CHAPTER 16

Reaction Rates

BIG Idea Every chemical reaction proceeds at a definite rate, but can be speeded up or slowed down by changing the conditions of the reaction.

16.1 A Model for Reaction Rates

MAIN Idea Collision theory is the key to understanding why some reactions are faster than others.

16.2 Factors Affecting Reaction Rates

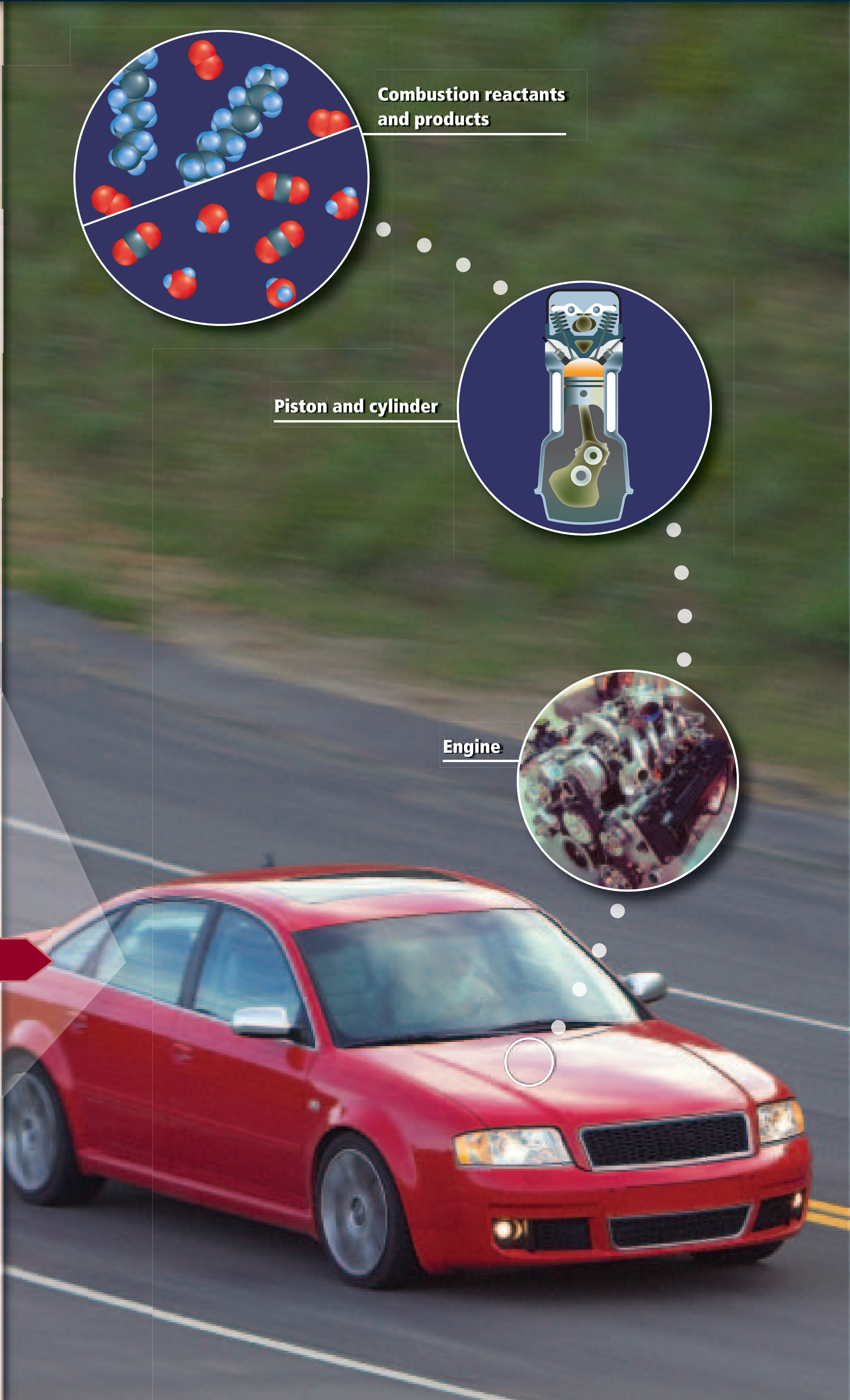
MAIN Idea Factors such as reactivity, concentration, temperature, surface area, and catalysts affect the rate of a chemical reaction.

16.3 Reaction Rate Laws

MAIN Idea The reaction rate law is an experimentally determined mathematical relationship that relates the speed of a reaction to the concentrations of the reactants.

16.4 Instantaneous Reaction Rates and Reaction Mechanisms

MAIN Idea The slowest step in a sequence of steps determines the rate of the overall chemical reaction.



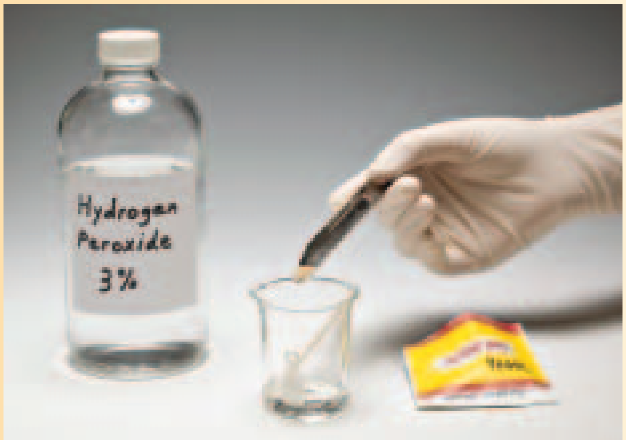
ChemFacts

- Most cars today still use the same combustion system invented by Alphonse Bear de Rochas in 1862.
- Regular, small explosions occurring in sequence in the cylinders of an automobile engine provide the energy to drive a car.
- In complete combustion, components of gasoline and oxygen combine in the cylinders to form carbon dioxide and water.

LAUNCH Lab

How can you accelerate a reaction?

Some chemical reactions go so slowly that nothing seems to be happening. In this lab, you can investigate one way of speeding up a slow reaction.



Procedure

1. Read and complete the lab safety form.
2. Create a *Before and After* table to record your observations.
3. Pour about 10 mL of **hydrogen peroxide** into a small **beaker or cup**. Observe the hydrogen peroxide. Complete the *Before* column with your initial observations.
   WARNING: ***Hydrogen peroxide is corrosive. Avoid contact with skin and eyes.***
4. Add 0.1 g of **baker's yeast** to the hydrogen peroxide. Stir gently with a **toothpick,** and observe the mixture again. Complete the *After* column with your observations.

Analysis

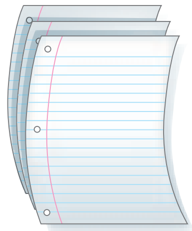
1. **Identify** the two products formed when hydrogen peroxide decomposes.
2. **Explain** why bubbles are produced in Step 4 but not in Step 3.

Inquiry What would happen if you added more or less yeast? What if you did not stir the mixture? Design an experiment to test one of these variables.

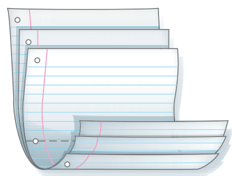
FOLDABLES™ Study Organizer

Reaction Rates Make the following Foldable to help you organize information about factors affecting reaction rates.

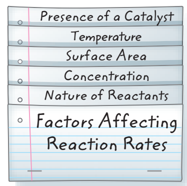
STEP 1 Stack three sheets of paper with the edges about 2 cm apart vertically. Keep the left and right edges even.



STEP 2 Fold up the bottom edges of the paper to form five equal tabs. Crease the fold to hold the tabs in place.



STEP 3 Staple along the fold. Label the tabs: *Nature of Reactants, Concentration, Surface Area, Temperature,* and *Presence of a Catalyst.*



FOLDABLES Use this Foldable with Section 16.2. As you read the section, define each factor and summarize its effect on reaction rate. Include examples in your summaries.

Chemistry Online

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Matt Meadows

Section 16.1

Objectives

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

Review Vocabulary

energy: the ability to do work or produce heat; it exists in two basic forms: potential energy and kinetic energy

New Vocabulary

reaction rate
collision theory
activated complex
activation energy

A Model for Reaction Rates

MAIN Idea Collision theory is the key to understanding why some reactions are faster than others.

Real-World Reading Link Which is faster: walking to school, or riding in a bus or car? Determining how fast a person can get to school is not all that different from calculating the rate of a chemical reaction. Either way, you are measuring change over time.

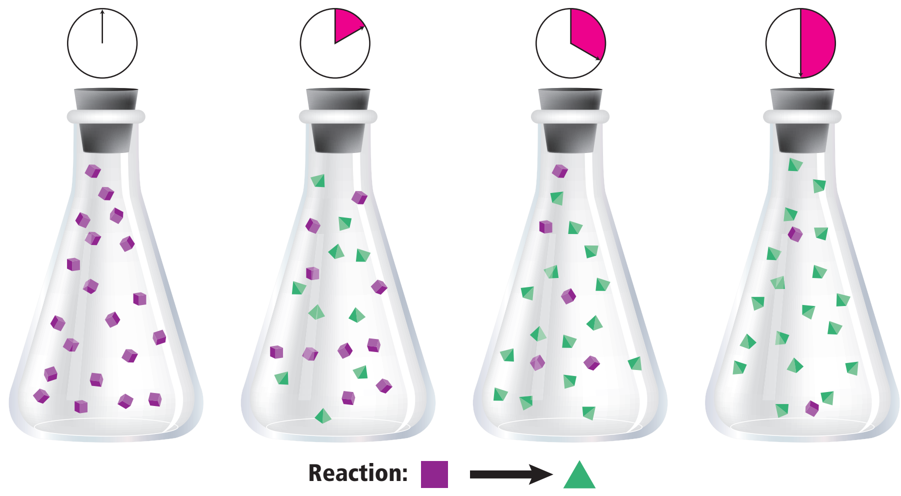
Expressing Reaction Rates

In the Launch Lab, you discovered that the decomposition of hydrogen peroxide can be a fast reaction, or it can be a slow one. However, *fast* and *slow* are inexact terms. Chemists, engineers, chefs, welders, concrete mixers, and others often need to be more specific. For example, a chef must know the rate at which a roast cooks to determine when it will be ready to serve. The person mixing the concrete must know the rate of mixing water, sand, gravel, and cement so that the resulting concrete can be poured at the correct consistency. Delaying pouring can result in concrete that is not strong enough for its purpose.

Think about how you express the speed or rate of a moving object. The speedometer of the speeding racer in **Figure 16.1** shows that the car is moving at 320 km/h. The speed of a sprinter on a track team might be expressed in meters per second (m/s). Generally, the average rate of an action or process is defined as 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 follows.

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

■ **Figure 16.1** The speedometer of the racer shows its speed in km/h or mph, both of which are the change in distance divided by the change in time. The sprinter's speed might be measured in m/s.



■ **Figure 16.2** Over time, the reactant changes to a product. The rate of a chemical reaction can be expressed as a change in the number of moles of reactant or product during an interval of time.

Calculate *the rate of change for each interval.*

Figure 16.2 shows how a reaction proceeds from reactant to product over time. Notice that the amount of the reactant decreases as the amount of product increases. If you know the change in a product or a reactant during a segment of time, you can calculate the average rate of the reaction. 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 generally stated as the change in concentration of a reactant or product per unit of time, expressed as mol/(L • s). Brackets around the formula for a substance denote its molar concentration. For example, $[NO_2]$ represents the molar concentration of NO_2.

Reaction rates are determined experimentally by measuring the concentrations of reactants and/or products as an actual chemical reaction proceeds. Reaction rates cannot be calculated from balanced equations.

Suppose you wish to express the average rate of the following reaction during the time period beginning at time t_1 and ending at time t_2.

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

Calculating the rate at which the products of the reaction are produced results in a reaction rate with a positive value. The rate calculation based on the production of NO has the following form.

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

For example, if the concentration of NO is 0.000M at time $t_1 = 0.00$ 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.

$$\text{Average reaction rate} = \frac{0.010M - 0.000M}{2.00\text{ s} - 0.00\text{ s}}$$

$$= \frac{0.010M}{2.00\text{ s}} = 0.0050 \text{ mol/(L•s)}$$

Notice how the units work out:

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

VOCABULARY

SCIENCE USAGE V. COMMON USAGE

Concentration

Science usage: quantitative measure of the amount of solute in a given amount of solvent or solution

The solution has a concentration of six moles per liter.

Common usage: the focus of attention on a single object or purpose

The concentration of the audience was completely on the performer.

You can also 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 a negative value for this reaction rate? In this case, a negative value indicates that the concentration of CO decreases as the reaction proceeds. However, reaction rates must always be positive. When the rate is measured by the consumption of a reactant, scientists apply a negative sign to the calculation to get a positive reaction rate. Thus, the following form of the average rate equation is used to calculate the rate of consumption of a reactant.

