

CHAPTER 17

Reaction Kinetics

BIG IDEA

For chemical reactions to occur, the particles of the reactants must collide with sufficient kinetic energy and in the proper orientation.



ONLINE Chemistry
HMHSscience.com

SECTION 1

The Reaction Process

SECTION 2

Reaction Rate

ONLINE LABS

- Clock Reactions
- Rate of a Chemical Reaction
- A Leaky Reaction
- Reaction Action



GO ONLINE



Why It Matters Video
HMHSscience.com

Reaction Kinetics

The Reaction Process

Key Terms

reaction mechanism
intermediate

homogeneous reaction
collision theory

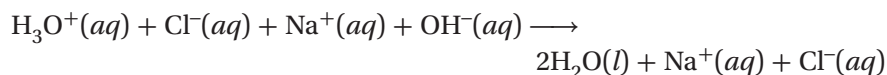
activation energy
activated complex

By studying many types of experiments, chemists have found that chemical reactions occur at widely differing rates. For example, in the presence of air, iron rusts very slowly, whereas the methane in natural gas burns rapidly when ignited. The speed of a chemical reaction depends on the energy pathway that a reaction follows and the changes that take place on the molecular level when substances interact. In this chapter, you will study the factors that affect how fast chemical reactions take place.

MAIN IDEA

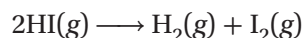
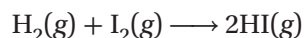
Some reactions have intermediate steps.

If you mix aqueous solutions of HCl and NaOH, an extremely rapid neutralization reaction occurs, as shown in **Figure 1.1**.



The reaction is practically instantaneous; the rate is limited only by the speed with which the H_3O^+ and OH^- ions can diffuse through the water to meet each other. On the other hand, reactions between ions of the same charge and between molecular substances are not instantaneous. Negative ions repel each other, as do positive ions. The electron clouds of molecules also repel each other strongly at very short distances. Therefore, only ions or molecules with very high kinetic energy can overcome repulsive forces and get close enough to react. In this section, we will limit our discussion to reactions between molecules.

Colorless hydrogen gas consists of pairs of hydrogen atoms bonded together as diatomic molecules, H_2 . Violet-colored iodine vapor is also diatomic, consisting of pairs of iodine atoms bonded together as I_2 molecules. A chemical reaction between these two gases at elevated temperatures produces hydrogen iodide, HI, a colorless gas. Hydrogen iodide molecules, in turn, tend to decompose and re-form hydrogen and iodine molecules, producing the violet gas shown in **Figure 1.2** on the next page. The following chemical equations describe these two reactions.



Such equations indicate only which molecular species disappear as a result of the reactions and which species are produced. **They do not show the reaction mechanism, the step-by-step sequence of reactions by which the overall chemical change occurs.**

Main Ideas

- ▶ Some reactions have intermediate steps.
- ▶ Molecular collisions need the right energy and orientation to react.
- ▶ Reactions occur only if there is enough energy.
- ▶ In a transition state, bonds are breaking as new bonds form.

FIGURE 1.1

Instantaneous Reaction As NaOH solution is poured into HCl solution, a very rapid neutralization reaction occurs. Excess NaOH turns the phenolphthalein indicator pink.



FIGURE 1.2

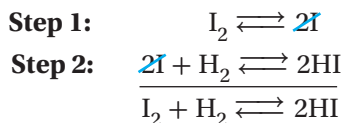
Intermediates Colorless hydrogen iodide gas, HI, decomposes into colorless hydrogen gas and violet iodine gas. Some of the hydrogen gas and iodine gas will re-form HI.



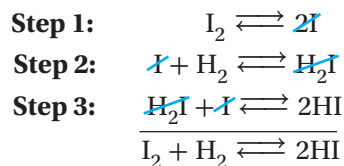
Although only the net chemical change is directly observable for most chemical reactions, experiments can often be designed that suggest the probable sequence of steps in a reaction mechanism. Each reaction step is usually a simple process. The equation for each step represents the *actual* atoms, ions, or molecules that participate in that step. Even a reaction that appears from its balanced equation to be a simple process may actually be the result of several simple steps.

For many years, the formation of hydrogen iodide, as shown in **Figure 1.2**, was considered a simple one-step process. It was thought to involve the interaction of two molecules, H_2 and I_2 , in the forward reaction and two HI molecules in the reverse reaction. Experiments eventually showed, however, that a direct reaction between H_2 and I_2 does not take place.

Alternative mechanisms for the reaction were proposed based on the experimental results. The steps in each reaction mechanism had to add together to give the overall equation. Note that two of the species in the mechanism steps— I and H_2I —do not appear in the net equation. **Species that appear in some steps but not in the net equation are known as intermediates.** (Notice that they cancel each other out in the following mechanisms.) The first possible mechanism has the following two-step pathway.



The second possible mechanism has a three-step pathway.



The reaction between hydrogen gas and iodine vapor to produce hydrogen iodide gas is an example of a **homogeneous reaction**, a reaction whose reactants and products exist in a single phase—in this case, the gas phase. This reaction system is also an example of a homogeneous chemical system, because all reactants and products in all intermediate steps are in the same phase.

✓ CHECK FOR UNDERSTANDING

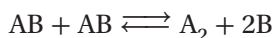
Propose Based on your knowledge of reaction mechanisms, propose at least one reason that a chemist working in industry might need to know all of the steps in a chemical reaction.

▶ MAIN IDEA

Molecular collisions need the right energy and orientation to react.

In order for reactions to occur between substances, their particles (molecules, atoms, or ions) must collide. Furthermore, these collisions must result in interactions. **The set of assumptions regarding collisions and reactions is known as collision theory.** Chemists use this theory to interpret many of their observations about chemical reactions.

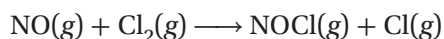
Consider what might happen on a molecular scale in one step of a homogeneous reaction system. We will analyze a proposed first step in a hypothetical decomposition reaction.



According to the collision theory, the two AB molecules must collide in order to react. Furthermore, they must collide with a favorable orientation and with enough energy to overcome electron-cloud repulsion and disrupt the bonds of the AB molecules. If they do so, AB bonds break, and A₂ bonds form, leading to the formation of the products, one A₂ molecule and two B atoms. An effective collision is modeled in **Figure 1.3a**.

If a collision is too gentle, the two molecules simply rebound from each other. This effect is illustrated in **Figure 1.3b**. Similarly, a collision in which the reactant molecules have an unfavorable orientation has little effect. The colliding molecules rebound without reacting. A collision that has poor orientation is shown in **Figure 1.3c**.

A chemical reaction produces new bonds 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. For example, if a chlorine molecule collides with the oxygen end of a nitrogen monoxide molecule, the following reaction may occur.



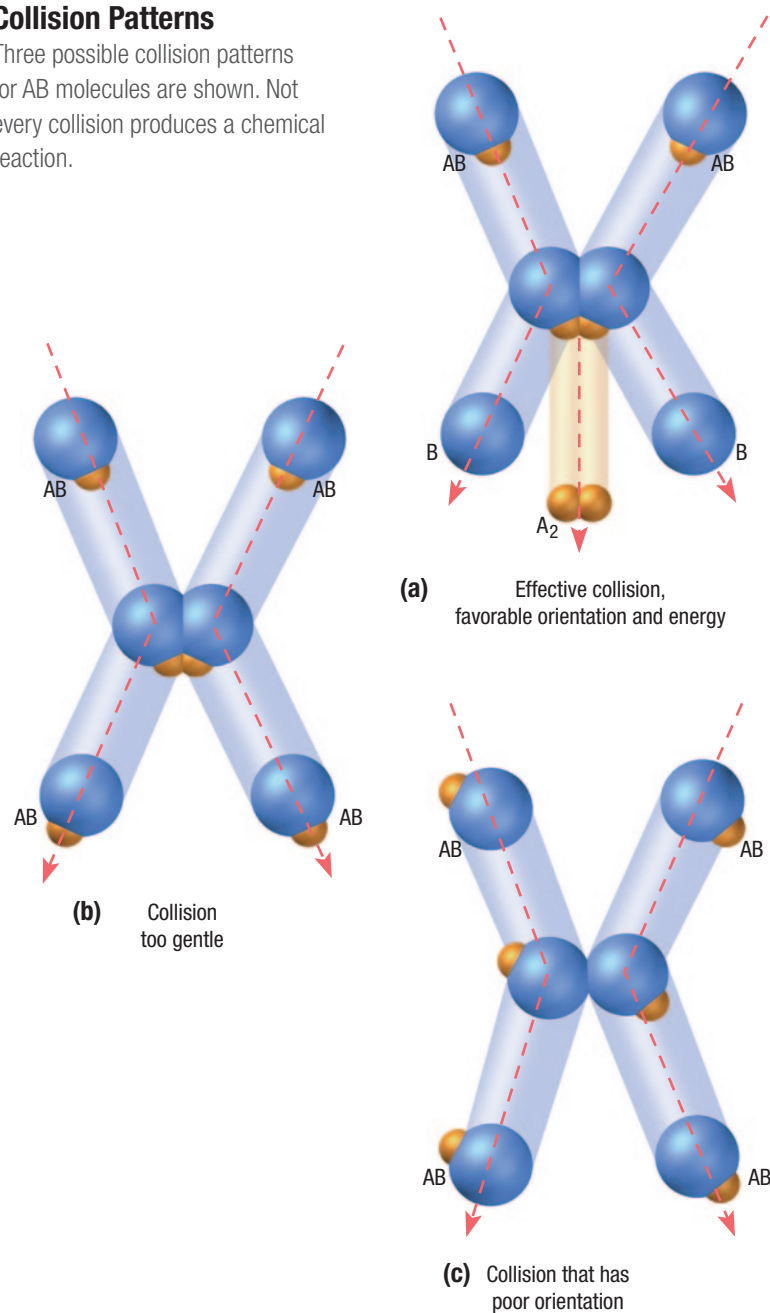
This reaction will not occur if the chlorine molecule strikes the nitrogen end of the molecule.

