



CHAPTER 14

THE PROCESS OF CHEMICAL REACTIONS

Have you ever considered becoming a chemical engineer? The men and women in this profession develop industrial processes for the large-scale production of the chemicals we use to fertilize and protect our crops; synthesize textiles, plastics, and other ubiquitous modern materials; cure our diseases; and so much more. Or, perhaps you have considered becoming a research chemist, who figures out new ways to make existing chemicals and ways to produce chemicals that have never existed before. Although these two careers require different sets of skills and aptitudes, they also have some concerns and traits in common. For example, both kinds of chemist need to understand the factors that affect the speed with which chemicals can be made, and to know the reasons why chemical changes do not always proceed to 100% products. Armed with this knowledge, chemical engineers and research chemists can develop ways to make chemical products more efficiently, more safely, and more economically.

This chapter introduces a model for visualizing the changes that take place in a reaction mixture as a chemical reaction proceeds. The model describes the requirements that must be met before a reaction can occur, and explains why certain factors speed the reaction up or slow it down. It will help us understand why some chemical reactions are significantly reversible and why such reactions reach a dynamic equilibrium with equal rates of change in both directions. It will also allow us to explore the factors that can push a chemical equilibrium forward to create more desired products or backwards to minimize the formation of unwanted products.



Research chemists want to know how they can produce chemicals of the highest purity in the shortest time.

- 14.1 Collision Theory: A Model for the Reaction Process
- 14.2 Rates of Chemical Reactions
- 14.3 Reversible Reactions and Chemical Equilibrium
- 14.4 Disruption of Equilibrium

Review Skills

The presentation of information in this chapter assumes that you can already perform the tasks listed below. You can test your readiness to proceed by answering the Review Questions at the end of the chapter. This might also be a good time to read the Chapter Objectives, which precede the Review Questions.

- Describe the particle nature of gases. (Section 3.1)
- Write or recognize the definitions of energy, kinetic energy, potential energy, heat, radiant energy, exergonic, exothermic, endergonic, endothermic, and catalyst. (Chapters 4 and 7 Glossaries.)
- Describe the relationship between average internal kinetic energy and temperature (Section 4.1)
- Describe the relationship between stability and potential energy. (Section 4.1)
- Explain why energy is required to break chemical bonds. (Section 4.1)
- Explain why energy is released when chemical bonds are formed. (Section 4.1)
- Explain why some chemical reactions release heat to their surroundings. (Section 7.4)
- Explain why some chemical reactions absorb heat from their surroundings. (Section 7.4)
- Write a general description of dynamic equilibrium. (Section 12.1)

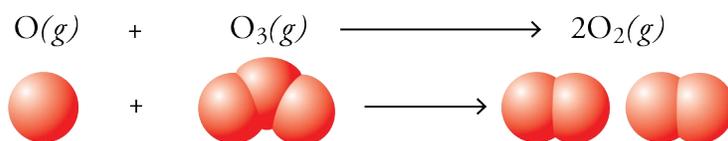
14.1 Collision Theory: A Model for the Reaction Process

Gasoline and oxygen coexist quietly until a spark from a spark plug propels them into violent reaction. Why? Why are ozone molecules in the stratosphere destroyed more rapidly in the presence of chlorine atoms released from CFC molecules? In order to understand these situations, we need to take a look at a model called **collision theory**, which is useful for visualizing the process of chemical change.

The Basics of Collision Theory

OBJECTIVE 2

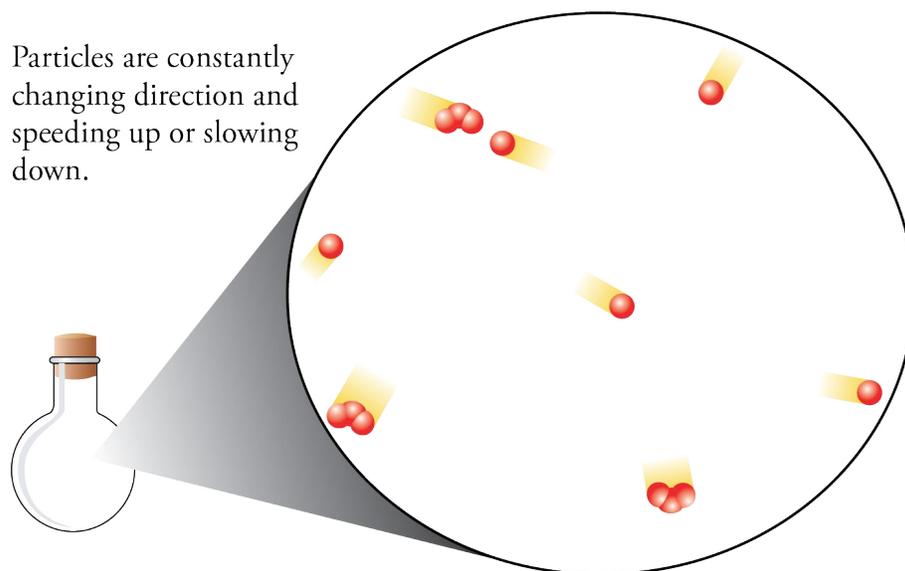
We will demonstrate the basic assumptions of collision theory by using it to describe the reaction of an oxygen atom and an ozone molecule to form two oxygen molecules.



Try to picture oxygen atoms and ozone molecules moving in a random way in the stratosphere. Some of the particles are moving with a high velocity and some are moving more slowly. The particles are constantly colliding, changing their direction of motion, and speeding up or slowing down (Figure 14.1). Some of the collisions between oxygen atoms and ozone molecules lead to the production of two oxygen molecules, but some of the collisions do not. To understand why some collisions are productive and others are not, we need to take a closer look at the events that take place in the reaction process.

Figure 14.1

Ozone Molecules, O_3 , and Oxygen Atoms, O



Particles are constantly changing direction and speeding up or slowing down.

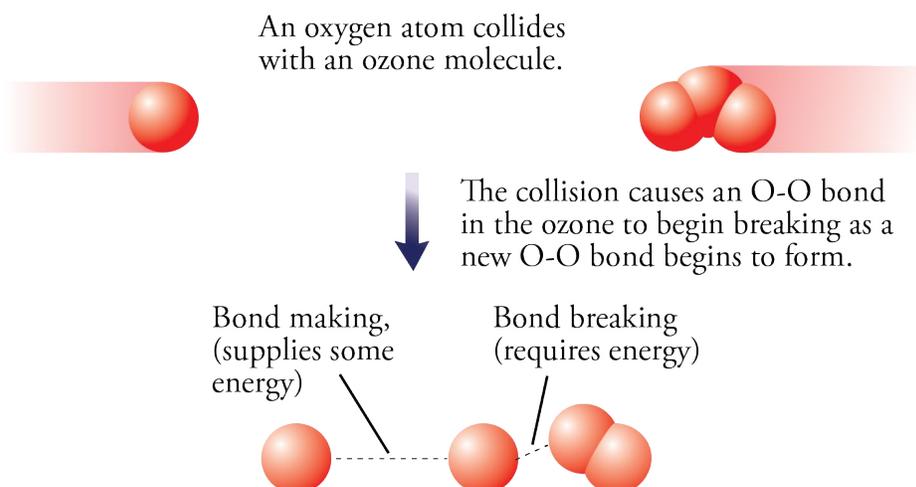
OBJECTIVE 2

OBJECTIVE 3

Step 1 Reactants collide: The process begins with a violent collision between an O atom and an O_3 molecule, which shakes them up and provides them with enough energy for the bond between two oxygen atoms in O_3 to begin to break. We saw in Section 4.1 that energy is required to break chemical bonds. At the same time as one $\text{O}-\text{O}$ bond is breaking, another $\text{O}-\text{O}$ bond begins to form between the original single oxygen atom and the oxygen atom breaking away from the O_3 molecule. We know from

Chapter 4 that bond making releases energy, which in this case can supply some of the energy necessary for the bond breaking. Initially, the bond breaking predominates over the bond making, so the energy released in bond making is not enough to compensate for the energy necessary for bond breaking. The extra energy necessary for the reaction comes from the kinetic energy of the moving particles as they collide (Figure 14.2).

OBJECTIVE 4



OBJECTIVE 2

OBJECTIVE 3

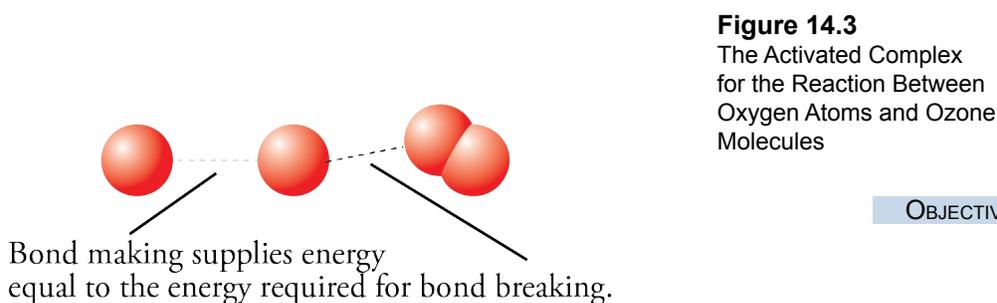
Figure 14.2

Initial Stage of a Reaction Between Two Particles

Initially, the energy required for bond breaking is greater than the energy supplied by bond making. The extra energy necessary for the reaction comes from the kinetic energy of the moving particles as they collide.

Step 2 Formation of activated complex: As the oxygen atoms of the O-O bond in the O₃ molecule separate, the attraction between them decreases, and as the attraction decreases, less energy is needed for moving the atoms even farther apart. Meanwhile, the oxygen atoms that are forming the new bond move closer together, attracting each other more strongly and releasing more energy. At a certain stage in the progress of the reaction, bond breaking and bond making are of equal importance. In other words, the energy necessary for bond breaking is balanced by the energy supplied by bond making. At this turning point, the particles involved in the reaction are joined in a structure known as the *activated complex*, or *transition state*, which is the least stable (and therefore the highest energy) intermediate in the most efficient pathway between reactants and products. In the activated complex for our reaction between an oxygen atom and an ozone molecule, the bond being broken and the bond forming have roughly equal strengths and lengths (Figure 14.3).

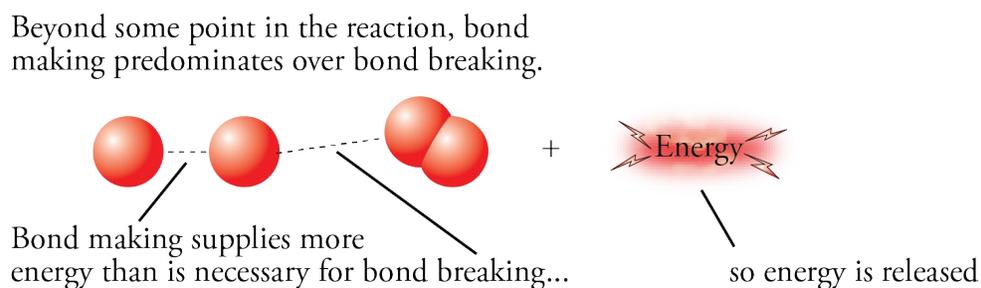
OBJECTIVE 2



OBJECTIVE 2

Step 3 Formation of product: As the reaction continues beyond the activated complex, the energy released in bond making becomes greater than the energy necessary for bond breaking, and energy is released (Figure 14.4).

Figure 14.4
Final Stage of a Reaction
Between Two Particles



OBJECTIVE 6

Thus, as the reaction begins, an input of energy is necessary to produce the activated complex; as the reaction proceeds, and the system shifts from the activated complex to products, energy is released. In a chemical reaction, the minimum energy necessary for reaching the activated complex and proceeding to products is called the **activation energy**. Only the collisions that provide a net kinetic energy equal to or greater than the activation energy can lead to products.

Remember that at any instant in time, the particles in a gas, liquid, or solid have a wide range of velocities and thus a wide range of kinetic energies. If you were riding on a particle—in a gas, for example—you would be constantly colliding with other particles, speeding up or slowing down, and increasing or decreasing your kinetic energy. Sometimes you collide with a slow moving particle while moving slowly yourself. This collision is not too jarring. It has a low net kinetic energy. Sometimes you collide with a fast moving particle while moving rapidly yourself. This collision is much more violent and has a much higher net kinetic energy.

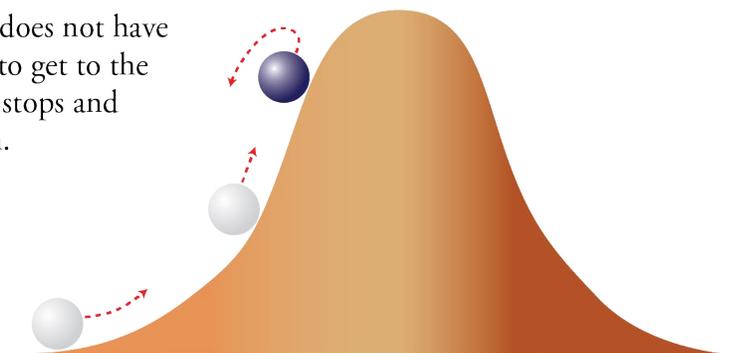
OBJECTIVE 6

If a collision does not provide enough kinetic energy to form an activated complex, the reaction does not proceed to products. Instead, the atoms in the bond that has begun to break pull back together, the atoms in the bond that has begun to form fall apart, and the particles accelerate apart unchanged. This is like the situation depicted in Figure 14.5, where a rolling ball rolls back down the same side of a hill it started up.

