CHAPTER 16

REACTION RATES
A forest fire is an enormous combustion reaction that can go on as long as it has fuel, oxygen, and heat. The air tanker in the photograph is dropping a fire-retardant mixture to slow the spread of one of these fires. Fire retardants, which usually contain chemicals such as water, ammonium sulfate, and ammonium phosphate, work by forming a barrier between the fuel (brush and trees) and the oxygen. These chemicals help firefighters slow and eventually stop the combustion reaction. In this chapter, you will learn about the many factors that affect how fast a chemical reaction takes place.

**START-UP ACTIVITY**

**Temperature and Reaction Rates**

**PROCEDURE**

1. Submerge one light stick in a bath of cold water (about 10°C).
2. Submerge a second light stick in a bath of hot water (about 50°C).
3. Allow each light stick to reach the same temperature as its bath.
4. Remove the light sticks, and activate them.
5. In a dark corner of the room, observe and compare the light intensities of the two sticks.

**ANALYSIS**

1. Which stick was brighter?
2. Light is emitted from the stick because of a chemical reaction. What can you conclude about how temperature affects this reaction?

**Pre-Reading Questions**

1. Give two examples of units that could be used to measure a car’s rate of motion.
2. What can you do to slow the rate at which milk spoils?
3. What is a catalytic converter in an automobile?
What Affects the Rate of a Reaction?

**Key Terms**
- chemical kinetics
- reaction rate

**Objectives**
1. Define the rate of a chemical reaction in terms of concentration and time.
2. Calculate the rate of a reaction from concentration-versus-time data.
3. Explain how concentration, pressure, and temperature may affect the rate of a reaction.
4. Explain why, for surface reactions, the surface area is an important factor.

**Rates of Chemical Change**

A *rate* indicates how fast something changes with time. In a savings account, the rate of interest tells how your money is growing over time. Speed is also a rate. From the speed of one of the race cars shown in Figure 1, you can tell the distance that the car travels in a certain time. If a car’s speed is 67 m/s (150 mi/h), you know that it travels a distance of 67 meters every second. Rates are always measured in a unit of something per time interval. The rate at which the car’s wheels turn would be measured in revolutions per second. The rate at which the car burns gasoline could be measured in liters per minute.

The rate of a chemical reaction measures how quickly reactants are changed into products. Some reactions are over in as little as $10^{-15}$ s; others may take hundreds of years. The study of reaction rates is called chemical kinetics.

**Figure 1**
The winner of the race is the car that has the highest rate of travel.
**Rate Describes Change over Time**

At 500°C, the compound dimethyl ether slowly decomposes according to the equation below to give three products—methane, carbon monoxide, and hydrogen gas.

\[ \text{CH}_3\text{OCH}_3(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g}) + \text{H}_2(\text{g}) \]

The concentration of dimethyl ether will keep decreasing during the reaction. Recall that the symbol \( \Delta \) represents a change in some quantity. If the concentration of dimethyl ether changes by \( \Delta[\text{CH}_3\text{OCH}_3] \) during a small time interval \( \Delta t \), then the rate of the reaction is defined as

\[ \text{rate} = \frac{-\Delta[\text{CH}_3\text{OCH}_3]}{\Delta t} \]

The sign is negative because, while \( \Delta [\text{CH}_3\text{OCH}_3] \) is negative, the rate during the reaction must be a positive number.

The chemical equation shows that for every mole of dimethyl ether that decomposes, 1 mol each of methane, carbon monoxide, and hydrogen is produced. Thus, the concentrations of \( \text{CH}_4, \text{CO} \), and \( \text{H}_2 \) will *increase* at the same rate that \( [\text{CH}_3\text{OCH}_3] \) *decreases*. This means that the rate for this reaction can be defined in terms of the changes in concentration of any one of the products, as shown below.

\[
\text{rate} = \frac{-\Delta[\text{CH}_3\text{OCH}_3]}{\Delta t} = \frac{\Delta[\text{CH}_4]}{\Delta t} = \frac{\Delta[\text{CO}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t}
\]

The concentrations of the products are all increasing, so the signs of their rate expressions are positive.

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**Quick LAB**

**Concentration Affects Reaction Rate**

**PROCEDURE**

1. Prepare two labeled beakers, one containing 0.001 M hydrochloric acid and the second containing 0.1 M hydrochloric acid.
2. Start a stopwatch at the moment you drop an effervescent tablet into the first beaker.
3. Stop the stopwatch when the tablet has finished dissolving.
4. Repeat steps 2–3 with a second effervescent tablet, using the second beaker.

**ANALYSIS**

1. What evidence is there that a chemical reaction occurred?
2. Were the dissolution times different? Did the tablet dissolve faster or slower in the more concentrated solution?
3. What conclusion can you draw about how the rate of a chemical reaction depends on the concentration of the reactants?
Balanced Coefficients Appear in the Rate Definition

Now consider the following reaction, which is the one illustrated in Figure 2 below.

\[
2N_2O_5(s) \rightarrow 4NO_2(g) + O_2(g)
\]

The stoichiometry is more complicated here because 2 mol of dinitrogen pentoxide produce 4 mol of nitrogen dioxide and 1 mol of oxygen. So, it is no longer true that the rate of decrease of the reactant concentration equals the rates of increase of the product concentrations. However, this difficulty can be overcome if, in order to define the reaction rate, we divide by the coefficients from the balanced equation. For this reaction, we get the following.

\[
\text{rate} = \frac{-\Delta[N_2O_5]}{2\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = \frac{\Delta[O_2]}{\Delta t}
\]

The definition of reaction rate developed in these two examples may be generalized to cover any reaction.

It is important to realize that a reaction does not have a single, specific rate. Reaction rates depend on conditions such as temperature and pressure. Also, the rate of a reaction changes during the reaction. Usually, the rate decreases gradually as the reaction proceeds. The rate becomes zero when the reaction is complete.

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**Figure 2**
Dinitrogen pentoxide decomposes to form oxygen and the orange-brown gas nitrogen dioxide.
Reaction Rates Can Be Measured

To measure a reaction rate, you need to be able to keep track of how the concentration of one or more reactants or products changes over time. There are many ways of tracking these changes depending on the reaction you are studying.