Average Reaction Rate Equation

$$\textbf{average reaction rate} = -\frac{\Delta[\text{reactant}]}{\Delta t}$$

Δ[reactant] represents the change in concentration of a reactant.

Δt represents the change in time.

The average reaction rate for the consumption of a reactant is the negative change in the concentration of the reactant divided by the elapsed time.

EXAMPLE Problem 16.1

Math Handbook
Solving Algebraic Equations
pages 954–955

Calculate Average Reaction Rates In a reaction between butyl chloride (C_4H_9Cl) and water, the concentration of C_4H_9Cl is 0.220M at the beginning of the reaction. At 4.00 s, the concentration of C_4H_9Cl is 0.100M. Calculate the average reaction rate over the given time period expressed as moles of C_4H_9Cl consumed per liter per second.

1 Analyze the Problem

You are given the initial and final concentrations of the reactant C_4H_9Cl 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.

Known	Unknown
$t_1 = 0.00$ s	Average reaction rate $=$? mol/(L•s)
$t_2 = 4.00$ s	
$[C_4H_9Cl]$ at $t_1 = 0.220M$	
$[C_4H_9Cl]$ at $t_2 = 0.100M$	

2 Solve for the Unknown

$$\text{Average reaction rate} = \frac{[C_4H_9Cl] \text{ at } t_2 - [C_4H_9Cl] \text{ at } t_1}{t_2 - t_1}$$

State the average reaction rate equation.

$$= -\frac{0.100M - 0.220M}{4.00 \text{ s} - 0.00 \text{ s}}$$

Substitute $t_2 = 4.00$ s, $t_1 = 0.00$ s, $[C_4H_9Cl]$ at $t_2 = 0.100$ M, and $[C_4H_9Cl]$ at $t_1 = 0.220M$.

$$= -\frac{0.100 \text{ mol/L} - 0.220 \text{ mol/L}}{4.00 \text{ s} - 0.00 \text{ s}}$$

Substitute mol/L for M and perform the calculations.

$$\text{Average reaction rate} = -\frac{-0.120 \text{ mol/L}}{4.00 \text{ s}} = \mathbf{0.0300 \text{ mol/(L•s)}}$$

3 Evaluate the Answer

The average reaction rate of 0.0300 moles C_4H_9Cl consumed per liter per second is reasonable based on the starting and ending amounts. The answer is correctly expressed in three significant figures.

Chemistry Online

Personal Tutor For help solving reaction rate problems, visit glencoe.com.

PRACTICE Problems Extra Practice Page 987 and glencoe.com

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

Experimental Data for $H_2 + Cl_2 \rightarrow 2HCl$			
Time (s)	$[H_2]$ (M)	$[Cl_2]$ (M)	$[HCl]$ (M)
0.00	0.030	0.050	0.000
4.00	0.020	0.040	

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. **Challenge** If the average reaction rate for the reaction, expressed in moles of HCl formed, is 0.0050 mol/L•s, what concentration of HCl would be present after 4.00 s?

Collision Theory

Have you ever watched children trying to break a piñata? Each hit with a stick can result in emptying the piñata of its contents, as shown in **Figure 16.3.** The reactants in a chemical reaction must also collide in order to form products. **Figure 16.3** also represents a reaction between the molecules A_2 and B_2 to form AB. The reactant molecules must come together in a collision in order to react and produce molecules of AB. The figure is an illustration of **collision theory,** which states that atoms, ions, and molecules must collide in order to react.

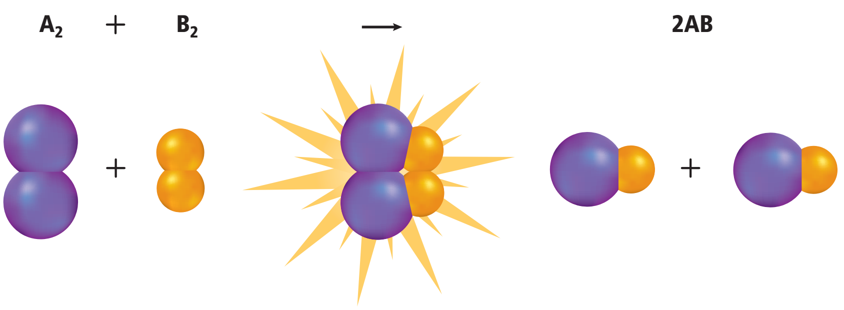
Reading Check **Predict** why a collision between two particles is necessary for a reaction to occur.

Look at the reaction between carbon monoxide (CO) gas and nitrogen dioxide (NO_2) gas at a temperature above 500 K.

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

The reactant molecules collide to produce carbon dioxide (CO_2) gas and nitrogen monoxide (NO) gas. However, calculations of the number of molecular collisions per second yield a puzzling result: only a small fraction of collisions produce reactions.

■ **Figure 16.3** Just as a stick must hit the piñata hard enough to break it open, particles in chemical reactions must collide with a sufficient amount of energy for a reaction to occur.



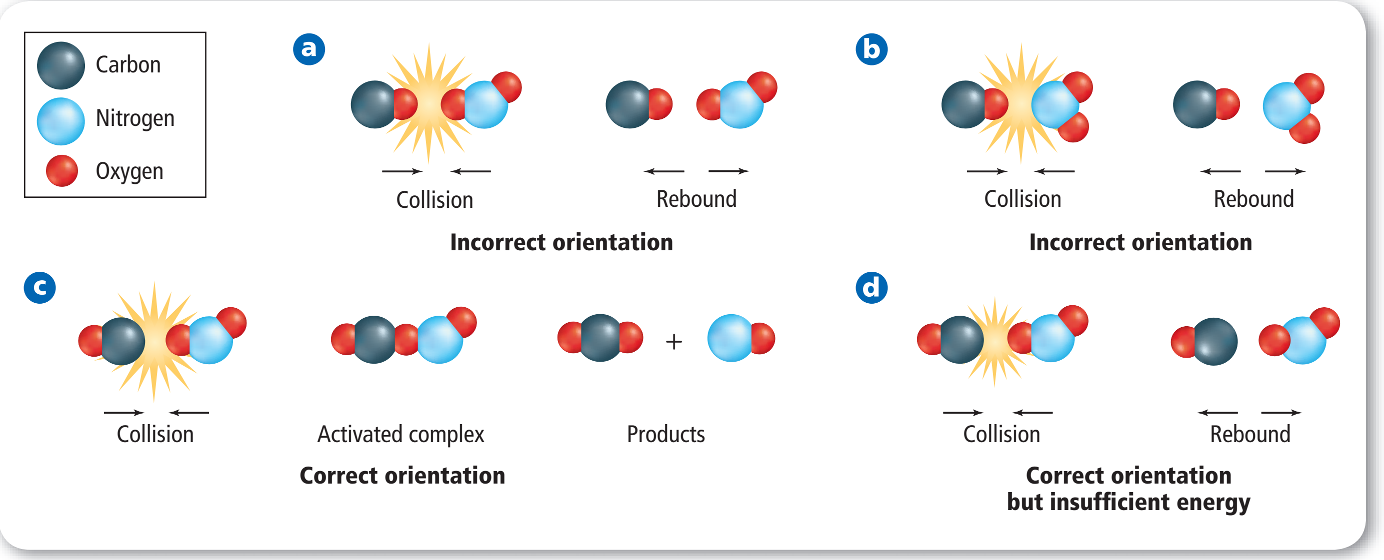


Figure 16.4 This figure shows four different collision orientations between CO molecules and NO_2 molecules. The collisions in **a** and **b** do not result in a reaction because the molecules are not in position to form bonds. The molecules in **c** collide in the correct orientation, and a reaction occurs. Although the molecules in **d** are also in the correct orientation, they have insufficient energy to react.

Concepts In Motion

Interactive Figure To see an animation of the effect of molecular orientation on collision effectiveness, visit glencoe.com.

Collision orientation and the activated complex Why do most collisions fail to produce products? What other factors must be considered? **Figure 16.4a** and **b** show one possible answer to this question. These illustrations indicate 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. This is the only way in which a temporary bond can form between the carbon atom and an oxygen atom. The collisions shown in **Figure 16.4a** and **b** do not lead to reactions because the molecules collide in unfavorable orientations. A carbon atom does not contact an oxygen atom at the instant of impact, so the molecules simply rebound.

When the orientation of colliding molecules is correct, as shown in **Figure 16.4c,** a reaction can occur. An oxygen atom is transferred from an NO_2 molecule to a CO molecule. When this occurs, a short-lived entity called an activated complex is formed, in this case OCONO. An **activated complex,** sometimes called a transition state, is a temporary, unstable arrangement of atoms in which old bonds are breaking and new bonds are forming. As a result, the activated complex might form products or might break apart to re-form the reactants.

Activation energy and reaction rate The collision depicted in **Figure 16.4d** does not lead to a reaction for a different reason—insufficient energy. Just as the piñata does not break open unless it is hit hard enough, no reaction occurs between the CO and NO_2 molecules unless they collide with sufficient energy. 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). **Table 16.1** summarizes the conditions under which colliding particles can react.

A high E_a means that relatively few collisions have the required energy to produce the activated complex, and the reaction rate is slow. A low E_a means that more collisions have sufficient energy to react, and the reaction rate is faster. 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 is required to move the cart, and it might take a long time to get it to the top. If the hill is low, less energy is required and the task might be accomplished faster.

Table 16.1	Collision Theory Summary
	1. Reacting substances (atoms, ions, or molecules) must collide.
	2. Reacting substances must collide in the correct orientation.
	3. Reacting substances must collide with sufficient energy to form an activated complex.

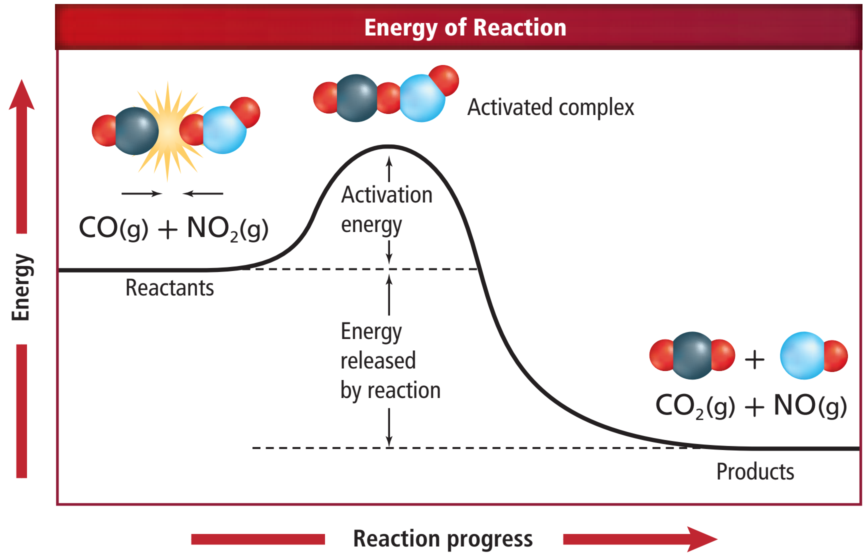


Figure 16.5 When an exothermic reaction occurs, molecules collide with enough energy to overcome the activation energy barrier. They form an activated complex, then release energy and form products at a lower energy level.

Graph Check

Explain how you can tell from the graph that the reaction described is an exothermic reaction.

Figure 16.5 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 15? Why? 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. Recall that reactions that lose energy are called exothermic reactions.

For many reactions, the process from reactants to products is reversible. **Figure 16.6** illustrates the reverse endothermic reaction between CO_2 and NO to re-form CO and NO_2. In this reaction, the reactants lie at a low energy level. They must overcome a significant activation energy to re-form CO and NO_2. This requires a greater input of energy than the forward reaction. If this reverse reaction is achieved, CO and NO_2 again lie at a high energy level.

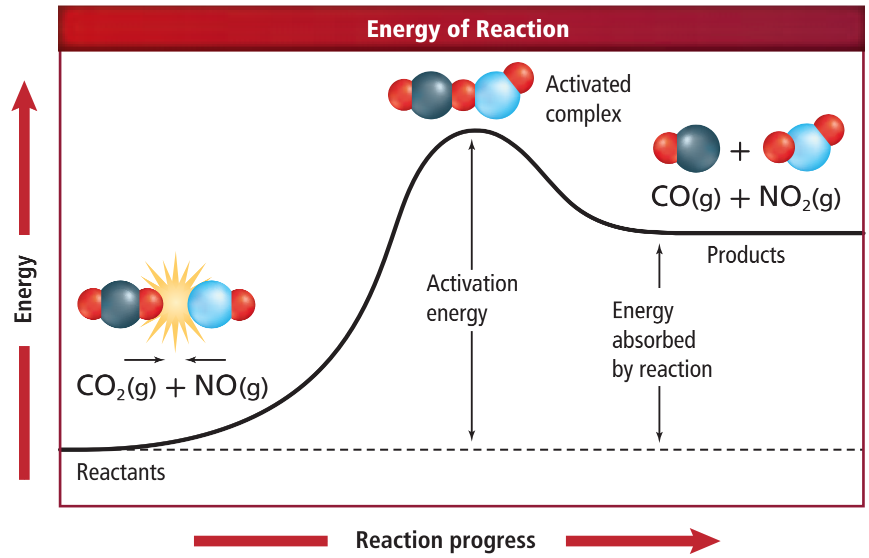


Figure 16.6 In the reverse reaction, which is endothermic, the reactant molecules are at a lower energy than the products. To react, the reactants must absorb enough energy to overcome the activation energy barrier and form higher-energy products.