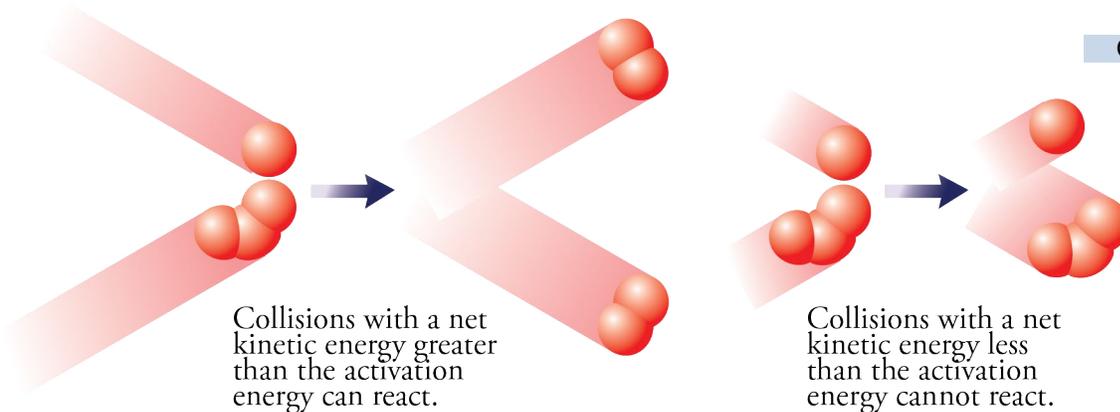
Figure 14.5
Not Enough Energy to
Get Over the Hill

OBJECTIVE 6

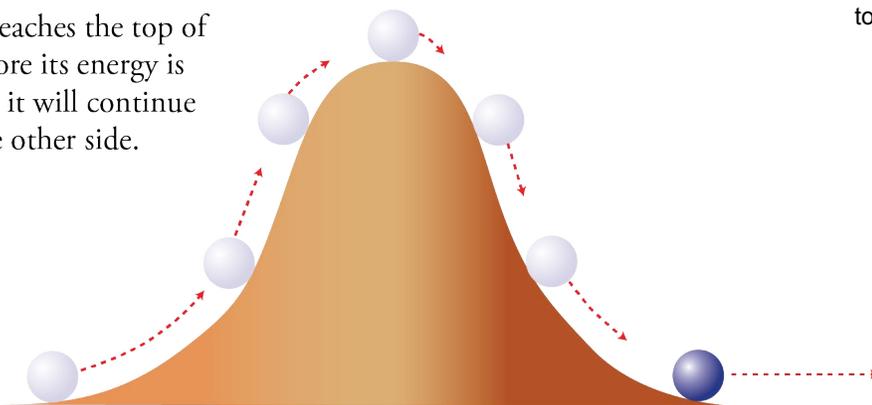
If a rolling ball does not have enough energy to get to the top of a hill, it stops and rolls back down.



The activation energy for the oxygen-ozone reaction is 17 kJ/mole O_3 . If the collision between reactants yields a net kinetic energy equal to or greater than the activation energy, the reaction can proceed to products (Figure 14.6). This is like a ball rolling up a hill with enough kinetic energy to reach the top of the hill, where it can roll down the other side (Figure 14.7)



If a ball reaches the top of a hill before its energy is depleted, it will continue down the other side.



The bonds between oxygen atoms in O_2 molecules are stronger and more stable than the bonds between atoms in the ozone molecules, so more energy is released in the formation of the new bonds than is consumed in the breaking of the old bonds. This leads to an overall release of energy, so the reaction is exothermic. The energies associated with chemical reactions are usually described in terms of kilojoules per mole, kJ/mole. If the energy is released, the value is described with a negative sign. Because 390 kJ of energy are evolved when one mole of ozone molecules react with oxygen atoms to form oxygen molecules, the energy of the reaction is -390 kJ/mole O_2 .

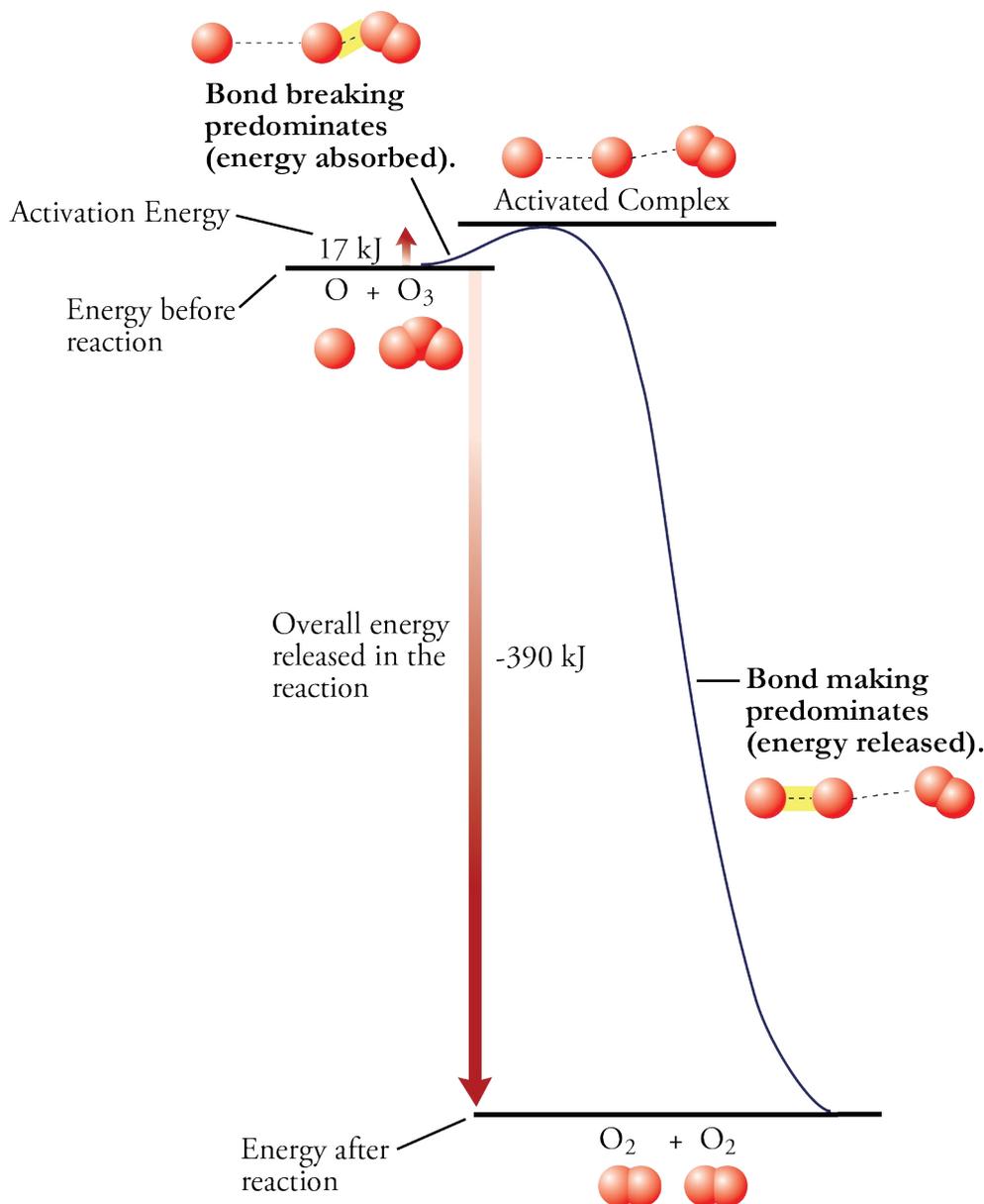
OBJECTIVE 5

Chemists often describe the progress of chemical reactions with energy diagrams such as Figure 14.8, which shows the energy changes associated with the O/O_3 reaction. It shows that the reactants must have enough kinetic energy to climb an energy hill before they can proceed on to products.

Figure 14.8

Energy Diagram for the Exergonic Reaction of an Oxygen Atom with an Ozone Molecule to Form Two Oxygen Molecules

OBJECTIVE 7



Endergonic Reactions

We know from Section 7.4 that if less energy is released in the formation of new bonds than is consumed in the breaking of old bonds, a reaction will be endergonic and will absorb energy overall as it takes place. If this energy comes from the motion (kinetic energy) of the reactants, the particles in the system will be moving more slowly after the reaction than before. The system will have lower kinetic energy, and the temperature will decrease. Because the system is at a lower temperature than the surroundings, it can absorb heat from the surroundings. Remember that when heat energy is absorbed in the process of a change, the change is called *endothermic*. The energies associated with

endergonic (or endothermic) changes are described with positive values. For example, 178 kJ of energy are necessary to convert one mole of calcium carbonate, CaCO_3 , to calcium oxide, CaO , and carbon dioxide, CO_2 . Thus the energy of reaction is +178 kJ/mole.

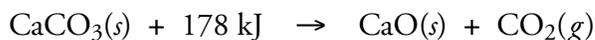


Figure 14.9 shows the energy diagram for a typical endergonic reaction.

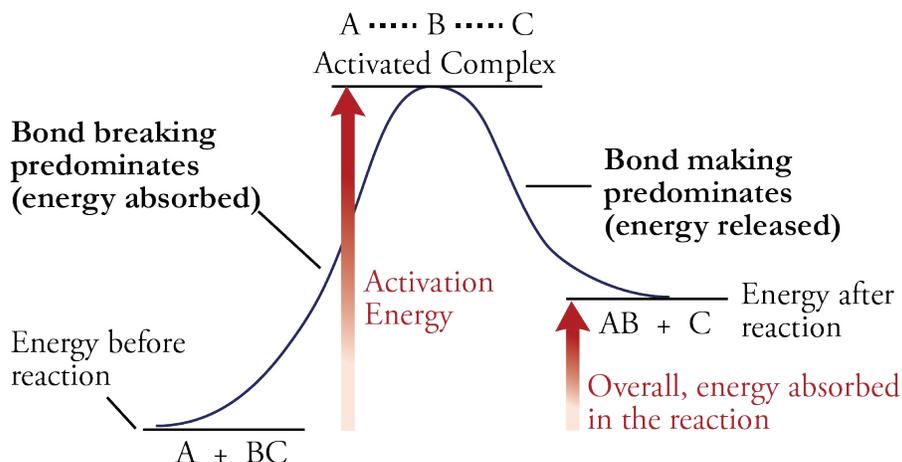


Figure 14.9
Energy Diagram for an Endergonic Reaction

OBJECTIVE 9

Even if a collision between two particles provides the activation energy, they still might not react. For the reaction to take place, the particles must collide in such a way as to allow the formation of the new bond or bonds to occur at the same time as the breaking of the old bond or bonds. For example, in the O_3/O reaction, the new bond must form between the free oxygen atom and one of the outer atoms in the O_3 molecule. Therefore, the free oxygen atom must collide with one of the outer oxygen atoms rather than with the central atom. The orientation of the particles in the first collision shown in Figure 14.10 can lead to reaction if the collision provides the activation energy. The orientation shown in the second collision is not likely to proceed to products.

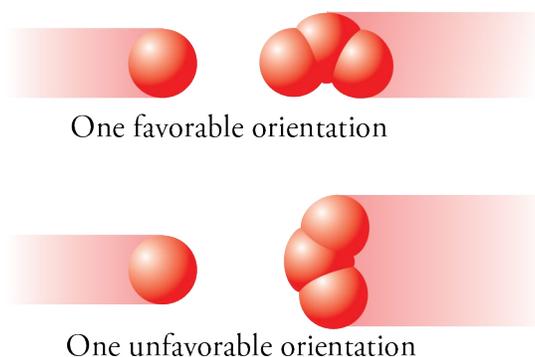


Figure 14.10
Oxygen Atoms Collision Orientation

OBJECTIVE 10

Summary of Collision Theory

Collision theory stipulates that three requirements must be met before a reaction between two particles is likely to take place.

1. **The reactant particles must collide.** The collision brings together the atoms that will form the new bonds, and the kinetic energy of the particles provides energy for the reaction to proceed.
2. **The collision must provide at least the minimum energy necessary to produce the activated complex.** It takes energy to initiate the reaction by converting the reactants into the activated complex. If the collision does not provide this energy, products cannot form.

OBJECTIVE 11

3. **The orientation of the colliding particles must favor the formation of the activated complex, in which the new bond or bonds are able to form as the old bond or bonds break.** Because the formation of the new bonds provides some of the energy necessary to break the old bonds, the making and breaking of bonds must occur more or less simultaneously. This is possible only when the particles collide in such a way that the bond-forming atoms are close to each other.

14.2 Rates of Chemical Reactions



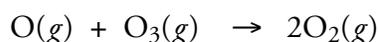
At normal temperatures, the CaCO_3 in limestone, such as in the cliffs above, can exist for centuries.

As you saw in the last section, the calcium carbonate in limestone can be converted into calcium oxide (lime) and carbon dioxide. At normal temperatures, this reaction is so slow that most limestone formations remain unreacted for thousands of years. Why, then, does it take place rapidly at $1200\text{ }^\circ\text{C}$? Similarly, why does the combustion of gasoline take place more quickly when the fuel air mixture in a cylinder of your car is compressed into a smaller volume by a moving piston? How does your car's catalytic converter speed the conversion of $\text{NO}(g)$ into $\text{N}_2(g)$ and $\text{O}_2(g)$? Now that we know more about the requirements for reaction, we can proceed to answer questions such as these.

In this section, we focus on the factors that affect **rates of chemical reactions**, which for a gas can be described as the number of product molecules that form per liter per second.

$$\text{rate of reaction} = \frac{\text{number of moles of product formed}}{\text{liter} \cdot \text{second}}$$

We can use the O/O_3 reaction described in the last section as an illustration of the factors affecting rate:



$$\text{rate of reaction} = \frac{\text{mol O}_2 \text{ formed}}{\text{L} \cdot \text{s}}$$

In the last section, we found that for a reaction between two particles to form products, the particles must collide with enough energy to reach the activated complex and with an orientation that allows the new bond or bonds to form as the old bond or bonds break. Any factor that affects these conditions will also affect the rate of the reaction. Let's look again at the chemical reaction between oxygen atoms and ozone molecules.

Temperature and Rates of Chemical Reactions

In general, increased temperature increases the rate of chemical reactions. There are two reasons for this. One is that increased temperature means increased average velocity of the particles. As heat is transferred to a system containing O_3 and O , for example, the particles move faster. This leads to an increase in the number of particles colliding per second—and therefore an increase in the amount of products formed per second.

Increased temperature also means an increase in the average net kinetic energy of the collisions between the particles in a system. This leads to an increase in the fraction of the collisions that have enough energy to reach the activated complex (the activation energy)—and thus to an increase in the rate of the reaction. For the reaction of O_3

OBJECTIVE 12



Heated to high temperature in an industrial plant, calcium carbonate, CaCO_3 , is quickly converted into lime, CaO , and carbon dioxide.

and O, an increase in temperature from 25 °C (298 K) to 35 °C (308 K) increases the fraction of the particles with the activation energy from 0.0010 to 0.0013. Figure 14.11 summarizes why reaction rates are increased by increased temperature.

