how the activation energy of the catalyzed reaction is lower and therefore the reaction produces the products at a faster rate than the uncatalyzed reaction does.



Note that the activation energy for the catalyzed reaction is much lower than for the uncatalyzed reaction. The lower activation energy for the catalyzed reaction means that more collisions have sufficient energy to initiate reaction. It might help you to visualize this relationship by thinking of the reaction's activation energy as a mountain range to be crossed, as shown in **Figure 17-12**. In this analogy, the tunnel, representing the catalyzed pathway, provides an easier and therefore quicker route to the other side of the mountains.

Another type of substance that affects reaction rates is called an inhibitor. Unlike a catalyst, which speeds up reaction rates, an **inhibitor** is a substance that slows down, or inhibits, reaction rates. Some inhibitors, in fact, actually prevent a reaction from happening at all.

In our fast-paced world, it might seem unlikely that it would be desirable to slow a reaction. But if you think about your environment, you can probably come up with several uses for inhibitors. One of the primary applications for inhibitors is in the food industry, where inhibitors are called preservatives. **Figure 17-13** shows how a commercially available fruit freshener



Figure 17-12

Compare the amount of time it would take this train to travel over or around the barrier with the time it takes to travel through the barrier. Obviously, travel is faster through the mountain with the aid of the tunnel.



Figure 17-13

The preservative that was applied to the apple on the left is an inhibitor that reacted with substances in the apple to slow the chemical reactions that cause the apple to brown.

inhibits fruit from browning once it is cut. These preservatives are safe to eat and give food a longer shelf-life. Another inhibitor is the compound maleic hydrazide ($C_4N_2H_4O_2$), which is used as a plant growth inhibitor and weed killer. Inhibitors also are important in biology. For example, a class of inhibitors called monoamine oxidase inhibitors blocks a chemical reaction that can cause depression.

Heterogeneous and homogeneous catalysts In order to reduce harmful engine emissions, automobiles manufactured today must have catalytic converters similar to the one described in **How It Works** at the end of the chapter. The most effective catalysts for this application are transition metal oxides and metals such as palladium and platinum. These substances catalyze reactions that convert nitrogen monoxide to nitrogen and oxygen, carbon monoxide to carbon dioxide, and unburned gasoline to carbon dioxide and water. Because the catalysts in a catalytic converter are solids and the reactions they catalyze are gaseous, the catalysts are called heterogeneous catalysts. A **heterogeneous catalyst** exists in a physical state different than that of the reaction it catalyzes. A catalyst that exists in the same physical state as the reaction it catalyzes is called a **homogeneous catalyst**. For example, if both an enzyme and the reaction it catalyzes are in aqueous solution, the enzyme is a homogeneous catalyst.



Topic: Industrial Catalysts

To learn more about industrial catalysts, visit the Chemistry Web site at chemistrymc.com

Activity: Research how catalysts help reactions to occur in industry that would not otherwise be able to proceed. Explain how scientists have been able to design materials that will only use catalysts at a certain time.

Section 17.2 Assessment

- 11.** How do temperature, concentration, and surface area affect the rate of a chemical reaction?
- 12.** How does the collision model explain the effect of concentration on the reaction rate?
- 13.** How does the activation energy of an uncatalyzed reaction compare with that of the catalyzed reaction?
- 14. Thinking Critically** For a reaction of A and B that proceeds at a specific rate, $x \text{ mol}/(\text{L}\cdot\text{s})$, what is the effect of decreasing the amount of one of the reactants?
- 15. Using the Internet** Conduct Internet research on how catalysts are used in industry, in agriculture, or in the treatment of contaminated soil, waste, or water. Write a short report summarizing your findings about one use of catalysts.



Objectives

- **Express** the relationship between reaction rate and concentration.
- **Determine** reaction orders using the method of initial rates.

Vocabulary

rate law
specific rate constant
reaction order
method of initial rates

In Section 17.1, you learned how to calculate the average rate of a chemical reaction given the initial and final times and concentrations. The word *average* is important because most chemical reactions slow down as the reactants are consumed. To understand why most reaction rates slow over time, recall that the collision theory states that chemical reactions can occur only when the reacting particles collide and that reaction rate depends upon reactant concentration. As reactants are consumed, fewer particles collide and the reaction slows. Chemists use the concept of rate laws to quantify the results of the collision theory in terms of a mathematical relationship between the rate of a chemical reaction and the reactant concentration.

Reaction Rate Laws

The equation that expresses the mathematical relationship between the rate of a chemical reaction and the concentration of reactants is called a **rate law**. For example, the reaction $A \rightarrow B$, which is a one-step reaction, has only one activated complex between reactants and products. The rate law for this reaction is expressed as

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

where k is the **specific rate constant**, or a numerical value that relates reaction rate and concentration of reactants at a given temperature. Units for the rate constant include $L/(\text{mol}\cdot\text{s})$, $L^2/(\text{mol}^2\cdot\text{s})$, and s^{-1} . Depending on the reaction conditions, especially temperature, k is unique for every reaction.

The rate law means that the reaction rate is directly proportional to the molar concentration of A. Thus, doubling the concentration of A will double the reaction rate. Increasing the concentration of A by a factor of 5 will increase the reaction rate by a factor of 5. The specific rate constant, k , does not change with concentration; however, k does change with temperature. A large value of k means that A reacts rapidly to form B. What does a small value of k mean?

Figure 17-14

Specific rate constants are determined experimentally. Scientists have a number of methods at their disposal that can be used to establish k for a given reaction.



a A spectrophotometer measures the absorption of specific wavelengths of light by a reactant or product as a reaction progresses to determine the specific rate constant for the reaction.

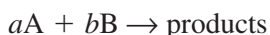
Reaction order In the expression $\text{Rate} = k[A]$, it is understood that the notation $[A]$ means the same as $[A]^1$. In other words, for reactant A, the understood exponent 1 is called the reaction order. The **reaction order** for a reactant defines how the rate is affected by the concentration of that reactant. For example, the rate law for the decomposition of H_2O_2 is expressed by the following equation.

$$\text{Rate} = k[\text{H}_2\text{O}_2]$$

Because the reaction rate is directly proportional to the concentration of H_2O_2 raised to the first power, $[\text{H}_2\text{O}_2]^1$, the decomposition of H_2O_2 is said to be first order in H_2O_2 . Because the reaction is first order in H_2O_2 , the reaction rate changes in the same proportion that the concentration of H_2O_2 changes. So if the H_2O_2 concentration decreases to one-half its original value, the reaction rate is halved as well.

Recall from Section 17.1 that reaction rates are determined from experimental data. Because reaction order is based on reaction rates, it follows that reaction order also is determined experimentally. Finally, because the rate constant describes the reaction rate, k , too, must be determined experimentally. **Figure 17-14** illustrates two of several experimental methods that are commonly used to measure reaction rates.