Thus, collision theory provides two reasons that a collision between reactant molecules may fail to produce a new chemical species: the collision is not energetic enough to supply the required energy, or the colliding molecules are not oriented in a way that enables them to react with each other.

FIGURE 1.3

Collision Patterns

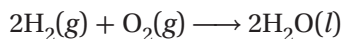
Three possible collision patterns for AB molecules are shown. Not every collision produces a chemical reaction.



▶ MAIN IDEA

Reactions occur only if there is enough energy.

Consider the reaction for the formation of water from the diatomic gases oxygen and hydrogen according to the following equation:



The enthalpy of formation is quite high: $\Delta H_f^0 = -285.8 \text{ kJ/mol}$ at 298.15 K. The free-energy change is also large: $\Delta G^0 = -237.1 \text{ kJ/mol}$. Why, then, don't oxygen and hydrogen combine spontaneously and immediately to form water when they are mixed at room temperature?

Hydrogen and oxygen gases exist as diatomic molecules. When the molecules approach each other, the electron clouds repel each other. For a reaction to occur, the colliding molecules must have enough kinetic energy to overcome the electron-cloud repulsion. The bonds of these molecular species must be broken in order for new bonds to be formed between oxygen and hydrogen atoms. Bond breaking is an endothermic process, and bond forming is exothermic. Even though the net process for forming water is exothermic, an initial input of energy is needed to overcome the repulsion forces that occur between reactant molecules when they are brought very close together. This initial energy input activates the reaction.

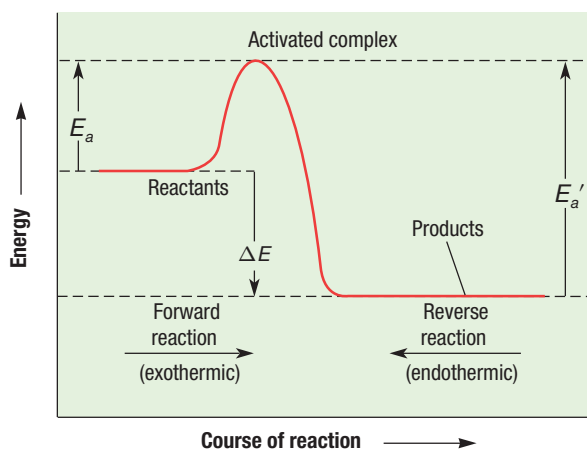
Once an exothermic reaction is started, the energy released is enough to sustain the reaction by activating other molecules. Thus, the reaction rate keeps increasing. It is limited only by the time required for reactant particles to acquire the energy and make contact. Energy from an outside source may start exothermic reactants along the pathway of reaction. A generalized reaction pathway for an exothermic reaction is shown as the forward reaction in **Figure 1.4**. The minimum amount of energy needed to activate this reaction is the activation energy represented by E_a . **Activation energy is the minimum energy required to transform the reactants into an activated complex.**

The reverse reaction, decomposition of water molecules, is endothermic, because the water molecules lie at an energy level lower than that of the hydrogen and oxygen molecules. The water molecules require a larger activation energy before they can decompose to re-form oxygen and hydrogen. The energy needed to activate an endothermic reaction is greater than that required for the original exothermic change and is represented by E_a' in **Figure 1.4**. The difference between E_a' and E_a is equal to the energy change in the reaction, ΔE . This energy change has the same numerical value for the forward reaction as it has for the reverse reaction but with the opposite sign.

FIGURE 1.4

Reaction Pathways The difference between the activation energies for the reverse and forward reactions of a reversible reaction equals the energy change in the reaction, ΔE . The quantity for ΔE is the same for both directions but is negative for the exothermic direction and positive for the endothermic direction.

Reaction Pathways for Forward and Reverse Reactions



▶ MAIN IDEA

In a transition state, bonds are breaking as new bonds form.

When molecules collide, some of their high kinetic energy is converted into internal potential energy within the colliding molecules. If enough energy is converted, molecules with suitable orientation become activated. New bonds can then form. In this brief interval of bond breakage and bond formation, the collision complex is in a *transition state*. Some partial bonding exists in this transitional structure. **A transitional structure that results from an effective collision and that persists while old bonds are breaking and new bonds are forming is called an activated complex.**

Figure 1.5 graphically breaks down the reaction pathway of the formation of hydrogen iodide gas into three steps. Beginning with the reactants, H_2 and I_2 , a certain amount of activation energy, E_{a1} , is needed to form the activated complex that leads to the formation of the intermediates H_2 and 2I . Then more activation energy, E_{a2} , is needed to form the activated complex leading to the intermediates H_2I and I . In order to arrive at the final product, 2HI , another increase in activation energy is necessary, as seen by the highest peak, labeled E_{a3} .

An activated complex is formed when an effective collision raises the internal energies of the reactants to their minimum level for reaction, as in Figure 1.4 (see previous page). Both forward and reverse reactions go through the same activated complex. A bond broken in the activated complex for the forward reaction must be re-formed in the activated complex for the reverse reaction. Observe that an activated complex occurs at a high-energy position along the reaction pathway.

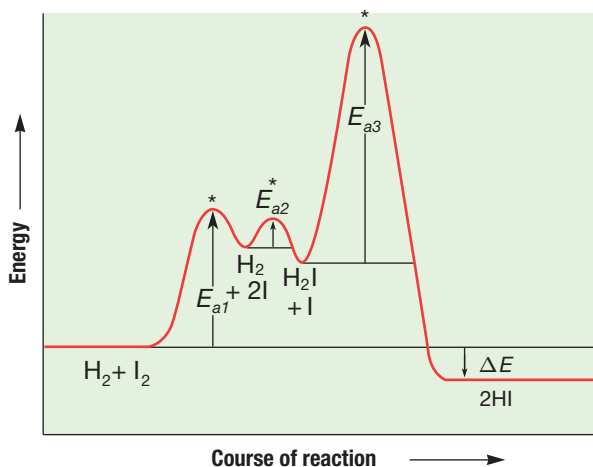
The kinetic-molecular theory states that the speeds and the kinetic energies of the molecules increase as the temperature increases. An increase in speed causes more collisions, which can cause an increase in the number of reactions. However, an increase in the reaction rate depends on more than simply the number of collisions, as Figure 1.3 (earlier in the section) illustrates. The collisions between molecules must possess sufficient energy to form an activated complex, or a reaction will not take place. Raising the temperature of a reaction means more molecules that have enough energy to exceed activation energy, increasing the reaction rate.

In its brief existence, the activated complex has partial bonding that is characteristic of both reactant and product. It may then re-form the original bonds and separate back into the reactant particles, or it may form new bonds and separate into product particles. The activated complex, unlike the relatively stable intermediate products, is a very short-lived molecular complex in which bonds are in the process of being broken and formed.

FIGURE 1.5

Activation Energy This energy profile graphically shows the formation of three activated complexes (*) during the gas-phase reaction $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$.