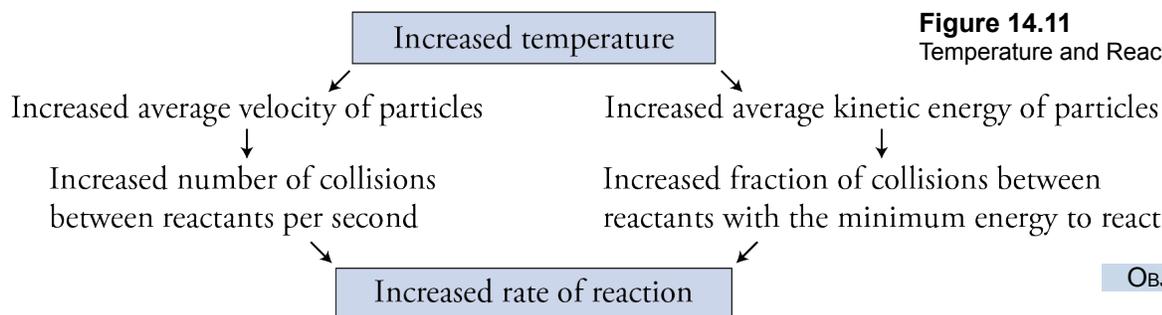


Figure 14.11
Temperature and Reaction Rate

OBJECTIVE 12

Concentration and Rates of Chemical Reactions

Another way to increase the rate of a chemical reaction is to increase the concentration of the reactant particles. **Concentration** can be described as the number of particles per unit volume. For gases, it is usually described as moles of gas particles per liter of container. Gas concentration can be increased by either increasing the number of reactant particles in a container or decreasing the volume of the container. Once again, let us consider the O_3/O reaction. The concentration of oxygen atoms in the system described in Figure 14.1 can be increased by either adding more oxygen atoms, O, or decreasing the volume of the container.

Increasing the concentration of one or both reactants will lead to shorter distances between reactant particles and to their occupying a larger percentage of the volume. With shorter distances between the particles and less empty space for them to move in without colliding, more collisions can be expected to occur per second. Figure 14.12 shows the container from Figure 14.1 after more oxygen atoms are added. At a constant temperature, increasing the concentration of oxygen atoms in the container will increase the rate of collisions between O and O_3 and increase the rate of the reaction. The same would be true if the concentration of O_3 were increased; increasing the concentration of O_3 would lead to an increase in the rate of the reaction.

OBJECTIVE 13

Increased concentration of oxygen atoms leads to increased rate of collision between oxygen atoms and ozone molecules.

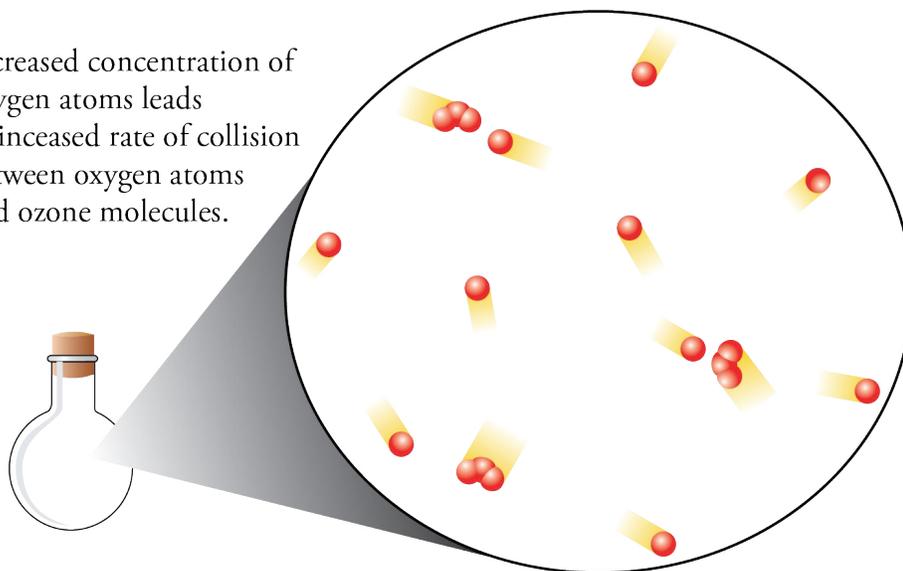


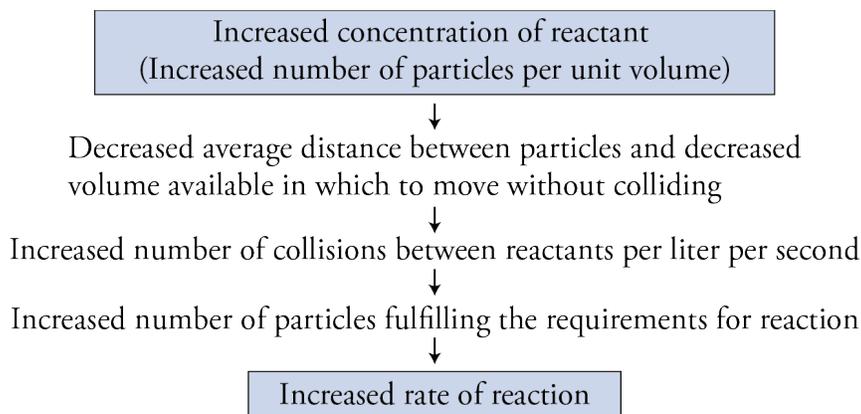
Figure 14.12
An Increase in One of the Reactants
Note that this image has twice as many oxygen atoms in the volume shown as the same volume in Figure 14.1.

OBJECTIVE 13

Figure 14.13 summarizes why increased concentration of a reactant leads to an increase in the rate of reaction.

Figure 14.13
Reactant Concentration and
Reaction Rate

OBJECTIVE 13



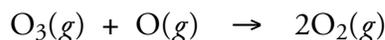
We can use similar reasoning to explain why the compression of fuel-air mixtures in the cylinders in a car engine speeds the reaction between the gaseous fuel and oxygen from the air. When a piston moves up in a cylinder, the decreased volume available to the reacting gases creates an increased concentration of each gas, which decreases the distance between the reacting molecules and decreases the volume available in which to move without colliding. This leads to more collisions between the reactants per second and a greater rate of reaction.

Catalysts

A catalyst is a substance that accelerates a chemical reaction without being permanently altered itself. Catalysts are employed by the chemical industry to increase the rates of 60-70% of the industry's reactions, and most of the important chemical reactions that take place in your body are regulated by catalysts called *enzymes*.

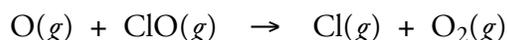
OBJECTIVE 14

One of the ways in which catalysts accelerate chemical reactions is by providing an alternative pathway between reactants and products that has a lower activation energy. Once again, the reaction between ozone molecules and oxygen atoms in the stratosphere provides an example.

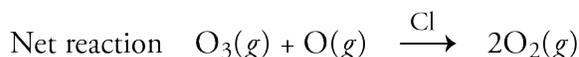


The activation energy for this reaction, as noted in Figure 14.8, is about 17 kJ/mole. At 25 °C (298 K), about one of every one thousand collisions (or 0.1%) between O_3 molecules and O atoms has a net kinetic energy large enough to form the activated complex and proceed to products. (This does not mean that 1/1000 of the collisions lead to products, however. The collisions must still have the correct orientation in order for the bond making and bond breaking to proceed at the same time.)

Chlorine atoms can catalyze this reaction in two steps:

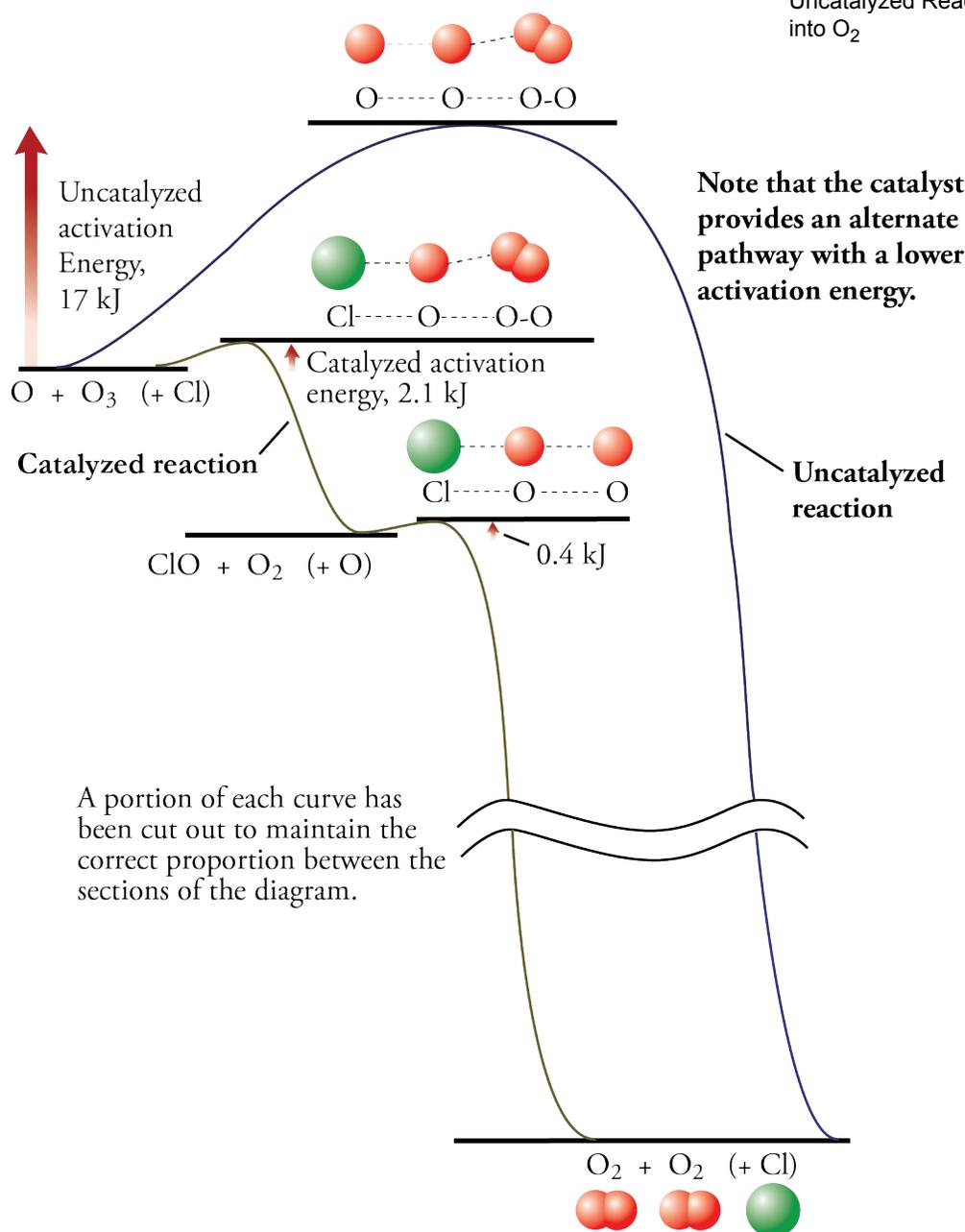


The net reaction that summarizes these two intermediate reactions is



Thus chlorine atoms provide a second pathway for the conversion of O_3 and O to O_2 , but there is another reason why the chlorine reactions speed the destruction of ozone. The reaction between O_3 and Cl that forms ClO and O_2 has an activation energy of 2.1 kJ/mole. At 25 °C, about three of every seven collisions (or 43%) have enough energy to form the activated complex. The reaction between O and ClO to form Cl and O_2 has an activation energy of only 0.4 kJ/mole. At 25 °C, about 85% of the collisions have at least this energy. Thus a much higher fraction of the collisions have the minimum energy necessary to react than in the direct reaction between O_3 and O , in which only 0.1% of the collisions have the activation energy or more (Figure 14.14).

OBJECTIVE 14



OBJECTIVE 14

Figure 14.15 summarizes why the rate of a catalyzed reaction would be expected to be greater than the rate of the same reaction without the catalyst.

Figure 14.15
Catalysts and
Reaction Rate

OBJECTIVE 15

The catalyst provides an alternate pathway with a lower activation energy.

A greater fraction of collisions have the activation energy.

A greater fraction of collisions lead to products.

Increased rate of reaction

Homogeneous and Heterogeneous Catalysts

If the reactants and the catalyst are all in the same state (all gases or all in solution) the catalyst is a **homogeneous catalyst**. The chlorine atoms are homogeneous catalysts for the reaction that converts O_3 and O into O_2 because the chlorine atoms and the reactants are all gases.

If the catalyst is not in the same state as the reactants, the catalyst is called a **heterogeneous catalyst**. A heterogeneous catalyst is usually a solid, and the reactants are either gases or liquids. For example, in Special Topic 9.2: *Air Pollution and Catalytic Converters*, you read that the catalyst in a car's catalytic converter, which helps convert gaseous nitrogen monoxide, $\text{NO}(g)$, into nitrogen gas, $\text{N}_2(g)$, and oxygen gas, $\text{O}_2(g)$, is a solid mixture of transition metals and transition metal oxides.

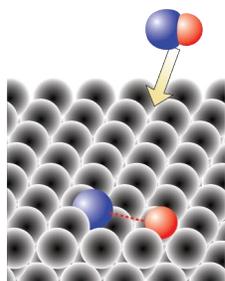
OBJECTIVE 16

Heterogeneous catalysis is thought to proceed in the four steps shown in Figure 14.16, which uses the catalytic conversion of NO to N_2 and O_2 in automobiles as an example. The model suggests that as exhaust from a car's engine passes over the solid catalyst—a transition metal like platinum, palladium, iridium, or rhodium—nitrogen monoxide molecules become attached to the catalyst's surface, bonds between nitrogen and oxygen atoms are broken, the atoms migrate across the surface, and new bonds form between nitrogen and oxygen atoms.