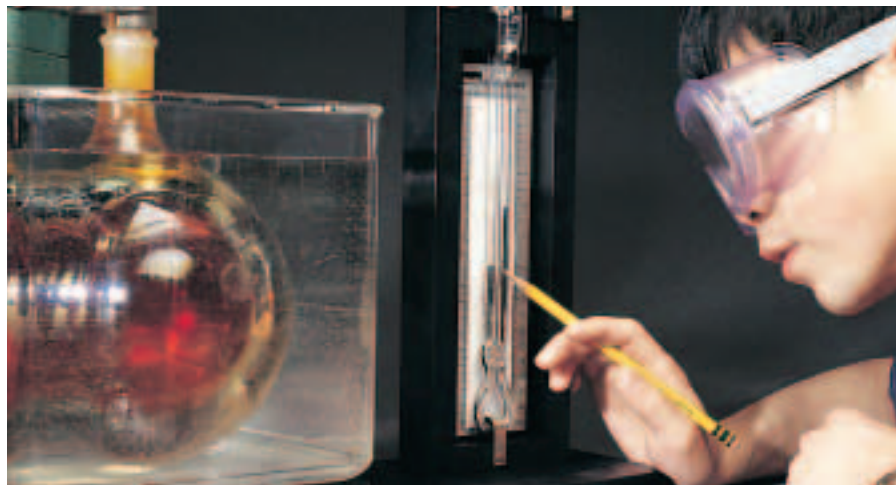
Other reaction orders The overall reaction order of a chemical reaction is the sum of the orders for the individual reactants in the rate law. Many chemical reactions, particularly those having more than one reactant, are not first order. Consider the general form for a chemical reaction with two reactants. In this chemical equation, a and b are coefficients.



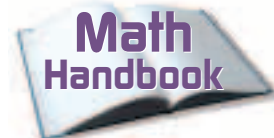
The general rate law for such a reaction is

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

where m and n are the reaction orders for A and B, respectively. Only if the reaction between A and B occurs in a single step (and with a single activated complex) does $m = a$ and $n = b$. That's unlikely, however, because single-step reactions are uncommon.



b A manometer measures pressure changes that result from the production of gas as a reaction progresses. The reaction rate is directly proportional to the rate at which the pressure increases.

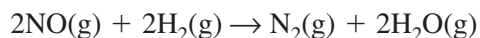


Review direct and inverse relationships in the **Math Handbook** on page 905 of this text.

CONNECTION

The time it takes for bonds to form and break during a chemical reaction is measured in femtoseconds. A femtosecond is one thousandth of a trillionth of a second. Until recently, scientists could only calculate and imagine the actual atomic activity of chemical bonding. In 1999, Dr. Ahmed Zewail of the California Institute of Technology won a Nobel Prize for his achievements in the field of femtochemistry. Zewail has developed an ultrafast laser device that can monitor and record chemical reactions in real time. Zewail's laser "flashes" every ten femtoseconds, allowing chemists to record changes in the wavelengths (colors) that vibrating molecules emitted during the course of a reaction. The changes correspond to bond formation and breakage and are mapped to the various intermediates and products that are formed during a reaction and that were previously impossible to witness.

For example, the reaction between nitrogen monoxide (NO) and hydrogen (H_2) is described by the following equation.



This reaction, which occurs in more than one step, has the following rate law.

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

This rate law was determined experimentally. The data tell that the rate depends on the concentration of the reactants as follows. If $[NO]$ doubles, the rate quadruples; if $[H_2]$ doubles, the rate doubles. The reaction is described as second order in NO, first order in H_2 , and third order overall because the sum of the orders for the individual reactants (the sum of the exponents) is $(2 + 1)$, or 3.

Determining Reaction Order

One common experimental method of evaluating reaction order is called the method of initial rates. The **method of initial rates** determines reaction order by comparing the initial rates of a reaction carried out with varying reactant concentrations. To understand how this method works, let's use the general reaction $aA + bB \rightarrow \text{products}$. Suppose that this reaction is carried out with varying concentrations of A and B and yields the initial reaction rates shown in **Table 17-3**.

Table 17-3

Experimental Initial Rates for $aA + bB \rightarrow \text{products}$			
Trial	Initial [A] (M)	Initial [B] (M)	Initial Rate (mol/(L·s))
1	0.100	0.100	2.00×10^{-3}
2	0.200	0.100	4.00×10^{-3}
3	0.200	0.200	16.0×10^{-3}

Recall that the general rate law for this type of reaction is

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

To determine m , the concentrations and reaction rates in Trials 1 and 2 are compared. As you can see from the data, while the concentration of B remains constant, the concentration of A in Trial 2 is twice that of Trial 1. Note that the initial rate in Trial 2 is twice that of Trial 1. Because doubling $[A]$ doubles the rate, the reaction must be first order in A. That is, because $2^m = 2$, m must equal 1. The same method is used to determine n , only this time Trials 2 and 3 are compared. Doubling the concentration of B causes the rate to increase by four times. Because $2^n = 4$, n must equal 2. This information suggests that the reaction is second order in B, giving the following overall rate law.

$$\text{Rate} = k[A]^1[B]^2$$

The overall reaction order is third order (sum of exponents $2 + 1 = 3$).

PRACTICE PROBLEMS

- 16.** Write the rate law for the reaction $aA \rightarrow bB$ if the reaction is third order in A. [B] is not part of the rate law.
- 17.** Given the following experimental data, use the method of initial rates to determine the rate law for the reaction $aA + bB \rightarrow \text{products}$. Hint: Any number to the zero power equals one. For example, $(0.22)^0 = 1$ and $(55.6)^0 = 1$.

Practice Problem 17 Experimental Data

Trial	Initial [A] (M)	Initial [B] (M)	Initial Rate (mol/(L·s))
1	0.100	0.100	2.00×10^{-3}
2	0.200	0.100	2.00×10^{-3}
3	0.200	0.200	4.00×10^{-3}

- 18.** Given the following experimental data, use the method of initial rates to determine the rate law for the reaction $\text{CH}_3\text{CHO(g)} \rightarrow \text{CH}_4\text{(g)} + \text{CO(g)}$.

Practice Problem 18 Experimental Data

Trial	Initial $[\text{CH}_3\text{CHO}]$ (M)	Initial rate (mol/(L·s))
1	2.00×10^{-3}	2.70×10^{-11}
2	4.00×10^{-3}	10.8×10^{-11}
3	8.00×10^{-3}	43.2×10^{-11}

In summary, the rate law for a reaction relates reaction rate, the rate constant k , and the concentration of the reactants. Although the equation for a reaction conveys a great deal of information, it is important to remember that the actual rate law and order of a complex reaction can be determined only by experiment.



For more practice determining reaction orders, go to **Supplemental Practice Problems** in Appendix A.

Section 17.3 Assessment

- 19.** What does the rate law for a chemical reaction tell you about the reaction?
- 20.** Use the rate law equations to show the difference between a first-order reaction having a single reactant and a second-order reaction having a single reactant.
- 21.** What relationship is expressed by the specific rate constant for a chemical reaction?
- 22. Thinking Critically** When giving the rate of a chemical reaction, explain why it is significant to know that the reaction rate is an average reaction rate.
- 23. Designing an Experiment** Explain how you would design an experiment to determine the rate law for the general reaction $aA + bB \rightarrow \text{products}$ using the method of initial rates.