Graph Check

Compare Figures 16.5 and **16.6** to determine whether the activation energy for the forward reaction is larger or smaller than the activation energy for the reverse reaction.

PROBLEM-SOLVING LAB

Interpret Data

How does the rate of decomposition vary over time? The compound dinitrogen pentoxide (N_2O_5) decomposes in air according to the equation

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

Knowing the rate of decomposition allows its concentration to be determined at any time.

Time (min)	$[N_2O_5]$ (mol/L)
0	0.01756
20.0	0.00933
40.0	0.00531
60.0	0.00295
80.0	0.00167
100.0	0.00094

Analysis

The table shows the results of an experiment in which the concentration of N_2O_5, was measured over time at normal atmospheric pressure and a temperature of 45°C.

Think Critically

1. **Calculate** the average reaction rate for each time interval: 0–20 min, 40–60 min, and 80–100 min. Express each rate as a positive number and in moles of N_2O_5 consumed per liter per minute.
2. **Express** the average reaction rate for each time interval in moles of NO_2 produced per liter per minute. Use the reaction equation to explain the relationship between these rates and those calculated in Question 1.
3. **Interpret** the data and your calculations in describing how the average rate of decomposition of N_2O_5 varies over time.
4. **Apply** collision theory to infer why the reaction rate varies as it does.

Spontaneity and Reaction Rate

Recall from Chapter 15 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. 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.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Here, $\Delta G = -458$ kJ at 298 K (25°C) and 1 atm pressure. Because ΔG is negative, the reaction is spontaneous. For the same reaction, $\Delta H = -484$ 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 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.

VOCABULARY

ACADEMIC VOCABULARY

Investigate
to observe by study or close examination
They decided to investigate how the mice were getting into the house.

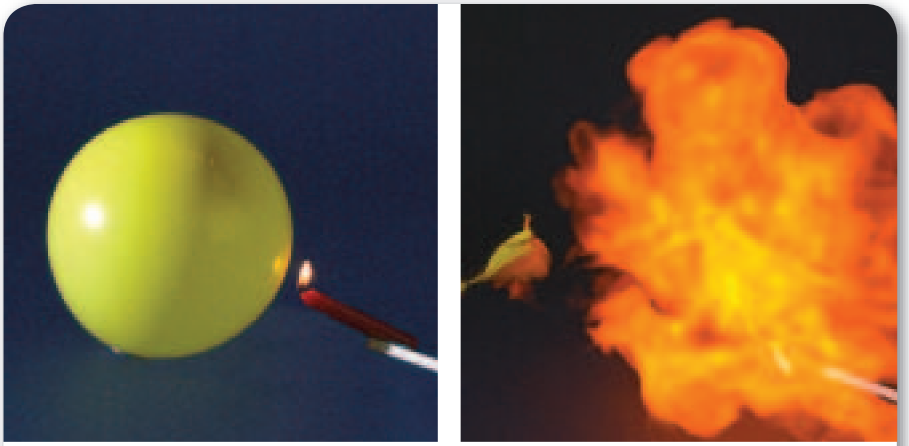


Figure 16.7 The hydrogen and oxygen in the balloon do not react until the balloon is touched by a flame. Then, an explosive reaction occurs.
Explain *the role of the flame.*

Figure 16.7 illustrates the reaction between hydrogen and oxygen in a similar way. The balloon is filled with a mixture of hydrogen gas and oxygen gas that appears not to react. When the lighted candle introduces additional energy, an explosive reaction occurs between the gases. Similarly, the air-fuel mixture in the cylinders of a car show little sign of reaction until a spark from a spark plug initiates a small explosion which produces energy to move the car. Logs on the forest floor combine slowly with oxygen in the air as they decompose, but they also combine with oxygen and burn rapidly in a forest fire once they are ignited.

As these examples show, reaction spontaneity in the form of ΔG implies nothing about the speed of the reaction; ΔG indicates only the natural tendency for a reaction or process to proceed. Factors other than spontaneity, however, do affect the rate of a chemical reaction. You will learn about these factors in the next section.

Section 16.1 Assessment

Section Summary

- 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.
- The rate of a chemical reaction is unrelated to the spontaneity of the reaction.

4. MAIN Idea **Relate** collision theory to reaction rate.
5. **Explain** what the reaction rate indicates about a particular chemical reaction.
6. **Compare** the concentrations of the reactants and products during the course of a chemical reaction (assuming no additional reactants are added).
7. **Explain** why the average rate of a reaction depends on the length of the time interval over which the rate is measured.
8. **Describe** the relationship between activation energy and the rate of a reaction.
9. **Summarize** what happens during the brief existence of an activated complex.
10. **Apply** collision theory to explain why collisions between two reacting particles do not always result in the formation of a product.
11. **Interpret** how the speed of a chemical reaction is related to the spontaneity of the reaction.
12. **Calculate** the average rate of a reaction between hypothetical molecules A and B if the concentration of A changes from 1.00M to 0.50M in 2.00 s.

Section 16.2

Objectives

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

Review Vocabulary

concentration: a quantitative measure of the amount of solute in a given amount of solvent or solution

New Vocabulary

catalyst
inhibitor
heterogeneous catalyst
homogeneous catalyst

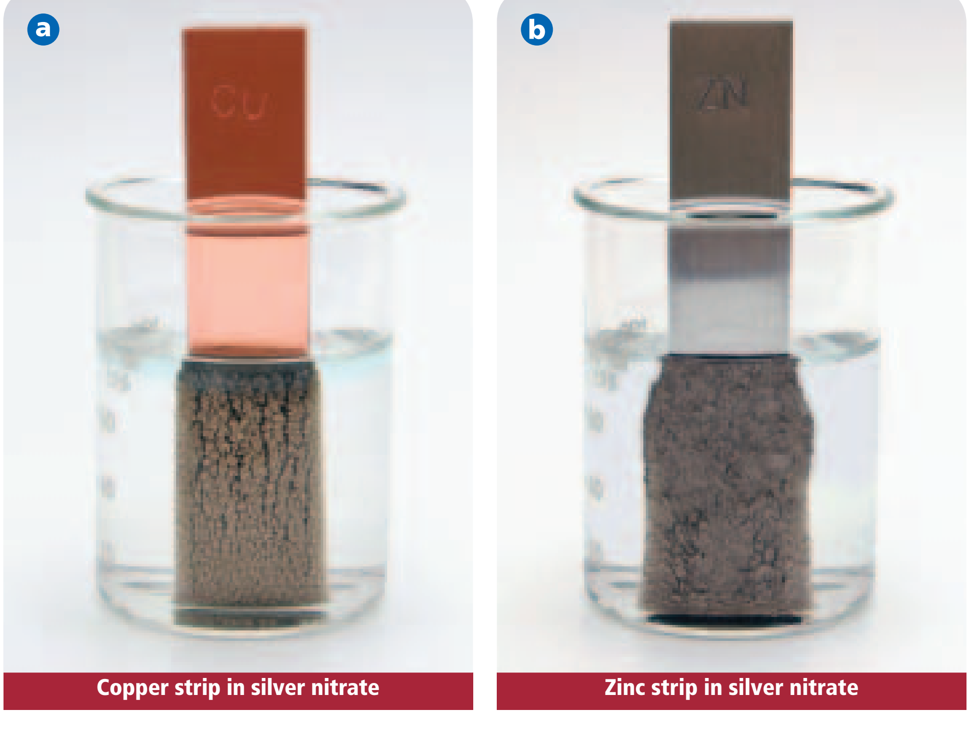
Factors Affecting Reaction Rates

MAIN Idea Factors such as reactivity, concentration, temperature, surface area, and catalysts affect the rate of a chemical reaction.

Real-World Reading Link How quickly do you think a forest fire would spread if the trees were far apart or the wood were damp? Similarly, the rate of a chemical reaction is dependent on a number of factors, including the concentrations and physical properties of the reactants.

The Nature of Reactants

Some substances react more readily than others. For example, copper and zinc are both metals and they have similar physical properties because of their relative positions of the periodic table, but they react at different rates when placed in aqueous silver nitrate solutions of equal concentration. When a copper strip is placed in 0.05*M* silver nitrate, as shown in **Figure 16.8a,** the copper and silver nitrate react to form silver metal and aqueous copper(II) nitrate. When a zinc strip is placed in 0.05*M* silver nitrate, as shown in **Figure 16.8b,** the zinc and silver nitrate react to form silver metal and aqueous zinc nitrate. You can see that the reactions are similar. However, compare the amounts of silver formed in the two photographs, which were taken after the same number of minutes had elapsed. **Figure 16.8** shows that more silver formed in the reaction of zinc and silver nitrate than in the reaction of copper and silver nitrate. The reaction of zinc with silver nitrate occurs faster because zinc is more reactive with silver nitrate than copper.



■ **Figure 16.8** Zinc is more reactive than copper, so it reacts with silver nitrate faster than copper does.
Write *the balanced equations for the reactions at right.*

The concentration of oxygen in the air surrounding the candle is about 20%.

The candle burns more rapidly because the jar contains almost 100% oxygen.

Figure 16.9 The brighter flame in the jar containing a greater amount of oxygen indicates an increase in reaction rate. The higher oxygen concentration accounts for the faster reaction.

Concentration

One way chemists can change the rate of a reaction is by changing the concentrations of the reactants. Remember that collision theory states that particles must collide in order to react. The more particles that are present, the more often collisions occur. Think about bumper cars at an amusement park. When more cars are in operation, the number of collisions increases. The same is true for a reaction in which Reactant A combines with Reactant B. At given concentrations of A and B, molecules of A and B collide to produce AB at a particular rate. What happens if the concentration of B is increased? Molecules of A collide with molecules of B more frequently because more molecules of B are available. More collisions ultimately increase the rate of reaction.

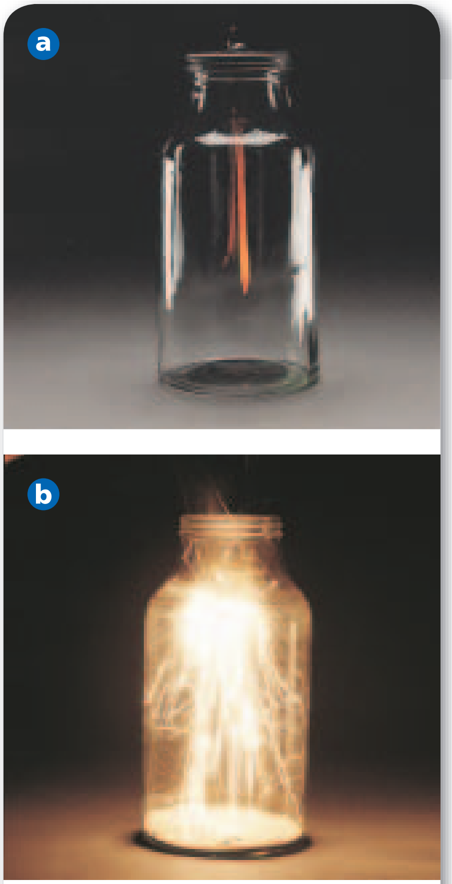
Reading Check **Predict** what would happen to the rate of the reaction if the concentration of A was increased.

Look at the reactions shown in **Figure 16.9.** The wax in the candle undergoes combustion. In the first photo, the candle burns in air. How does this compare with the second photo, in which the burning candle is placed inside a jar containing nearly 100% oxygen—approximately five times the concentration of oxygen in air? According to collision theory, the higher concentration of oxygen increases the collision frequency between the wax molecules in the candle and oxygen molecules. As a result, the rate of the reaction increases, resulting in a larger, brighter flame.

FOLDABLES
Incorporate information from this section into your Foldable.

Surface Area

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



■ **Figure 16.10** The greater surface area of the steel wool means that more collisions can occur between the metal and oxygen.

For the same mass, many small particles have more total surface area than one large particle. For example, observe the reactions shown in **Figure 16.10.** The hot nail glows in oxygen in **Figure 16.10a,** but the same mass of steel wool in **Figure 16.10b** bursts into flames. Increasing the surface area of a reactant speeds up the rate of reaction by increasing the collision rate between reacting particles.