For the reaction in Figure 2, you could measure how quickly the concentration of one product changes by measuring a change in color. Because nitrogen dioxide is the only gas in the reaction that has a color, you could use the red-brown color of the gas mixture to calculate $[\text{NO}_2]$. On the other hand, because the pressure of the system changes during the reaction, you could measure this change and, with help from the gas laws, calculate the concentrations.

Concentrations Must Be Measured Often

Remember that the $\Delta t$ that occurs in the equations defining reaction rate is a small time interval. This means that studies of chemical kinetics require that concentrations be measured frequently. Table 1 shows the results from a study of the following reaction.

$$2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)$$

The NO$_2$ concentrations were used to calculate the reaction rate in this example, but $[\text{N}_2\text{O}_3]$ or $[\text{O}_2]$ data could also have been used. As expected, the reaction rate decreases with time. It takes about 900 s before the reaction is 99% complete, and at that point, the rate is only $6.2 \times 10^{-7}$ M/s.

Reaction rates are generally expressed, as they are here, in moles per liter-second or M/s.

Notice in the table how the rate is calculated from pairs of data points—two different time readings and two different concentrations of NO$_2$. For example, the last rate in the table comes from the calculation shown below.

$$\text{rate} = \frac{\Delta [\text{NO}_2]}{4\Delta t} = \frac{0.01616 \text{ M} - 0.01272 \text{ M}}{4(80.0 \text{ s} - 60.0 \text{ s})} = 4.30 \times 10^{-5} \text{ M/s}$$

This result shows the rate of the reaction after it has been going on for about 70 s.

Table 1  Concentration Data and Calculations for the Decomposition of $\text{N}_2\text{O}_5$

<table>
<thead>
<tr>
<th>$t$ (s)</th>
<th>$[\text{NO}_2]$ (M)</th>
<th>$\Delta [\text{NO}_2]$ (M)</th>
<th>$\Delta t$ (s)</th>
<th>$\Delta [\text{NO}_2]/\Delta t$ (M/s)</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>$4.68 \times 10^{-3}$</td>
<td>20.0</td>
<td>$2.34 \times 10^{-4}$</td>
<td>$5.85 \times 10^{-5}$</td>
</tr>
<tr>
<td>20.0</td>
<td>0.00468</td>
<td>$4.22 \times 10^{-3}$</td>
<td>20.0</td>
<td>$2.11 \times 10^{-4}$</td>
<td>$5.28 \times 10^{-5}$</td>
</tr>
<tr>
<td>40.0</td>
<td>0.00890</td>
<td>$3.82 \times 10^{-3}$</td>
<td>20.0</td>
<td>$1.91 \times 10^{-4}$</td>
<td>$4.78 \times 10^{-5}$</td>
</tr>
<tr>
<td>60.0</td>
<td>0.01272</td>
<td>$3.44 \times 10^{-3}$</td>
<td>20.0</td>
<td>$1.72 \times 10^{-4}$</td>
<td>$4.30 \times 10^{-5}$</td>
</tr>
<tr>
<td>80.0</td>
<td>0.01616</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chemists often use graphs to help them think about chemical changes. Graphs are especially helpful in the field of chemical kinetics. For one example of how a graph can be useful, we can take another look at the decomposition reaction $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$. Figure 3 is a graph that keeps track of this reaction with three curves, which show how the concentrations of the reactant and the products change with time. Notice that the concentration of dinitrogen pentoxide steadily falls. Also note that the concentration of oxygen and the concentration of nitrogen dioxide steadily increase.

Finally, notice that the graph also shows that the concentration of nitrogen dioxide increases four times faster than the concentration of oxygen increases. This result agrees with the 4:1 ratio of nitrogen dioxide to oxygen in the balanced equation.

Now, when some quantity is plotted versus time, the slope of the line tells you how fast that quantity is changing with time. So the slopes of the three curves in Figure 3 measure the rates of change of each concentration. The slope of a curve at a particular point is just the slope of a straight line drawn as a tangent to the curve at that point. Because oxygen is a product and its coefficient in the equation is 1, the slope of the O$_2$ curve is simply the reaction rate.

$$\text{slope of O}_2 \text{ curve} = \frac{\Delta[\text{O}_2]}{\Delta t} = \text{rate of the reaction}$$

A line has been drawn as a tangent to the O$_2$ curve at $t = 70$ s. Its slope was measured in the usual way as rise/run and is $4.30 \times 10^{-5}$ M/s. This value agrees with the rate calculated in Table 1 at the same instant.
SAMPLE PROBLEM A

Calculating a Reaction Rate

The data below were collected during a study of the following reaction.

\[2\text{Br}^- (aq) + \text{H}_2\text{O}_2(aq) + 2\text{H}_3\text{O}^+(aq) \rightarrow \text{Br}_2(aq) + 4\text{H}_2\text{O}(l)\]

<table>
<thead>
<tr>
<th>Time t (s)</th>
<th>[H_3O^+] (M)</th>
<th>[Br_2] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0500</td>
<td>0</td>
</tr>
<tr>
<td>85</td>
<td>0.0298</td>
<td>0.0101</td>
</tr>
<tr>
<td>95</td>
<td>0.0280</td>
<td>0.0110</td>
</tr>
<tr>
<td>105</td>
<td>0.0263</td>
<td>0.0118</td>
</tr>
</tbody>
</table>

Use two methods to calculate what the reaction rate was after 100 s.