Instantaneous Reaction Rates and Reaction Mechanisms

Objectives

- **Calculate** instantaneous rates of chemical reactions.
- **Understand** that many chemical reactions occur in steps.
- **Relate** the instantaneous rate of a complex reaction to its reaction mechanism.

Vocabulary

instantaneous rate
complex reaction
reaction mechanism
intermediate
rate-determining step

The average reaction rate you learned to calculate in Section 17.3 gives important information about the reaction over a period of time. However, chemists also may need to know at what rate the reaction is proceeding at a specific time. A pharmacist developing a new drug treatment might need to know the progress of a reaction at an exact instant. This information makes it possible to adjust the product for maximum performance. Can you think of other situations where it might be critical to know the specific reaction rate at a given time?

Instantaneous Reaction Rates

The decomposition of hydrogen peroxide (H_2O_2) is represented as follows.



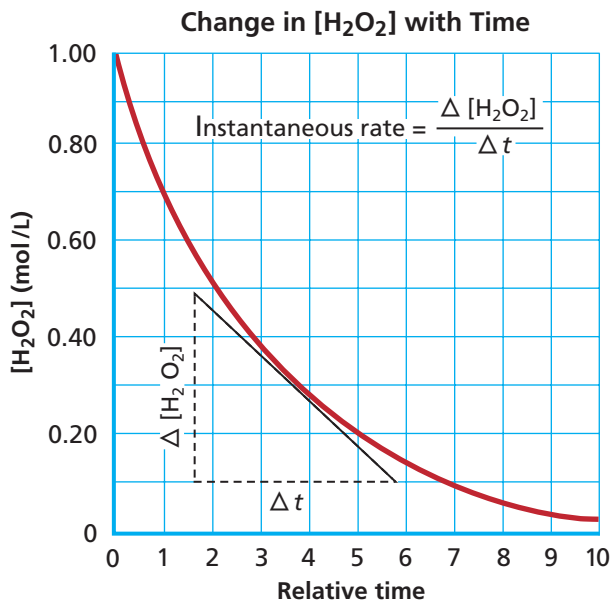
For this reaction, the decrease in H_2O_2 concentration over time is shown in **Figure 17-15**. The curved line shows how the reaction rate decreases as the reaction proceeds. The **instantaneous rate**, or the rate of decomposition at a specific time, can be determined by finding the slope of the straight line tangent to the curve at that instant. This is because the slope of the tangent to the curve at a particular point is $\Delta[\text{H}_2\text{O}_2]/\Delta t$, which is one way to express the reaction rate. In other words, the rate of change in H_2O_2 concentration relates to one specific point (or instant) on the graph.

Another way to determine the instantaneous rate for a chemical reaction is to use the experimentally determined rate law, given the reactant concentrations and the specific rate constant for the temperature at which the reaction occurs. For example, the decomposition of dinitrogen pentoxide (N_2O_5) into nitrogen dioxide (NO_2) and oxygen (O_2) is given by the following equation.



Figure 17-15

The instantaneous rate for a specific point in the reaction progress can be determined from the tangent to the curve that passes through that point. The equation for the slope of the line ($\Delta y/\Delta x$) is the equation for instantaneous rate in terms of $\Delta[\text{H}_2\text{O}_2]$ and Δt :

$$\text{instantaneous rate} = \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t}$$


The experimentally determined rate law for this reaction is

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

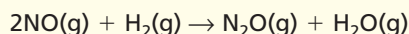
where $k = 1.0 \times 10^{-5} \text{ s}^{-1}$. If $[\text{N}_2\text{O}_5] = 0.350M$, the instantaneous reaction rate would be calculated as

$$\begin{aligned}\text{Rate} &= (1.0 \times 10^{-5} \text{ s}^{-1})(0.350 \text{ mol/L}) \\ &= 3.5 \times 10^{-6} \text{ mol/(L}\cdot\text{s)}\end{aligned}$$

EXAMPLE PROBLEM 17-2

Calculating Instantaneous Reaction Rates

The following equation is first order in H_2 and second order in NO with a rate constant of $2.90 \times 10^2 \text{ (L}^2\text{/(mol}^2\cdot\text{s))}$.



Calculate the instantaneous rate when the reactant concentrations are $[\text{NO}] = 0.00200M$ and $[\text{H}_2] = 0.00400M$.

1. Analyze the Problem

The rate law can be expressed by $\text{Rate} = k[\text{NO}]^2[\text{H}_2]$. Therefore, the instantaneous reaction rate can be determined by inserting reactant concentrations and the specific rate constant into the rate law equation.

Known

$$[\text{NO}] = 0.00200M$$

$$[\text{H}_2] = 0.00400M$$

$$k = 2.90 \times 10^2 \text{ (L}^2\text{/(mol}^2\cdot\text{s))}$$

Unknown

$$\text{Rate} = ? \text{ mol/(L}\cdot\text{s)}$$

2. Solve for the Unknown

Insert the known quantities into the rate law equation.

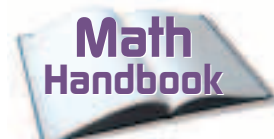
$$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$$

$$\text{Rate} = 2.90 \times 10^2 \text{ (L}^2\text{/(mol}^2\cdot\text{s))}(0.00200 \text{ mol/L})^2(0.00400 \text{ mol/L})$$

$$\text{Rate} = 4.64 \times 10^{-6} \text{ mol/(L}\cdot\text{s)}$$

3. Evaluate the Answer

Are the units correct? Units in the calculation cancel to give $\text{mol/(L}\cdot\text{s)}$, which is the common unit for the expression of reaction rates. Is the magnitude reasonable? A magnitude of approximately $10^{-6} \text{ mol/(L}\cdot\text{s)}$ fits with the quantities given and the rate law equation.



Review solving algebraic equations in the **Math Handbook** on page 897 of this text.

PRACTICE PROBLEMS

Use the rate law in Example Problem 17-2 and the concentrations given in each practice problem to calculate the instantaneous rate for the reaction between NO and H_2 .

24. $[\text{NO}] = 0.00500M$ and $[\text{H}_2] = 0.00200M$

25. $[\text{NO}] = 0.0100M$ and $[\text{H}_2] = 0.00125M$

26. $[\text{NO}] = 0.00446M$ and $[\text{H}_2] = 0.00282M$



For more practice calculating instantaneous reaction rates, go to **Supplemental Practice Problems** in Appendix A.

Careers Using Chemistry

Food Technologist

Everyone needs to eat, and in today's fast-paced world, we've become accustomed to having safe, convenient, and nutritious food at our fingertips, ready to toss in the microwave. Food technologists help make nutrition in our fast-paced lifestyle more convenient by developing new ways to process, preserve, package, and store food.