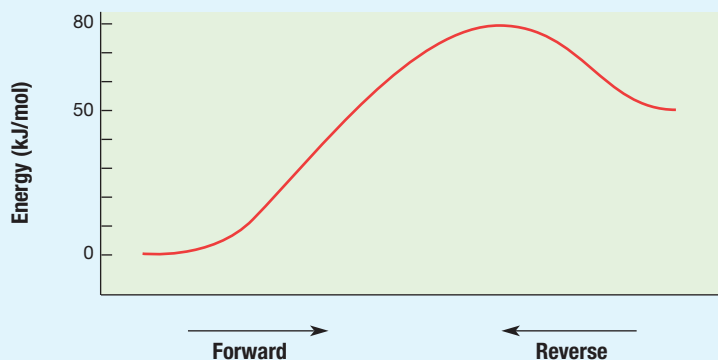
Activation Energy Peaks in the Formation of Activated Complexes





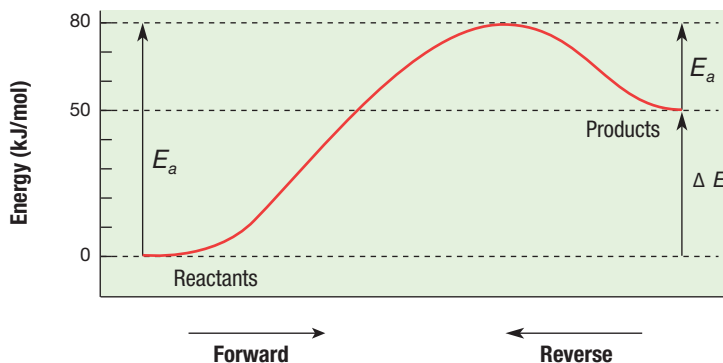
Energy Diagrams

Sample Problem A Copy the energy diagram below, and label the reactants, products, ΔE , E_a , and E_a' . Determine the value of $\Delta E_{\text{forward}}$, $\Delta E_{\text{reverse}}$, E_a , and E_a' .



SOLVE

The energy level of reactants is always at the left-hand end of such a curve, and the energy level of products is always at the right-hand end. The energy change in the reaction, ΔE , is the difference between these two energy levels. The activation energy differs in the forward and reverse directions. It is the minimum energy needed to achieve effective reaction in either direction. As E_a , it is the difference between the reactant energy level and the peak in the curve. As E_a' , it is the difference between the product energy level and the peak in the curve.



$$\Delta E_{\text{forward}} = \text{energy of products} - \text{energy of reactants}$$

$$\Delta E_{\text{forward}} = 50 \text{ kJ/mol} - 0 \text{ kJ/mol} = +50 \text{ kJ/mol}$$

$$\Delta E_{\text{reverse}} = \text{energy of reactants} - \text{energy of products}$$

$$\Delta E_{\text{reverse}} = 0 \text{ kJ/mol} - 50 \text{ kJ/mol} = -50 \text{ kJ/mol}$$

$$E_a = \text{energy of activated complex} - \text{energy of reactants}$$

$$E_a = 80 \text{ kJ/mol} - 0 \text{ kJ/mol} = 80 \text{ kJ/mol}$$

$$E_a' = \text{energy of activated complex} - \text{energy of products}$$

$$E_a' = 80 \text{ kJ/mol} - 50 \text{ kJ/mol} = 30 \text{ kJ/mol}$$

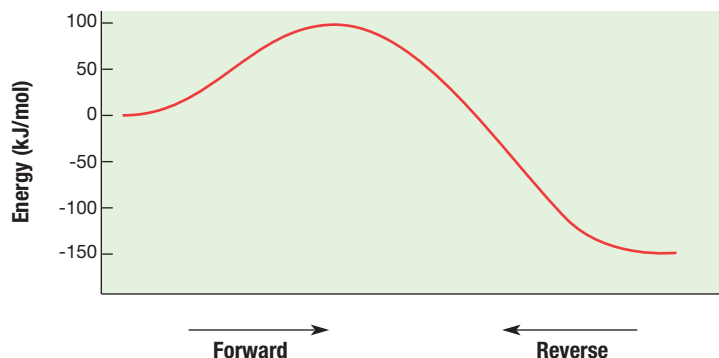
Continued

Energy Diagrams (continued)

Practice

Answers in Appendix E

- Use the method shown in the sample problem to redraw and label the following energy diagram. Determine the value of $\Delta E_{\text{forward}}$, $\Delta E_{\text{reverse}}$, E_a , and E_a' .
 - Is the forward reaction shown in the diagram exothermic or endothermic? Explain your answer.



- Draw and label an energy diagram similar to the one shown in the sample problem for a reaction in which $E_a = 125$ kJ/mol and $E_a' = 86$ kJ/mol. Place the reactants at energy level zero.
 - Calculate the values of $\Delta E_{\text{forward}}$ and $\Delta E_{\text{reverse}}$.
 - Is this reaction endothermic or exothermic? Explain your answer.
- Draw and label an energy diagram for a reaction in which $E_a = 154$ kJ/mol and $\Delta E = 136$ kJ/mol.
 - Calculate the activation energy, E_a' , for the reverse reaction.



SECTION 1 FORMATIVE ASSESSMENT

▶ Reviewing Main Ideas

- What is meant by *reaction mechanism*?
- What factors determine whether a molecular collision produces a reaction?
- What is activation energy?
- What is an activated complex?
- How is activation energy of the forward and reverse reactions related to the energy of reaction?
- What is the difference between an activated complex and an intermediate?

- Explain why, even though a collision may have energy in excess of the activation energy, a reaction may not occur.

✔ Critical Thinking

- ANALYZING INFORMATION** Which corresponds to the faster rate: a mechanism with a small activation energy or one with a large activation energy? Explain your answer.

SECTION 2

Main Ideas

- ▶ Several factors can influence reaction rates.
- ▶ Concentration and reaction rate are related.

Reaction Rate

Key Terms

reaction rate	catalysis	order
chemical kinetics	homogeneous catalyst	rate-determining step
heterogeneous reaction	heterogeneous catalyst	
catalyst	rate law	

The change in concentration of reactants per unit time as a reaction proceeds is called the reaction rate. The study of reaction rates is concerned with the factors that affect the rate and with the mathematical expressions that reveal the specific dependencies of the rate on concentration. **The area of chemistry that is concerned with reaction rates and reaction mechanisms is called chemical kinetics.**

▶ MAIN IDEA

Several factors can influence reaction rates.

For reactions to occur, particles must come into contact in a favorable orientation and with enough energy for activation. Thus, the rate of a reaction depends on the collision frequency of the reactants and on the collision efficiency. Any change in reaction conditions that affects the collision frequency, the collision efficiency, or the collision energy affects the reaction rate. At least five important factors influence the rate of a chemical reaction.

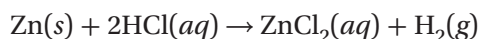
Nature of Reactants

Substances vary greatly in their tendencies to react. For example, hydrogen combines vigorously with chlorine under certain conditions. Under the same conditions, it may react only slowly with nitrogen. Sodium and oxygen combine much more rapidly than iron and oxygen under similar conditions. Bonds are broken, and other bonds are formed in reactions. The rate of reaction depends on the particular reactants and reaction conditions.

Surface Area

Gaseous mixtures and dissolved particles can mix and collide freely; therefore, reactions involving them can occur rapidly. In heterogeneous reactions, the reaction rate depends on the area of contact of the reaction substances. **Heterogeneous reactions involve reactants in two different phases.** These reactions can occur only when the two phases are in contact. Thus, the surface area of a solid reactant is an important factor in determining rate. An increase in surface area increases the rate of heterogeneous reactions.

Solid zinc reacts with aqueous hydrochloric acid to produce zinc chloride and hydrogen gas according to the following equation:



This reaction occurs at the surface of the zinc solid. A cube of zinc measuring 1 cm on each edge presents only 6 cm² of contact area. The same amount of zinc in the form of a fine powder might provide a contact area thousands of times greater than the original area. Consequently, the reaction rate of the powdered solid is much faster.

A lump of coal burns slowly when kindled in air. The rate of burning can be increased by breaking the lump into smaller pieces, exposing more surface area. If the piece of coal is powdered and then ignited while suspended in air, it burns explosively. This is the cause of some explosions in coal mines.

Temperature

An increase in temperature increases the average kinetic energy of the particles in a substance; this can result in a greater number of effective collisions when the substance is allowed to react with another substance. If the number of effective collisions increases, the reaction rate will increase.

To be effective, the energy of the collisions must be equal to or greater than the activation energy. At higher temperatures, more particles possess enough energy to form the activated complex when collisions occur. Thus, a rise in temperature produces an increase in collision energy as well as in collision frequency.

Decreasing the temperature of a reaction system has the opposite effect. The average kinetic energy of the particles decreases, so they collide less frequently and with less energy, producing fewer effective collisions. Beginning near room temperature, the reaction rates of many common reactions roughly double with each 10 K (10°C) rise in temperature. This rule of thumb should be used with caution, however. The actual rate increase with a given rise in temperature must be determined experimentally.

Concentration

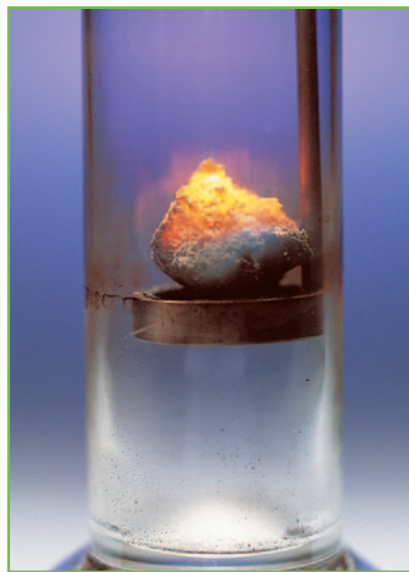
Pure oxygen has five times the concentration of oxygen molecules that air has at the same pressure; consequently, a substance that oxidizes in air oxidizes more vigorously in pure oxygen. For example, in **Figure 2.1**, the light produced when the lump of charcoal is burned in pure oxygen is much more intense than the light produced when the charcoal lump is heated in air until combustion begins. The oxidation of charcoal is a heterogeneous reaction system in which one reactant is a gas. The reaction rate depends not only on the amount of exposed charcoal surface but also on the concentration of the reacting species, O₂.