1 **Gather information.**

During the interval \(\Delta t = 10\) s between \(t = 95\) s and \(t = 105\) s, the changes in the concentrations of hydronium ion and bromine were

\[\Delta [\text{H}_3\text{O}^+] = (0.0263\ \text{M}) - (0.0280\ \text{M}) = -0.0017\ \text{M}\]

\[\Delta [\text{Br}_2] = (0.0118\ \text{M}) - (0.0110) = 0.0008\ \text{M}\]

2 **Plan your work.**

For this reaction, two definitions of the reaction rate are as follows.

\[\text{rate} = \frac{-\Delta [\text{H}_3\text{O}^+]}{2\Delta t} = \frac{\Delta [\text{Br}_2]}{\Delta t}\]

3 **Calculate.**

From the change in hydronium ion concentration,

\[\text{rate} = \frac{-\Delta [\text{H}_3\text{O}^+]}{2\Delta t} = \frac{(-0.0017\ \text{M})}{2(10\ \text{s})} = 8.5 \times 10^{-5}\ \text{M/s}\]

From the change in bromine concentration,

\[\text{rate} = \frac{\Delta [\text{Br}_2]}{\Delta t} = \frac{0.0008\ \text{M}}{10\ \text{s}} = 8 \times 10^{-5}\ \text{M/s}\]

4 **Verify your results.**

The two ways of solving the problem provide approximately the same answer.

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**PRACTICE**

1 For the reaction in **Sample Problem A**, write the expressions that define the rate in terms of the hydrogen peroxide and bromide ion concentrations.

2 The initial rate of the \(\text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g)\) reaction is \(7.3 \times 10^{-6}\ \text{M/s}\). What are the rates of concentration change for the two gases?

3 Use the data from **Sample Problem A** to calculate the reaction rate after 90 s.
**Factors Affecting Rate**

Concentration, pressure, temperature, and surface area are the most important factors on which the rate of a chemical reaction depends. Consider each of these effects for a type of reaction that is already familiar to you—combustion.

You know that the more fuel and oxygen there is, the faster a fire burns. This is an example of the general principle that the rate of a chemical reaction increases as the concentration of a reactant increases.

Many combustion processes, such as those of sulfur or wood, take place at a surface. The larger the surface area, the greater the chances that each particle will be involved in a reaction.

**Concentration Affects Reaction Rate**

Though there are exceptions, almost all reactions, including the one shown in Figure 4, increase in rate when the concentrations of the reactants are increased.

It is easy to understand why reaction rates increase as the concentrations of the reactants increase. Think about the following reaction taking place within a container.

\[
\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)
\]

Clearly, the reaction can take place only when a nitrogen dioxide molecule collides with a carbon monoxide molecule. If the concentration of NO\(_2\) is doubled, there are twice as many nitrogen dioxide molecules, and so the number of collisions with CO molecules will double. Only a very small fraction of those collisions will actually result in a reaction. Even so, the possibility that each reaction will take place is twice as much when the NO\(_2\) concentration is doubled.

Reaction rates decrease with time because the reaction rate depends on the concentration of the reactants. As the reaction proceeds, the reactant is consumed and its concentration declines. This change in concentration, in turn, decreases the reaction rate.

*Figure 4*

Carbon burns faster in pure oxygen a than in air b because the concentration of the reacting species, O\(_2\), is greater.
Concentration Affects Noncollision Reaction Rates

Not all reactions require a collision. The gas cyclopropane has a molecule in which three bonded carbon atoms form a triangle, with two hydrogen atoms attached to each carbon atom. Above room temperature, cyclopropane slowly changes into propene.

\[(\text{CH}_2)_3(g) \rightarrow \text{CH}_2=\text{CH}-\text{CH}_3(g)\]

A collision is not necessary for this reaction, but the rate of the reaction still increases as the concentration of cyclopropane increases. In fact, the rate doubles if the \((\text{CH}_2)_3\) concentration doubles. This is not surprising. Because there are twice as many molecules, their reaction is twice as likely, and so the reaction rate doubles.

Pressure Affects the Rates of Gas Reactions

Pressure has almost no effect on reactions taking place in the liquid or solid states. However, it does change the rate of reactions taking place in the gas phase, such as the reaction shown in Figure 5.

As the gas laws confirm, doubling the pressure of a gas doubles its concentration. So changing the pressure of a gas or gas mixture is just another way of changing the concentration.

Temperature Greatly Influences the Reaction Rate

All chemical reactions are affected by temperature. In almost every case, the rate of a chemical reaction increases with increasing temperature. The increase in rate is often very large. A temperature rise of only 10%, say from 273 K to 300 K, will frequently increase the reaction rate tenfold. Our bodies work best at around 37°C or 310 K. Even a 1°C change in body temperature affects the rates of the body’s chemical reactions enough that we may become ill as a result.

Figure 5
This reaction between two gases, ammonia and hydrogen chloride, forms solid ammonium chloride in a white ring near the center of the glass tube.
Chapter 16

Temperature Affects Reactions in Everyday Life

The fact that reaction rates respond to temperature changes is part of everyday life. In the kitchen, we increase the temperature to speed up the chemical processes of cooking food, and we lower the temperature to slow down the chemical processes of food spoilage. When you put food in a refrigerator, you slow down the chemical reactions that cause food, such as the grapes shown in Figure 6 to decompose. Most manufacturing operations use either heating or cooling to control their processes for optimal performance.

Why do chemical reactions increase in rate so greatly when the temperature rises? You have seen, in discussing reactions such as $\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$, that a collision between molecules (or other particles, such as ions or atoms) is necessary for a reaction to occur. A common misconception is that a rise in temperature increases the number of collisions and thereby boosts the reaction rate. It is true that a temperature rise does increase the collision frequency somewhat, but that effect is small. The main reason for the increase in reaction rate is that a temperature rise increases the fraction of molecules that have an energy great enough for collision to lead to reaction. If they are to react, molecules must collide with enough energy to rearrange bonds. A rise in temperature means that many more molecules have the required energy.

Surface Area Can Be an Important Factor

Most of the reactions that we have considered so far happen uniformly in three-dimensional space. However, many important reactions—such as precipitations, corrosions, and many combustions—take place at surfaces. The definition of rate given earlier does not apply to surface reactions. Even so, these reactions respond to changes in concentration, pressure, and temperature in much the same way as do other reactions.

A feature of surface reactions is that the amount of matter that reacts is proportional to the surface area. As Figure 7 shows, you get a bigger blaze with small pieces of wood, because the surface area of many small pieces is greater than that of one larger piece of wood.