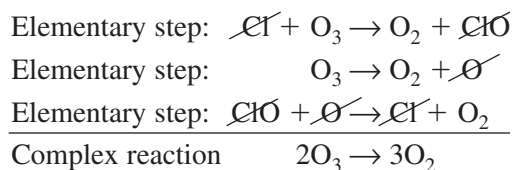
Food technologists are also called food chemists, food scientists, and food engineers. They find ways to make food products more healthful, more convenient, and better tasting. Part of their job is searching for ways to stop or slow chemical reactions and lengthen the shelf life of food. Food technologists might find careers in the food industry, universities, or the federal government.

Reaction Mechanisms

Most chemical reactions consist of a sequence of two or more simpler reactions. For example, recent evidence indicates that the reaction $2\text{O}_3 \rightarrow 3\text{O}_2$ occurs in three steps after intense ultraviolet radiation from the sun liberates chlorine atoms from certain compounds in Earth's stratosphere. Steps 1 and 2 in this reaction may occur simultaneously or in reverse order.

1. Chlorine atoms decompose ozone according to the equation $\text{Cl} + \text{O}_3 \rightarrow \text{O}_2 + \text{ClO}$.
2. Ultraviolet radiation causes the decomposition reaction $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$.
3. ClO produced in the reaction in step 1 reacts with O produced in step 2 according to the equation $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$.

Each of the reactions described in steps 1 through 3 is called an elementary step. These three elementary steps comprise the complex reaction $2\text{O}_3 \rightarrow 3\text{O}_2$. A **complex reaction** is one that consists of two or more elementary steps. The complete sequence of elementary steps that make up a complex reaction is called a **reaction mechanism**. Adding the elementary steps in steps 1 through 3 and canceling formulas that occur in equal amounts on both sides of the reaction arrow produce the net equation for the complex reaction as shown below:



Because chlorine atoms react in step 1 of the reaction mechanism and are re-formed in step 3, chlorine is said to catalyze the decomposition of ozone. Do you know why? Because ClO and O are formed in the reactions in steps 1 and 2, respectively, and are consumed in the reaction in step 3, they are called intermediates. In a complex reaction, an **intermediate** is a substance produced in one elementary step and consumed in a subsequent elementary step. Catalysts and intermediates do not appear in the net chemical equation.

Rate-determining step You have probably heard the expression, “A chain is no stronger than its weakest link.” Chemical reactions, too, have a “weakest link” in that a complex reaction can proceed no faster than the slowest of its elementary steps. In other words, the slowest elementary step in a reaction mechanism limits the instantaneous rate of the overall reaction.

Figure 17-16

In an automobile assembly plant, the process that is most time consuming limits the production rate. For example, because it takes longer to install the onboard computer system than it takes to attach the hood assembly, the computer installation is a rate-determining step.



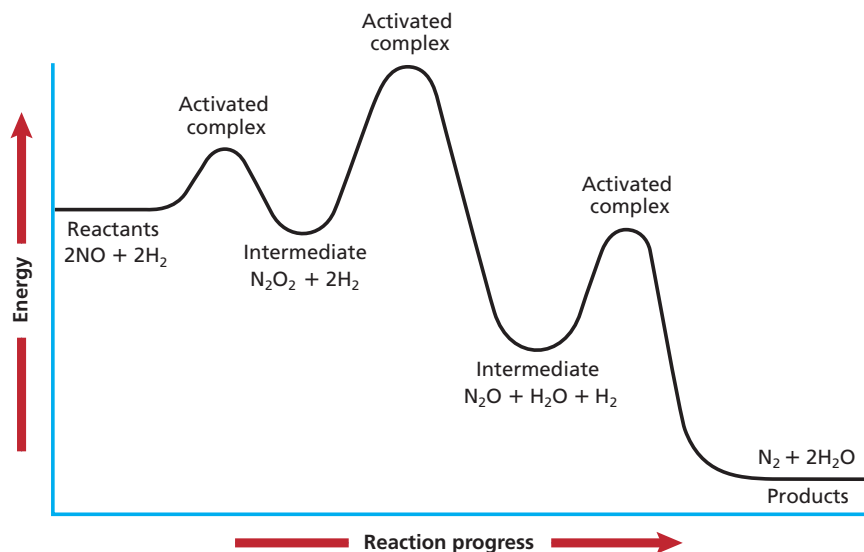
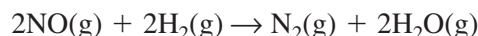


Figure 17-17

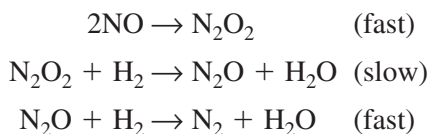
The three peaks in this energy diagram correspond to activation energies for the intermediate steps of the reaction. The middle hump represents the highest energy barrier to overcome; therefore, the reaction involving $\text{N}_2\text{O}_2 + 2\text{H}_2$ is the rate-determining step.

For that reason, the slowest of the elementary steps in a complex reaction is called the **rate-determining step**. Figure 17-16 illustrates this concept in a manufacturing plant.

To see how the rate-determining step affects reaction rate, again consider the gas-phase reaction between hydrogen and nitrogen monoxide discussed earlier in the chapter.



A proposed mechanism for this reaction consists of the following elementary steps.



Although the first and third elementary steps occur relatively fast, the middle step is the slowest, and it limits the overall reaction rate. It is the rate-determining step. The relative energy levels of reactants, intermediates, products, and activated complex are illustrated in Figure 17-17.

Chemists can make use of instantaneous reaction rates, reaction orders, and rate-determining steps to develop efficient ways to manufacture products such as pharmaceuticals. By knowing which step of the reaction is slowest, a chemist can work to speed up that rate-determining step and thereby increase the rate of the overall reaction.

Section 17.4 Assessment

27. How can the rate law for a chemical reaction be used to determine an instantaneous reaction rate?
28. Compare and contrast an elementary chemical reaction with a complex chemical reaction.
29. What is a reaction mechanism? An intermediate?
30. **Thinking Critically** How can you determine whether a product of one of the elementary steps in a complex reaction is an intermediate?
31. **Communicating** How would you explain the significance of the rate-determining step in a chemical reaction?



Concentration and Reaction Rate

The collision theory describes how the change in concentration of one reactant affects the rate of chemical reactions. In this laboratory experiment you will observe how concentration affects the reaction rate.

Problem

How does the concentration of a reactant affect the reaction rate?

Objectives

- **Sequence** the acid concentrations from the most to the least concentrated.
- **Observe** which concentration results in the fastest reaction rate.

Materials

graduated pipette	magnesium ribbon
10-mL	emery cloth or fine
safety pipette filler	sandpaper
6M hydrochloric acid	scissors
distilled water	plastic ruler
25 mm × 150 mm	tongs
test tubes (4)	watch with second hand
test-tube rack	stirring rod

Safety Precautions



- Always wear safety goggles and an apron in the lab.
- Never pipette any chemical by mouth.
- No open flame.

Pre-Lab

1. Read the entire CHEMLAB. Prepare all written materials that you will take into the laboratory. Be sure to include safety precautions, procedure notes, and a data table.