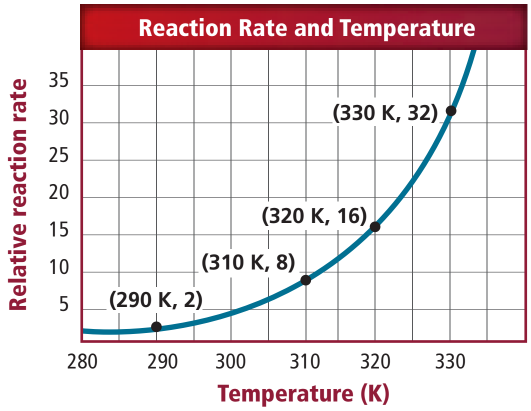
Temperature

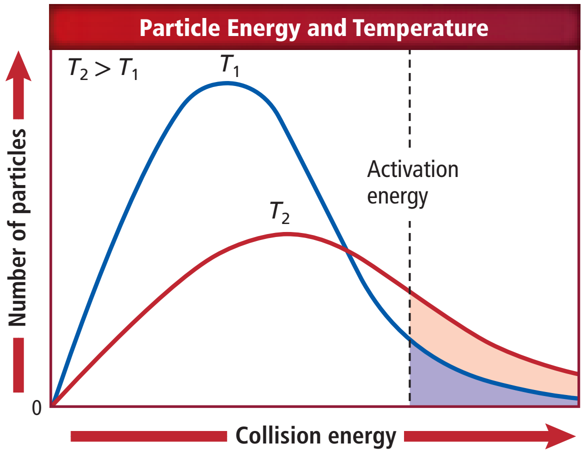
Increasing the temperature of a reaction generally increases the rate of a reaction. For example, you know that the reactions that cause foods to spoil occur faster at room temperature than when the foods are refrigerated. The graph in **Figure 16.11** illustrates that increasing the temperature by 10 K can approximately double the rate of a reaction. How can such a small increase in temperature have such a significant effect?

Recall from Chapter 13 that 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 does not account for the increase in reaction rate with increasing temperature. To better understand how reaction rate varies with temperature, examine the second graph in **Figure 16.11.** This graph compares the numbers of particles that have sufficient energy to react at temperatures T_1 and T_2, where T_2 is greater than T_1. The dotted line indicates the activation energy (E_a) for the reaction. The shaded area under each curve represents the number of collisions that have energy equal to or greater than the activation energy. How do the shaded areas compare? The number of high-energy collisions at the higher temperature, T_2, is greater than the number at the lower temperature, T_1. Therefore, as the temperature increases, more collisions result in a reaction.

Graph Check **Determine** the relative reaction rate at 325 K.

■ **Figure 16.11** Increasing the temperature of a reaction increases the frequency of collisions and therefore the rate of the reaction. Increasing the temperature also raises the kinetic energy of the particles. More of the collisions at high temperatures have enough energy to overcome the activation energy barrier and react.





MiniLab

Examine Reaction Rate and Temperature

What is the effect of temperature on a common chemical reaction?

Procedure

1. Read and complete the lab safety form.
2. Break a single **effervescent tablet** into four equal pieces.
3. Use a **balance** to measure the mass of one piece of the tablet. Measure 50 mL of room-temperature **water** (approximately 20°C) into a **250-mL beaker.** Use a **nonmercury thermometer** to measure the temperature of the water.
4. With a **stopwatch** or a **clock with a second hand** ready, add the piece of tablet to the water. Record the amount of time elapsed between when the tablet hits the water and when all of the solid has dissolved.
5. Repeat Steps 3 and 4, this time gradually warming the 50 mL of water to about 50°C on a **hot plate**. Maintain the temperature (equilibrate) throughout the run.

Analysis

1. **Identify** the initial mass, the final mass, and t_1 and t_2 for each trial run.
2. **Calculate** the reaction rate by finding the mass of reactant consumed per second for each run.
3. **Describe** the relationship between reaction rate and temperature for this reaction.
4. **Predict** what the reaction rate would be if the reaction were carried out at 40°C and explain the basis for your prediction. To test your prediction, repeat the reaction at 40°C using another piece of tablet.
5. **Evaluate** how well your prediction for the reaction rate at 40°C compares to the measured reaction rate.

Catalysts and Inhibitors

The temperature and the concentration of reactants affect the rate of a reaction, but 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 the decomposition of glucose in a living cell. Increasing the temperature and/or the concentration of reactants is not an option because doing so might harm or kill the cell.

Catalysts 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 being consumed in the reaction. Catalysts are used extensively in manufacturing because producing more of a product quickly reduces its cost. A catalyst does not yield more product and is not included in either the reactants or the products of the reaction. Thus, catalysts are not included in chemical equations.

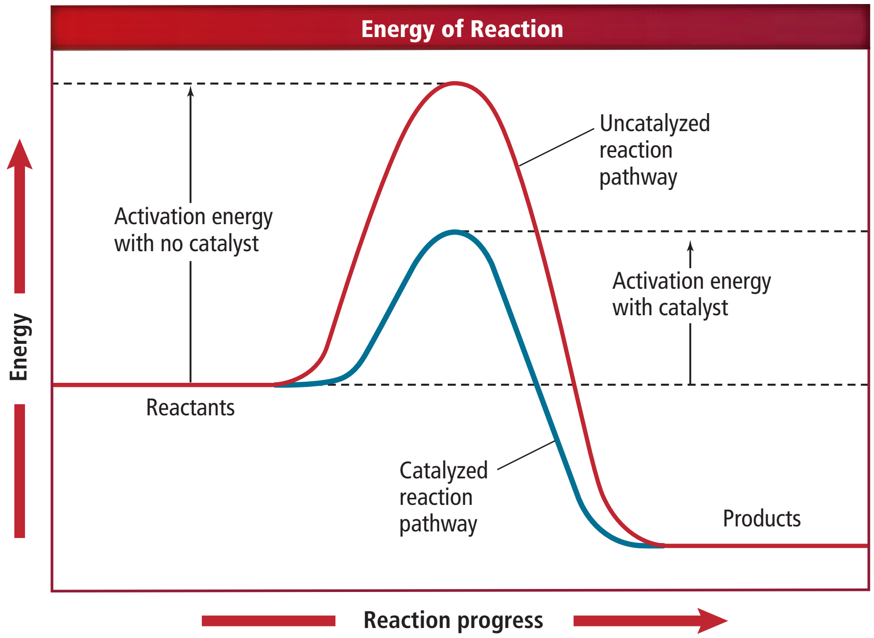
Inhibitors Another type of substance that affects reaction rates is called an inhibitor. Unlike a catalyst, which speeds up reaction rates, an **inhibitor** is a substance that slows down, or inhibits, reaction rates. Some inhibitors prevent a reaction from happening at all.

How catalysts and inhibitors work A catalyst lowers the activation energy required for a reaction to take place at a given temperature. Recall that a low activation energy means that more of the collisions between particles will have sufficient energy to overcome the activation energy barrier and bring about a reaction. By lowering the activation energy, a catalyst increases the average reaction rate.

Real World Chemistry
Excluding Oxygen

Food Preservation Foods often spoil because they react with oxygen. Many methods of food preservation maintain product freshness by excluding oxygen. For example, apples stored in an atmosphere of carbon dioxide can be kept fresh long after harvest. Foods such as crackers and popcorn are often packaged in an atmosphere of an unreactive gas such as nitrogen or argon.

■ **Figure 16.12** The activation energy of the catalyzed reaction is lower than that of the uncatalyzed reaction. Thus the catalyzed reaction produces products at a faster rate than the uncatalyzed reaction does.



Graph Check

Determine from the graph how the use of a catalyst affects the energy released in the reaction.

Figure 16.12 shows the energy diagram for an exothermic chemical reaction. The red line represents the reaction pathway with no catalyst present. The blue line represents the catalyzed reaction pathway. Note that the activation energy for the catalyzed reaction is much lower than for the uncatalyzed reaction. You can think of the reaction's activation energy as an obstacle to be cleared, as shown in **Figure 16.13.** In this analogy, much less energy is required for the horse and rider to clear the lower barrier than to jump the higher hurdle.

Inhibitors can act in a variety of ways. Some block lower energy pathways and thus raise the activation energy of a reaction. Others react with the catalyst and destroy it or prevent it from performing its function. In biological reactions, an inhibitor might bind the enzyme that catalyzes a reaction and prevent the reaction from occurring. In the food industry, inhibitors are called preservatives or antioxidants. Preservatives are safe to eat and give food longer shelf lives.

■ **Figure 16.13** A higher activation energy means that reacting particles must have more energy in order to react. The horse and rider exert little energy jumping the low barrier. Greater speed and energy are needed to clear the higher hurdle.

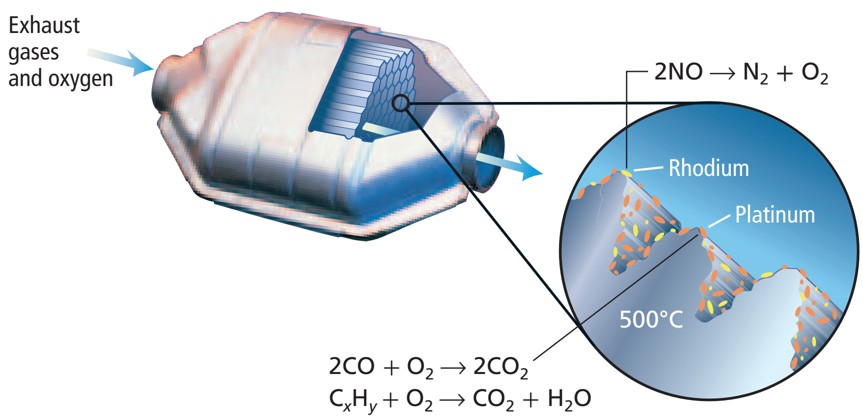


Figure 16.14 The inside of a catalytic converter is coated with particles of rhodium and platinum. At 500°C, rhodium catalyzes the conversion of nitrogen oxide (NO) to nitrogen (N_2) and oxygen (O_2). Platinum catalyzes the conversion of carbon monoxide (CO) to carbon dioxide (CO_2) and converts any unburned gasoline, represented by C_xH_y, to carbon dioxide and water vapor (H_2O).

Heterogeneous and homogeneous catalysts Today's automobiles are required by law to be equipped with catalytic converters. **Figure 16.14** shows the reactions within a catalytic converter that convert harmful exhaust gases to acceptable substances. Nitrogen monoxide is converted to nitrogen and oxygen, carbon monoxide to carbon dioxide, and unburned gasoline to carbon dioxide and water. The most effective catalysts for this application are transition metal oxides and metals such as rhodium and platinum. 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.** In the Launch Lab, you used a heterogenous catalyst (yeast) to speed up the decomposition of hydrogen peroxide. The same result can be obtained by using a potassium iodide (KI) solution. Iodide ions (I^- (aq)), present in the same physical state as the hydrogen peroxide molecules, act as a homogeneous catalyst in the decomposition.

Section 16.2 Assessment

Section Summary

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

13. MAIN Idea **Explain** why magnesium metal reacts with hydrochloric acid (HCl) at a faster rate than iron does.
14. **Explain** how collision theory accounts for the effect of concentration on reaction rate.
15. **Explain** the difference between a catalyst and an inhibitor.
16. **Describe** the effect on the rate of a reaction if one of the reactants is ground to a powder rather than used as a single chunk.
17. **Infer** If increasing the temperature of a reaction by 10 K approximately doubles the reaction rate, what would be the effect of increasing the temperature by 20 K?
18. **Research** 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 the role of a catalyst in one of these applications.

Section 16.3

Reaction Rate Laws

MAIN Idea **The reaction rate law is an experimentally determined mathematical relationship that relates the speed of a reaction to the concentrations of the reactants.**

Real-World Reading Link When a bicyclist switches from first gear to second gear, the bicycle travels a greater distance with each revolution of the pedals. In the same way, when a chemist increases the concentration of a reactant, the rate of the reaction increases.

Objectives

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

Review Vocabulary

reactant: the starting substance in a chemical reaction

New Vocabulary

rate law
specific rate constant
reaction order
method of initial rates

Writing Reaction Rate Laws

In Section 16.1, you learned how to calculate the average rate of a chemical reaction. The word *average* is important because most chemical reactions slow down as the reactants are consumed and fewer particles are available to collide. Chemists quantify the results of collision theory in an equation called a rate law. A **rate law** expresses the relationship between the rate of a chemical reaction and the concentration of reactants. For example, the reaction $A \longrightarrow B$ is a one-step reaction. The rate law for this reaction is expressed as follows.