In homogeneous reaction systems, reaction rates depend on the concentration of the reactants. Predicting the mathematical relationship between rate and concentration is difficult, because most chemical reactions occur in a series of steps and only one of these steps determines the reaction rate. If the number of effective collisions increases, the rate increases as well. In general, an increase in rate is expected if the concentration of one or more of the reactants is increased.

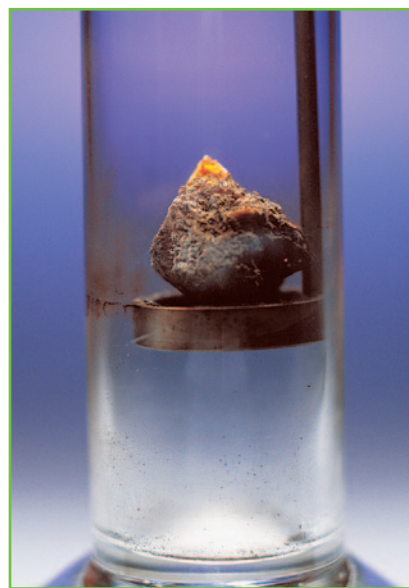
FIGURE 2.1

Concentration and Reaction

Rate A greater concentration increases the number of effective collisions, so the reaction rate increases.



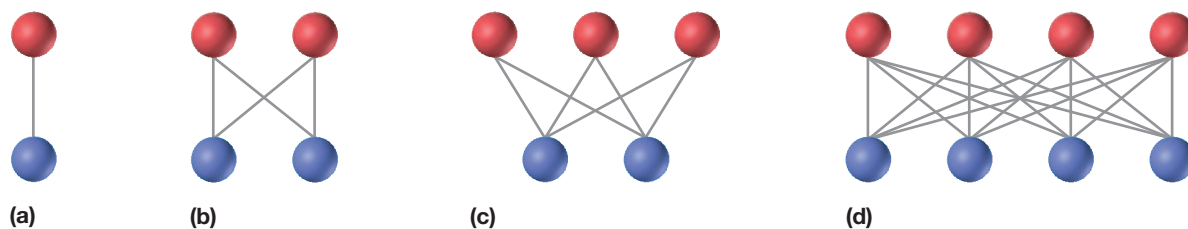
(a) Pure oxygen has five times the concentration of oxygen molecules compared to air, so the charcoal will burn more intensely.



(b) Air contains substances in addition to oxygen, so oxygen molecules have fewer chances to collide with the charcoal to react.

FIGURE 2.2

Collisions and Reaction Rates



Consider the model depicted in **Figure 2.2**. In the system with only two molecules, shown in **Figure 2.2a**, only one collision can possibly occur. When there are four molecules in the system, as in **Figure 2.2b**, there can be four possible collisions. With temperature and pressure under constant conditions, as the number of molecules in the system increases, so does the total number of possible collisions between them. **Figures 2.2c** and **d** show a five- and eight-molecule system, allowing six and sixteen possible collisions, respectively. Lowering the concentration should have the opposite effect. The actual effect of concentration changes on reaction rate, however, must be determined experimentally.

FIGURE 2.3

Reaction Rate and Catalysts

The reaction rate of the decomposition of hydrogen peroxide, H_2O_2 , can be increased by using a catalyst. The catalyst used here is manganese dioxide, MnO_2 , a black solid. A 30% H_2O_2 solution is added dropwise onto the MnO_2 in the beaker and rapidly decomposes to O_2 and H_2O . Both the oxygen and water appear as gases, because the energy released by the reaction causes much of the water to vaporize.

CRITICAL THINKING

Describe Research and describe at least two important chemical reactions in the human body that require catalysts.

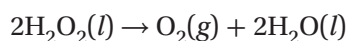


Presence of Catalysts

Some chemical reactions proceed quite slowly. Sometimes their reaction rates can be increased dramatically by the presence of a catalyst.

A catalyst is a substance that changes the rate of a chemical reaction without itself being consumed. The action of a catalyst is called catalysis.

The catalysis of the decomposition reaction of hydrogen peroxide by manganese dioxide is shown in **Figure 2.3**. A catalyst provides a reaction mechanism with an alternate pathway, which has a lower activation energy. Think of it as driving through a tunnel in a mountain, rather than driving up the mountain and down the other side. The catalyst may be effective in forming an alternative activated complex that requires a lower activation energy—as suggested in the energy profiles of the decomposition of hydrogen peroxide, H_2O_2 , shown on the next page in **Figure 2.4**—via the following equation:



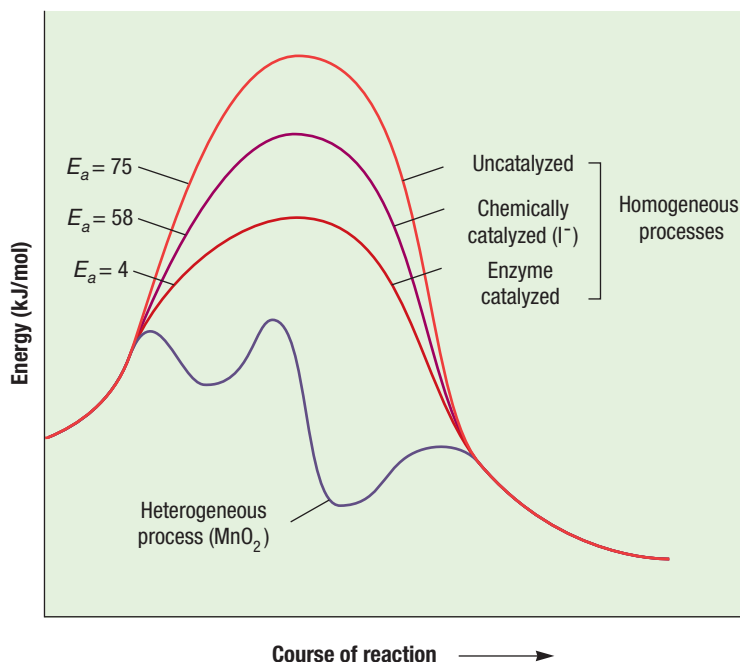
Catalysts do not appear among the final products of reactions they accelerate. They may participate in one step along a reaction pathway and be regenerated in a later step. In large, cost-sensitive reaction systems, catalysts are recovered and reused. **A catalyst that is in the same phase as all the reactants and products in a reaction system is called a homogeneous catalyst. When its phase is different from that of the reactants, it is called a heterogeneous catalyst.** Metals are often used as heterogeneous catalysts. The catalysis of many reactions is promoted by adsorption of reactants on the metal surfaces, which increases the concentration of the reactants. In the chapter “Biochemistry,” you will learn about enzymes, biological catalysts to facilitate chemical reactions in living organisms.

FIGURE 2.4

Reaction Pathways and Catalysts

A catalyst reduces the activation energy for a chemical reaction.

Comparison of Pathways for the Decomposition of H_2O_2 by Various Catalysts

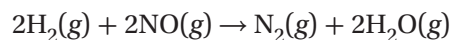


MAIN IDEA

Concentration and reaction rate are related.

The relationship between the rate of a reaction and the concentration of one reactant is determined experimentally by first keeping the concentrations of other reactants and the temperature of the system constant. Then the reaction rate is measured for various concentrations of the reactant in question. A series of such experiments reveals how the concentration of each reactant affects the reaction rate.

Hydrogen gas reacts with nitrogen monoxide gas at constant volume and at an elevated constant temperature, via the following equation.



Four moles of reactant gases produce three moles of product gases; thus, the pressure of the system diminishes as the reaction proceeds. The rate of the reaction can, therefore, be determined by measuring the change of pressure in the vessel with time.

Suppose a series of experiments is conducted using the same initial concentration of nitrogen monoxide but different initial concentrations of hydrogen. The initial reaction rate is found to vary directly with the hydrogen concentration: doubling the concentration of H_2 doubles the rate, tripling the concentration of H_2 triples the rate, and so on.

WHY IT MATTERS

Explosives

S.T.E.M.

In a tiny fraction of a second, the reactions of explosives such as nitroglycerin, trinitrotoluene (TNT), and dynamite are over. These materials are primarily organic substances containing mostly carbon, hydrogen, oxygen, and nitrogen atoms held together by relatively weak bonds. When “set off,” explosive materials experience rapid decomposition. The released elements immediately react to form gaseous N_2 , CO, CO_2 , and NO_2 . The bonds in these small molecules are much stronger than those in the original explosive material, and so an enormous amount of energy is released. In addition, the sudden formation of gaseous material causes a tremendous increase in pressure that provides the force to demolish an unwanted building or break rocks for building roads.