Reaction Time Data		
Test tube	[HCl] (M)	Time (s)
1		
2		
3		
4		

2. Use emery paper or sand paper to polish the magnesium ribbon until it is shiny. Use scissors to cut the magnesium into four 1-cm pieces.
3. Place the four test tubes in the test-tube rack. Label the test tubes #1 (6.0M HCl), #2 (3M HCl), #3 (1.5M HCl), and #4 (0.75M HCl).

4. Form a hypothesis about how the chemical reaction rate is related to reactant concentration.
5. What reactant quantity is held constant? What are the independent and dependent variables?
6. What gas is produced in the reaction between magnesium and hydrochloric acid? Write the balanced formula equation for the reaction.
7. Why is it important to clean the magnesium ribbon? If one of the four pieces is not thoroughly polished, how will the rate of the reaction involving that piece be affected?

Procedure

1. Use a safety pipette to draw 10 mL of 6.0M hydrochloric acid (HCl) into a 10-mL graduated pipette.
2. Dispense the 10 mL of 6.0M HCl into test tube #1.
3. Draw 5.0 mL of the 6.0M HCl from test tube #1 with the empty pipette. Dispense this acid into test tube #2 and use the pipette to add an additional

5.0 mL of distilled water to the acid. Use the stirring rod to mix thoroughly. This solution is 3.0M HCl.

4. Draw 5.0 mL of the 3.0M HCl from test tube #2 with the empty pipette. Dispense this acid into test tube #3 and use the pipette to add an additional 5.0 mL of distilled water to the acid. Use the stirring rod to mix thoroughly. This solution is 1.5M HCl.
5. Draw 5.0 mL of the 1.5M HCl from test tube #3 with the empty pipette. Dispense this acid into test tube #4 and use the pipette to add an additional 5.0 mL of distilled water to the acid. Use the stirring rod to mix thoroughly. This solution is 0.75M HCl.
6. Draw 5.0 mL of the 0.75M HCl from test tube #4 with the empty pipette. Neutralize and discard it in the sink.
7. Using the tongs, place a 1-cm length of magnesium ribbon into test tube #1. Record the time in seconds that it takes for the bubbling to stop.
8. Repeat step 7 using the remaining three test tubes of HCl and the three remaining pieces of magnesium ribbon. Record in your data table the time (in seconds) it takes for the bubbling to stop.

Cleanup and Disposal

1. Place acid solutions in an acid discard container. Your teacher will neutralize the acid for proper disposal.
2. Wash thoroughly all test tubes and lab equipment.
3. Discard other materials as directed by your teacher.
4. Return all lab equipment to its proper place.

Analyze and Conclude

1. **Analyzing** In step 6, why is 5.0 mL HCl discarded?
2. **Making and Using Graphs** Plot the concentration of the acid on the x -axis and time it takes for the bubbling to stop on the y -axis. Draw a smooth curve through the data points.
3. **Interpreting Graphs** Is the curve in question 2 linear or nonlinear? What does the slope tell you?
4. **Drawing a Conclusion** Based on your graph, what do you conclude about the relationship between the acid concentration and the reaction rate?



5. **Hypothesizing** Write a hypothesis using the collision theory, reaction rate, and reactant concentration to explain your results.
6. **Designing an Experiment** Write a brief statement of how you would set up an experiment to test your hypothesis.
7. **Error Analysis** Compare your experimental results with those of several other students in the laboratory. Explain the differences.

Real-World Chemistry

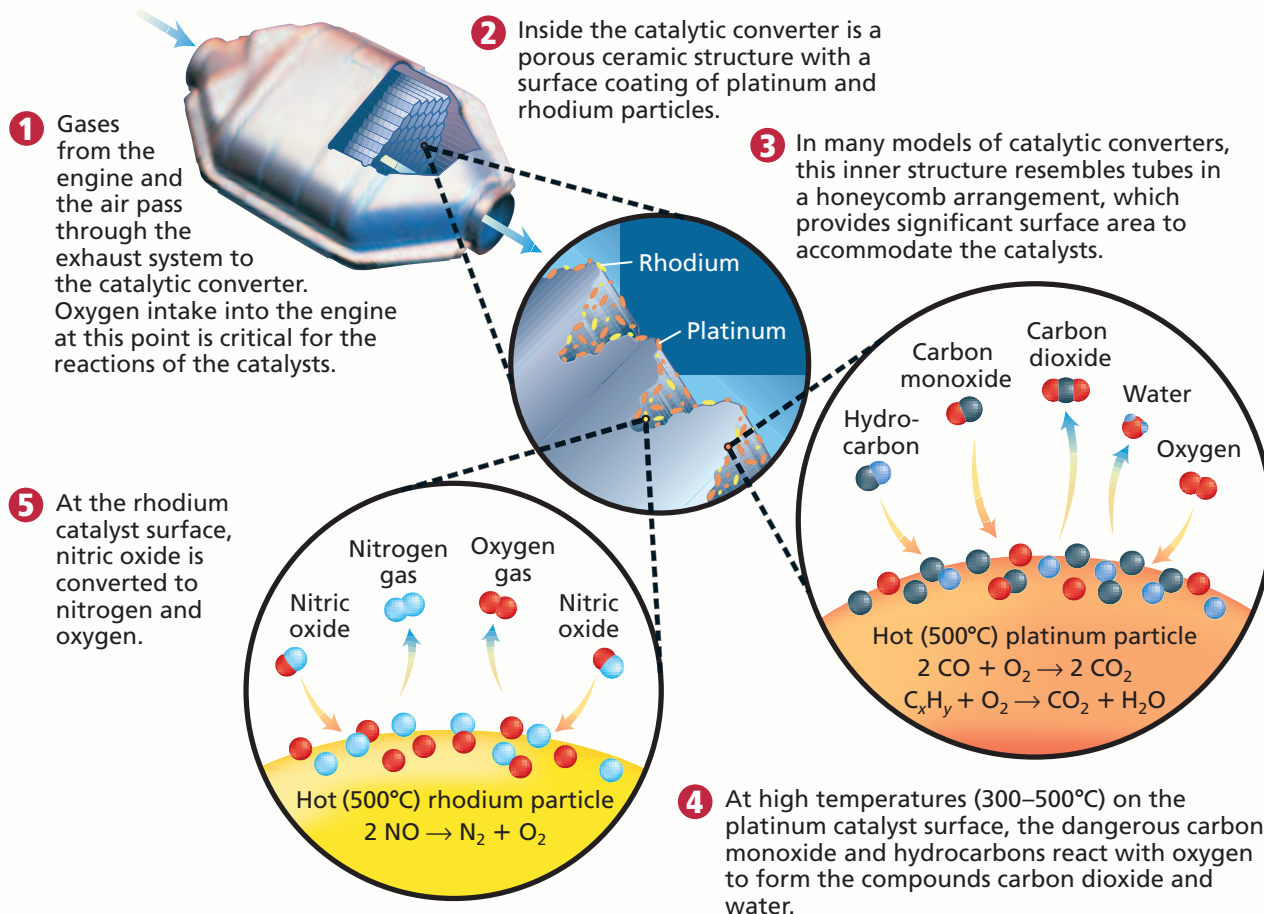
1. Describe a situation that may occur in your daily life that exemplifies the effect of concentration on the rate of a reaction.
2. Some hair-care products, such as hot-oil treatments, must be heated before application. Explain in terms of factors affecting reaction rates why heat is required.