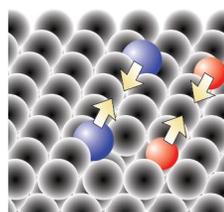
Figure 14.16

A Proposed Mechanism for the Conversion of $\text{NO}(g)$ to $\text{N}_2(g)$ and $\text{O}_2(g)$ aided by a Transition Metal Solid in a Catalytic Converter

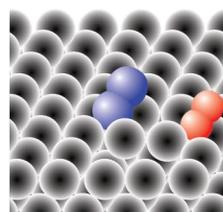
OBJECTIVE 16



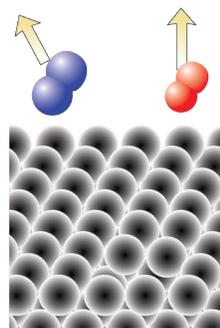
Step 1 - The reactant molecules are adsorbed, and the bonds are weakened.



Step 2 - The atoms migrate across the catalyst.



Step 3 - New bonds form.



Step 4 - The products leave the catalyst.

SPECIAL TOPIC 14.1 Green Chemistry—The Development of New and Better Catalysts

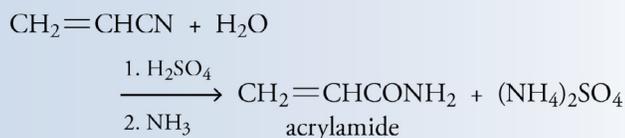
Because catalysts are used by the chemical industry to produce many essential products, the discovery of new and better catalysts is important for meeting the goals of Green Chemistry (Special Topic 1.1: *Green Chemistry*) As catalysts improve, less energy will be required for the production of industrial chemicals, and raw material and by-products will become more benign.

The Monsanto Company, as an example, received the 1996 Alternate Synthetic Pathways Award—a Presidential Green Chemistry Challenge Award—for improving the methods used in the production of their herbicide Roundup[®]. Formerly, the synthesis of this product required the use of ammonia, formaldehyde, hydrogen cyanide, and hydrochloric acid. All of these substances pose dangers to the workers using them and to the environment, but hydrogen cyanide in particular is extremely toxic. Another problem was that the overall process produced up to one kilogram of cyanide- and formaldehyde-containing waste for every seven kilograms of product. When Monsanto developed a process that used a new metallic copper catalyst for making Roundup[®], they were able to eliminate cyanide and formaldehyde from the procedure and generate no waste at all.

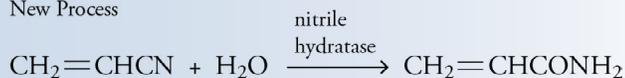
Biocatalysts—catalysts produced by living organisms—are another important category of new

catalysts being developed for industry. Enzymes are biocatalysts capable of forming very specific products very quickly. In some cases, their use in industrial reactions eliminates the need for hazardous reactants or the production of hazardous by-products. For example, the conventional synthesis of acrylamide (used to make dyes, adhesives, and permanent-press fabrics) uses sulfuric acid in the first step of a two step process and ammonia in the second step. Both of these substances can be difficult or even dangerous to handle. The conventional synthesis forms acrylamide and the waste product ammonium sulfate. An alternative technique, using an enzyme called nitril hydratase, eliminates the need for the sulfuric acid and ammonia and does not produce ammonium sulfate.

Old Process



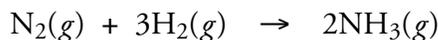
New Process



14.3 Reversible Reactions and Chemical Equilibrium

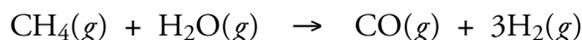
Our next step in understanding chemical change is to apply what we have learned about rates of reactions to explore what happens when a reaction is reversible. Let's take a look at a real world example that we can use to illustrate our main points.

Let's say you become so interested in chemistry that you decide to train to be an industrial chemist. Your first professional assignment is to design a procedure for making hydrogen gas that will then be used to make ammonia for fertilizers.

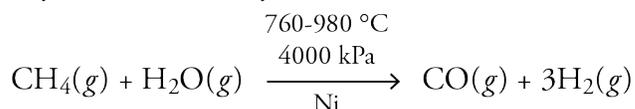


After searching the chemical literature, you compile a list of all the reactions that lead to the formation of hydrogen gas, and then shorten it by eliminating all but the reactions whose initial reactants are inexpensive, readily available, and relatively nontoxic. The following reaction between methane, CH_4 (the primary component of natural gas),

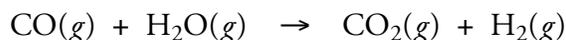
and water vapor fits these criteria.



You decide to focus on this reaction and to research the conditions under which it is likely to produce high purity hydrogen gas as quickly as possible. You know that rates of chemical reactions can be increased by increasing the concentration of reactants, raising the temperature, and by adding a catalyst. Another search of the chemical literature shows you that the reaction between methane gas and water vapor runs most quickly (and yields a high concentration of gases) when it takes place over a nickel catalyst at a total gas pressure of about 4000 kPa and a temperature between 760 °C and 980 °C. This process, called steam re-forming, is summarized by the equation below. The mixture of carbon monoxide and hydrogen gas formed in this process is used to make (synthesize) so many other chemicals that it is called *synthesis gas*.



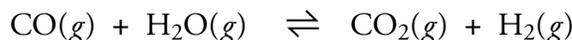
The reaction between methane and water described above produces a significant amount of hydrogen gas, but industrial chemists are always searching for ways to increase the overall yield of their conversions. Therefore, your next step is to look for a way of using the carbon monoxide formed in the reaction to make even more hydrogen gas. You discover that carbon monoxide will react with water vapor to yield carbon dioxide and hydrogen gas (Figure 14.17).



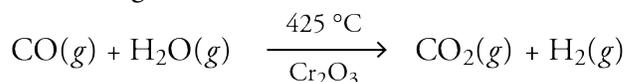
Your first thought is that this reaction should be run in the same reaction vessel as the first reaction, but further study shows that at the temperature of the first reaction (760-980 °C), the reaction between CO and H₂O does not give a very high yield of hydrogen gas. At this temperature, the reaction is significantly reversible. As soon as CO₂ and H₂ form, they begin to react with each other to reform CO and H₂O.



The two competing changes are summarized in a single reaction equation written with a double arrow (to show the reaction's reversible nature).



If you were riding on one of the hydrogen atoms, you would find yourself sometimes on an H₂ molecule and sometimes on an H₂O molecule, constantly going back and forth. Although the hydrogen yield of this reversible process is low at 760-980 °C, it is much higher at the lower temperature of 425 °C (for reasons explained below). Therefore, your best overall plan for making H₂(g) is to run the methane-water reaction in one vessel at 760-980 °C, transfer the products of this reaction to another container, add more water vapor, and run the reaction between carbon monoxide and water in the second container at 425 °C. The rate of the second reaction is further increased by allowing the reactants to combine over a chromium(III) oxide catalyst. (Note that because the reaction at 425 °C yields a high percentage of products, the equation below has a single arrow.)





Chemical plants make a mixture of hydrogen gas and carbon monoxide gas called synthesis gas.

A shift converter converts carbon monoxide and water into more hydrogen gas and carbon dioxide.

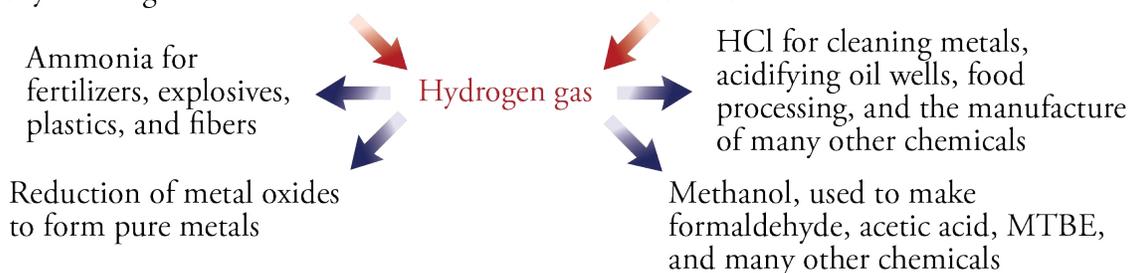
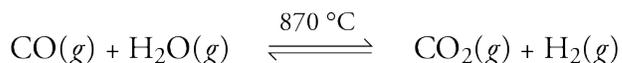


Figure 14.17
Production and Use of Hydrogen Gas

Reversible Reactions and Dynamic Equilibrium

Let's look more closely at the events taking place in the reaction between carbon monoxide gas and water vapor, and at their effect on reaction rates. Because this reaction is significantly reversible at 870 °C, we write its equation at this temperature with a double arrow.



Picture a system in which 1.0 mole of $\text{CO}(g)$ and 1.0 mole of $\text{H}_2\text{O}(g)$ are added to a 1.0 L container at 870 °C. As the reaction proceeds and the concentrations of CO and H_2O diminish, the rate of the forward reaction decreases. At the start of the reaction, there is no carbon dioxide or hydrogen gas in the container, so the rate of the reverse reaction is initially zero. But, as the concentrations of CO_2 or H_2 increase, the rate of the reverse reaction increases.

As long as the rate of the forward reaction is greater than the rate of the reverse reaction, the concentrations of the reactants (CO and H_2O) will steadily decrease, and the concentrations of products (CO_2 and H_2) will constantly increase. These changes lead to a decrease in the forward rate of the reaction and an increase in the rate of the reverse reaction, a trend that continues until the two rates become equal (Figure

OBJECTIVE 17

OBJECTIVE 18

OBJECTIVE 19

OBJECTIVE 17

OBJECTIVE 20

14.18). At this point, our system has reached a dynamic equilibrium. Because all of the reactants and products are gaseous, this system is an example of a **homogeneous equilibrium**, an equilibrium system in which all of the components are in the same state.

OBJECTIVE 17

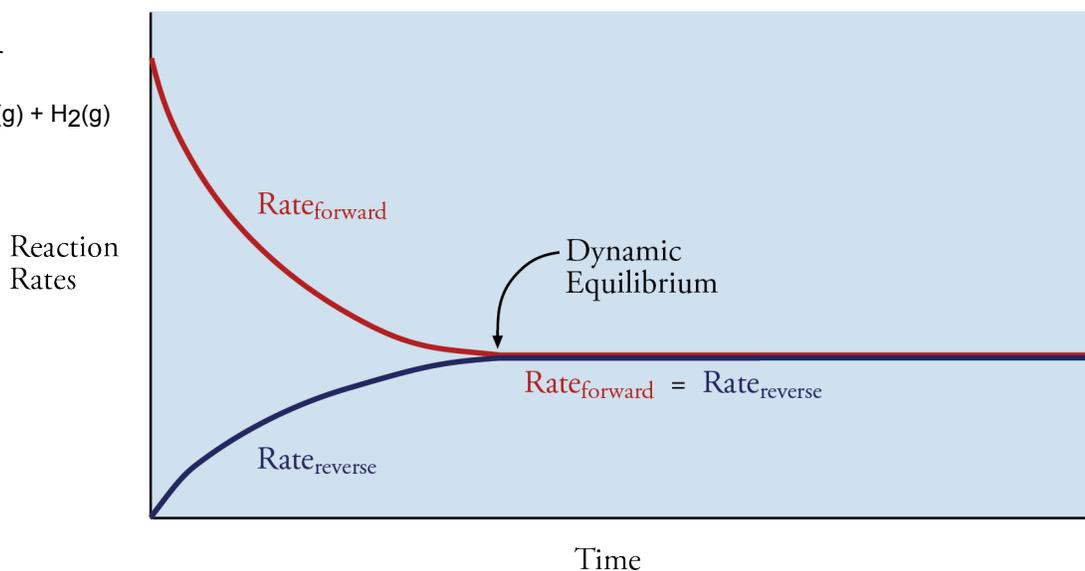
OBJECTIVE 21

In a dynamic equilibrium for a reversible chemical reaction, the forward and reverse reaction rates are equal, so although reactants and products are constantly changing back and forth, there is no net change in the amount of either. In our example, the CO and H₂O are constantly reacting to form CO₂ and H₂, but CO₂ and H₂ are reacting to reform CO and H₂O at the same rate. Note that although the concentrations of reactants and products become constant, they do not become equal (Figure 14.19).

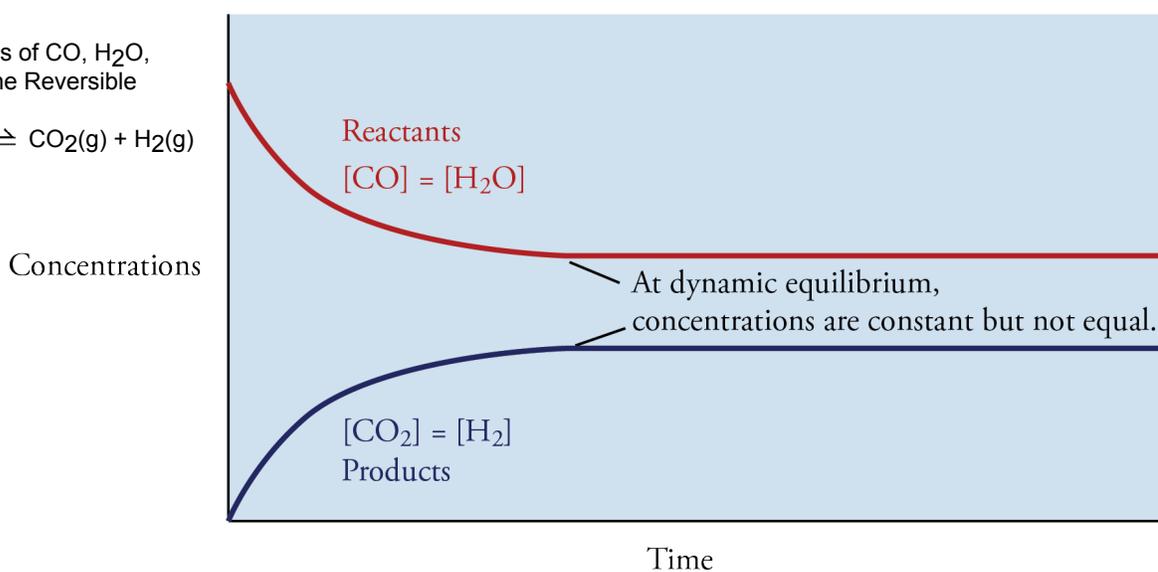
As long as the system remains in a dynamic equilibrium, the concentrations of CO, H₂O, CO₂, and H₂ remain constant, and the rates of the forward and reverse reactions also remain constant (Figures 14.18 and 14.19). This condition continues unless something occurs to disrupt the equilibrium. (You will see a list of ways that equilibrium systems can be disrupted later in this section.)