CHECK FOR UNDERSTANDING

Describe The feature on this page, “Why It Matters: Explosives,” describes why TNT and dynamite explosions occur very quickly. Describe a chemical reaction with a very slow reaction rate.

We can represent this proportion mathematically. If R represents the reaction rate and $[H_2]$ is the concentration of hydrogen in moles per liter, the mathematical relationship between rate and concentration can be expressed as follows:

$$R \propto [H_2]$$

The \propto is a symbol that is read “is proportional to.”

Now suppose the same initial concentration of hydrogen is used, but the initial concentration of nitrogen monoxide is varied. The initial reaction rate is found to increase fourfold when the NO concentration is doubled and ninefold when the concentration of NO is tripled. Thus, the reaction rate varies directly with the square of the nitrogen monoxide concentration, as described by the following proportion:

$$R \propto [NO]^2$$

Because R is proportional to $[H_2]$ and to $[NO]^2$, it is proportional to their product:

$$R \propto [H_2][NO]^2$$

By introduction of an appropriate proportionality constant, k , the expression becomes an equality:

$$R = k[H_2][NO]^2$$

An equation that relates reaction rate and concentrations of reactants is called the **rate law for the reaction**. It is applicable for a specific reaction at a given temperature. A rise in temperature increases the reaction rates of reactions, so the value of k usually increases as the temperature increases.

Using the Rate Law

The general form for the rate law is given by the following equation:

$$R = k[A]^n[B]^m$$

The reaction rate is represented by R , k is the specific rate constant, and $[A]$ and $[B]$ represent the molar concentrations of reactants. The respective powers to which the concentrations are raised are represented by n and m . The rate law is applicable for a specific reaction at a given set of conditions and must be determined from experimental data.

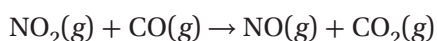
The power to which a reactant concentration is raised is called the **order in that reactant**. The value of n is said to be the order of the reaction with respect to $[A]$, so the reaction is said to be “ n th order in A.” Similarly, for the value of m , the reaction is said to be “ m th order in B.” The orders, or powers, n and m , are usually small integers or zero.

An order of *one* for a reactant means the reaction rate is directly proportional to the concentration of that reactant. An order of *two* means the reaction rate is directly proportional to the *square* of the reactant concentration. An order of *zero* means that the rate does not depend on the concentration of the reactant, *as long as some of the reactant is present*. The sum of all of the reactant orders is called the *order of the reaction*, or *overall order*. The overall order of the reaction is equal to the sum of the reactant orders, or $n + m$. Some examples of observed rate laws are shown below. Some of these reactions involve nitrogen oxides, which are highly reactive gases that contribute to the formation of smog that can blanket an entire city, as shown in **Figure 2.5**.



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

second order in NO,
second order overall



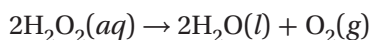
$$R = k[\text{NO}_2]^2$$

second order in NO_2 ,
zero order in CO,
second order overall



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

second order in NO_2 ,
second order overall



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

first order in H_2O_2 ,
first order overall

Important to understand is that orders in the rate law must be determined from experiment and cannot be predicted from the reaction stoichiometry.

Rate Constant

The *rate constant* (k) is the proportionality constant relating the rate of the reaction to the concentrations of reactants. It is important to remember the following about the value of k :

1. Once the reaction orders (powers) are known, the value of k can be determined from experimental data.
2. The value of k is for a *specific reaction*; k has a different value for other reactions, even at the same conditions.
3. The units of k depend on the *overall order of the reaction*.
4. The value of k *does not change* for different concentrations of reactants or products. So the value of k for a reaction remains the same throughout the reaction and does not change with time.
5. The value of k is for the reaction *at a specific temperature*; if we increase the temperature of the reaction, the value of k increases.
6. The value of k changes (becomes larger) if a *catalyst* is present.

FIGURE 2.5

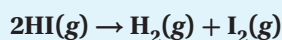
Smog A cloud of polluted air, commonly known as smog, settles over a city. Smog is common in industrialized areas, where highly reactive gases and particulate matter are released into the air. The rate of the reaction that produces smog is determined by the amount of sunlight present.





Determining Rate Law and Rate Constant

Sample Problem B Three experiments that have identical conditions were performed to measure the initial rate of the reaction



The results for the three experiments in which only the HI concentration was varied are as follows:

Experiment	[HI] (M)	Rate (M/s)
1	0.015	1.1×10^{-3}
2	0.030	4.4×10^{-3}
3	0.045	9.9×10^{-3}

Write the rate law for the reaction. Find the value and units of the specific rate constant, k .

1 ANALYZE

The general rate law for this reaction has the form $R = k[\text{HI}]^n$. We need to deduce the value of the power n .

2 PLAN

Find the ratio of the reactant concentrations between two experiments, such as 1 and 2, $\frac{[\text{HI}]_2}{[\text{HI}]_1}$. Then, see how the ratio of concentration affects the ratio of rates, $\frac{R_2}{R_1}$.

3 SOLVE

Concentration ratio: $\frac{[\text{HI}]_2}{[\text{HI}]_1} = \frac{0.030 \text{ M}}{0.015 \text{ M}} = 2.0$; rate ratio: $\frac{R_2}{R_1} = \frac{4.4 \times 10^{-3} \text{ M/s}}{1.1 \times 10^{-3} \text{ M/s}} = 4.0$

Thus, when the concentration changes by a factor of 2, the rate changes by a factor of 4, or 2^2 , so the rate law is $R = k[\text{HI}]^2$.

To find the value of k , we can rearrange the rate law and substitute known values for any one experiment. Do the following for Experiment 1:

$$k = \frac{R}{[\text{HI}]^2} = \frac{1.1 \times 10^{-3} \text{ M/s}}{(0.015 \text{ M})^2} = 4.9 \text{ M}^{-1}\text{s}^{-1}$$

4 CHECK YOUR WORK

By comparing items 1 and 3 in the table, we see that when [HI] is tripled, the rate changes by a factor of 9, or 3^2 . This rate change confirms that the order is 2. The same value of k can be calculated from any other experiment. Thus, the rate law and k are correct.

Practice

Answers in Appendix E

- For the reaction $3\text{A} \rightarrow \text{C}$, the initial concentration of A was 0.2 M, and the reaction rate was 1.0 M/s. When [A] was doubled, the reaction rate increased to 4.0 M/s. Determine the rate law for the reaction.
- The rate law for a reaction is found to be $\text{rate} = k[\text{X}]^3$. By what factor does the rate increase if [X] is tripled?



Determining Rate Law and Rate Constant

Sample Problem C Three experiments were performed to measure the initial rate of the reaction



Conditions were identical in the three experiments except that the concentrations of reactants varied. The results are as follows:

Experiment	[A] (M)	[B] (M)	Rate (M/s)
1	2.4	4.8	6.0×10^{-9}
2	2.4	2.4	3.0×10^{-9}
3	7.2	4.8	5.4×10^{-8}

Write the rate law for the reaction. Find the value and units of the specific rate constant, k .

1 ANALYZE

The general rate law for this reaction has the form $R = k[A]^n[B]^m$. We need to calculate the values of the powers n and m .

2 PLAN

Find the ratio of the reactant concentrations between two experiments that have the same [A] but different [B]. Then, see how this ratio affects the ratio of rates, $\frac{R_2}{R_1}$; this ratio of rates lets us find the value of m . A similar approach of comparing two experiments that have the same [B] but a different [A] lets us find the value of n .

3 SOLVE

First compare Experiments 1 and 2, which have the same [A], to find m :

$$\text{Concentration ratio: } \frac{[B]_1}{[B]_2} = \frac{4.8 \text{ M}}{2.4 \text{ M}} = 2.0; \text{ rate ratio: } \frac{R_1}{R_2} = \frac{6.0 \times 10^{-9} \text{ M/s}}{3.0 \times 10^{-9} \text{ M/s}} = 2.0$$

Thus, when the concentration of B changes by a factor of 2, the rate changes by a factor of 2, or 2^1 . So m is 1, and the reaction is first order in B.

Then, compare Experiments 1 and 3, which have the same [B], to find n :

$$\text{Concentration ratio: } \frac{[A]_3}{[A]_1} = \frac{7.2 \text{ M}}{2.4 \text{ M}} = 3.0; \text{ rate ratio: } \frac{R_3}{R_1} = \frac{5.4 \times 10^{-8} \text{ M/s}}{6.0 \times 10^{-9} \text{ M/s}} = 9.0$$

Thus, when the concentration of A changes by a factor of 3, the rate changes by a factor of 9, or 3^2 . So n is 2, and the reaction is second order in A.

The rate law is $R = k[A]^2[B]$.