Figure 6
The reactions that cause food such as these grapes to spoil occur much more slowly when food is placed in a refrigerator or freezer.
### UNDERSTANDING KEY IDEAS

1. What does the word *rate* mean in everyday life, and what do chemists mean by *reaction rate*?

2. What is the name given to the branch of chemistry dealing with reaction rates? Why are such studies important?

3. Why is a collision between molecules necessary in many reactions?

4. How may reaction rates be measured?

5. Explain why reactant concentration influences the rate of a chemical reaction.

6. Give examples of the strong effect that temperature has on chemical reactions.

7. What is unique about surface reactions?

### CRITICAL THINKING

8. Why must coefficients be included in the definition of reaction rate?

9. Calculating the reaction rate from a product appeared to give an answer different from that calculated from a reactant. Suggest a possible explanation.

10. The usual unit for reaction rate is M/s. Suggest a different unit that could be used for reaction rate, and explain why this unit would be appropriate.

11. Explain why an increase in the frequency of collisions is not an adequate explanation of the effect of temperature on reaction rate.

12. Would the factors that affect the rate of a chemical reaction influence a physical change in the same way? Explain, and give an example.

13. Why does pressure affect the rates of gas reactions?
How Can Reaction Rates Be Explained?

**Objectives**

1. **Write** a rate law using experimental rate-versus-concentration data from a chemical reaction.
2. **Explain** the role of activation energy and collision orientation in a chemical reaction.
3. **Describe** the effect that catalysts can have on reaction rate and how this effect occurs.
4. **Describe** the role of enzymes as catalysts in living systems, and give examples.

**Rate Laws**

You have learned that the rate of a chemical reaction is affected by the concentration of the reactant or reactants. The **rate law** describes the way in which reactant concentration affects reaction rate. A rate law may be simple or very complicated, depending on the reaction.

By studying rate laws, chemists learn how a reaction takes place. Researchers in chemical kinetics can often make an informed guess about the **reaction mechanism**. In other words, they can create a model to explain how atoms move in rearranging themselves from reactants into products.

### Determining a General Rate Law Equation

For a reaction that involves a single reactant, the rate is often proportional to the concentration of the reactant raised to some power. That is, the rate law takes the following form.

\[
\text{rate} = k[\text{reactant}]^n
\]

This is a general expression for the rate law. The exponent, \(n\), is called the **order** of the reaction. It is usually a whole number, often 1 or 2, but it could be a fraction. Occasionally, \(n\) equals 0, which means that the reaction rate is independent of the reactant concentration. The term \(k\) is the **rate constant**, a proportionality constant that varies with temperature.

Reaction orders cannot be determined from a chemical equation. They must be found by experiment. For example, you might guess that \(n = 1\) for the following reaction.

\[
\text{CH}_3\text{CHO}(g) \rightarrow \text{CH}_4(g) + \text{CO}(g)
\]

However, experiments have shown that the reaction order is 1.5.
Determining a Rate Law

Three experiments were performed to measure the initial rate of the reaction $2\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g)$. Conditions were identical in the three experiments, except that the hydrogen iodide concentrations varied. The results are shown below.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[HI] (M)</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.015</td>
<td>$1.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>0.030</td>
<td>$4.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>0.045</td>
<td>$9.9 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

1 **Gather information.**

The general rate law for this reaction is as follows: $\text{rate} = k[\text{HI}]^n$

$n = ?$

2 **Plan your work.**

Find the ratio of the reactant concentrations between experiments 1 and 2, $\frac{[\text{HI}]_2}{[\text{HI}]_1}$

Then see how this affects the ratio $\frac{\text{rate}_2}{\text{rate}_1}$ of the reaction rates.

3 **Calculate.**

$$\frac{[\text{HI}]_2}{[\text{HI}]_1} = \frac{0.030 \text{ M}}{0.015 \text{ M}} = 2.0$$

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{4.4 \times 10^{-3} \text{ M/s}}{1.1 \times 10^{-3} \text{ M/s}} = 4.0$$

Thus, when the concentration changes by a factor of 2, the rate changes by 4, or $2^2$. Hence $n$, the reaction order, is 2.

4 **Verify your results.**

On inspecting items 1 and 3 in the table, one sees that when the concentration triples, the rate changes by a factor of 9, or $3^2$. This confirms that the order is 2.

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**PRACTICE HINT**

To find a reaction order, compare a rate ratio with a concentration ratio.

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**PRACTICE**

1 In a study of the $2\text{NH}_3(g) \rightarrow \text{N}_2(g) + 3\text{H}_2(g)$ reaction, when the ammonia concentration was changed from $3.57 \times 10^{-3}$ M to $5.37 \times 10^{-3}$ M, the rate increased from $2.91 \times 10^{-5}$ M/s to $4.38 \times 10^{-5}$ M/s. Find the reaction order.

2 What is the order of a reaction if its rate increases by a factor of 13 when the reactant concentration increases by a factor of 3.6?

3 What concentration increase would cause a tenfold increase in the rate of a reaction of order 2?

4 When the $\text{CH}_3\text{CHO}$ concentration was doubled in a study of the $\text{CH}_3\text{CHO}(g) \rightarrow \text{CH}_4(g) + \text{CO}(g)$ reaction, the rate changed from $7.9 \times 10^{-5}$ M/s to $2.2 \times 10^{-4}$ M/s. Confirm that the order is 3/2.
Rate Laws for Several Reactants

When a reaction has more than one reactant, a term in the rate law corresponds to each. There are three concentration terms in the rate law for the following reaction.

\[2\text{Br}^- (aq) + \text{H}_2\text{O}_2(aq) + 2\text{H}_3\text{O}^+(aq) \rightarrow \text{Br}_2(aq) + 4\text{H}_2\text{O}(l)\]

There is an order associated with each term:

\[\text{rate} = k[\text{Br}^-]^{n_1}[\text{H}_2\text{O}_2]^{n_2}[\text{H}_3\text{O}^+]^{n_3}\]

For example, \(n_1\) is the reaction order with respect to \(\text{Br}^-\).

To be sure of the orders of reactions that have several reactants, one must perform many experiments. Often the concentration of only a single reactant is varied during a series of experiments. Then a new series is begun and a second reactant is varied, and so on.