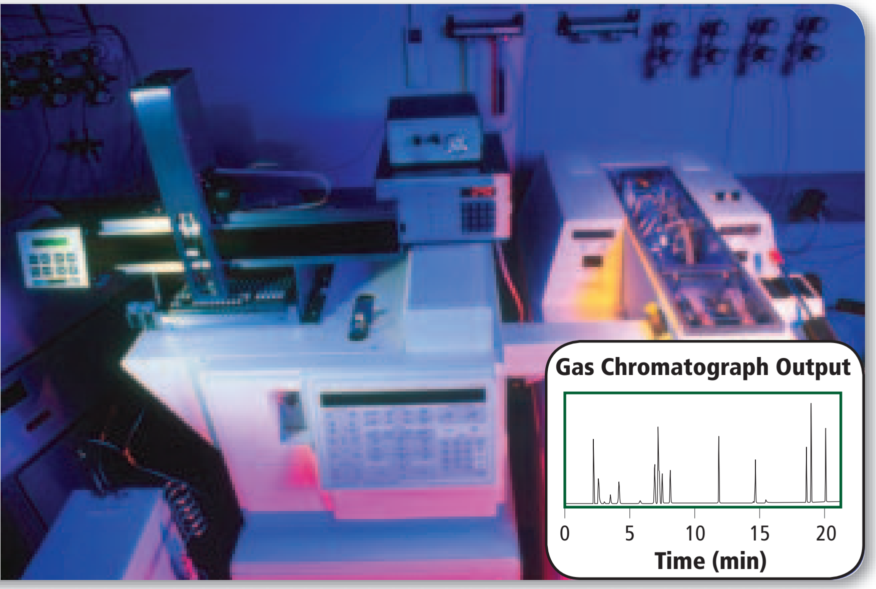
One-Step Reaction Rate Law

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

[A] represents the concentration of a reactant; *k* is a constant.

The rate of a one-step reaction is the product of the concentration of the reactant and a constant.

The symbol k is the **specific rate constant,** a numerical value that relates the reaction rate and the concentrations of reactants at a given temperature. The specific rate constant is unique for every reaction and can have a variety of units including $L/(mol{\cdot}s)$, $L^2/(mol^2{\cdot}s)$, and s^{-1}. A rate law must be determined experimentally as illustrated in **Figure 16.15.**



■ **Figure 16.15** To determine the rate of a reaction, samples of the reaction mixture are withdrawn at regular intervals while the reaction is proceeding. The samples are immediately injected into a gas chromatograph, which separates the components and helps identify them.

The rate law shows that the reaction rate is directly proportional to the molar concentration of A. 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.

First-order reaction rate laws In the expression $Rate = k[A]$, it is understood that the notation [A] means the same as $[A]^1$. 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.

$$\text{Rate} = k[H_2O_2]$$

Because the reaction rate is directly proportional to the concentration of H_2O_2 raised to the first power ($[H_2O_2]^1$), 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 also reduced by one-half.

Recall that reaction rates are determined from experimental data. Because reaction order is based on reaction rates, it follows that reaction order is also determined experimentally. Finally, because the rate constant, k, describes the reaction rate, it must also be determined experimentally. The graph in **Figure 16.16** shows how the initial reaction rate for the decomposition of H_2O_2 changes with the concentration of H_2O_2.

Reading Check **Infer** If the reaction order for a reactant is first order, how will the rate of the reaction change if the concentration of the reactant is tripled?

Other-order reaction rate laws 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 that have 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.

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

The general rate law for such a reaction is described below.

The General Rate Law

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

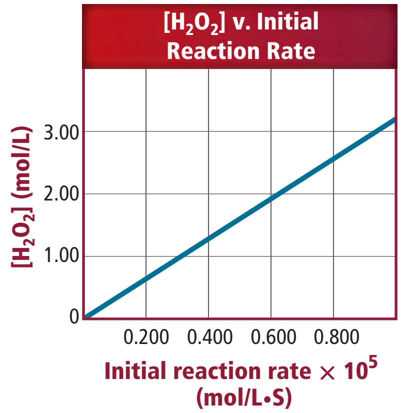
[A] and [B] represent the concentrations of reactants A and B. The exponents *m* and *n* are the reaction orders.

The rate of a reaction is equal to the product of k and the concentrations of the reactants each raised to a power (order) that is determined experimentally.

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 is unlikely, however, because single-step reactions are not common. For example, consider the reaction between nitrogen monoxide (NO) and hydrogen (H_2), which is described by the following equation.

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

Figure 16.16 The graph shows a direct relationship between the concentration of H_2O_2 and the rate of the decomposition.



Graph Check
Apply Using the graph, determine the initial reaction rate when $[H_2O_2]$ is 1.50 mol/L.

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

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

The rate law was determined from experimental data that indicate 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. The overall order is the sum of the orders for the individual reactants (the sum of the exponents), which is $(2 + 1)$, or 3.

Reading Check **Explain** how you can determine the overall order of the reaction from the rate equation.

VOCABULARY

WORD ORIGIN

Initial

adjective from Latin *initium*, meaning *of or relating to the beginning*

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. The initial rate measures how fast the reaction proceeds at the moment at which the reactants are mixed and the concentrations of the reactants are known. To understand how this method works, consider the general reaction $a\text{A} + b\text{B} \longrightarrow$ products. Suppose that the reaction is carried out three times with varying concentrations of A and B and yields the initial reaction rates shown in **Table 16.2.** Recall that the general rate law for this type of reaction is as follows.

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

To determine m, the exponent of [A], compare the concentrations and reaction rates in Trials 1 and 2. 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, the exponent of [B], except 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.

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

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

Table 16.2 **Experimental Initial Rates for $a\text{A} + b\text{B} \longrightarrow$ 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	16.00×10^{-3}

PRACTICE Problems

Extra Practice Page 987 and glencoe.com

19. Write the rate law for the reaction $aA \longrightarrow bB$ if the reaction is third order in A. [B] is not part of the rate law.

20. The rate law for the reaction $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ is first order in O_2 and third order overall. What is the rate law for the reaction?

21. Given the experimental data below, use the method of initial rates to determine the rate law for the reaction $aA + bB \longrightarrow$ products. *(Hint: Any number to the zero power equals one. For example, $(0.22)^0 = 1$ and $(55.6)^0 = 1$.)*

Practice Problem 21 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}

22. Challenge The rate law for the reaction $CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$ is Rate $= k[CH_3CHO]^2$. Use this information to fill in the missing experimental data below.

Practice Problem 22 Experimental Data

Trial	Initial [CH_3CHO](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}	

Section 16.3 Assessment

Section Summary

- 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.

23. MAIN Idea **Explain** what the rate law for a chemical reaction tells you about the reaction.

24. Apply the rate-law equations to show the difference between a first-order reaction with a single reactant and a second-order reaction with a single reactant.

25. Explain the function of the specific rate constant in a rate-law equation.

26. Explain Under what circumstance is the specific rate constant (k), not a constant. What does the size of k indicate about the rate of a reaction?

27. Suggest a reason why, when given the rate of a chemical reaction, it is important to know that the reaction rate is an average reaction rate.

28. Explain how the exponents in the rate equation for a chemical reaction relate to the coefficients in the chemical equation.

29. Determine the overall reaction order for a reaction between A and B for which the rate law is rate $= k[A]^2[B]^2$.

30. Design an Experiment Explain how you would design an experiment to determine the rate law for the general reaction $aA + bB \longrightarrow$ products using the method of initial rates.

Section 16.4

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.

Review Vocabulary

decomposition reaction: a chemical reaction that occurs when a single compound breaks down into two or more elements or new compounds

New Vocabulary

instantaneous rate
complex reaction
reaction mechanism
intermediate
rate-determining step

Instantaneous Reaction Rates and Reaction Mechanisms

MAIN Idea The slowest step in a sequence of steps determines the rate of the overall chemical reaction.

Real-World Reading Link Buying lunch in the cafeteria is a series of steps: picking up a tray and tableware, choosing food items, and paying the cashier. The first two steps might go rapidly, but a long line at the cashier will slow down the whole experience. Similarly, a reaction can go no faster than its slowest step.

Instantaneous Reaction Rates

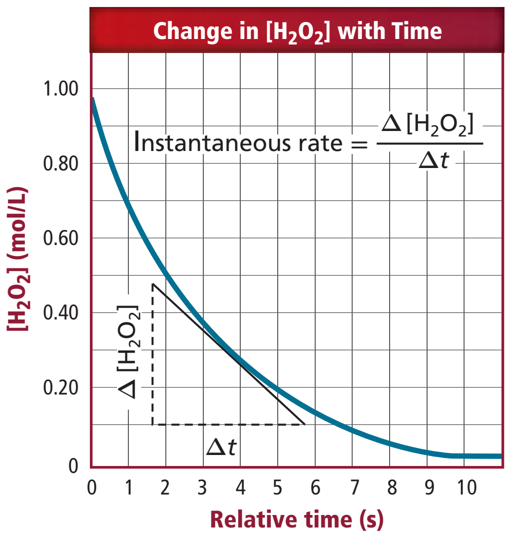
Chemists often need to know more than the average reaction rate. A pharmacist developing a new drug treatment might need to know the progress of a reaction at an exact instant. Consider the decomposition of hydrogen peroxide (H_2O_2), which is represented as follows.

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

For this reaction, the decrease in H_2O_2 concentration over time is shown in **Figure 16.17.** The curved line shows how the reaction rate decreases as the reaction proceeds. The **instantaneous rate** is the slope of the straight line tangent to the curve at a specific time. The expression $\Delta[H_2O_2]/\Delta t$ 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.

You can determine the instantaneous rate for a reaction in another way if you are given the reactant concentrations at a given temperature and know the experimentally determined rate law and the specific rate constant at that temperature.

Figure 16.17 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.



Slope of line $= \frac{\Delta x}{\Delta y}$

Instantaneous rate $= \frac{\Delta[H_2O_2]}{\Delta t}$

$\frac{\Delta x}{\Delta y} = \frac{\Delta[H_2O_2]}{\Delta t}$

Graph Check
Identify the variables that are plotted on the *y*-axis and on the *x*-axis.

Consider, the decomposition of dinitrogen pentoxide (N_2O_5) into nitrogen dioxide (NO_2) and oxygen (O_2), which proceeds as follows.

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

The experimentally determined rate law for this reaction is

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

where $k = 1.0 \times 10^{-5}\ s^{-1}$. If $[N_2O_5] = 0.350M$, the instantaneous reaction rate would be calculated as

$$\text{rate} = (1.0 \times 10^{-5}\ s^{-1})(0.350\ \text{mol/L}) = 3.5 \times 10^{-6}\ \text{mol/(L}\cdot\text{s)}$$

EXAMPLE Problem 16.2

Math Handbook
Dimensional Analysis
page 956

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

$$2NO(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$$

Calculate the instantaneous rate when the reactant concentrations are $[NO] = 0.00200M$ and $[H_2] = 0.00400M$.

1 Analyze the Problem

The rate law can be expressed by rate $= k[NO]^2[H_2]$. Therefore, the instantaneous reaction rate can be determined by inserting reactant concentrations and the specific rate constant into the rate law equation.

Known

$[NO] = 0.00200M$

$[H_2] = 0.00400M$

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

Unknown

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

2 Solve for the Unknown

rate $= k[NO]^2[H_2]$ — **State the rate law.**

rate $= (2.90 \times 10^2\ \text{L}^2/(\text{mol}^2 \cdot \text{s}))(0.00200\ \text{mol/L})^2(0.00400\ \text{mol/L})$ — **Substitute $k = 2.90 \times 10^2\ (\text{L}^2/(\text{mol}^2 \cdot \text{s}))$, $[NO] = 0.00200M$, and $[H_2] = 0.00400M$.**

rate $= 4.64 \times 10^{-6}\ \text{mol/(L}\cdot\text{s)}$ — **Multiply the numbers and units.**

3 Evaluate the Answer

Units in the calculation cancel to give mol/(L•s), which is a common unit for reaction rates. A magnitude of approximately 10^{-6} mol/(L•s) fits with the quantities given and the rate law equation. The answer is correctly expressed with three significant figures.

PRACTICE Problems

Extra Practice Page 988 and glencoe.com

Use the rate law in Example Problem 16.2 and the concentrations given in Practice Problems 31 and 32 to calculate the instantaneous rate for the reaction between NO and H_2.

31. $[NO] = 0.00500M$ and $[H_2] = 0.00200M$

32. $[NO] = 0.0100M$ and $[H_2] = 0.00125M$

33. Challenge Calculate [NO] for the reaction in Example Problem 16.2 if the rate is 9.00×10^{-5} mol/(L•s) and $[H_2]$ is $0.00300M$.

Reaction Mechanisms

Most chemical reactions consist of sequences of two or more simpler reactions. For example, recent evidence indicates that the reaction $2O_3 \longrightarrow 3O_2$ 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 might occur simultaneously or in reverse order.

1. Chlorine atoms decompose ozone according to the equation $Cl + O_3 \longrightarrow O_2 + ClO$.
2. Ultraviolet radiation causes the decomposition reaction $O_3 \longrightarrow O + O_2$.
3. ClO produced in the reaction in Step 1 reacts with O produced in Step 2 according to the equation $ClO + O \longrightarrow Cl + O_2$.

Each of the reactions described in Steps 1 through 3 is called an elementary step. These elementary steps, illustrated in **Figure 16.18,** comprise the complex reaction $2O_3 \longrightarrow 3O_2$. A **complex reaction** is one that consists of two or more elementary steps. A **reaction mechanism** is the complete sequence of elementary steps that makes up a complex reaction. Adding elementary 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.