To find the value of k , we can rearrange the rate law and substitute known values for any one experiment. Do the following for Experiment 1:

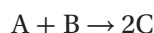
$$k = \frac{R}{[A]^2[B]} = \frac{6.0 \times 10^{-9} \text{ M/s}}{(2.4 \text{ M})^2(4.8 \text{ M})} = 2.2 \times 10^{-10} \text{ M}^{-2}\text{s}^{-1}$$

4 CHECK YOUR WORK

The same value of k can be calculated from the data for any other experiment. So the rate law and the calculation of k are correct.

Rate Laws and Reaction Pathway

The rate law depends on the reaction mechanism. For a reaction that occurs in a *single step*, the reaction rate of that step is proportional to the product of the reactant concentrations, each of which is raised to its stoichiometric coefficient. For example, suppose one molecule of gas A collides with one molecule of gas B to form two molecules of substance C, according to the following equation:



One particle of each reactant is involved in each collision. Thus, doubling the concentration of either reactant will double the collision frequency. It will also double the reaction rate *for this step*. Therefore, the rate for this step is directly proportional to the concentration of A and B. The rate law for this one-step forward reaction follows:

$$R_{\text{forward}} = k_{\text{forward}}[A][B]$$

Now suppose the reaction is reversible. In the reverse step, two molecules of C must decompose to form one molecule of A and one of B, or $2C \rightarrow A + B$.

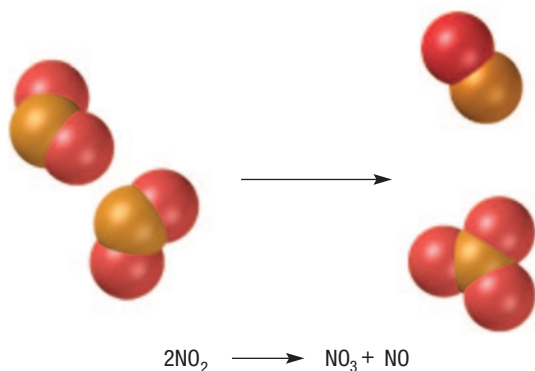
Thus, the reaction rate for this reverse step is directly proportional to $[C] \times [C]$. The rate law for the reverse step is $R_{\text{reverse}} = k_{\text{reverse}}[C]^2$.

The power to which the molar concentration of each reactant is raised in the rate laws above corresponds to the coefficient for the reactant in the balanced chemical equation. Such a relationship holds *only* if the reaction follows a simple one-step path, that is, if the reaction occurs at the molecular level exactly as written in the chemical equation.

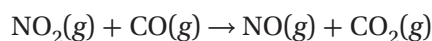
If a chemical reaction proceeds in a sequence of steps, the rate law is determined from the slowest step because it has the lowest rate. **This slowest-rate step is called the rate-determining step for the chemical reaction.**

FIGURE 2.6

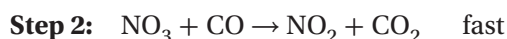
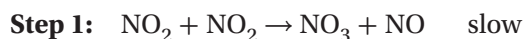
Formation of Intermediate Species This diagram is a representation of Step 1 in the reaction of nitrogen dioxide and carbon monoxide. Notice the formation of the intermediate species NO_3 after two molecules of NO_2 collide.



Consider the reaction of nitrogen dioxide and carbon monoxide.



The reaction is believed to be a two-step process represented by the following mechanism:



In the first step, shown in **Figure 2.6**, two molecules of NO_2 collide, forming the intermediate species NO_3 . This molecule then collides with one molecule of CO and reacts quickly to produce one molecule each of NO_2 and CO_2 . The first step is the slower of the two and is therefore the rate-determining step. We can write the rate law from this rate-determining step, which has two molecules of NO_2 as the reactants.

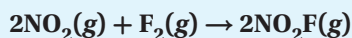
$$R = k[\text{NO}_2]^2$$

The rate law does not include $[\text{CO}]$, because CO reacts after the rate-determining step and its concentration does not affect the rate.



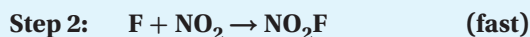
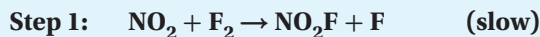
Determining Rate-Determining Step and Law and Rate Constant

Sample Problem D Nitrogen dioxide and fluorine react in the gas phase according to the following equation.



The rate law is $k[\text{NO}_2][\text{F}_2]$.

A proposed mechanism for this reaction follows.



Identify the rate-determining step.

SOLVE

If we combine these two steps, the intermediate, F, cancels out, and we are left with the original equation. Since the rate law is first order in both NO and F₂, they react in the slower rate-determining step. Thus, **Step 1 is the rate-determining step.**

Determining Effects on Reaction Rate

Sample Problem E A reaction involving reactants X and Y was found to occur by a one-step mechanism: $\text{X} + 2\text{Y} \rightarrow \text{XY}_2$. Write the rate law for this reaction, and then determine the effect of each of the following on the reaction rate:

- doubling the concentration of X
- doubling the concentration of Y
- using one-third the concentration of Y

SOLVE

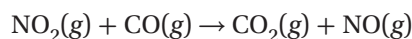
Because the equation represents a single-step mechanism, the rate law can be written from the equation (otherwise, it could not be). The rate will vary directly with the concentration of X, which has an implied coefficient of 1 in the equation. And the rate will vary directly with the square of the concentration of Y, which has the coefficient of 2: $R = k[\text{X}][\text{Y}]^2$.

- Doubling the concentration of X will double the rate ($R = k[2\text{X}][\text{Y}]^2$).
- Doubling the concentration of Y will increase the rate fourfold ($R = k[\text{X}][2\text{Y}]^2$).
- Using one-third the concentration of Y will reduce the rate to one-ninth of its original value ($R = k[\text{X}][\frac{1}{3}\text{Y}]^2$).

Practice

Answers in Appendix E

- The rate of a hypothetical reaction involving L and M is found to double when the concentration of L is doubled and to increase fourfold when the concentration of M is doubled. Write the rate law for this reaction.
- At temperatures below 498 K, the following reaction takes place.



Doubling the concentration of NO₂ quadruples the rate of CO₂ formed if the CO concentration is held constant. However, doubling the concentration of CO has no effect on the rate of CO₂ formation. Write a rate-law expression for this reaction.

QUESTION

How do the type of reactants, surface area of reactants, concentration of reactants, and catalysts affect the rates of chemical reactions?

PROCEDURE

Remove all combustible material from the work area. Wear safety goggles and an apron. Record all your results in a data table.

1. Add 10 mL of vinegar to each of three test tubes. To one test tube, add a 3 cm piece of magnesium ribbon; to a second, add a 3 cm zinc strip; and to a third, add a 3 cm copper strip. (All metals should be the same width.) If necessary, polish the metals with sandpaper until they are shiny.
2. Using tongs, hold a paper clip in the hottest part of the burner flame for 30 s. Repeat with a ball of steel wool 2 cm in diameter.

3. To one test tube, add 10 mL of vinegar; to a second, add 5 mL of vinegar plus 5 mL of water; and to a third, add 2.5 mL of vinegar plus 7.5 mL of water. To each of the three test tubes, add a 3 cm piece of magnesium ribbon.

4. Using tongs, hold a sugar cube and try to ignite it with a match. Then try to ignite it in a burner flame. Rub paper ash on a second cube, and try to ignite it with a match.

DISCUSSION

1. What are the rate-influencing factors in each step of the procedure?
2. What were the results from each step of the procedure? How do you interpret each result?

MATERIALS

- Bunsen burner
- paper ash
- copper foil strip
- graduated cylinder, 10 mL
- magnesium ribbon
- matches
- paper clip
- sandpaper
- steel wool
- 2 sugar cubes
- white vinegar
- zinc strip
- 6 test tubes, 16 × 150 mm
- tongs

SAFETY

Wear safety goggles and an apron.

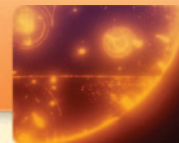
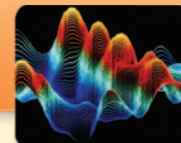
**SECTION 2 FORMATIVE ASSESSMENT****▶ Reviewing Main Ideas**

1. What is studied in the branch of chemistry that is known as chemical kinetics?
2. List five important factors that influence the rate of chemical reactions.
3. What is a catalyst? Explain the effect of a catalyst on the rate of chemical reactions. How does a catalyst influence the activation energy required by a particular reaction?

4. What is meant by a rate law for a chemical reaction?

✓ Critical Thinking

5. **RELATING IDEAS** Using the ideas of reaction kinetics, explain the purpose of food refrigeration.



New Generation Catalysts

S.T.E.M.

To see an important example of *heterogeneous catalysis*, you do not need to look any farther than the streets near your home. The *catalytic converter*, an important part of a vehicle's exhaust system, uses metal catalysts to reduce harmful gaseous pollutants.