**Figure 8** shows the results of changing conditions during a study of the reaction represented by the equation below.

\[\text{NO}(g) + \text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g)\]

This is an important reaction because it participates in the destruction of the ozone layer high in the atmosphere. There are two terms in the rate law for this reaction, which is shown below.

\[\text{rate} = k[\text{NO}]^{n_1}[\text{O}_3]^{n_2}\]

In this case, it turns out that \(n_1 = n_2 = 1\). The fact that the orders for each reactant are equal to one suggests that this reaction has a simple one-step mechanism in which an oxygen atom is transferred when the two reactant molecules collide.
Rate-Determining Step Controls Reaction Rate

Although a chemical equation can be written for the overall reaction, it does not usually show how the reaction actually takes place. For example, the reaction shown below is believed to take place in four steps, in the mechanism that follows.

\[ 2\text{Br}^- (aq) + \text{H}_2\text{O}_2 (aq) + 2\text{H}_3\text{O}^+ (aq) \rightarrow \text{Br}_2 (aq) + 4\text{H}_2\text{O} (l) \]

The order with respect to each of the three reactants was found to be 1.

(1) \[ \text{Br}^- (aq) + \text{H}_3\text{O}^+ (aq) \rightleftharpoons \text{HBr} (aq) + \text{H}_2\text{O} (l) \]
(2) \[ \text{HBr} (aq) + \text{H}_2\text{O}_2 (aq) \rightarrow \text{HOBr} (aq) + \text{H}_2\text{O} (l) \]
(3) \[ \text{Br}^- (aq) + \text{HOBr} (aq) \rightleftharpoons \text{Br}_2 (aq) + \text{OH}^- (aq) \]
(4) \[ \text{OH}^- (aq) + \text{H}_3\text{O}^+ (aq) \rightleftharpoons 2\text{H}_2\text{O} (l) \]

These four steps add up to the overall reaction that was shown above. Three of the steps are shown as equilibria; these are fast reactions. Step 2, however, is slow. If one step is slower than the others in a sequence of steps, it will control the overall reaction rate, because a reaction cannot go faster than its slowest step. Such a step is known as the \textit{rate-determining step}. Step 2 is the rate-determining step of the mechanism shown by steps 1–4. Species such as HOBr that form during a reaction but are then consumed are called \textit{intermediates}.

**Quick LAB**

**Modeling a Rate-Determining Step**

**SAFETY PRECAUTIONS**

**PROCEDURE**

1. Attach a \textbf{large-bore funnel} above a \textbf{small-bore funnel} onto a \textbf{ring stand}. Set a large \textbf{bowl} on the table, directly below the funnels.
2. Pour one cup of \textbf{sand} into the top funnel, and start a \textbf{stopwatch}.
3. When the last of the sand has fallen into the bowl, stop the stopwatch.
4. Write down the elapsed time.

5. Repeat steps 1 through 4 using the large-bore funnel above a \textbf{medium-bore funnel}.
6. Repeat steps 1 through 4 using the medium-bore funnel above the small-bore funnel.
7. Repeat steps 1 through 4 using the small-bore funnel above the large-bore funnel.

**ANALYSIS**

1. Which combination of funnels made the process go the fastest?
2. Which funnel controlled the rate of the process?
3. Does reversing the order of the two funnels in a trial change the results? Explain.
4. What strengths does this process have as a model for a chemical reaction? What weaknesses does it have?
**Reaction Pathways and Activation Energy**

If two molecules approach each other, the outer electrons of each molecule repel the outer electrons of the other. So, ordinarily, the molecules just bounce off each other. For two molecules to react, they must collide violently enough to overcome the mutual repulsion, so that the electron clouds of the two molecules merge to some extent. This merging may lead to a distortion of the shapes of the colliding molecules and, ultimately, to the creation of new bonds.

Violent collisions happen only when the colliding pair of molecules have an unusually large amount of energy. The kinetic energies of individual gas molecules vary over a wide range. Only the molecules with especially high kinetic energy are likely to react. The other molecules must wait until a succession of “lucky” collisions brings their kinetic energies up to the necessary amount.

The minimum energy that a pair of colliding molecules (or atoms or ions) need to have before a chemical change becomes a possibility is called the **activation energy** of the reaction. It is represented by the symbol \( E_a \). No reaction is possible if the colliding pair has less energy than \( E_a \).

**Activation-Energy Diagrams Model Reaction Progress**

Imagine rolling a ball toward a speed bump in a parking lot. If you do not give the ball enough kinetic energy, it will roll partway up the bump, stop, reverse its direction, and come back toward you. If you give it enough energy, the ball will make it just to the top of the bump and stay there for a moment. After that, it may go either way. Given plenty of energy, the ball will pass easily over the bump. Then, gaining more kinetic energy as it descends, it will roll away down the far side of the speed bump.

The model of the ball and speed bump provides a good analogy of the reaction between two colliding molecules. Without enough kinetic energy, the two molecules will not change chemically. With a combined kinetic energy equal to the activation energy, the molecules reach a state where there is a 50:50 chance of either returning to the initial state without reacting, or of being rearranged and becoming products. This point, similar to the top of the speed bump, is called the **activated complex** or **transition state** of the reaction.

**Figure 9a** is a graph of how the energy changes as a pair of hydrogen iodide molecules collide, form an activated complex, and then go on to become hydrogen and iodine molecules. As a chemical equation, the process could be written as follows.

\[
2\text{HI} \rightarrow \text{H}_2\text{I}_2 \rightarrow \text{H}_2 + \text{I}_2
\]

Initial state  Activated complex  Final state
(reactant)         (products)

In the initial state, the bonds are between the hydrogen and iodine atoms, H–I. In the activated complex, four weak bonds link the four atoms into a deformed square. In the final state the bonds link hydrogen to hydrogen, H–H, and iodine to iodine, I–I.
Hydrogen Bromide Requires a Different Diagram

**Figure 8b** similarly represents how potential energy changes with reaction progress for the reaction below.

\[
2\text{HBr} \rightarrow \text{H}_2\text{Br}_2 \rightarrow \text{H}_2 + \text{Br}_2
\]

(initial state) activated (final state)

(reactant) complex (products)

One difference between the two graphs is that the activation energy is lower in the case of hydrogen bromide. Because the activation energy of HBr is lower than that of HI, a larger fraction of the HBr molecules have enough energy to clear the activation energy barrier than in the HI case. As a result, hydrogen bromide decomposes more quickly than hydrogen iodide does.