How It Works

Catalytic Converter

Concerns for our environment have made a huge impact in the products and processes we use every day. The catalytic converter is one of those impacts.

When a combustion engine converts fuel into energy, the reactions of the combustion process are incomplete. Incomplete combustion results in the production of poisonous carbon monoxide and undesirable nitrogen oxides. Since 1975, catalytic converters have reduced the exhaust emissions that contribute to air pollution by approximately 90%.



Thinking Critically

1. Inferring Why is it necessary to have additional air in exhaust before it enters the catalytic converter?

2. Hypothesizing A catalytic converter is not effective when cold. Use the concept of activation energy to explain why.

Summary

17.1 A Model for Reaction Rates

- The rate of a chemical reaction is expressed as the rate at which a reactant is consumed or the rate at which a product is formed.
- Reaction rates are generally calculated and expressed in moles per liter per second (mol/(L·s)).
- In order to react, the particles in a chemical reaction must collide in a correct orientation and with sufficient energy to form the activated complex.
- The rate of a chemical reaction is unrelated to the spontaneity of the reaction.

17.2 Factors Affecting Reaction Rates

- Key factors that influence the rate of chemical reactions include reactivity, concentration, surface area, temperature, and catalysts.
- Catalysts increase the rates of chemical reactions by lowering activation energies.
- Raising the temperature of a reaction increases the rate of the reaction by increasing the collision frequency and the number of collisions forming the activated complex.

17.3 Reaction Rate Laws

- The mathematical relationship between the rate of a chemical reaction at a given temperature and the concentrations of reactants is called the rate law.
- The rate law for a chemical reaction is determined experimentally using the method of initial rates.

17.4 Instantaneous Reaction Rates and Reaction Mechanisms

- The instantaneous rate for a chemical reaction is calculated from the rate law, the specific rate constant, and the concentrations of all reactants.
- Most chemical reactions are complex reactions consisting of two or more elementary steps.
- A reaction mechanism is the complete sequence of elementary steps that make up a complex reaction.
- For a complex reaction, the rate-determining step limits the instantaneous rate of the overall reaction.

Key Equations and Relationships

• Average rate = $\frac{\Delta \text{quantity}}{\Delta t}$
(p. 529)

• Rate = $k[A]$
(p. 542)

• Rate = $k[A]^m[B]^n$
(p. 543)

Vocabulary

- | | | |
|-----------------------------------|------------------------------------|-----------------------------------|
| • activated complex (p. 532) | • homogeneous catalyst (p. 541) | • rate law (p. 542) |
| • activation energy (p. 533) | • inhibitor (p. 540) | • reaction mechanism (p. 548) |
| • catalyst (p. 539) | • instantaneous rate (p. 546) | • reaction order (p. 543) |
| • collision theory (p. 532) | • intermediate (p. 548) | • reaction rate (p. 530) |
| • complex reaction (p. 548) | • method of initial rates (p. 544) | • specific rate constant (p. 542) |
| • heterogeneous catalyst (p. 541) | • rate-determining step (p. 549) | • transition state (p. 532) |

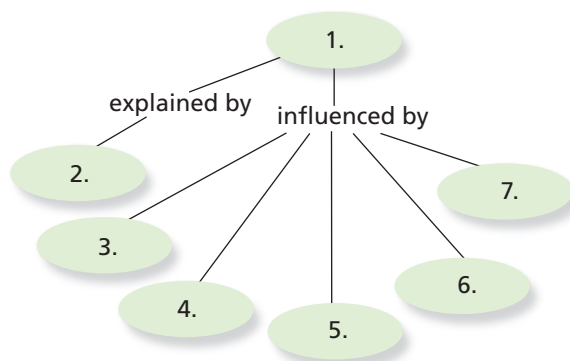




Go to the Chemistry Web site at chemistrymc.com for additional Chapter 17 Assessment.

Concept Mapping

- 32.** Complete the following concept map using the following terms: surface area, collision theory, temperature, reaction rates, concentration, reactivity, catalyst.



Mastering Concepts

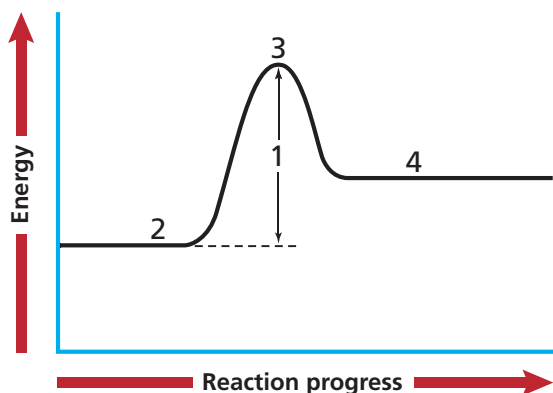
- 33.** For a specific chemical reaction, assume that the change in free energy (ΔG) is negative. What does this information tell you about the rate of the reaction? (17.1)
- 34.** How would you express the rate of the chemical reaction $A \rightarrow B$ based on the concentration of reactant A? How would that rate compare with the reaction rate based on the product B? (17.1)
- 35.** What does the activation energy for a chemical reaction represent? (17.1)
- 36.** What is the role of the activated complex in a chemical reaction? (17.1)
- 37.** Suppose two molecules that can react collide. Under what circumstances do the colliding molecules not react? (17.1)
- 38.** How is the activation energy for a chemical reaction related to whether or not a collision between molecules initiates a reaction? (17.1)
- 39.** In the activated complex for a chemical reaction, what bonds are broken and what bonds are formed? (17.1)
- 40.** If $A \rightarrow B$ is exothermic, how does the activation energy for the forward reaction compare with the activation energy for the reverse reaction ($A \leftarrow B$)? (17.1)
- 41.** What role does the reactivity of the reactants play in determining the rate of a chemical reaction? (17.2)
- 42.** Explain why a crushed solid reacts with a gas more quickly than a large chunk of the same solid. (17.2)
- 43.** What do you call a substance that increases the rate of a chemical reaction without being consumed in the reaction? (17.2)
- 44.** In general, what is the relationship between reaction rate and reactant concentration? (17.2)
- 45.** In general, what is the relationship between reaction rate and temperature? (17.2)
- 46.** Distinguish between a homogeneous catalyst and a heterogeneous catalyst. (17.2)
- 47.** Explain how a catalyst affects the activation energy for a chemical reaction. (17.2)
- 48.** Use the collision theory to explain why increasing the concentration of a reactant usually increases the reaction rate. (17.2)
- 49.** Use the collision theory to explain why increasing the temperature usually increases the reaction rate. (17.2)
- 50.** In a chemical reaction, what relationship does the rate law describe? (17.3)
- 51.** What is the name of the proportionality constant in the mathematical expression that relates reaction rate and reactant concentration? (17.3)
- 52.** What does the order of a reactant tell you about the way the concentration of that reactant appears in the rate law? (17.3)
- 53.** Why does the specific rate constant for a chemical reaction often double for each increase of 10 K? (17.3)
- 54.** Explain why the rates of most chemical reactions decrease over time. (17.3)
- 55.** In the method of initial rates used to determine the rate law for a chemical reaction, what is the significance of the word initial? (17.3)
- 56.** If a reaction has three reactants and is first order in one, second order in another, and third order in the third, what is the overall order of the reaction? (17.3)
- 57.** What do you call the slowest of the elementary steps that make up a complex reaction? (17.4)
- 58.** What is an intermediate in a complex reaction? (17.4)
- 59.** Distinguish between an elementary step, a complex reaction, and a reaction mechanism. (17.4)
- 60.** Under what circumstances is the rate law for the reaction $2A + 3B \rightarrow \text{products}$ correctly written as $\text{Rate} = k[A]^2[B]^3$? (17.3)