Elementary step:	$Cl + O_3 \longrightarrow ClO + O_2$
Elementary step:	$O_3 \longrightarrow O + O_2$
Elementary step:	$ClO + O \longrightarrow Cl + O_2$
Complex reaction:	$2O_3 \longrightarrow 3O_2$

Because chlorine atoms react in Step 1 and are re-formed in Step 3, chlorine is said to catalyze the decomposition of ozone. Because ClO and O are formed in Steps 1 and 2, respectively, and are consumed in the reaction in Step 3, they are called intermediates. An **intermediate** is a substance produced in one elementary step and consumed in a subsequent elementary step. Like catalysts, intermediates do not appear in the net chemical equation.

CAREERS IN CHEMISTRY

Chemical Engineer An understanding of reaction mechanisms is vital to chemical engineers. Their jobs often include scaling up a laboratory synthesis of a substance to large-scale production in a manufacturing plant. They must design the production facility and monitor its safe and efficient operation. For more information on chemistry careers, visit glencoe.com.

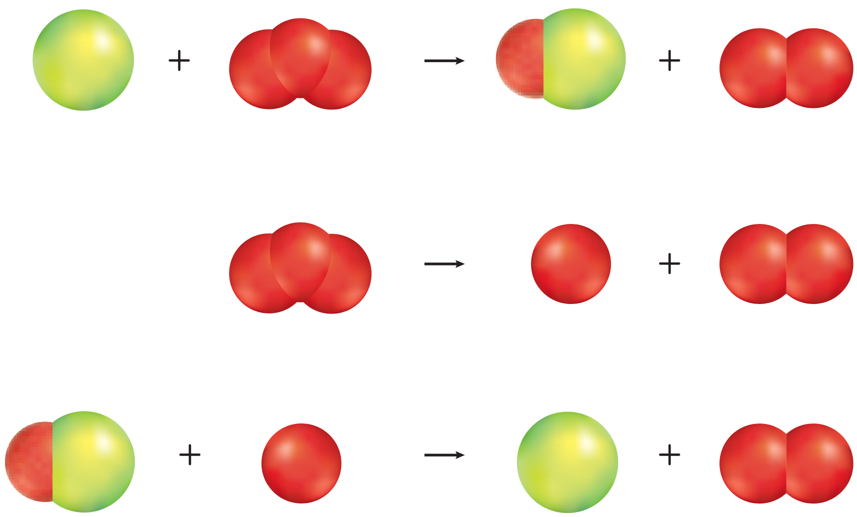


Figure 16.18 ClO and O are intermediates in the three elementary steps of the complex reaction producing oxygen gas (O_2) from ozone (O_3).
Infer *What is the function of chlorine (Cl) in the complex reaction?*

Connection to Physics Investigating reaction mechanisms

How is it possible to discover the presence of intermediates and determine their role in a chemical reaction? Learning how particles change their identities in the course of a chemical reaction means detecting evidence of bonds breaking and bonds forming. These processes take an extremely short period of time—time measured in femtoseconds. A femtosecond (fs) is one-thousandth of a trillionth of a second (0.000000000000001 second). Until recently, scientists could only calculate and imagine the actual atomic activity that occurs when bonds are broken and new bonds are made.

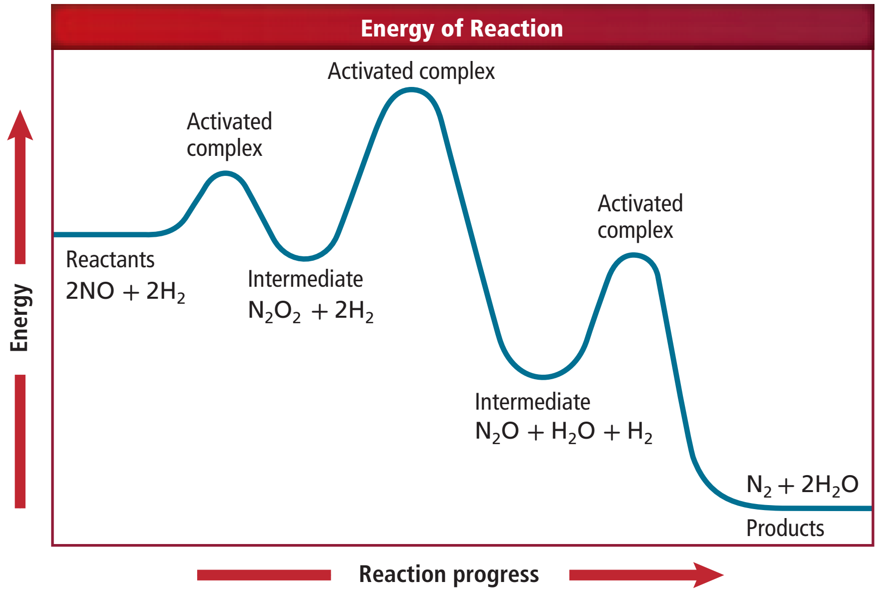
In 1999, Dr. Ahmed Zewail of the California Institute of Technology won a Nobel Prize for his achievements in the field of femtochemistry. Zewail developed an ultrafast laser device that can record pictures of chemical reactions as they happen. The laser "flashes" every 10 femtoseconds to record the movements of particles just as if they were being recorded on frames taken by a movie camera. Thus, a femtosecond recording of molecular motion could have as many as 10^{14} frames per second. The molecular motion corresponds to bond formation and breakage and can be related to the various possible intermediates and the products that are formed during a reaction. Zewail was able to witness an interaction between benzene (C_6H_6) and iodine (I_2) over a period of 1500 fs. A collision of iodine with benzene resulted in the breaking of the bond between the iodine atoms, after which the two atoms moved apart from one another. Technology such as this allows chemists to test their hypotheses about possible intermediates and reaction mechanisms.

Reading Check **Explain** the importance of the methods of femtochemistry to the study of reaction mechanisms.

Rate-determining step Every complex reaction has an elementary step that is slower than all the other steps. The slowest elementary step in a complex reaction is called the **rate-determining step.** A reaction cannot go faster than its slowest elementary step. An analogy for the rate-determining step is shown in **Figure 16.19.**

Figure 16.19 At highway toll booths, drivers must slow down and stop as tolls are paid. Although they can resume their speeds after paying the toll, the pause affects their overall rate of travel. In a similar way, the overall rate of a chemical reaction is dependent on how fast the slowest elementary step proceeds.

Figure 16.20 The three peaks in this energy diagram correspond to activation energies for the elementary steps of the reaction. The middle hump represents the highest energy barrier to overcome; therefore, the reaction involving $N_2O_2 + 2H_2$ is the rate-determining step.



Graph Check

Determine from the graph whether the overall reaction is exothermic or endothermic.

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

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

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

$$\begin{array}{rcll} 2NO & \longrightarrow & N_2O_2 & \text{(fast)} \\ N_2O_2 + H_2 & \longrightarrow & N_2O + H_2O + H_2 & \text{(slow)} \\ N_2O + H_2 & \longrightarrow & N_2 + H_2O & \text{(fast)} \end{array}$$

The first and third elementary steps occur relatively fast, so the slow middle step is the rate-determining step. **Figure 16.20** shows how energy changes as this complex reaction proceeds. Each step of the reaction has its own activation energy. Activation energy for Step 2 is higher than for Steps 1 and 3, which is why Step 2 is the rate-determining step.

Section 16.4 Assessment

Section Summary

- The reaction mechanism of a chemical reaction must be determined experimentally.
- For a complex reaction, the rate-determining step limits the instantaneous rate of the overall reaction.

34. MAIN Idea **Compare and contrast** an elementary chemical reaction with a complex chemical reaction.
35. **Explain** how the rate law for a chemical reaction is used to determine the instantaneous rate of the reaction.
36. **Define** a reaction mechanism and an intermediate.
37. **Distinguish** between an intermediate and an activated complex.
38. **Relate** the size of the activation energy of an elementary step in a complex reaction to the rate of that step.
39. **Calculate** A reaction between A and B to form AB is first order in A and first order in B. The rate constant, k, equals 0.500 mol/(L•s). What is the rate of the reaction when $[A] = 2.00 \times 10^{-2}M$ and $[B] = 1.50 \times 10^{-2}M$?

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Chemistry & Health

Reaction Rate and Body Temperature

Imagine that you're late for school and rush outside without putting on your jacket. It's a chilly day, and soon you begin to shiver. Shivering is an automatic response by your body that helps maintain your normal body temperature, which is important.

What is normal body temperature?

Normal human body temperature is approximately 37°C, but it can vary with age, gender, time of day, and level of activity. Your temperature goes up when you engage in strenuous activities or when the temperature of the air around you is high. It can also go down when you take a cold shower or forget to wear your jacket in cold weather.

Chemical reactions heat the body Inside each cell of the body, food is metabolized to produce energy that is either used or stored in large molecules called adenosine triphosphate (ATP). When energy is needed, ATP splits into adenosine diphosphate (ADP) and a phosphate group (P_i) and energy is released.

$$\text{ATP} \longrightarrow \text{ADP} + \text{P}_i + \text{Energy}$$

Reactions such as this require enzymes that regulate their rates. These enzymes are protein catalysts that are most efficient within the range of normal human body temperatures. Without the help of enzymes and a temperature near 37°C, reactions such as this one could not occur at a rate that would meet the needs of the body. Outside this temperature range, reaction rates are slower, as shown in **Figure 1.**

Regulating body temperature The area of the brain called the hypothalamus regulates body temperature by a complex feedback system. The system maintains a balance between the thermal energy released by chemical reactions within the body and the thermal energy exchanged between the body and the environment.

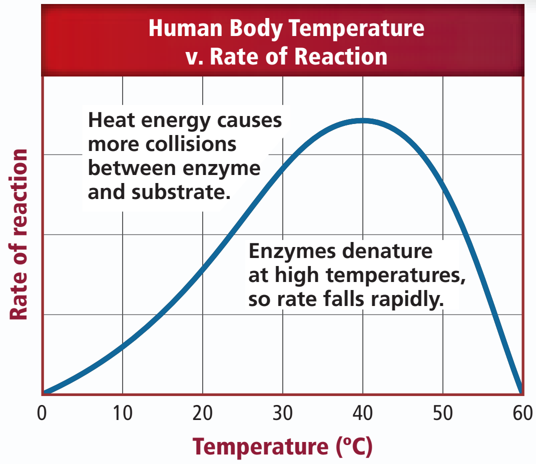


Figure 1 Optimum temperature for humans is close to 37°C. Excessive thermal energy results in the breakdown of a protein's structure, preventing it from functioning as it should.

Hypothermia—low body temperature

When hypothermia is detected, the hypothalamus begins actions that increase the release of thermal energy. Shivering is the rapid contractions of muscles that result from chemical reactions that release thermal energy. The body also begins actions to conserve thermal energy, including reducing blood flow to the skin.

Hyperthermia—high body temperature

Excessive thermal energy, either from the environment or because of increased chemical reactions within the body, causes the body to respond by sweating. Blood vessels near the skin's surface dilate, and heart and lung functions increase. These actions result in an increase in the release of thermal energy to the environment. The entire system of temperature control is designed to keep reactions within the body occurring at the optimal rate.

WRITING in Chemistry

Research Write a patient-information brochure about the medical treatment of hypothermia and hyperthermia. Describe any long term effects these conditions might have and how they might be prevented. Visit glencoe.com to learn more about rates of reactions.

CHEMLAB

Chemistry Online

Probeware Alternate CBL instructions can be found at glencoe.com.

OBSERVE HOW CONCENTRATION AFFECTS REACTION RATE

Background: Collision theory describes how a change in concentration of one reactant affects the rate of a chemical reaction.

Question: *How does the concentration of a reactant affect the reaction rate?*

Materials

10-mL graduated pipette
safety pipette filler
6*M* hydrochloric acid
distilled water
25-mm × 150-mm test tubes, labeled *1–4*
test-tube rack
magnesium ribbon
emery cloth or fine sandpaper
scissors
plastic ruler
tongs
watch with second hand or stopwatch
stirring rod

Safety Precautions

WARNING: ***Never pipette any chemical by mouth. Hydrochloric acid is corrosive. Avoid contact with skin and eyes.***

Procedure

1. Read and complete the lab safety form.
2. Use a safety pipette to draw 10 mL of 6.0*M* hydrochloric acid (HCl) into a 10-mL graduated pipette.
3. Dispense the 10 mL of 6.0*M* HCl into Test Tube 1.
4. Draw 5.0 mL of the 6.0*M* HCl from Test Tube 1 with the pipette. Dispense this acid into Test Tube 2. Use the pipette to add an additional 5.0 mL of distilled water. Mix with the stirring rod. This solution is 3.0*M* HCl.
5. Draw 5.0 mL of the 3.0*M* HCl from Test Tube 2 and dispense it into Test Tube 3. Add 5.0 mL of distilled water and stir. This solution is 1.5*M* HCl.
6. Draw 5.0 mL of the 1.5*M* HCl from Test Tube 3 and dispense it into Test Tube 4. Add 5.0 mL of distilled water and stir. This solution is 0.75*M* HCl.
7. Draw 5.0 mL of the 0.75*M* HCl from Test Tube 4. Neutralize and discard it in the sink.