In an automobile engine, hydrocarbon molecules in gasoline or diesel fuel undergo a combustion reaction with oxygen from air to make carbon dioxide, CO_2 , and water. The correct stoichiometric ratio of fuel to oxygen is required for the fuel to be completely burned in the reaction. Additional reaction products are formed when not enough oxygen or excess oxygen is present. These products include carbon monoxide, CO , and NO_x compounds, such as nitric oxide, NO , and nitrogen dioxide, NO_2 . There is also leftover unburned fuel, which is called a volatile organic compound (VOC).

The Clean Air Act, last amended in 1990, regulates automobile emissions of CO , NO_x , and VOCs. In addition to being harmful themselves, NO_x compounds, CO , and VOCs react with sunlight to make ozone, O_3 . In the lower atmosphere, ozone is a major part of photochemical smog. NO_x gases can also mix with rainwater to produce acid rain.

Catalytic converters use precious-metal catalysts to change the gases coming from the engine into less-harmful gases. A combination of rhodium and platinum, and sometimes palladium, is used to convert nitrogen compounds back into N_2 and O_2 . This combination also converts CO into CO_2 and converts VOCs into CO_2 and water. The catalysts need O_2 from the air and temperatures above approximately 500°F to work properly. The temperatures are achieved from the normal operation of the car engine.

Up to 90% of CO , NO_x , and VOCs are typically eliminated from automobile exhaust by a catalytic converter. Although catalytic converters are beneficial to our environment, they could still be improved. To this end, researchers at the Department of Energy's Oak Ridge National Laboratory (ORNL) in Tennessee are developing a new generation of catalysts to remove pollutants from engine exhausts. In particular, they are working on the problem of inhibition in catalytic converters. This happens when pollutant molecules

occupy too many of the active sites on catalytic surfaces, which has the effect of clogging the converter. A combination of copper, cobalt, and cerium oxides shows promise in solving this problem.

Another problem ORNL is working on is low-temperature exhaust gases. The improved efficiency of newer engines has reduced the waste heat lost through the exhaust system. The problem is that catalysts currently in use operate better at high temperature. The mixed metal oxide catalyst described above may hold promise for working at lower temperatures.

ORNL is also working on an improved catalyst to speed up the synthesis of nylon, an important polymer used for cloth, cookware, machinery, and electronics. Researchers have discovered that a catalyst made of a mixture of manganese and cerium oxides is very selective for carbon-hydrogen bonds. These bonds must be broken to take cyclohexane to the next step in the synthesis of nylon. In addition to being selective, the catalyst is very porous. This gives it a large surface area, which speeds up the process, resulting in more nylon being made in less time.

Questions

1. Catalysts lower the activation energy of chemical reactions. How does this benefit the environment?
2. Chlorine free radicals are produced in the upper atmosphere when ultraviolet radiation interacts with chlorofluorocarbons (CFCs). The free radicals catalyze the conversion of ozone to oxygen. How is this catalysis harmful to humans?



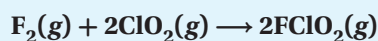
Scientist Sheng Dai at the Department of Energy's Oak Ridge National Laboratory

Factors such as surface area and temperature affect the rate of reactions because they affect the frequency and energy of collisions between particles. The concentrations of reactants can also affect the frequency of collisions. If other factors are

kept constant, the rates of most chemical reactions will be determined by the concentrations of reactants. Thus, it is possible to write an equation called a *rate law* that relates the rate of a reaction to the concentrations of reactants.

Sample Problem

Fluorine gas reacts with chlorine dioxide according to the following equation.



Use the following experimental data to write a rate law for this reaction.

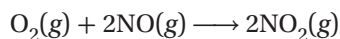
TRIAL	CONCENTRATION OF F_2	CONCENTRATION OF ClO_2	RATE (MOL/L•S)
1	0.10 M	0.10 M	1.1×10^{-3}
2	0.20 M	0.10 M	2.2×10^{-3}
3	0.10 M	0.20 M	2.2×10^{-3}
4	0.20 M	0.20 M	4.4×10^{-3}

To write the rate law, first examine the data to see how the rate of reaction changes as the concentrations of the reactants change.

- When $[\text{F}_2]$ doubles and $[\text{ClO}_2]$ remains constant, the rate of reaction doubles from 1.1×10^{-3} mol/L•s to 2.2×10^{-3} mol/L•s. So the rate is directly proportional to $[\text{F}_2]$, or $R \propto [\text{F}_2]$.
- When $[\text{ClO}_2]$ doubles and $[\text{F}_2]$ remains constant, the rate of reaction also doubles from 1.1×10^{-3} mol/L•s to 2.2×10^{-3} mol/L•s. So the rate is directly proportional to $[\text{ClO}_2]$, or $R \propto [\text{ClO}_2]$.
- Because rate is proportional to both $[\text{F}_2]$ and $[\text{ClO}_2]$, you can write the rate law $R = k[\text{F}_2][\text{ClO}_2]$. The data from Trial 4 help confirm the rate law, because when both $[\text{F}_2]$ and $[\text{ClO}_2]$ double, the rate increases by a factor of four, from 1.1×10^{-3} mol/L•s to 4.4×10^{-3} mol/L•s.

Practice

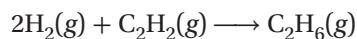
1. Nitrogen monoxide and oxygen react to produce nitrogen dioxide according to the following equation:



Use the data in the following table to write a rate law for this reaction.

TRIAL	$[\text{O}_2]$	$[\text{NO}]$	REACTION RATE (MOL/L•S)
1	1.20×10^{-2} M	1.40×10^{-2} M	3.30×10^{-3}
2	2.40×10^{-2} M	1.40×10^{-2} M	6.60×10^{-3}
3	1.20×10^{-2} M	2.80×10^{-2} M	1.32×10^{-2}

2. Hydrogen reacts with ethyne, C_2H_2 , to produce ethane, C_2H_6 , as shown below:



Use the data in the following table to write a rate law for this reaction.

TRIAL	$[\text{H}_2]$	$[\text{C}_2\text{H}_2]$	REACTION RATE (MOL/L•MIN)
1	0.20 M	0.20 M	1.5×10^{-4}
2	0.40 M	0.20 M	3.0×10^{-4}
3	0.20 M	0.40 M	1.5×10^{-4}

CHAPTER 17 Summary

BIG IDEA For chemical reactions to occur, the particles of the reactants must collide with sufficient kinetic energy and in the proper orientation.

SECTION 1 The Reaction Process

- The step-by-step process by which an overall chemical reaction occurs is called the *reaction mechanism*.
- In order for chemical reactions to occur, the particles of the reactants must collide.
- Activation energy is needed to merge valence electrons and to loosen bonds sufficiently for molecules to react.
- An activated complex is formed when an effective collision between molecules of reactants raises the internal energy to the minimum level necessary for a reaction to occur.

KEY TERMS

reaction mechanism
intermediate
homogeneous reaction
collision theory
activation energy
activated complex

SECTION 2 Reaction Rate

- The rate of reaction is influenced by the following factors: nature of reactants, surface area, temperature, concentration of reactants, and the presence of catalysts.
- The rates at which chemical reactions occur can sometimes be experimentally measured and expressed in terms of mathematical equations called *rate laws*.
- Rate laws are determined by studying how reaction rate depends on concentration.

KEY TERMS

reaction rate
chemical kinetics
heterogeneous reaction
catalyst
catalysis
homogeneous catalyst
heterogeneous catalyst
rate law
order
rate-determining step

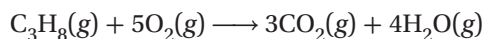


SECTION 1

The Reaction Process

REVIEWING MAIN IDEAS

- What is the collision theory?
 - According to this theory, what two conditions must be met for a collision between reactant molecules to be effective in producing new chemical species?
- What condition must be met for an activated complex to result from the collision of reactant particles?
 - Where, in terms of energy, does the activated complex occur along a typical reaction pathway?
- In a reversible reaction, how does the activation energy required for the exothermic change compare with the activation energy required for the endothermic change?
- Would you expect the following equation to represent the mechanism by which propane, C_3H_8 , burns? Why or why not?

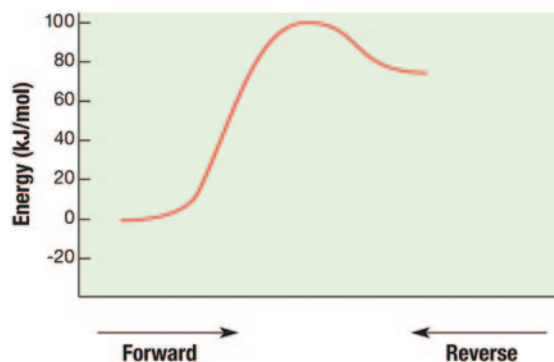


- The decomposition of nitrogen dioxide, $2NO_2 \longrightarrow 2NO + O_2$, occurs in a two-step sequence at elevated temperatures. The first step is $NO_2 \longrightarrow NO + O$. Predict a possible second step that, when combined with the first step, gives the complete reaction.