Figure 14.18

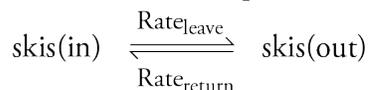
The Rates of Reaction for the Reversible Reaction
 $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$

**Figure 14.19**

The Concentrations of CO, H₂O, CO₂, and H₂ for the Reversible Reaction
 $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$



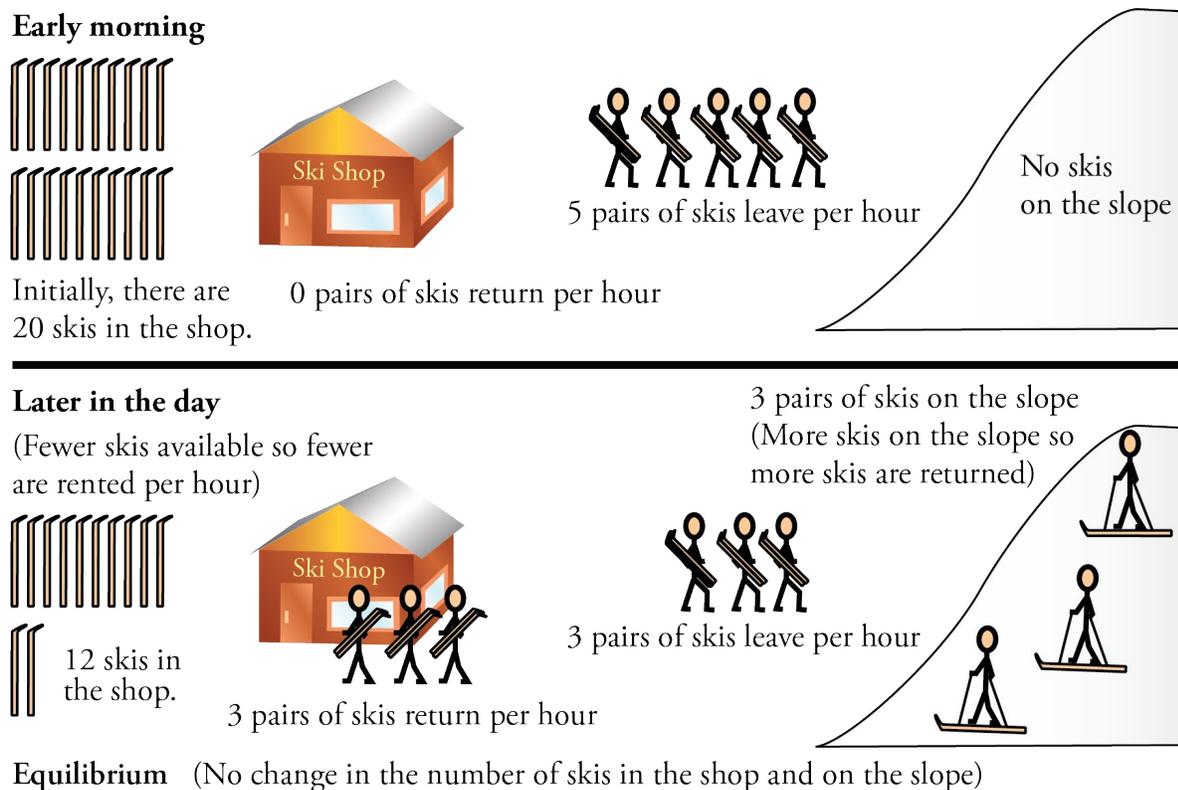
An analogy can be used to illustrate the idea of dynamic equilibrium. Suppose that you have left your job as an industrial chemist in order to start a ski rental shop near the Squaw Valley ski resort in California. To prepare for opening day, you purchase all the skis, boots, poles, and other accessories that you think will be necessary. When you open your doors for business, the skis begin to leave the store at a certain rate, $\text{Rate}_{\text{leave}}$, and by the end of the day, a few of the skis are returned at a rate represented by $\text{Rate}_{\text{return}}$. This sets up a reversible process with two opposing rates of change.



At the beginning of the first day of business, you have many different sizes and styles of ski boots and skis, so very few people are turned away without equipment. As the day progresses, you begin to run out of some sizes and styles that people want, so more people leave without renting anything. Thus the rate at which the skis leave the store is at its peak at the beginning of the first day and diminishes steadily.

As long as the skis are going out of the store faster than they are coming in, the number of your skis on the ski slopes increases. This leads to a greater probability that some people will decide to stop skiing and return their equipment to the store. Thus the rate of return increases steadily. Eventually, the increasing $\text{Rate}_{\text{return}}$ becomes equal to the decreasing $\text{Rate}_{\text{leave}}$. At this point, although skis will be constantly going out and coming back in, there will be no net change in the number of skis in the store and the skis that your customers have outside the store. The system will have reached a dynamic equilibrium, and as long as the conditions for your business remain unchanged, this dynamic equilibrium will continue (Figure 14.20). (We will return to this analogy later to illustrate how changes in certain conditions can disrupt an equilibrium system.)

Figure 14.20
Ski Shop Equilibrium

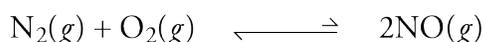


Equilibrium Constants

All reversible chemical reactions spontaneously progress toward an equilibrium mixture of constant concentrations of reactants and products. At equilibrium, some reactions yield more products than reactants; others yield more reactants than products. For example, sulfur dioxide, SO_2 , formed in forest fires and nitrogen dioxide, NO_2 , formed in electrical storms, react in the atmosphere to yield sulfur trioxide, SO_3 (which reacts with water to form sulfuric acid, one of the components of acid rain) and nitrogen monoxide, NO . At normal temperatures, this reaction has a 99.92% yield, so it goes almost to completion.

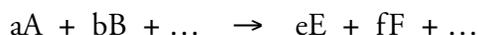


At the other extreme, nitrogen gas and oxygen gas, which under the high temperature conditions inside a car's engine react to form a significant amount of nitrogen monoxide gas, behave quite differently at room temperature. At 25 °C, the equilibrium mixture of N_2 , O_2 , and NO gases has about $1 \times 10^{-31}\%$ of the $\text{N}_2(g)$ and $\text{O}_2(g)$ converted into $\text{NO}(g)$.



OBJECTIVE 22

The extent to which reversible reactions proceed toward products before reaching equilibrium can be described with an **equilibrium constant**, which is derived from the ratio of the concentrations of products to the concentrations of reactants at equilibrium. For homogeneous equilibria, the concentrations of all reactants and products can be described in moles per liter, and the concentration of each is raised to a power equal to its coefficient in a balanced equation for the reaction. The following shows the general form for the **equilibrium constant expression**:

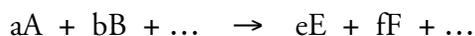


OBJECTIVE 22

$$\text{Equilibrium constant} = K_C = \frac{[E]^e [F]^f \dots}{[A]^a [B]^b \dots}$$

In this general equilibrium constant equation, the lowercase letters represent coefficients and the upper case letters represent chemical formulas. The brackets around a formula represent the concentration of that substance in moles per liter. Because the key variables are concentrations of reactants and products, the equilibrium constant has the symbol K_C .

Gases in equilibrium constant expressions are often described with pressures instead of concentrations (mol/L). When an equilibrium constant is derived from gas pressures, we represent it with the symbol K_P .



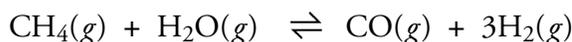
OBJECTIVE 23

$$\text{Equilibrium constant} = K_P = \frac{P_E^e P_F^f \dots}{P_A^a P_B^b \dots}$$

The values for K_C and K_P for the same reaction can be different, so it is important to specify whether you are using K_P or K_C .

EXAMPLE 14.1 - Writing Equilibrium Constant Expressions

The first step in the process you designed for producing hydrogen was to react methane gas with water vapor to form carbon monoxide and hydrogen gases. Write the equilibrium constant expressions for K_C and K_P for the following equation for this reaction.



Solution

The coefficient before H_2 is 3, so we raise the concentration or pressure to the third power.

$$K_C = \frac{[\text{CO}] [\text{H}_2]^3}{[\text{CH}_4] [\text{H}_2\text{O}]} \quad K_P = \frac{P_{\text{CO}} P_{\text{H}_2}^3}{P_{\text{CH}_4} P_{\text{H}_2\text{O}}}$$

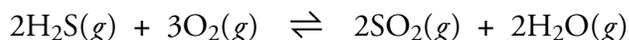
Note that the concentration of H_2 in the K_C expression and the pressure of H_2 in the K_P expression must be raised to the third power, because in the balanced equation, hydrogen has a coefficient of 3. Students commonly forget to do this.

OBJECTIVE 22

OBJECTIVE 23

EXERCISE 14.1 - Writing Equilibrium Constant Expressions

Sulfur dioxide, SO_2 , one of the intermediates in the production of sulfuric acid, can be made from the reaction of hydrogen sulfide gas with oxygen gas. Write the equilibrium constant expressions for K_C and K_P for the following equation for this reaction.



OBJECTIVE 22

OBJECTIVE 23

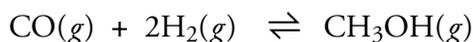
Determination of Equilibrium Constant Values

One way to determine the value of an equilibrium constant is to run the reaction in the laboratory, wait for it to reach equilibrium, determine the concentrations or partial pressures of reactants and products, and plug them into the equilibrium constant expression. Note that equilibrium constants are usually described without units.

OBJECTIVE 24

EXAMPLE 14.2 - Equilibrium Constant Calculation

Methanol is a common substance used both as a solvent and as a reactant in the synthesis of many other substances. Methanol can be made from synthesis gas, a mixture of $\text{CO}(g)$ and $\text{H}_2(g)$. When a mixture of these gases is allowed to come to equilibrium over a copper oxide catalyst at 200°C , the partial pressures of the gases are 0.96 atm for $\text{CO}(g)$, 1.92 atm for $\text{H}_2(g)$, and 0.11 atm for $\text{CH}_3\text{OH}(g)$. What is K_P for this reaction at 200°C ?



Solution

$$K_P = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} P_{\text{H}_2}^2} = \frac{0.11 \text{ atm}}{0.96 \text{ atm} (1.92 \text{ atm})^2} = 0.031 \frac{1}{\text{atm}^2} \text{ or } 0.031$$

OBJECTIVE 24

EXERCISE 14.2 - Equilibrium Constant Calculation

OBJECTIVE 24

Ethanol, C_2H_5OH , can be made from the reaction of ethylene gas, C_2H_4 , and water vapor. A mixture of $C_2H_4(g)$ and $H_2O(g)$ is allowed to come to equilibrium in a container at $110^\circ C$, and the partial pressures of the gases are found to be 0.35 atm for $C_2H_4(g)$, 0.75 atm for $H_2O(g)$, and 0.11 atm for $C_2H_5OH(g)$. What is K_P for this reaction at $110^\circ C$?

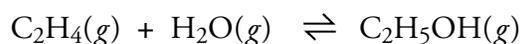


Table 14.1 shows K_P values for some gas phase homogeneous equilibria at $25^\circ C$.

Table 14.1

Equilibrium Constants for Homogeneous Equilibria at $25^\circ C$

Reaction	K_P Expression	K_P
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	$K_P = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}}$	6.8×10^{24}
$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$	$K_P = \frac{P_{COCl_2}}{P_{CO} P_{Cl_2}}$	6.5×10^{11}
$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$	$K_P = \frac{P_{NO_2}^2}{P_{NO}^2 P_{O_2}}$	2.2×10^{12}
$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$	$K_P = \frac{P_{SO_3} P_{NO}}{P_{SO_2} P_{NO_2}}$	1.7×10^6
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	$K_P = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$	5.8×10^5
$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$	$K_P = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}$	1.0×10^5
$2NO_2(g) \rightleftharpoons N_2O_4(g)$	$K_P = \frac{P_{N_2O_4}}{P_{NO_2}^2}$	6.7
$SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g)$	$K_P = \frac{P_{SO_2Cl_2}}{P_{SO_2} P_{Cl_2}}$	1.4×10^{-18}
$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$	$K_P = \frac{P_{C_2H_4} P_{H_2}}{P_{C_2H_6}}$	1.2×10^{-18}
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	$K_P = \frac{P_{NO}^2}{P_{N_2} P_{O_2}}$	4.7×10^{-31}

Equilibrium Constants and Extent of Reaction

Equilibrium constants indicate the extent to which reactions yield products as they progress toward equilibrium. The larger a value for K , the farther the reaction shifts toward products before the rates of the forward and reverse reactions become equal and the concentrations of reactants and products stop changing. The following generalizations provide guidelines for interpreting equilibrium constant values.

- $K > 10^2$ Products favored at equilibrium
 $K < 10^{-2}$ Reactants favored at equilibrium
 $10^{-2} < K < 10^2$ Neither reactants nor products favored

OBJECTIVE 25

EXAMPLE 14.3 - Predicting the Extent of Reaction

Using the information on Table 14.1, predict whether each of the following reversible reactions favors reactants, products, or neither at 25 °C.

OBJECTIVE 25

- a. Carbon monoxide gas and chlorine gas combine to make phosgene gas, COCl_2 , a poison gas used in World War I.
- b. Ethylene, used to make polyethylene plastics, can be formed from the following reaction:



Solution

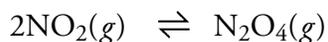
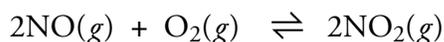
- a. **Favors Products** – The equilibrium constant given in Table 14.1 is 6.5×10^{11} . Reactions, like this one, with extremely large equilibrium constants, can be considered to go to completion and are often described with single arrows.
- b. **Favors Reactants** – The highly unfavorable equilibrium constant for this reaction (1.2×10^{-18}) seems to suggest that this would be a poor way to make $\text{C}_2\text{H}_4(g)$, but in fact, the equilibrium constant gets much larger, and more favorable toward products, as the temperature rises. At 800-900 °C, ethylene gas is produced in a much larger proportion.