8. Using tongs, place a 1-cm length of magnesium ribbon into Test Tube 1. Record in your data table the time in seconds it takes for the bubbling to stop.
9. Repeat Step 8 using the remaining three test tubes. Record the time in seconds it takes for the bubbling to stop in each test tube.
10. **Cleanup and Disposal** Place acid solutions in an acid discard container. Thoroughly wash all test tubes and lab equipment. Discard other materials as directed by your teacher. Return all lab equipment to its proper place.

Analyze and Conclude

1. **Make a Graph** Plot the concentration of the acid on the *x*-axis and the reaction time on the *y*-axis. Draw a smooth curve through the data points.
2. **Conclude** Based on your graph, what is the relationship between the acid concentration and the reaction rate?
3. **Hypothesize** Write a hypothesis using collision theory, reaction rate, and reactant concentration to explain your results.
4. **Error Analysis** Compare your experimental results with those of other students in the laboratory. Explain the differences.

INQUIRY EXTENSION

Design an Experiment Based on your observations and results, would temperature variations affect reaction rates? Plan an experiment to test your hypothesis.

Matt Meadows

Study Guide

BIG Idea Every chemical reaction proceeds at a definite rate, but can be speeded up or slowed down by changing the conditions of the reaction.

Section 16.1 A Model for Reaction Rates

MAIN Idea Collision theory is the key to understanding why some reactions are faster than others.

Vocabulary

- activated complex (p. 564)
- activation energy (p. 564)
- collision theory (p. 563)
- reaction rate (p. 561)

Key Concepts

- 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.

$$\text{average reaction rate} = -\frac{\Delta[\text{reactant}]}{\Delta t}$$

- 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.
- The rate of a chemical reaction is unrelated to the spontaneity of the reaction.

Section 16.2 Factors Affecting Reaction Rates

MAIN Idea Factors such as reactivity, concentration, temperature, surface area, and catalysts affect the rate of a chemical reaction.

Vocabulary

- catalyst (p. 571)
- heterogeneous catalyst (p. 573)
- homogeneous catalyst (p. 573)
- inhibitor (p. 571)

Key Concepts

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

Section 16.3 Reaction Rate Laws

MAIN Idea The reaction rate law is an experimentally determined mathematical relationship that relates the speed of a reaction to the concentrations of the reactants.

Vocabulary

- method of initial rates (p. 576)
- rate law (p. 574)
- reaction order (p. 575)
- specific rate constant (p. 574)

Key Concepts

- The mathematical relationship between the rate of a chemical reaction at a given temperature and the concentrations of reactants is called the rate law.

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

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

- The rate law for a chemical reaction is determined experimentally using the method of initial rates.

Section 16.4 Instantaneous Reaction Rates and Reaction Mechanisms

MAIN Idea The slowest step in a sequence of steps determines the rate of the overall chemical reaction.

Vocabulary

- complex reaction (p. 580)
- instantaneous rate (p. 578)
- intermediate (p. 580)
- rate-determining step (p. 581)
- reaction mechanism (p. 580)

Key Concepts

- The reaction mechanism of a chemical reaction must be determined experimentally.
- For a complex reaction, the rate-determining step limits the instantaneous rate of the overall reaction.

Section 16.1

Mastering Concepts

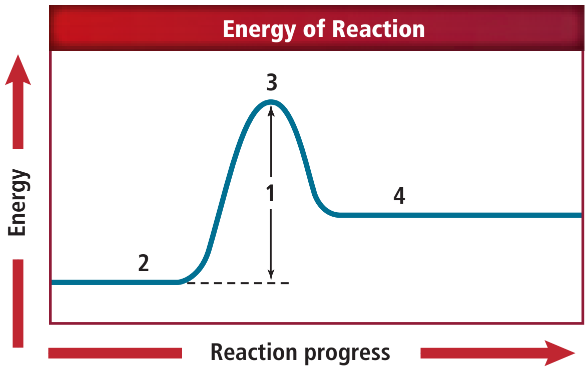
40. What happens to the concentrations of the reactants and products during the course of a chemical reaction?

41. Explain what is meant by the average rate of a reaction.

42. How would you express the rate of the chemical reaction $A \longrightarrow B$ based on the concentration of Reactant A? How would that rate compare with the reaction rate based on the Product B?

43. What is the role of the activated complex in a chemical reaction?

44. Suppose two molecules that can react collide. Under what circumstances do the colliding molecules not react?



■ **Figure 16.21**

45. **Figure 16.21** is an energy level diagram for a reaction. Match the appropriate number with the quantity it represents.

a. reactants
b. activated complex
c. products
d. activation energy

46. If $A \longrightarrow B$ is exothermic, how does the activation energy for the forward reaction compare with the activation energy for the reverse reaction ($A \longleftarrow B$)?

Mastering Problems

47. In the gas-phase reaction, $I_2 + Cl_2 \longrightarrow 2ICl$, $[I_2]$ changes from 0.400*M* at 0.00 min to 0.300*M* at 4.00 min. Calculate the average reaction rate in moles of I 2 consumed per liter per minute.

48. In a reaction $Mg(s) + 2HCl(aq) \longrightarrow H_2(g) + MgCl_2(aq)$, 6.00 g of Mg was present at 0.00 min. After 3.00 min, 4.50 g of Mg remained. Express the average rate as mol Mg consumed/min.

49. If a chemical reaction occurs at the 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?

Section 16.2

Mastering Concepts

50. What role does the reactivity of the reactants play in determining the rate of a chemical reaction?

51. In general, what is the relationship between reaction rate and reactant concentration?

52. Apply collision theory to explain why increasing the concentration of a reactant usually increases the reaction rate.

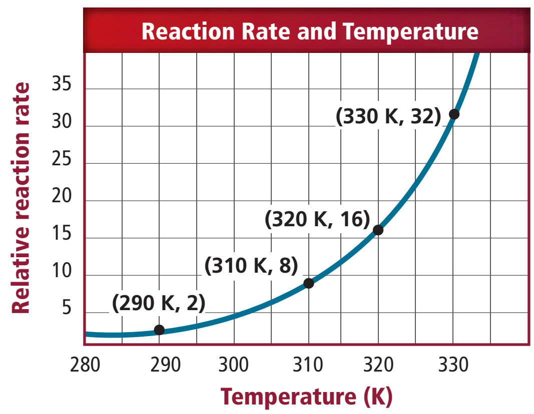
53. Explain why a crushed solid reacts with a gas more quickly than a large chunk of the same solid.

54. **Food Preservation** Apply collision theory to explain why foods usually spoil more slowly when refrigerated than at room temperature.

55. Apply collision theory to explain why powdered zinc reacts to form hydrogen gas faster than large pieces of zinc when both are placed in hydrochloric acid solution.

56. Hydrogen peroxide decomposes to water and oxygen gas more rapidly when manganese dioxide is added. The manganese dioxide is not consumed in the reaction. Explain the role of the manganese dioxide.

Mastering Problems



■ **Figure 16.22**

57. Examine **Figure 16.22,** which relates relative reaction rate and temperature. Approximately how does the reaction rate change for each increase of 10 K?

58. Suppose that a large volume of 3% hydrogen peroxide decomposes to produce 12 mL of oxygen gas in 100 s at 298 K. Estimate how much oxygen gas would be produced by an identical solution in 100 s at 308 K.

59. Using the information in Question 58, estimate how much oxygen gas would be produced in an identical solution in 100 seconds at 318 K. Estimate the time needed to produce 12 mL of oxygen gas at 288 K.

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Section 16.3

Mastering Concepts

60. In the method of initial rates used to determine the rate law for a chemical reaction, what is the significance of the word *initial*?

61. Why must the rate law for a chemical reaction be based on experimental evidence rather than the balanced equation for the reaction?

62. Assume that the rate law for a generic chemical reaction is rate = $[A][B]^3$. What is the reaction order in A, the reaction order in B, and the overall reaction order?

63. Consider the generic chemical reaction: $A + B \longrightarrow AB$. Based on experimental data, the reaction is second order in Reactant A. If the concentration of A is halved, and all other conditions remain unchanged, how does the reaction rate change?

Mastering Problems

64. The instantaneous rate data in **Table 16.3** were obtained for the reaction $H_2(g) + 2NO(g) \longrightarrow H_2O(g) + N_2O(g)$ at a given temperature and concentration of NO. How does the instantaneous rate of this reaction change as the initial concentration of H_2 is changed? Based on the data, is $[H_2]$ part of the rate law? Explain.

Table 16.3 Reaction Between $H_2(g)$ and NO(g)

$[H_2]$ (mol/L)	Instantaneous Rate (mol/L·s)
0.18	6.00×10^{-3}
0.32	1.07×10^{-2}
0.58	1.93×10^{-2}

65. Suppose that a generic chemical reaction has the rate law of rate = $[A]^2[B]^3$ and that the reaction rate under a given set of conditions is 4.5×10^{-4} mol/(L·min). If the concentrations of both A and B are doubled and all other reaction conditions remain constant, how will the reaction rate change?

66. The experimental data in **Table 16.4** were obtained for the decomposition of azomethane ($CH_3N_2CH_3$) at a particular temperature according to the equation $CH_3N_2CH_3(g) \longrightarrow C_2H_6(g) + N_2(g)$. Use the data to determine the reaction's experimental rate law.

Table 16.4 Decomposition of Azomethane

Experiment Number	Initial $[CH_3N_2CH_3]$	Initial Reaction Rate
1	0.012*M*	2.5×10^{-6} mol/(L·s)
2	0.024*M*	5.0×10^{-6} mol/(L·s)

67. Use the data in **Table 16.4** to calculate the value of the specific rate constant, *k*.

68. At the same temperature, predict the reaction rate when the initial concentration of $CH_3N_2CH_3$ is 0.048*M*. Use the data in **Table 16.4.**

Section 16.4

Mastering Concepts

69. Distinguish between a complex reaction, a reaction mechanism, and an elementary step.

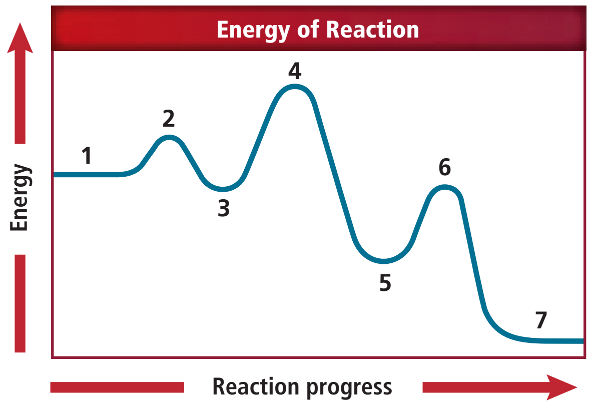
70. Suppose that a chemical reaction takes place in a two-step mechanism.

Step 1 (fast) $A + B \longrightarrow C$

Step 2 (slow) $C + D \longrightarrow E$

Which step in the reaction mechanism is the rate-determining step? Explain.

71. In the reaction described in Question 70, what are Steps 1 and 2 called? What is substance C called?



■ **Figure 16.23**

72. In **Figure 16.23,** identify each of the labels 1, 2, 3, 4, 5, and 6 as one of the following: activated complex, intermediate, reactants, or products.

Mastering Problems

73. Dinitrogen pentoxide decomposes in chloroform at a rate of 2.48×10^{-4} mol/(L·min) at a particular temperature according to the equation $2N_2O_5 \longrightarrow 4NO_2 + O_2$. The reaction is first order in N_2O_5. Given an initial concentration 0.400 mol/L, what is the rate constant for the reaction? What is the approximate $[N_2O_5]$ after the reaction proceeds for 1.30 h?

74. Radioactive decay is first order in the decaying isotope. For example, strontium-90 contained in fallout from nuclear explosions decays to yttrium-90 and a beta particle. Write the rate law for the decay of strontium-90.

Mixed Review

75. Evaluate the validity of this statement: You can determine the rate law for a chemical reaction by examining the mole ratio of reactants in the balanced equation. Explain your answer.

76. The concentration of Reactant A decreases from 0.400 mol/L at 0.00 min to 0.384 mol/L at 4.00 min. Calculate the average reaction rate during this time period. Express the rate in mol/(L • min).

77. The mass of a sample of magnesium is obtained and the sample is placed in a container of hydrochloric acid. A chemical reaction occurs according to the equation $Mg(s) + 2HCl(aq) \rightarrow H_2(g) + MgCl_2(aq)$. Use the data in **Table 16.5** to calculate the volume of hydrogen gas produced at STP during the 3.00-min reaction? *(Hint: 1 mol of an ideal gas occupies 22.4 L at STP)*

Table 16.5 Reaction of Magnesium and Hydrochloric Acid

Time (min)	Mass of Magnesium (g)	Volume of Hydrogen at STP (L)
0.00	6.00	0.00
3.00	4.50	?