61. How does the activation energy of the rate-determining step in a complex reaction compare with the activation energies of the other elementary steps? (17.4)

Mastering Problems

A Model for Reaction Rates (17.1)

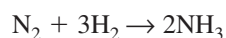
62. In the gas-phase reaction $\text{I}_2 + \text{Cl}_2 \rightarrow 2\text{ICl}$, the $[\text{I}_2]$ changes from 0.400M at time = 0 to 0.300M at time = 4.00 min . Calculate the average reaction rate in moles I_2 consumed per liter per minute.
63. If a chemical reaction occurs at a rate of 2.25×10^{-2} moles per liter per second at 322 K , what is the rate expressed in moles per liter per minute?
64. On the accompanying energy level diagram, match the appropriate number with the quantity it represents.
- reactants
 - activated complex
 - products
 - activation energy



65. Given the following data for the decomposition of hydrogen peroxide, calculate the average reaction rate in moles H_2O_2 consumed per liter per minute for each time interval.

Decomposition of H_2O_2	
Time (min)	$[\text{H}_2\text{O}_2]\text{ (M)}$
0	2.50
2	2.12
5	1.82
10	1.48
20	1.00

66. At a given temperature and for a specific time interval, the average rate of the following reaction is 1.88×10^{-4} moles N_2 consumed per liter per second.



Express the reaction rate in moles H_2 consumed per liter per second and in moles NH_3 produced per liter per second.

Factors Affecting Reaction Rates (17.2)

67. Estimate the rate of the reaction described in problem 63 at 332 K . Express the rate in moles per liter per second.
68. Estimate the rate of the reaction described in problem 63 at 352 K and with $[\text{I}_2]$ doubled (assume the reaction is first order in I_2).

Reaction Rate Laws (17.3)

69. Nitrogen monoxide gas and chlorine gas react according to the equation $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$. Use the following data to determine the rate law for the reaction by the method of initial rates. Also, calculate the value of the specific rate constant.

2NO + Cl₂ Reaction Data

Initial $[\text{NO}]\text{ (M)}$	Initial $[\text{Cl}_2]\text{ (M)}$	Initial rate (mol/(L·min))
0.50	0.50	1.90×10^{-2}
1.00	0.50	7.60×10^{-2}
1.00	1.00	15.20×10^{-2}

70. Use the following data to determine the rate law and specific rate constant for the reaction $2\text{ClO}_2(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{ClO}_3^-(\text{aq}) + \text{ClO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$.

2ClO₂(aq) + 2OH[−](aq) Reaction Data

Initial $[\text{ClO}_2]\text{ (M)}$	Initial $[\text{OH}^-]\text{ (M)}$	Initial rate (mol/(L·min))
0.0500	0.200	6.90
0.100	0.200	27.6
0.100	0.100	13.8

Instantaneous Reaction Rates and Reaction Mechanisms (17.4)

71. The gas-phase reaction $2\text{HBr} + \text{NO}_2 \rightarrow \text{H}_2\text{O} + \text{NO} + \text{Br}_2$ is thought to occur by the following mechanism.
- $$\text{HBr} + \text{NO}_2 \rightarrow \text{HOBr} + \text{NO} \quad \Delta H = 4.2\text{ kJ} \quad (\text{slow})$$
- $$\text{HBr} + \text{HOBr} \rightarrow \text{H}_2\text{O} + \text{Br}_2 \quad \Delta H = -86.2\text{ kJ} \quad (\text{fast})$$

Draw the energy diagram that depicts this reaction mechanism. On the diagram, show the energy of the reactants, energy of the products, and relative activation energies of the two elementary steps.

- 72.** Are there any intermediates in the complex reaction described in problem 71? Explain why or why not. If any intermediates exist, what are their formulas?
- 73.** Given the rate law $\text{Rate} = k[\text{A}][\text{B}]^2$ for the generic reaction $\text{A} + \text{B} \rightarrow \text{products}$, the value for the specific rate constant ($4.75 \times 10^{-7} \text{ L}^2/(\text{mol}^2 \cdot \text{s})$), the concentration of A (0.355 M), and the concentration of B (0.0122 M), calculate the instantaneous reaction rate.

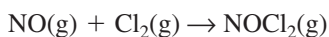
Mixed Review

Sharpen your problem-solving skills by answering the following.

- 74.** Use the method of initial rates and the following data to determine and express the rate law for the reaction $\text{A} + \text{B} \rightarrow 2\text{C}$.

A + B → 2C Reaction Data		
Initial [A] (M)	Initial [B] (M)	Initial rate (mol C/(L·s))
0.010	0.010	0.0060
0.020	0.010	0.0240
0.020	0.020	0.0960

- 75.** The concentration of reactant A decreases from 0.400 mol/L at time = 0 to 0.384 mol/L at time = 4.00 min . Calculate the average reaction rate during this time period. Express the rate in $\text{mol}/(\text{L} \cdot \text{min})$.
- 76.** It is believed that the following two elementary steps make up the mechanism for the reaction between nitrogen monoxide and chlorine:



Write the equation for the overall reaction and identify any intermediates in the reaction mechanism.

- 77.** One reaction that takes place in an automobile's engine and exhaust system is described by the equation $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$. This reaction's rate law at a particular temperature is given by the relationship $\text{rate} = 0.50 \text{ L}/(\text{mol} \cdot \text{s})[\text{NO}_2]^2$. What is the reaction's initial, instantaneous rate at $[\text{NO}_2] = 0.0048 \text{ mol/L}$?
- 78.** At 232 K , the rate of a certain chemical reaction is $3.20 \times 10^{-2} \text{ mol}/(\text{L} \cdot \text{min})$. Predict the reaction's approximate rate at 252 K .