Notice in both **Figure 9** graphs that the initial states are not at the same energy as the final states. Note also that the products have a lower energy than the reactants in the case of the HI decomposition reaction in **Figure 9a**, while the opposite is true for hydrogen bromide decomposition in **Figure 9b**. This distinction reflects the fact that hydrogen iodide decomposition is exothermic,

\[
2\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g) \quad \Delta H = -53 \text{ kJ}
\]

while the decomposition of hydrogen bromide is endothermic.

\[
2\text{HBr}(g) \rightarrow \text{H}_2(g) + \text{Br}_2(g) \quad \Delta H = 73 \text{ kJ}
\]
Not All Collisions Result in Reaction

Much of what we know about the collisions of molecules (and atoms) has come from studies of reactions between gases. However, it is believed that collisions happen similarly in solution. The principles of rate laws and activation energies apply in reactions that occur in solutions as well as in gas-phase reactions.

Collision between the reacting molecules is necessary for almost all reactions. Collision is not enough, though. The molecules must collide with enough energy to overcome the activation energy barrier. But another factor is also important. **Figure 10** illustrates the need for adequate energy and correct orientation in a collision.

A chemical reaction produces new bonds, and those bonds are formed between specific atoms in the colliding molecules. Unless the collision brings the correct atoms close together and in the proper orientation, the molecules will not react, no matter how much kinetic energy they have. For example, if a chlorine molecule collides with the oxygen end of the nitrogen monoxide molecule, the following reaction may occur.

\[
\text{NO}(g) + \text{Cl}_2(g) \rightarrow \text{NOCl}(g) + \text{Cl}(g)
\]

This reaction will not occur if the chlorine molecule strikes the nitrogen end of the molecule.

---

**Figure 10**
A reaction will not occur if the collision occurs too gently, as in **a**, or with the wrong orientation as in **b**. An effective collision, as in **c**, must deliver sufficient energy and bring together the atoms that bond in the products.
Catalysts Increase Reaction Rate

Adding more reactant will usually increase the rate of a reaction. Adding extra product will sometimes cause the rate to decrease. Often, adding substances called catalysts to a reaction mixture will increase the reaction rate, even though the catalyst is still present and unchanged at the end of the reaction. The process, which is called catalysis, is shown in Figure 11.

Hydrogen peroxide solution, commonly used as a mild antiseptic and as a bleaching agent, decomposes only very slowly when stored in a bottle, forming oxygen as shown in the following equation.

\[ 2\text{H}_2\text{O}_2(aq) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) \]

Adding a drop of potassium iodide solution speeds up the reaction. On the other hand, adding a few crystals of insoluble manganese dioxide, MnO\textsubscript{2}(s), causes a violent decomposition to occur. The iodide ion, I\textsuperscript{−}(aq), and manganese dioxide are two of many catalysts for the decomposition of hydrogen peroxide.

Catalysis is widely used in the chemical industry, particularly in the making of gasoline and other petrochemicals. Catalysts save enormous amounts of energy. As you probably know, carbon monoxide is a poisonous gas that is found in automobile exhaust. The following oxidation reaction could remove the health hazard, but this reaction is very slow.

\[ 2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g) \]

It is the job of the catalytic converter, built into the exhaust system of all recent models of cars, to catalyze this reaction.

Catalysis does not change the overall reaction at all. The stoichiometry and thermodynamics of the reaction are not changed. The changes affect only the path the reaction takes from reactant to product.
Catalysts Lower the Activation Energy Barrier

Catalysis works by making a different pathway available between the reactants and the products. This new pathway has a different mechanism and a different rate law from that of the uncatalyzed reaction. The catalyzed pathway may involve a surface reaction, as in the decomposition of hydrogen peroxide catalyzed by manganese dioxide, and in biological reactions catalyzed by enzymes. Or, the catalytic mechanism may take place in the same phase as the uncatalyzed reaction.

The iodide-catalyzed decomposition of hydrogen peroxide is an example of catalysis that does not involve a surface. It probably works by the following mechanism.

1. \( \text{I}^- (aq) + \text{H}_2\text{O}_2(aq) \rightarrow \text{IO}^- (aq) + \text{H}_2\text{O}(l) \)
2. \( \text{IO}^- (aq) + \text{H}_2\text{O}_2(aq) \rightarrow \text{I}^- (aq) + \text{O}_2(g) + \text{H}_2\text{O}(l) \)

Notice that the iodide ion, \( \text{I}^- \), consumed in step 1 is regenerated in step 2, and the hypiodite ion, \( \text{IO}^- \), generated in step 1 is consumed in step 2. In principle, a single iodide ion could break down an unlimited amount of hydrogen peroxide. This is the characteristic of all catalytic pathways—the catalyst is never used up. It is regenerated and so becomes available for use again and again.

Each pathway corresponds to a different mechanism, a different rate law, and a different activation energy. Figure 12 shows the potential energy profiles for the uncatalyzed reaction and for catalysis by three different catalysts. Because the catalyzed pathways have lower activation energy barriers, the catalysts speed up the rate of the reaction.
Enzymes Are Catalysts Found in Nature
The most efficient of the three catalysts compared in Figure 12 is an enzyme. Enzymes are large protein molecules. Their biological role is to catalyze metabolic processes that otherwise would happen too slowly to help the organism. For example, the enzyme lactase catalyzes the reaction of water with the sugar lactose, present in milk. People whose bodies lack the ability to produce lactase have what is known as lactose intolerance.

Enzymes are very specific and catalyze only one reaction. This is because the surface of an enzyme molecule has a detailed arrangement of atoms that interacts with the target molecule (lactose, for instance). The enzyme site and the target molecule are often said to have a “lock and key” relationship to each other.