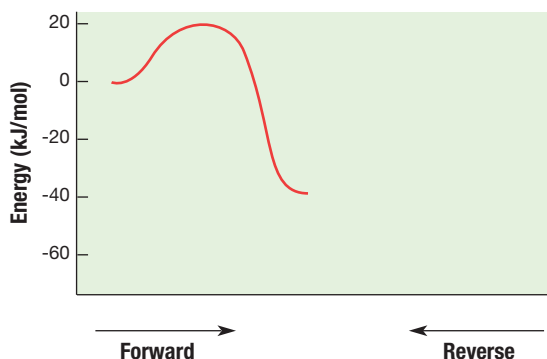
PRACTICE PROBLEMS

- For each of the energy diagrams provided below, label the reactants, products, ΔE , E_a , and E_a' . Also determine the values of ΔE for the forward and reverse reactions, and determine the values of E_a and E_a' . (Hint: See Sample Problem A.)

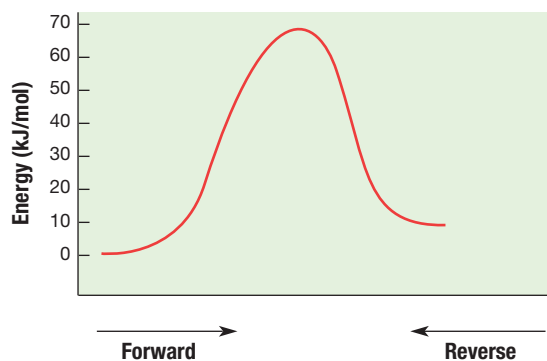
(a)



(b)



(c)



7. Draw and label energy diagrams that depict the following reactions, and determine all remaining values. Place the reactants at energy level zero.
- $\Delta E_{\text{forward}} = -10 \text{ kJ/mol}$, $E_a' = 40 \text{ kJ/mol}$
 - $\Delta E_{\text{forward}} = -95 \text{ kJ/mol}$, $E_a = 20 \text{ kJ/mol}$
 - $\Delta E_{\text{reverse}} = -40 \text{ kJ/mol}$, $E_a' = 30 \text{ kJ/mol}$

SECTION 2

Reaction Rate

REVIEWING MAIN IDEAS

- Define the rate-determining step for a chemical reaction.
- Write the general equation for the rate law, and label the various factors.

PRACTICE PROBLEMS

- Determine the overall balanced equation for a reaction that has the following proposed mechanism, and write an acceptable rate law. (Hint: See Sample Problem C.)
Step 1: $\text{B}_2 + \text{B}_2 \longrightarrow \text{E}_3 + \text{D}$ slow
Step 2: $\text{E}_3 + \text{A} \longrightarrow \text{B}_2 + \text{C}_2$ fast
 - Give the order of the reaction with respect to each reactant.
 - What is the overall order of the reaction?
- A reaction that involves reactants A and B is found to occur in the one-step mechanism $2\text{A} + \text{B} \longrightarrow \text{A}_2\text{B}$. Write the rate law for this reaction, and predict the effect of doubling the concentration of either reactant on the overall reaction rate. (Hint: See Sample Problem C.)
- A chemical reaction is expressed by the balanced chemical equation $\text{A} + 2\text{B} \longrightarrow \text{C}$. Three reaction-rate experiments yield the following data.

Experiment number	Initial [A]	Initial [B]	Initial rate of formation of C
1	0.20 M	0.20 M	$2.0 \times 10^{-4} \text{ M/min}$
2	0.20 M	0.40 M	$8.0 \times 10^{-4} \text{ M/min}$
3	0.40 M	0.40 M	$1.6 \times 10^{-3} \text{ M/min}$

- Determine the rate law for the reaction.
- Calculate the value of the specific rate constant.
- If the initial concentrations of both A and B are 0.30 M, at what initial rate is C formed?
- What is the order of the reaction with respect to A?
- What is the order of the reaction with respect to B?

Mixed Review

REVIEWING MAIN IDEAS

- Draw and label energy diagrams that depict the following reactions, and determine all remaining values. Place the reactants at energy level zero.
 - $\Delta E = +30 \text{ kJ/mol}$ $E_a' = 20 \text{ kJ/mol}$
 - $\Delta E = -30 \text{ kJ/mol}$ $E_a = 20 \text{ kJ/mol}$
- A particular reaction is found to have the following rate law:

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

How is the rate affected by each of the following changes?

- The initial concentration of A is cut in half.
 - The initial concentration of B is tripled.
 - The concentration of A is doubled, but the concentration of B is cut in half.
 - A catalyst is added.
- For each of the following pairs, choose the substance or process that you would expect to react more rapidly.
 - granulated sugar or powdered sugar
 - zinc in HCl at 298.15 K or zinc in HCl at 320 K
 - 5 g of thick platinum wire or 5 g of thin platinum wire
 - The following data relate to the reaction $\text{A} + \text{B} \longrightarrow \text{C}$. Find the order with respect to each reactant.

[A] (M)	[B] (M)	Rate (M/s)
0.08	0.06	0.012
0.08	0.03	0.006
0.04	0.06	0.003

CRITICAL THINKING

- 17. Predicting Outcomes** The balanced equation for a rapid homogeneous reaction between two gases is as follows: $4A + B \longrightarrow 2C + 2D$. Because the simultaneous collision of four molecules of one reactant with one molecule of the other reactant is extremely improbable, what would you predict about the nature of the reaction mechanism for this reaction system?
- 18. Evaluating Ideas**
- How can you justify calling the reaction pathway that is shown in **Figure 1.4** the minimum-energy pathway for reaction?
 - What significance is associated with the maximum-energy region of this minimum-energy pathway?
- 19. Applying Models** Explain why there is a danger of explosion in places such as coal mines, sawmills, and grain elevators, where large amounts of dry, powdered combustible materials are present.
- 20. Evaluating Methods** What property would you measure to determine the reaction rate for the following reaction? Justify your choice.

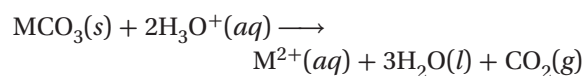


RESEARCH AND WRITING

- 21.** Look for situations around your house in which processes are speeded up by an increase in temperature or slowed down by a decrease in temperature. Make a list, and discuss the different processes.

ALTERNATIVE ASSESSMENT

- 22.** 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.



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.

Standards-Based Assessment

Record your answers on a separate piece of paper.

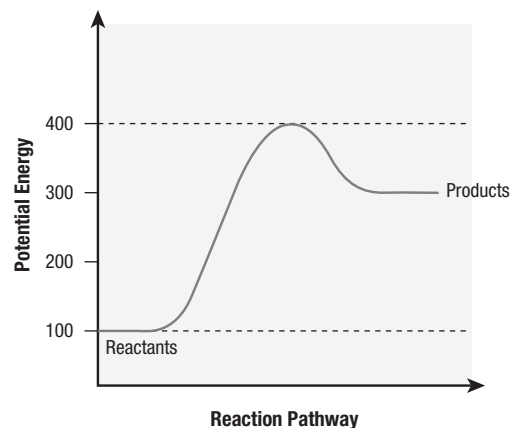
MULTIPLE CHOICE

- A transition structure that results from an effective energetic collision between reactants is the —
 - order of the reaction
 - rate law
 - overall reaction
 - activated complex
- How does the potential energy of the activated complex compare with the energies of the reactants and products?
 - It is less than both the energy of the reactants and the energy of the products.
 - It is less than the energy of the reactants but greater than the energy of the products.
 - It is greater than the energy of the reactants but less than the energy of the products.
 - It is greater than both the energy of the reactants and the energy of the products.
- If a collision between molecules is very gentle, the molecules are —
 - more likely to be oriented favorably
 - less likely to be oriented favorably
 - likely to react
 - likely to rebound without reacting
- Which of the explanations below describes why catalysts can increase reaction rates?
 - Adding a catalyst adds more molecules.
 - Adding a catalyst adds heat to the reaction.
 - Adding a catalyst adds electricity to the reaction.
 - Adding a catalyst provides an alternate reaction mechanism having a lower potential-energy barrier between reactants and products.

- A rate law relates —
 - reaction rate and temperature
 - reaction rate and concentration
 - temperature and concentration
 - energy and concentration
- In a graph of how energy changes with reaction progress, the activated complex appears at the —
 - left end of the curve
 - right end of the curve
 - bottom of the curve
 - peak of the curve
- A certain reaction is zero order in reactant A and second order in reactant B. What happens to the reaction rate when the concentrations of both reactants are doubled?
 - The reaction rate remains the same.
 - The reaction rate increases by a factor of two.
 - The reaction rate increases by a factor of four.
 - The reaction rate increases by a factor of eight.

GRIDDED RESPONSE

- Using the graph below, determine the value of ΔE for the reaction pathway shown.



Test Tip

If you are permitted to, draw a line through each incorrect answer choice as you eliminate it.