Thinking Critically

- 79. Using Numbers** Draw a diagram that shows all of the possible collision combinations between two molecules of reactant A and two molecules of reactant B. Now, increase the number of molecules of A from two to four and sketch each possible A–B collision combination. By what factor did the number of collision combinations increase? What does this imply about the reaction rate?
- 80. Applying Concepts** Use the collision theory to explain two reasons why increasing the temperature of a reaction by 10 K often doubles the reaction rate.
- 81. Formulating Models** Create a table of concentrations, starting with 0.100 M concentrations of all reactants, that you would propose in order to establish the rate law for the reaction $a\text{A} + b\text{B} + c\text{D} \rightarrow \text{products}$ using the method of initial rates.

Writing in Chemistry

- 82.** Research the way manufacturers in the United States produce nitric acid from ammonia. Write the reaction mechanism for the complex reaction. If catalysts are used in the process, explain how they are used and how they affect any of the elementary steps.
- 83.** Write an advertisement that explains why Company A's lawn care product (fertilizer or weed killer) works better than the competition's because of the smaller sized granules. Include applicable diagrams.

Cumulative Review

Refresh your understanding of previous chapters by answering the following.

- 84.** Classify each of the following elements as a metal, nonmetal, or metalloid. (Chapter 6)
- molybdenum
 - bromine
 - arsenic
 - neon
 - cerium
- 85.** Balance the following equations. (Chapter 10)
- $\text{Sn}(\text{s}) + \text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SnO}_2 + \text{H}_2$
 - $\text{C}_8\text{H}_{18}(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
 - $\text{Al}(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Al}_2(\text{SO}_4)_3(\text{aq}) + \text{H}_2(\text{g})$
- 86.** What mass of iron(III) chloride is needed to prepare 1.00 L of a 0.255 M solution? (Chapter 15)
- 87.** ΔH for a reaction is negative. Compare the energy of the products and the reactants. Is the reaction endothermic or exothermic? (Chapter 16)

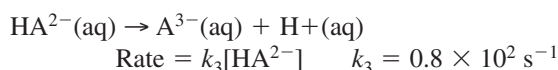
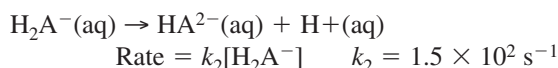
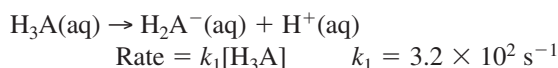
STANDARDIZED TEST PRACTICE

CHAPTER 17

Use these questions and the test-taking tip to prepare for your standardized test.

- The rate of a chemical reaction is all of the following EXCEPT
 - the speed at which a reaction takes place.
 - the change in concentration of a reactant per unit time.
 - the change in concentration of a product per unit time.
 - the amount of product formed in a certain period of time.

- The complete dissociation of acid H_3A takes place in three steps:



overall reaction: $\text{H}_3\text{A}(\text{aq}) \rightarrow \text{A}^{3-}(\text{aq}) + 3\text{H}^+(\text{aq})$

When the reactant concentrations are $[\text{H}_3\text{A}] = 0.100M$, $[\text{H}_2\text{A}^-] = 0.500M$, and $[\text{HA}^{2-}] = 0.200M$, which reaction is the rate-determining step?

- $\text{H}_3\text{A}(\text{aq}) \rightarrow \text{H}_2\text{A}^-(\text{aq}) + \text{H}^+(\text{aq})$
 - $\text{H}_2\text{A}^-(\text{aq}) \rightarrow \text{HA}^{2-}(\text{aq}) + \text{H}^+(\text{aq})$
 - $\text{HA}^{2-}(\text{aq}) \rightarrow \text{A}^{3-}(\text{aq}) + \text{H}^+(\text{aq})$
 - $\text{H}_3\text{A}(\text{aq}) \rightarrow \text{A}^{3-}(\text{aq}) + 3\text{H}^+(\text{aq})$
- Which of the following is NOT an acceptable unit for expressing a reaction rate?
 - M/min
 - L/s
 - $\text{mol}/(\text{mL} \cdot \text{h})$
 - $\text{mol}/(\text{L} \cdot \text{min})$

Interpreting Tables Use the table to answer questions 4–6.

Reaction: $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$

Experimental Data Collected for Reaction			
Time (min)	$[\text{SO}_2\text{Cl}_2] (M)$	$[\text{SO}_2] (M)$	$[\text{Cl}_2] (M)$
0.0	1.00	0.00	0.00
100.0	0.87	0.13	0.13
200.0	0.74	?	?

- What is the average reaction rate for this reaction, expressed in moles SO_2Cl_2 consumed per liter per minute?
 - $1.30 \times 10^{-3} \text{ mol}/(\text{L} \cdot \text{min})$
 - $2.60 \times 10^{-1} \text{ mol}/(\text{L} \cdot \text{min})$
 - $7.40 \times 10^{-3} \text{ mol}/(\text{L} \cdot \text{min})$
 - $8.70 \times 10^{-3} \text{ mol}/(\text{L} \cdot \text{min})$
- On the basis of the average reaction rate, what will the concentrations of SO_2 and Cl_2 be at 200.0 min?
 - 0.130M
 - 0.260M
 - 0.39M
 - 0.52M
- How long will it take for half of the original amount of SO_2Cl_2 to decompose at the average reaction rate?
 - 285 min
 - 335 min
 - 385 min
 - 500 min
- Which of the following does NOT affect reaction rate?
 - catalysts
 - surface area of reactants
 - concentration of reactants
 - reactivity of products
- The reaction between persulfate ($\text{S}_2\text{O}_8^{2-}$) and iodide (I^-) ions is often studied in student laboratories because it occurs slowly enough for its rate to be measured:

$$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq})$$

This reaction has been experimentally determined to be first order in $\text{S}_2\text{O}_8^{2-}$ and first order in I^- . Therefore, what is the overall rate law for this reaction?

 - $\text{Rate} = k[\text{S}_2\text{O}_8^{2-}]^2[\text{I}^-]$
 - $\text{Rate} = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$
 - $\text{Rate} = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]^2$
 - $\text{Rate} = k[\text{S}_2\text{O}_8^{2-}]^2[\text{I}^-]^2$

- The rate law for the reaction $\text{A} + \text{B} + \text{C} \rightarrow \text{products}$ is:

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

If $k = 6.92 \times 10^{-5} \text{ L}^2/(\text{mol}^2 \cdot \text{s})$, $[\text{A}] = 0.175M$, $[\text{B}] = 0.230M$, and $[\text{C}] = 0.315M$, what is the instantaneous reaction rate?

- $6.68 \times 10^{-7} \text{ mol}/(\text{L} \cdot \text{s})$
- $8.77 \times 10^{-7} \text{ mol}/(\text{L} \cdot \text{s})$
- $1.20 \times 10^{-6} \text{ mol}/(\text{L} \cdot \text{s})$
- $3.81 \times 10^{-6} \text{ mol}/(\text{L} \cdot \text{s})$

TEST-TAKING TIP

Watch the Little Words Underline words like *least*, *not*, and *except* when you see them in test questions. They change the meaning of the question!