Hydrogen peroxide is a toxic metabolic product in higher animals, and the enzyme catalase is present in their blood and other tissues to destroy H₂O₂. On the other hand, the bombardier beetle stores a supply of hydrogen peroxide for use as a defense mechanism. When threatened by a predator, the beetle injects catalase into its hydrogen peroxide store. The rapidly released oxygen gas provides pressure for a spray of irritating liquid that the beetle can squirt at its enemy, as shown in Figure 13.

PRACTICE PROBLEMS
6. What is the order of a reaction if its rate triples when the reactant concentration triples?
7. The reaction CH₃NC(g) → CH₃CN(g) is of order 1, with a rate of 1.3 × 10⁻⁴ M/s when the reactant concentration was 0.040 M. Predict the rate when [CH₃NC] = 0.025 M.
8. The following data relate to the reaction A + B → C. Find the order with respect to each reactant.

CRITICAL THINKING
9. Which corresponds to the faster rate: a mechanism with a small activation energy or one with a large activation energy?
10. If the reaction NO₂(g) + CO(g) → NO(g) + CO₂(g) proceeds by a one-step mechanism, what is the rate law?
11. What happens if a pair of colliding molecules possesses less energy than E_a?
12. Why is the phrase “lock and key” used to describe enzyme catalysis?
13. How are a catalyst and an intermediate similar? How are they different?
14. Draw a diagram similar to Figure 10 to show (a) an unsuccessful and (b) a successful collision between H₂(g) and Br₂(g).
CHAPTER HIGHLIGHTS

SECTION ONE  What Affects the Rate of a Reaction?
- The rate of a chemical reaction is calculated from changes in reactant or product concentration during a small time interval.
- Reaction rates generally increase with reactant concentration or, in the case of gases, pressure.
- Rate increases with temperature because at a higher temperature a greater fraction of collisions have enough energy to cause a reaction.

SECTION TWO  How Can Reaction Rates Be Explained?
- Rate laws, which are used to suggest mechanisms, are determined by studying how reaction rate depends on concentration.
- An activated complex occupies the energy high point on the route from reactant to product.
- Catalysts provide a pathway of lower activation energy.
- Enzymes are biological catalysts that increase the rates of reactions important to an organism.

KEY TERMS
- chemical kinetics
- reaction rate
- rate law
- reaction mechanism
- order
- rate-determining step
- intermediate
- activation energy
- activated complex
- catalyst
- catalysis
- enzyme

KEY IDEAS

KEY SKILLS

Calculating a Reaction Rate
Sample Problem A  p. 581

Determining a Rate Law
Sample Problem B  p. 587
**CHAPTER REVIEW**

**USING KEY TERMS**

1. Define reaction rate.

2. Explain the difference between a reaction rate and a rate law.

3. What is a mechanism, and what is its rate-determining step?

4. Explain why the names *activated complex* and *transition state* are suitable for describing the highest energy point on a reaction’s route from reactant to product.

5. Explain the role of an intermediate in a reaction mechanism.

6. What are enzymes, and what common features do they all share?

**UNDERSTANDING KEY IDEAS**

**What Affects the Rate of a Reaction?**

7. What unit is most commonly used to express reaction rate?

8. Explain how to calculate a reaction rate from concentration-versus-time data.

9. Explain how a graph can be useful in defining and measuring the rate of a chemical reaction.

10. Suggest ways of measuring concentration in a reaction mixture.

11. Why is it necessary to divide by the coefficient in the balanced chemical equation when calculating a reaction rate? When can that step be omitted?

12. What does $\Delta[A]$ mean if A is the reactant in a chemical reaction?

13. In a graph like the one in Figure 14, what are the signs of the slopes for reactants and for products?

14. Explain the effect that area has on reactions that occur on surfaces.

**How Can Reaction Rates Be Explained?**

15. Why are reaction orders not always equal to the coefficients in a chemical equation?

16. Write the general expression for the rate law of a reaction with three reactants A, B, and C.

17. Explain what a catalyst is and how it works.

18. Sketch a diagram showing how the potential energy changes with the progress of an endothermic reaction. Label the curve “Initial state,” “Final state,” and “Transition state.” Then, draw a second curve to show the change brought about by a catalyst.

19. How do enzymes differ from other catalysts?
29. Using chemical terminology, explain the purpose of food refrigeration.

30. Why do reptiles move more sluggishly in cold weather?

CRITICAL THINKING

31. Why is it necessary, in defining the rate of a reaction, to require that $\Delta t$ be small?

32. Explain why, unlike gas-phase reactions, a reaction in solution is hardly affected at all by pressure.

33. Could a catalyzed reaction pathway have an activation energy higher than the uncatalyzed reaction? Explain.

34. Would you expect the concentration of a catalyst to appear in the rate law of a catalyzed reaction? Explain.

ALTERNATIVE ASSESSMENT

35. Boilers are sometimes used to heat large buildings. Deposits of CaCO$_3$, MgCO$_3$, and FeCO$_3$ can hinder the boiler operation. Aqueous solutions of hydrochloric acid are commonly used to remove these deposits. The general equation for the reaction is written below.

$$\text{MCO}_3(s) + 2\text{H}_3\text{O}^+(aq) \rightarrow \text{M}^{2+}(aq) + 3\text{H}_2\text{O}(l) + \text{CO}_2(g)$$

In the equation, M stands for Ca, Mg, or Fe. Design an experiment to determine the effect of various HCl concentrations on the rates of this reaction. Present your design to the class.

CONCEPT MAPPING

36. Use the following terms to create a concept map: activation energy, alternative reaction pathway, catalysts, enzymes, and reaction rate.
The graph relates to an experiment in which the concentrations of bromide ion, hydrogen peroxide, and bromine were monitored as the following reaction took place.

$$2\text{Br}^- (aq) + \text{H}_2\text{O}_2 (aq) + 2\text{H}_3\text{O}^+ (aq) \rightarrow \text{Br}_2 (aq) + 4\text{H}_2\text{O} (l)$$

37. The three curves are lettered a, b, and c. Which curves have positive slopes and which have negative slopes?

38. Associate each curve with one of the species being monitored.

39. What were the initial concentrations of bromine and hydrogen peroxide?

40. Measure the slope of each of the three curves at $t = 500$ s.

41. From each slope calculate a reaction rate. Do your three values agree?

42. Graphing Calculator

**Reaction Order**

The graphing calculator can run a program that can tell you the order of a chemical reaction, provided you indicate the reactant concentrations and reaction rates for two experiments involving the same reaction.