78. If the concentration of a reaction product increases from 0.0882 mol/L to 0.1446 mol/L in 12.0 minutes, what is the average reaction rate during the time interval?

79. A two-step mechanism has been proposed for the decomposition of nitryl chloride (NO_2CL).

Step 1: $NO_2Cl(g) \rightarrow NO_2(g) + Cl(g)$

Step 2: $NO_2Cl(g) + Cl(g) \rightarrow NO_2(g) + Cl_2(g)$

What is the overall reaction? Identify any intermediates in the reaction sequence, and explain why they are called intermediates.

80. Compare and contrast the reaction energy diagrams for the overall decomposition of nitryl chloride by the mechanism in Problem 79 under two assumptions: A—that the first step is slower; B—that the second step is slower.

81. Automobile Engine The following reaction takes place in an automobile's engine and exhaust system.

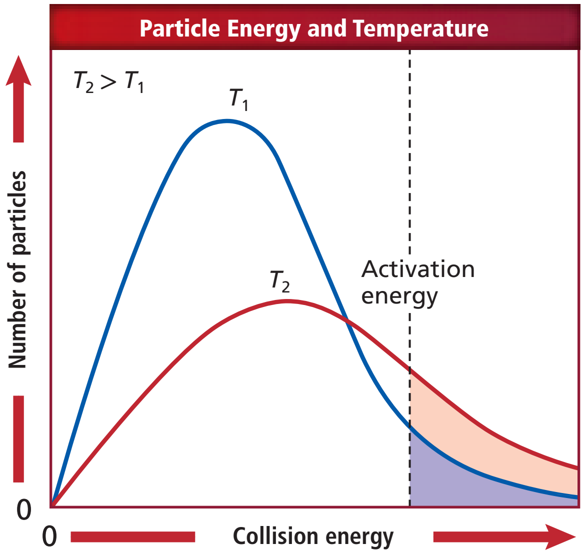
$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The reaction's rate law at a particular temperature is Rate $= 0.50\ L/(mol \cdot s)[NO_2]^2$. What is the reaction's initial, instantaneous rate when $[NO_2] = 0.0048$ mol/L?

82. The concentrations in a chemical reaction are expressed in moles per liter and time is expressed in seconds. If the overall rate law is third-order, what are the units for the rate and the rate constant?

Think Critically

83. Visualize the reaction energy diagram for a one-step, endothermic chemical reaction. Compare the heights of the activation energies for the forward and reverse reactions.



■ **Figure 16.24**

84. Differentiate between the shaded areas in **Figure 16.24** at temperatures T_1 and T_2 on the basis of the number of collisions per unit time that might occur with energy equal to or greater than the activation energy.

85. Apply the method of initial rates to determine the order of a chemical reaction with respect to Reactant X. Create a set of hypothetical experimental data that would lead you to conclude that the reaction is second order in X.

86. Formulate a rationale to explain how a complex chemical reaction might have more than one rate-determining elementary step.

87. Construct 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 tell you about the reaction rate?

88. Apply collision theory to explain two reasons why increasing the temperature of a reaction by 10 K often doubles the reaction rate.

89. 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 $aA + bB + cD \rightarrow$ products using the method of initial rates.

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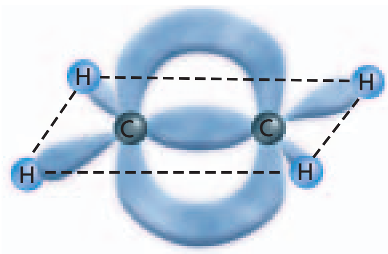
Challenge Problem

90. **Hydrocarbons** Heating cyclopropane (C_3H_6) converts it to propene ($CH_2{=}CHCH_3$). The rate law is first order in cyclopropane. If the rate constant at a particular temperature is 6.22×10^{-4} s^1 and the concentration of cyclopropane is held at 0.0300 mol/L, what mass of propene is produced in 10.0 min in a volume of 2.50 L?

Cumulative Review

91. For the following categories of elements, state the possible number(s) of electrons in their outermost orbitals in the ground state? *(Chapter 5)*
a. p-block elements
b. nitrogen-group elements
c. d-block elements
d. noble-gas elements
e. s-block elements

92. Classify each of the following elements as a metal, nonmetal, or metalloid. (*Chapter* 6)
a. molybdenum
b. bromine
c. arsenic
d. neon
e. cerium



Ethene

■ **Figure 16.25**

93. Using **Figure 16.25,** determine how many sigma and pi bonds are contained in a single ethene molecule. (*Chapter 8*)

94. Balance the following equations. (*Chapter 9*)
a. $Sn(s) + NaOH(aq) \longrightarrow Na_2SnO_2 + H_2$
b. $C_8H_{18}(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$
c. $Al(s) + H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + H_2(g)$

95. What mass of iron(III) chloride is needed to prepare 1.00 L of a 0.255*M* solution? (*Chapter 14*)

96. What information must you know to calculate the boiling point elevation of a solution of hexane in benzene? *(Chapter 14)*

97. ΔH for a reaction is negative. Compare the energy of the products and the reactants. Is the reaction endothermic or exothermic? (*Chapter 15*)

Additional Assessment

WRITING in Chemistry

98. **Pharmaceuticals** Imagine that your nation is experiencing an influenza epidemic. Fortunately, scientists have recently discovered a new catalyst that increases the rate of production of an effective flu medicine. Write a newspaper article describing how the catalyst works. Include a reaction energy diagram and an explanation detailing the importance of the discovery.

99. **Lawn Care** Write an advertisement that explains that Company A's fertilizer works better than Company B's fertilizer because it has smaller sized granules. Include applicable diagrams.

DBQ Document-Based Questions

Chemical Indicators *Phenolphthalein is a chemical indicator used to show the presence of a base. The data in* **Table 16.6** *presents the decrease in phenolphthalein concentration with time when a 0.0050M phenolphthalein solution is added to a solution that has a concentration of hydroxide ion equal to 0.61M.*

Table 16.6 Reaction Between Phenolphthalein and Excess Base

Concentration of Phenolphthalein (*M*)	Time (s)
0.0050	0.0
0.0040	22.3
0.0020	91.6
0.0010	160.9
0.00050	230.3
0.00015	350.7

Data obtained from: Bodner Research Web. 2006. "Chemical Kinetics," *General Chemistry Help.*

100. What is the average rate of the reaction in the first 22.3 s expressed in moles of phenolphthalein consumed per liter per second?

101. What is the average rate of the reaction as the phenolphthalein concentration decreases from 0.00050*M* to 0.00015*M*?

102. The rate law is rate = k[phenolphthalein]. If the rate constant for the reaction is 1.0×10^{-2} s^{-1}, what is the instantaneous rate of reaction when the concentration of phenolphthalein is 0.0025*M*?

Cumulative

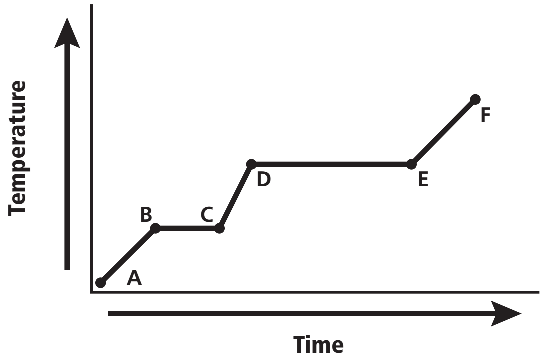
Standardized Test Practice

Multiple Choice

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

2. How can colloids be distinguished from solutions?
   A. Dilute colloids have particles that can be seen with the naked eye.
   B. Colloid particles are much smaller than solvated particles.
   C. Colloid particles that are dispersed will settle out of the mixture in time.
   D. Colloids will scatter light beams that are shone through them.

Use the graph below to answer Questions 3 and 4.



3. During which segment is this substance undergoing melting?
   A. segment AB
   B. segment BC
   C. segment CD
   D. segment DE

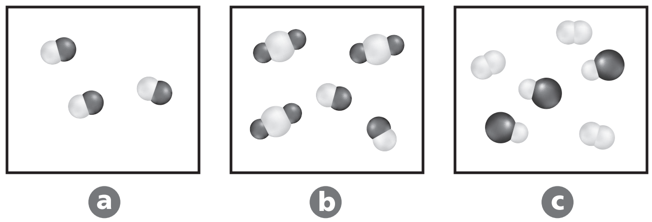
4. As the substance heats from point C to point D, which is true of the substance?
   A. potential energy increases, kinetic energy decreases
   B. potential energy increases, kinetic energy increases
   C. potential energy remains constant, kinetic energy increases
   D. potential energy decreases, kinetic energy remains constant

5. How much water must be added to 6.0 mL of a 0.050*M* stock solution to dilute it to 0.020*M*?
   A. 15 mL
   B. 9.0 mL
   C. 6.0 mL
   D. 2.4 mL

6. Which is NOT an acceptable unit for expressing a reaction rate?
   A. *M*/min
   B. L/s
   C. mol/(mL•h)
   D. mol/(L•min)

7. Which is the strongest type of intermolecular bond?
   A. ionic bond
   B. dipole-dipole force
   C. dispersion force
   D. hydrogen bond

Use the diagram below to answer Questions 8 and 9.



8. Which sample could contain particles of oxygen gas?
   A. a
   B. b
   C. c
   D. Both a and b

9. Which sample could contain particles of magnesium fluoride?
   A. a
   B. b
   C. c
   D. Both a and b

10. How many moles are in 4.30×10^2 g of calcium phosphate ($Ca_3(PO_4)_2$)?
   A. 0.721 moles
   B. 1.39 moles
   C. 1.54 moles
   D. 3.18 moles

Short Answer

Use the following information to answer Question 11.

The complete dissociation of acid H_3A takes place in three steps:	
$H_3A(aq) \longrightarrow H_2A^-(aq) + H^+(aq)$	rate $= k_1[H_3A]$ $k_1 = 3.2 \times 10^2\ s^{-1}$
$H_2A^-(aq) \longrightarrow HA_2^-(aq) + H^+(aq)$	rate $= k_2[H_2A^-]$ $k_2 = 1.5 \times 10^2\ s^{-1}$
$HA^{2-}(aq) \longrightarrow A^{3-}(aq) + H^+(aq)$	rate $= k_3[HA^{2-}]$ $k_3 = 0.8 \times 10^2\ s^{-1}$
overall reaction: $H_3A(aq) \longrightarrow A^{3-}(aq) + 3H^+(aq)$	

11. When the reactant concentrations are $[H_3A] = 0.100M$, $[H_2A^-] = 0.500M$, and $[HA^{2-}] = 0.200M$, which reaction is the rate-determining step? Explain how you can tell.

12. The rate law for $A + B + C \longrightarrow$ products is: rate $= k[A]^2[C]$. If $k = 6.92 \times 10^{-5}\ L^2/(mol^2{\bullet}s)$, $[A] = 0.175M$, $[B] = 0.230M$, and $[C] = 0.315M$, what is the instantaneous reaction rate?

Extended Response

Use the following reaction to answer Questions 13 to 15.

Sodium nitride (Na_3N) breaks down to form sodium metal and nitrogen gas.

13. Write the balanced chemical equation for the reaction.

14. Classify the type of reaction. Explain your answer.

15. Show the steps to determine the amount of nitrogen gas that can be produced from 32.5 grams of sodium nitride.

SAT Subject Test: Chemistry

Use the table below to answer Questions 16 to 18.

Reaction: $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$			
Experimental Data Collected for Reaction			
Time (min)	$[SO_2Cl_2]$ (M)	$[SO_2]$ (M)	$[Cl_2]$ (M)
0.0	1.00	0.00	0.00
100.0	0.87	0.13	0.13
200.0	0.74	?	?

16. What is the average reaction rate for this reaction, expressed in moles SO_2Cl_2 consumed per liter per minute?

A. 1.30×10^{-3} mol/(L•min)
B. 2.60×10^{-1} mol/(L•min)
C. 7.40×10^{-3} mol/(L•min)
D. 8.70×10^{-3} mol/(L•min)
E. 2.60×10^{-3} mol/(L•min)

17. On the basis of the average reaction rate, what will the concentrations of SO_2 and Cl_2 be at 200.0 min?

A. $0.13M$
B. $0.26M$
C. $0.39M$
D. $0.52M$
E. $0.87M$

18. How long will it take for half of the original amount of SO_2Cl_2 to decompose at the average reaction rate?

A. 285 min
B. 335 min
C. 385 min
D. 401 min
E. 516 min

19. A sample of argon gas is compressed into a volume of 0.712 L by a piston exerting 3.92 atm of pressure. The piston is released until the pressure of the gas is 1.50 atm. What is the new volume of the gas?

A. 0.272 L
B. 3.67 L
C. 5.86 L
D. 4.19 L
E. 1.86 L

NEED EXTRA HELP?																			
If You Missed Question . . .	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Review Section . . .	16.1	14.1	15.3	15.3	14.2	16.1	12.2	3.4	3.4	10.3	16.4	16.4	9.1	9.2	11.2	16.3	16.3	16.3	13.1