EXERCISE 14.3 - Predicting the Extent of Reaction

Using the information on Table 14.1, predict whether each of the following reversible reactions favors reactants, products, or neither at 25 °C.

OBJECTIVE 25

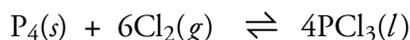
- a. This reaction is partially responsible for the release of pollutants from automobiles.
- b. The $\text{NO}_2(g)$ molecules formed in the reaction in part (a) can combine to form N_2O_4 .



The brown gas nitrogen dioxide, NO_2 , is one cause of the haze over this skyline.

Heterogeneous Equilibria

When the reactants and products for a reversible reaction are not all in the same phase (gas, liquid, solid, or aqueous), the equilibrium is called a **heterogeneous equilibrium**. For example, liquid phosphorus trichloride (used to make pesticides, gasoline additives, and other important substances) is made by passing chlorine gas over gently heated solid phosphorus.



The equilibrium constant expression below is the one derived from the guidelines used for homogeneous equilibria.

$$K' = \frac{[\text{PCl}_3]^4}{[\text{P}_4] [\text{Cl}_2]^6}$$

As you will see, this is not the most common form of the equilibrium constant expression for the reaction. The more common form leaves out the pure solid and liquid.

$$K_C = \frac{1}{[\text{Cl}_2]^6}$$

OBJECTIVE 26

When all reactants are gases, the concentrations in the equilibrium expression are described in moles per liter. Pure liquids and solids are treated differently, however, because, unlike gases, the concentrations of liquids and solids remain constant even when the amount of substance or the volume of the container change. To illustrate this, let's consider a reaction vessel with a constant volume in which a mixture of $\text{P}_4(s)$, $\text{Cl}_2(g)$, and $\text{PCl}_3(l)$ has come to equilibrium.

When more Cl_2 gas is added to the system, the new gas mixes easily with the gas already in the container, and because the moles of Cl_2 increase but the volume is constant, the concentration of Cl_2 increases. The concentration of Cl_2 could also be changed if the volume of the container could change. If the gas were compressed, the concentration would increase, and if the gas were allowed to expand, the concentration would decrease (Figure 14.21).

Note, however, that the concentrations of solids and liquids cannot be changed in these ways. If the number of moles of $\text{P}_4(s)$ in the container is doubled, its volume doubles too, leaving the concentration (mol/L) of the phosphorus constant. Increasing or decreasing the total volume of the container will not change the volume occupied by the solid phosphorus, so the concentration (mol/L) of the $\text{P}_4(s)$ also remains constant with changes in the volume of the container. Similarly, the concentration of liquid PCl_3 is also independent of the volume of the container and the amount of PCl_3 present (Figure 14.21). By convention, the constant concentrations of pure solids and liquids are understood to be incorporated into the equilibrium constant itself and left out of the equilibrium constant expression.

$$K' = \frac{[\text{PCl}_3]^4}{[\text{P}_4] [\text{Cl}_2]^6}$$

OBJECTIVE 22

OBJECTIVE 23

$$\frac{K' [\text{P}_4]}{[\text{PCl}_3]^4} = \frac{1}{[\text{Cl}_2]^6} = K_C \quad \text{or} \quad K_P = \frac{1}{P_{\text{Cl}_2}^6}$$

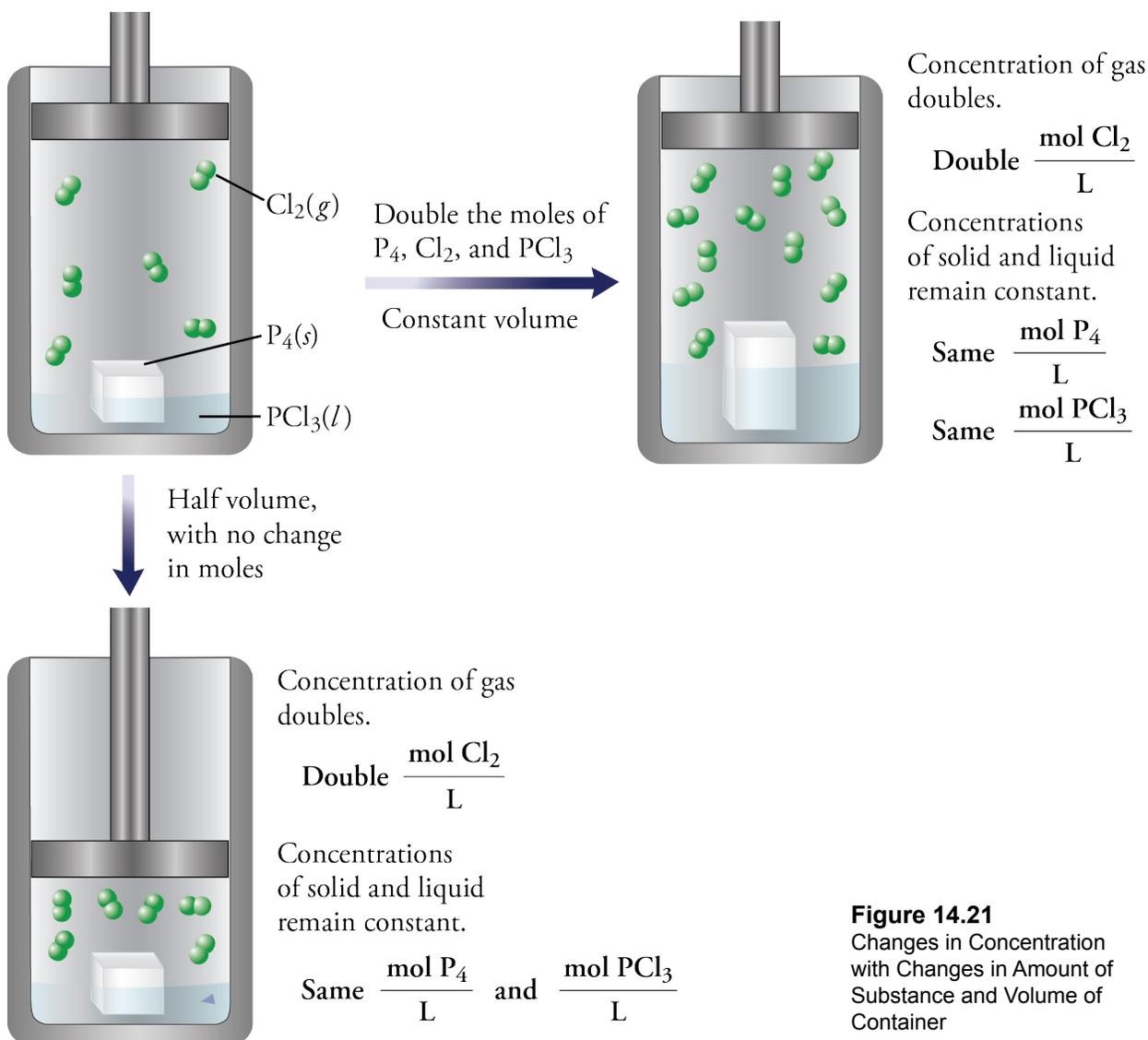
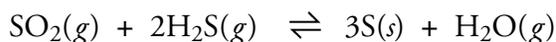


Figure 14.21
 Changes in Concentration
 with Changes in Amount of
 Substance and Volume of
 Container

EXAMPLE 14.4 - Writing Equilibrium Constant Expressions for Heterogeneous Equilibria

One of the steps in the production of sulfuric acid is to make solid sulfur from the reaction of sulfur dioxide gas and hydrogen sulfide gas. Write K_C and K_P expressions for this reaction.

OBJECTIVE 24



Solution

The solid does not appear in the K_C and K_P expressions.

$$K_C = \frac{[\text{H}_2\text{O}]}{[\text{SO}_2][\text{H}_2\text{S}]^2} \quad K_P = \frac{P_{\text{H}_2\text{O}}}{P_{\text{SO}_2} P_{\text{H}_2\text{S}}^2}$$

OBJECTIVE 22

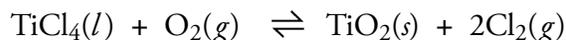
OBJECTIVE 23



White paint contains titanium dioxide.

EXERCISE 14.4 - Writing Equilibrium Constants for Heterogeneous Equilibria

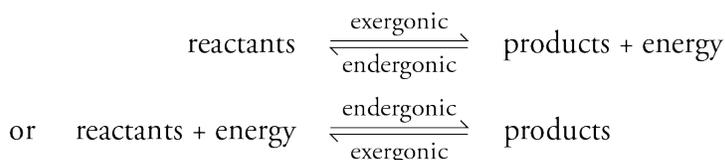
The following equation describes one of the steps in the purification of titanium dioxide, used as a white pigment in paints. Liquid titanium(IV) chloride reacts with oxygen gas to form solid titanium dioxide and chlorine gas. Write K_C and K_P expressions for this reaction.



Equilibrium Constants and Temperature

Changing temperature always causes a shift in equilibrium systems—sometimes toward more products and sometimes toward more reactants. For example, some industrial reactions that yield an equilibrium mixture with less than 1% products at room temperature will yield more than 99% products at higher temperature. This shift in equilibrium systems is reflected in changes in equilibrium constants that accompany changes in temperature.

Before we tackle the question of why changing temperature affects equilibrium systems, let's quickly establish some key characteristics of energy changes in chemical reactions. Remember that chemical reactions are either endergonic (absorb energy as the reaction forms weaker chemical bonds) or exergonic (evolve energy as the reaction leads to stronger bonds). In a reversible reaction, if the forward reaction is exergonic, the reverse reaction is endergonic. If the forward reaction is endergonic, the reverse reaction is exergonic.



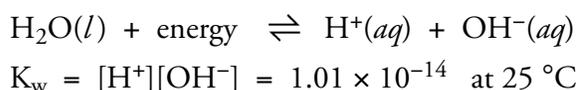
OBJECTIVE 27

Increased temperature increases the rate of both the forward and the reverse reactions, but it increases the rate of the endergonic reaction more than it increases the rate of the exergonic reaction. Therefore, increasing the temperature of a chemical system at equilibrium will disrupt the balance of the forward and reverse rates of reaction and shift the system in the direction of the endergonic reaction.

OBJECTIVE 28

- If the forward reaction is endergonic, increased temperature will shift the system toward more products, increasing the ratio of products to reactants and increasing the equilibrium constant.
- If the forward reaction is exergonic and the reverse reaction is endergonic, increased temperature will shift the system toward more reactants, decreasing the ratio of products to reactants and decreasing the equilibrium constant.

For example, pure water ionizes in a reversible endergonic reaction that forms hydrogen ions, H^+ (which form hydronium ions, H_3O^+) and hydroxide ions, OH^- . The equilibrium constant for this reaction is called the **water dissociation constant**, K_w .



Because the forward reaction is endergonic, increased temperature drives the system to products, increasing the value for the water dissociation constant. Table 14.2 shows K_w values for this reaction at different temperatures.

Table 14.2

Water Dissociation Constants at Various Temperatures

Temperature	K_w
0 °C	1.14×10^{-15}
10 °C	2.92×10^{-15}
25 °C	1.01×10^{-14}
30 °C	1.47×10^{-14}
40 °C	2.92×10^{-14}
50 °C	5.47×10^{-14}
60 °C	9.61×10^{-14}

The reaction between carbon monoxide gas and water vapor to form carbon dioxide gas and hydrogen gas is exothermic, meaning that energy is evolved as the reaction proceeds in the forward direction. Therefore, increased temperature favors the reverse reaction, shifting the system toward more reactants and decreasing the equilibrium constant for the reaction.



The fact that higher temperature leads to a lower percentage of $\text{CO}(g)$ and $\text{H}_2\text{O}(g)$ converted to $\text{CO}_2(g)$ and $\text{H}_2(g)$ creates a dilemma for the industrial chemist designing the process for making hydrogen gas. To maximize the percent yield, the reaction should be run at as low a temperature as possible, but at low temperature, the rates of the forward and reverse reactions are both very low, so it takes a long time for the system to come to equilibrium. Some chemical plants in the U.S. have solved this problem by setting up two chambers for the reaction, one at high temperature to convert some of the $\text{CO}(g)$ and $\text{H}_2\text{O}(g)$ to $\text{CO}_2(g)$ and $\text{H}_2(g)$ quickly, and a low temperature section to complete the process.

OBJECTIVE 29

You can visit the textbook's Web site to see how concentration or gas pressures of reactants and products at equilibrium can be calculated from initial concentrations of reactants and products and equilibrium constants.

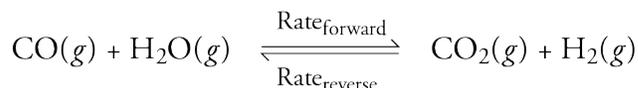
You can visit the textbook's Web site to see how the pH scale for describing acidic and basic solutions is defined.

You can visit the textbook's Web site to see how weak acids are described with equilibrium constants.

14.4 Disruption of Equilibrium

Chemical systems at equilibrium are actually somewhat rare outside the laboratory. For example, the concentrations of reactants and products of the reactions taking place in your body are constantly changing, leading to changes in the forward and reverse reaction rates. These constant fluctuations prevent the reactions from ever reaching equilibrium. In most industrial procedures, the products of reversible reactions are purposely removed as they form, preventing the reverse rate of the reaction from ever rising to match the rate of the forward reaction.

In general, equilibrium systems are easily disrupted. Every time you take a bottle of vinegar from a cool pantry and hold it in your warm hand, you increase the temperature of the solution and disrupt the equilibrium between acetic acid and its ions. To illustrate the conditions that lead to disruption of equilibria and to show why they do so, let's return to our example of making hydrogen gas from carbon monoxide and water vapor.