**Go to Appendix C.** If you are using a TI-83 Plus, you can download the program RXNORDER and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. At the prompts, enter the reactant concentrations and reaction rates. Run the program as needed to find the order of the following reactions. (All rates are given in M/s.)

a. $2\text{N}_2\text{O}_5 (g) \rightarrow 4\text{NO}_2 (g) + \text{O}_2 (g)$
   
   $\text{N}_2\text{O}_5$: conc. 1 = 0.025 M; conc. 2 = 0.040 M
   
   rate 1 = $8.1 \times 10^{-5}$; rate 2 = $1.3 \times 10^{-4}$

b. $2\text{NO}_2 (g) \rightarrow 2\text{NO} (g) + \text{O}_2 (g)$
   
   $\text{NO}_2$: conc. 1 = 0.040 M; conc. 2 = 0.080 M
   
   rate 1 = 0.0030; rate 2 = 0.012

c. $2\text{H}_2\text{O}_2 (g) \rightarrow 2\text{H}_2\text{O} (g) + \text{O}_2 (g)$
   
   $\text{H}_2\text{O}_2$: conc. 1 = 0.522 M; conc. 2 = 0.887 M
   
   rate 1 = $1.90 \times 10^{-4}$; rate 2 = $3.23 \times 10^{-4}$

d. $2\text{NOBr} (g) \rightarrow 2\text{NO} (g) + \text{Br}_2 (g)$
   
   $\text{NOBr}$: conc. 1 = 1.27 $\times 10^{-4}$ M; conc. 2 = $4.04 \times 10^{-4}$ M
   
   rate 1 = $6.26 \times 10^{-5}$; rate 2 = $6.33 \times 10^{-4}$

e. $2\text{HI} (g) \rightarrow \text{H}_2 (g) + \text{I}_2 (g)$
   
   $\text{HI}$: conc. 1 = $4.18 \times 10^{-4}$ M; conc. 2 = $8.36 \times 10^{-4}$ M
   
   rate 1 = $3.86 \times 10^{-5}$; rate 2 = $1.54 \times 10^{-4}$
UNDERSTANDING CONCEPTS

Directions (1–3): For each question, write on a separate sheet of paper the letter of the correct answer.

1. How does the potential energy of the activated complex compare with the potential energies of the reactants and products?
   A. lower than the potential energies of products and of reactants
   B. higher than the potential energies of products and of reactants
   C. lower than the potential energy of products but higher than potential energy of reactants
   D. higher than the potential energy of products but lower than potential energy of reactants

2. Where does the activated complex appear in a graph of how potential energy changes with reaction progress?
   F. at the left end of the curve
   G. at the right end of the curve
   H. at the lowest point on the curve
   I. at the highest point on the curve

3. Why is chemical kinetics useful?
   A. Catalysts decrease chemical costs.
   B. The rate law suggests possible reaction mechanisms.
   C. Thermodynamic data can be obtained from activation energies.
   D. The rate law enables the complete equation of the reaction to be derived.

Directions (4–5): For each question, write a short response.

4. How and why is the rate of the chemical reaction \( (\text{CH}_2)_3(g) \rightarrow \text{CH}_2\text{CHCH}_3(g) \) affected by pressure?

5. Explain why the biological process of converting glucose into carbon dioxide and water occurs at a much lower temperature than combustion, even though the energy released is the same.

READING SKILLS

Directions (6–7): Read the passage below. Then answer the questions.

The energy of a corrosion reaction is used to prepare a meal that has a self-contained heat source. The heat comes from a packet containing a powder made of a magnesium-iron alloy and a separate packet of salt water. When the contents of the two packets mix, the reaction between the metal, salt water, and oxygen in the air releases enough energy to heat the food by 100°C in 15 minutes. The process is used to provide heated food or beverages to military personnel, truck drivers, and sports fans.

6. Heat can also be generated by using sodium metal in place of the magnesium iron alloy. Why would this reaction be less suitable for heating food?
   F. Sodium is too expensive to use for this purpose.
   G. The reaction with sodium generates too much energy.
   H. The reaction between sodium and salt water would proceed too slowly.
   I. The toxic salts of sodium might contaminate the food, making it inedible.

7. How would the usefulness of the reaction for heating foods change if large granules of the alloy were used instead of a powder?
INTERPRETING GRAPHICS

Directions (8–11): For each question below, record the correct answer on a separate sheet of paper.
The diagrams below show activation energies for the decomposition of HI and HBr. Use them to answer questions 8 through 11.

Activation Energies for the Decomposition of HI and HBr

8. Which of these decomposition reactions is endothermic?
   A. HBr only
   B. HI only
   C. both HBr and HI
   D. neither HBr nor HI

9. Which of these reactions requires an input of energy to initiate the decomposition?
   F. HBr only
   G. HI only
   H. both HBr and HI
   I. neither HBr nor HI

10. Why does hydrogen bromide decompose more quickly than hydrogen iodide?
    A. Bromine is a smaller atom than iodine.
    B. The activation energy for hydrogen bromide is smaller.
    C. Hydrogen bromide forms an activated complex but hydrogen iodide does not.
    D. The difference in energy between reactants and products is larger for hydrogen bromide.

11. How would each curve above change if a catalyst were added?
    F. The activation energy decreases and the energy of the reactants and products both decrease.
    G. The activation energy increases and the energy of the reactants and products both decrease.
    H. The activation energy decreases and the energy of the reactants and products remains the same.
    I. The activation energy increases and the energy of the reactants and products remains the same.

When using a graph to answer a question, make sure you know what variables are represented on the x- and y-axes before answering the question.