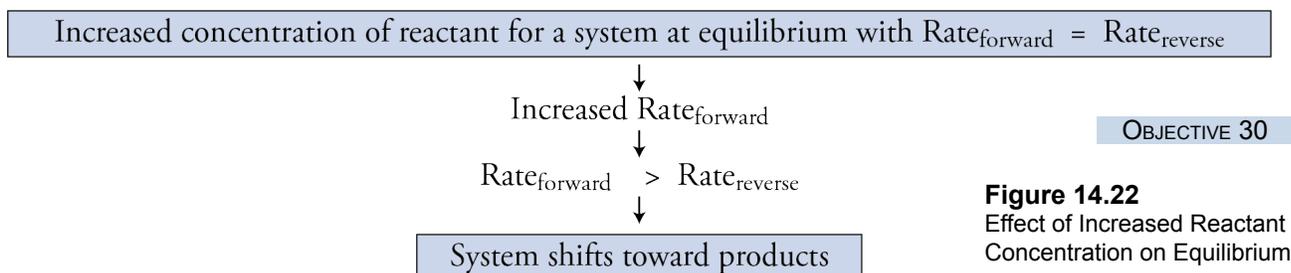
The Effect of Changing Concentrations on Equilibrium Systems

OBJECTIVE 30

Any change in the concentration of a reactant or product in a chemical system at equilibrium will destroy the balance of the forward and reverse reaction rates and create a non-equilibrium situation, which in some cases will lead to a shift toward more reactants and in others a shift toward more products. One common means of shifting an equilibrium system toward the formation of more products is to increase the concentration of one of the reactants. Imagine that our system containing $\text{CO}(g)$, $\text{H}_2\text{O}(g)$, $\text{CO}_2(g)$, and $\text{H}_2(g)$ is in equilibrium, so that the rate of the forward change is equal to the rate of the reverse change. If more water vapor is added to the system, collisions between CO molecules and H_2O molecules will be more frequent, and $\text{Rate}_{\text{forward}}$ will increase. Initially, the rate of the reverse reaction, $\text{Rate}_{\text{reverse}}$, will not be affected, so the two rates will no longer be the same, and the system will no longer be at equilibrium.

OBJECTIVE 30

To reiterate, the addition of water vapor to our equilibrium system causes $\text{Rate}_{\text{forward}}$ to be greater than $\text{Rate}_{\text{reverse}}$, so the products will be made faster than the reactants are reformed. The concentration of the reactants $\text{CO}(g)$ and $\text{H}_2\text{O}(g)$ will decrease, and the concentration of the products $\text{CO}_2(g)$ and $\text{H}_2(g)$ will increase. Chemists describe this situation by saying that the increase of one or more reactants shifts a system initially at equilibrium toward products (Figure 14.22).



As the concentrations of $\text{CO}_2(g)$ and $\text{H}_2(g)$ increase, $\text{Rate}_{\text{reverse}}$ increases, and as the concentrations of $\text{CO}(g)$ and $\text{H}_2\text{O}(g)$ decrease, $\text{Rate}_{\text{forward}}$ decreases. If there are no further disruptions of the system, it will arrive at a new equilibrium with $\text{Rate}_{\text{forward}}$ and $\text{Rate}_{\text{reverse}}$ once again equal. Note that at this new equilibrium, both $\text{Rate}_{\text{forward}}$ and $\text{Rate}_{\text{reverse}}$ are higher (Figure 14.23).

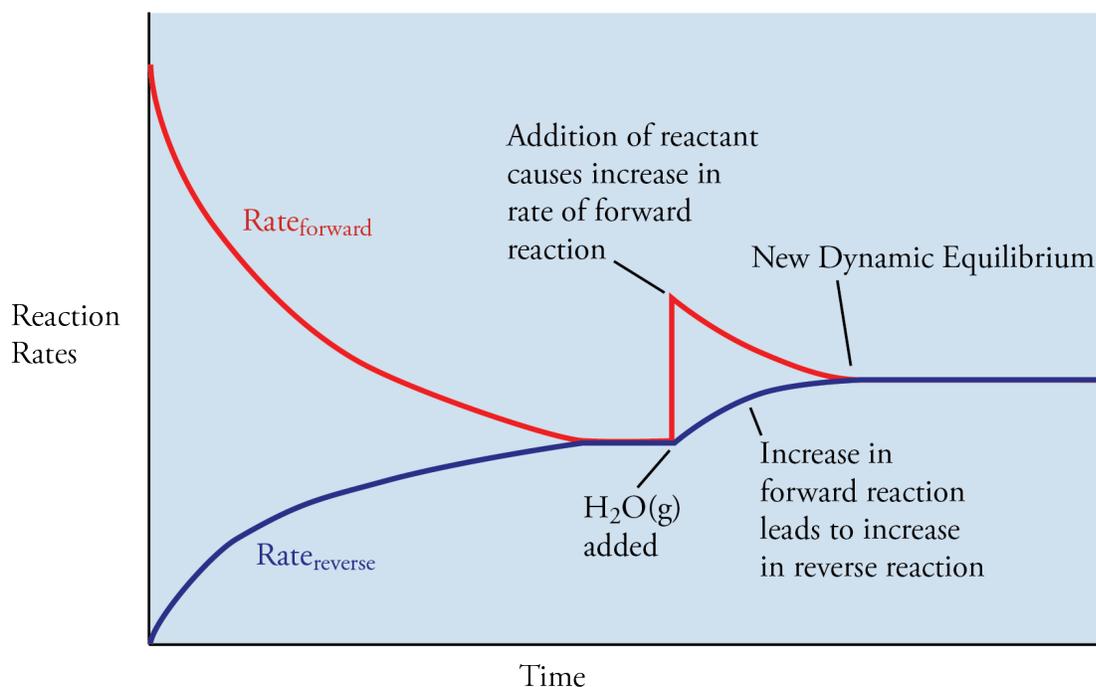


Figure 14.23

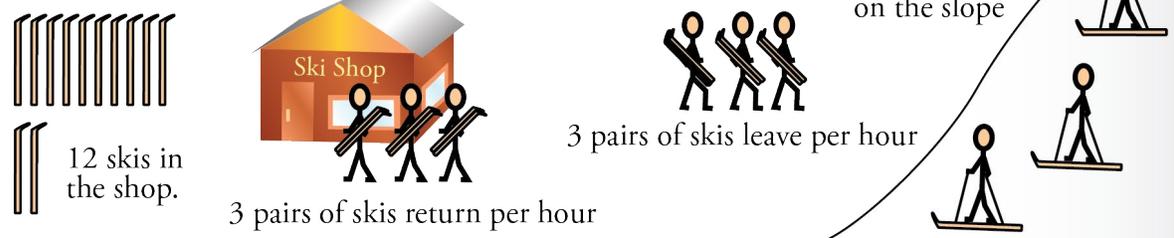
Change in the Rates of Reaction when a Reactant is Added to an Equilibrium System for the Reversible Reaction: $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$

OBJECTIVE 30

Back at your ski shop, you might encounter a similar situation. When we last looked in on the business, we saw a dynamic equilibrium in which the rate at which skis left the shop, $\text{Rate}_{\text{leave}}$, was equal to the rate at which they were being returned, $\text{Rate}_{\text{return}}$. If you buy more skis and equipment, however, you will be more likely to have what your customers want, so you will turn fewer customers away without skis. Thus the rate at which the skis leave the shop, $\text{Rate}_{\text{leave}}$, will increase, making $\text{Rate}_{\text{leave}}$ greater than $\text{Rate}_{\text{return}}$. In time, though, as the number of your skis out on the slopes increases, more people will decide to stop skiing and return the equipment. Eventually, the $\text{Rate}_{\text{return}}$ will increase until it is once again equal to $\text{Rate}_{\text{leave}}$. However, both the rate at which skis leave the shop and the rate at which they return will be greater at this new equilibrium (Figure 14.24 on the next page).

Before buying more skis

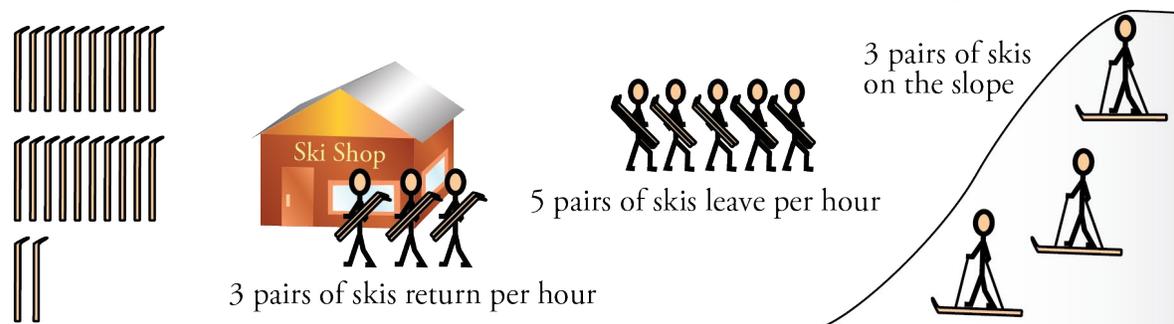
There are 12 skis in the shop.



Equilibrium (No change in the number of skis in the shop and on the slope)

Immediately after buying more skis

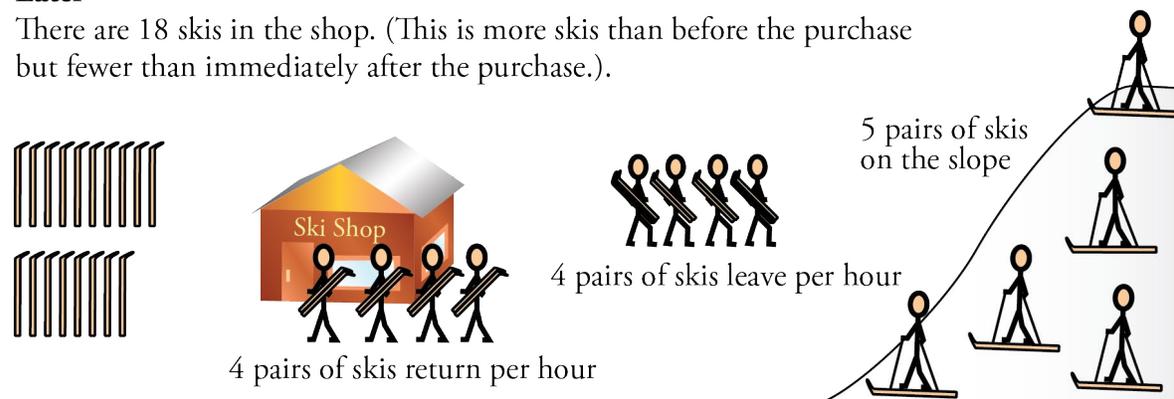
There are 22 skis in the shop. (With more skis in the shop, more are rented per hour.)



More skis leave than return, so the equilibrium is disrupted.

Later

There are 18 skis in the shop. (This is more skis than before the purchase but fewer than immediately after the purchase.)



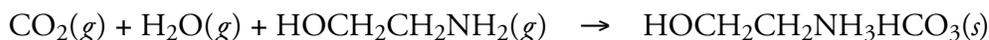
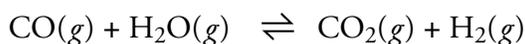
New equilibrium (No change in the number of skis in the shop and on the slope)

Figure 14.24

Ski Shop Equilibrium and Increased Stock

Another way to disrupt an equilibrium system and shift it toward products is to remove one or more of the products as they form. (We mentioned above that this is the practice in most industrial procedures.) For example, the reaction of $\text{CO}(g)$ and $\text{H}_2(g)$ from $\text{CO}_2(g)$ and $\text{H}_2(g)$ can be driven toward products by the removal of $\text{CO}_2(g)$ as it forms. This is done in the industrial process by reacting the $\text{CO}_2(g)$ with some of the

excess water vapor and monoethanolamine, $\text{HOCH}_2\text{CH}_2\text{NH}_2$.



The removal of $\text{CO}_2(g)$ decreases its concentration, decreasing the frequency of collisions between $\text{CO}_2(g)$ and $\text{H}_2(g)$ and therefore decreasing the rate of the reverse reaction, $\text{Rate}_{\text{reverse}}$. This change makes $\text{Rate}_{\text{forward}}$ greater than $\text{Rate}_{\text{reverse}}$, shifting the system toward the formation of more products (Figure 14.25).

OBJECTIVE 31

Decreased concentration of one product for a system at equilibrium with $\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

↓
Decreased $\text{Rate}_{\text{reverse}}$

↓
 $\text{Rate}_{\text{forward}} > \text{Rate}_{\text{reverse}}$

↓
System shifts toward products

OBJECTIVE 31

Figure 14.25
Effect of Decreased
Concentration of
Product on Equilibrium

As the concentration of products increases, $\text{Rate}_{\text{reverse}}$ increases. As the concentration of reactants decreases, $\text{Rate}_{\text{forward}}$ decreases. If no further changes are made to the system, it will return to a new dynamic equilibrium with $\text{Rate}_{\text{forward}}$ equaling $\text{Rate}_{\text{reverse}}$ (Figure 14.26).

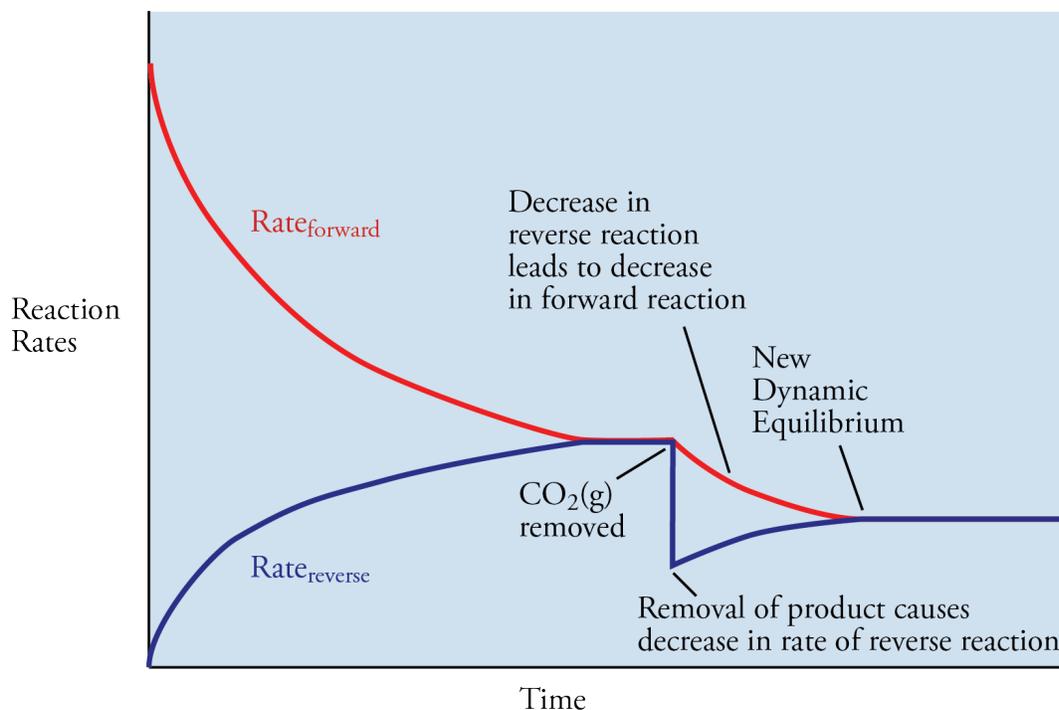


Figure 14.26

Change in the Rates of Reaction when a Product is Removed from an Equilibrium System for the Reversible Reaction: $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$

OBJECTIVE 31

You can visit the textbook's Web site to read about how changing volume affects gas phase reactions at equilibrium.

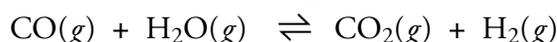
Le Chatelier's Principle

OBJECTIVE 32

OBJECTIVE 33

Whenever an equilibrium system is disrupted, it will move toward a new equilibrium by shifting either toward the formation of more products (and less reactants) or the formation of more reactants (and less products). We can predict the direction in which a system will shift by thinking about the effect of the proposed changes on $\text{Rate}_{\text{forward}}$ and $\text{Rate}_{\text{reverse}}$, but we can often arrive at the correct prediction more easily by applying a guideline called **Le Chatelier's principle**. This principle states that if a system at equilibrium is altered in a way that disrupts the equilibrium, the system will shift in such a way as to counter the change.

For example, we can use this principle to predict the direction in which the following equation shifts when water vapor is added to the system at equilibrium.



OBJECTIVE 32

OBJECTIVE 33

Le Chatelier's principle tells us that the system will shift toward products in order to decrease the increased concentration of $\text{H}_2\text{O}(g)$, partially counteracting the change that disrupted the equilibrium system.

Likewise, we can use Le Chatelier's principle to predict the effect of temperature on the following equilibrium for which the forward reaction is exothermic.



OBJECTIVE 32

OBJECTIVE 33

Le Chatelier's principle tells us that if we decrease the temperature for this system at equilibrium, the system will shift to partially counteract this change and increase the temperature. Thus we predict that decreased temperature will shift the system toward products, because the exothermic forward reaction releases energy and leads to an increase in temperature.

Table 14.3 summarizes the effects of changes in concentrations of reactants and products and changes in temperature of equilibrium systems.

Table 14.3

Summary of the Shifts in Equilibrium Predicted by Le Chatelier's Principle

OBJECTIVE 32

OBJECTIVE 33

Reaction	Cause of Disruption	To Counteract Change	Direction of Shift
All	Add reactant(s)	Decrease reactant(s)	To products
All	Add product(s)	Decrease product(s)	To reactants
All	Remove reactant(s)	Increase reactant(s)	To reactants
All	Remove product(s)	Increase products(s)	To products
Endothermic forward reaction	Increase temperature	Decrease temperature	To products
Endothermic forward reaction	Decrease temperature	Increase temperature	To reactants
Exothermic forward reaction	Increase temperature	Decrease temperature	To reactants
Exothermic forward reaction	Decrease temperature	Increase temperature	To products

The Effect of Catalysts on Equilibria

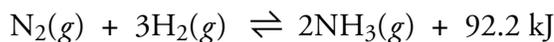
OBJECTIVE 34

The presence of a catalyst has no effect on the equilibrium concentrations of reactants and products. Catalysts speed both the forward and reverse rates to the same degree. The system will reach equilibrium more quickly, but the ratio of the concentrations of products to reactants—and thus the value of the equilibrium constant—is unchanged.

We can illustrate a situation of this kind using our ski rental analogy. You decide to “catalyze” your ski rental business by constructing a drive up window to increase the convenience of renting and returning skis. Because checking out the skis is easier now, $\text{Rate}_{\text{leave}}$ increases. Because returning skis is also easier now, $\text{Rate}_{\text{return}}$ also increases. If both of these rates increase equally, there will be no net change in the number of skis in the shop or on the slopes at any time.

EXAMPLE 14.5 - Predicting the Effect of Disruptions on Equilibrium

Ammonia gas, which is used to make fertilizers and explosives, is made from the reaction of nitrogen gas and hydrogen gas. The forward reaction is exothermic. Predict whether each of the following changes in an equilibrium system of nitrogen, hydrogen, and ammonia will shift the system to more products, to more reactants, or neither. Explain each answer in two ways, (1) by applying Le Chatelier’s principle and (2) by describing the effect of the change on the forward and reverse reaction rates.



- The concentration of N_2 is increased by the addition of more N_2 .
- The concentration of ammonia gas is decreased.
- The temperature is increased from 25°C to 500°C .
- An iron catalyst is added.

Solution

- The concentration of N_2 is increased by the addition of more N_2 .
 - Using Le Chatelier’s Principle, we predict that the system will shift to more products to partially counteract the increase in N_2 .
 - The increase in the concentration of nitrogen speeds the forward reaction without initially affecting the rate of the reverse reaction. The equilibrium is disrupted, and the system shifts toward more products because the forward rate is greater than the reverse rate.
- The concentration of ammonia is decreased.
 - Using Le Chatelier’s Principle, we predict that the system will shift toward more products to partially counteract the decrease in the concentration of ammonia.
 - The decrease in the concentration of ammonia decreases the rate of the reverse reaction. It does not initially affect the forward rate. The equilibrium is disrupted, and the system shifts toward more products because the forward rate is greater than the reverse rate.
- The temperature is increased from 25°C to 400°C .
 - Using Le Chatelier’s Principle, we predict that the system shifts in the endothermic direction to partially counteract the increase in temperature. Because the forward reaction is exothermic, the reverse reaction must be endothermic. As the system shifts toward more reactants, energy is absorbed, and the temperature decreases.
 - The increased temperature increases the rates of both the forward and reverse reactions, but it has a greater effect on the endothermic reaction. Thus the system shifts toward more reactants because the reverse rate becomes greater than the forward rate.

(continued)

OBJECTIVE 32

OBJECTIVE 33

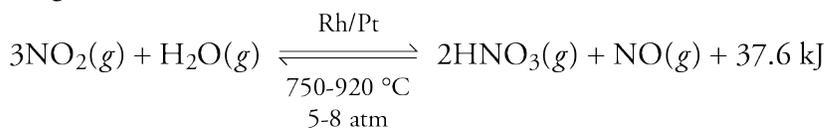
- d. An iron catalyst is added.
1. Le Chatelier's Principle does not apply here.
 2. The catalyst speeds the forward and the reverse rates equally. Thus there is no shift in the equilibrium. (The purpose of the catalyst is to bring the system to equilibrium faster.)

EXERCISE 14.5 - Predicting the Effect of Disruptions on Equilibrium

OBJECTIVE 32

OBJECTIVE 33

Nitric acid can be made from the exothermic reaction of nitrogen dioxide gas and water vapor in the presence of a rhodium and platinum catalyst at 750-920 °C and 5-8 atm. Predict whether each of the following changes in the equilibrium system will shift the system to more products, to more reactants, or neither. Explain each answer in two ways, (1) by applying Le Chatelier's principle and (2) by describing the effect of the change on the forward and reverse reaction rates.



- a. The concentration of H₂O is increased by the addition of more H₂O.
- b. The concentration of NO₂ is decreased.
- c. The concentration of HNO₃ is decreased by removing the nitric acid as it forms.
- d. The temperature is decreased from 1000 °C to 800 °C.
- e. The Rh/Pt catalyst is added to the equilibrium system.

SPECIAL TOPIC 14.2 The Big Question—How Did We Get Here?

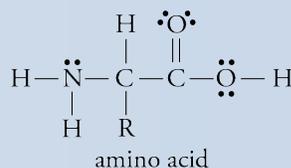
How did the human species come to be? This is a huge, multifaceted question being investigated from many different angles, not all of which are the province of science. Scientists have generally focused on four aspects of it:

- The creation of matter, including elements
- The formation of the molecules necessary for life
- The collection of these molecules into simple organisms
- The evolution of more complex organisms, including ourselves

Physicists are working to discover how matter was created, and biologists are attempting to explain how simple organisms formed and evolved into organisms that are more complex. Chemists get the middle ground, the problem of how biomolecules (molecules important to biological systems) originally formed from the elements. This alone is a huge topic, so we will limit our discussion

here to a theory that attempts to explain how some simple precursors of important biomolecules might have formed on Earth billions of years ago.

To explain how living organisms grow and reproduce, we need to explain how certain chemicals, such as amino acids and proteins, are formed. Amino acids have the following general structure, with R representing one of several groups that make one amino acid different from another.



When two or more amino acids are linked together, the product is called a peptide. Protein molecules, which

(continued)

showed that this reaction takes place at the temperatures of the hydrothermal vents (350 °C) if the reactants are combined at high pressure.

One of the perceived weaknesses of Wächtershäuser's theory was the need for ammonia. Some scientists questioned whether it would be present in high enough concentrations for the conversion of pyruvic acid to amino acids, but Brandes has done experiments that show that ammonia is formed when a mixture of water and nitrogen oxides known to be found in the vents is heated to 500 °C and compressed to 500 atm. Experiments done by Brandes duplicating the conditions at hydrothermal vents also show a 40% conversion of pyruvic acid and

ammonia to the amino acid alanine. Wächtershäuser and Huber have demonstrated the conversion of amino acids to peptides in the laboratory.

Do these experiments show that the first amino acids and proteins on Earth were made in this way? No. There are other plausible explanations, and at this point, there is no general agreement on which explanation is best. In fact, as of this writing, Wächtershäuser's theory is a minority view, but it is gaining in popularity. The search for an explanation of the origin of biomolecules continues, each step leading us closer to a better understanding of the physical world and how it came to be.

Chapter Glossary

Collision theory A model for the process of chemical change.

Activation energy The minimum energy necessary for reactants to reach the activated complex and proceed to products.

Rate of chemical reactions The number of product molecules that form (perhaps described as moles of product formed) per liter of container per second.

Concentration The number of particles per unit volume. For gases, it is usually described in terms of moles of gas particles per liter of container. Substances in solution are described with molarity (moles of solute per liter of solution).

Homogeneous catalyst A catalyst that is in the same phase as the reactants (so that all substances are gases or all are in solution).

Heterogeneous catalyst A catalyst that is not in the same phase as the reactants, e.g. a solid catalyst for a gas phase reaction.

Homogeneous equilibrium An equilibrium system in which all of the components are in the same phase (gas, liquid, solid, or aqueous).

Equilibrium constant A value that describes the extent to which reversible reactions proceed toward products before reaching equilibrium.

Equilibrium constant expression An expression showing the ratio of the concentrations of products to the concentrations of reactants for a reversible reaction at equilibrium. For homogeneous equilibria, the concentrations of all reactants and products are described in moles per liter, and the concentration of each is raised to a power equal to its coefficient in a balanced equation for the reaction.

Heterogeneous equilibrium An equilibrium in which the reactants and products are not all in the same phase (gas, liquid, solid, or aqueous).

Water dissociation constant, K_w The equilibrium constant for the reaction:

$$\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq)$$

Le Chatelier's principle If a system at equilibrium is altered in a way that disrupts the equilibrium, the system will shift so as to counter the change.

You can test yourself on the glossary terms at the textbook's Web site.

The goal of this chapter is to teach you to do the following.

1. Define all of the terms in the Chapter Glossary.

Section 14.1 Collision Theory: A Model for the Process of Chemical Reactions

2. Use collision theory to describe the general process that takes place as a system moves from reactants to products in a reaction between two reactants, such as the reaction between $\text{O}(g)$ and $\text{O}_3(g)$.
3. Explain why two particles must collide before a reaction between them can take place, referring to the role of the motion of the particles in providing energy for the reaction.
4. Explain why it is usually necessary for the new bonds in a chemical reaction's products to form at the same time as the old bonds in the reactants are broken.
5. Identify the sign (positive or negative) for the heat of reaction for an exothermic reaction.
6. Explain why a collision between reactant particles must have a certain minimum energy (activation energy) in order to proceed to products.
7. Draw an energy diagram for a typical exergonic reaction, showing the relative energies of the reactants, the activated complex, and the products. Using arrows show the activation energy and the overall energy of the reaction.
8. Identify the sign (positive or negative) for the overall energy of reaction for an endothermic reaction.
9. Draw an energy diagram for a typical endergonic reaction, showing the relative energies of the reactants, the activated complex, and the products. Using arrows show the activation energy and the overall energy of the reaction.
10. Explain why two reactant particles must collide with the correct orientation if a reaction between them is likely to take place.
11. List the three requirements that must be met before a reaction between two particles is likely to take place.

Section 14.2 Rates of Chemical Reactions

12. Give two reasons why increased temperature usually increases the rate of chemical reactions.
13. Explain why increased concentration of a reactant will lead to an increase in the rate of a chemical reaction.
14. Explain why chlorine atoms speed the conversion of ozone molecules, O_3 , and oxygen atoms, O , to oxygen molecules, O_2 . Include the change in the activation energy of the catalyzed reaction compared to the uncatalyzed reaction and the effect that this change has on the fraction of collisions having the minimum energy necessary for reaction.
15. Explain why the rate of a catalyzed reaction is expected to be greater than the rate of the same reaction without the catalyst.
16. Describe the four steps thought to occur in heterogeneous catalysis.

Section 14.3 Reversible Reactions and Chemical Equilibrium

17. Given an equation for a reversible chemical reaction, describe the changes that take place in the reaction vessel from the time when the reactants are first added to the container until a dynamic equilibrium is reached.
18. Explain why the rate of the forward reaction in a chemical change is at its peak when the reactants are first added to the container and why this rate diminishes with time.
19. Explain why the rate of the reverse reaction in a chemical change is zero when the reactants are first added to a container and why this rate increases with time.
20. With reference to the changing forward and reverse reaction rates, explain why any reversible reaction moves toward a dynamic equilibrium with equal forward and reverse reactions rates.
21. Describe the changes that take place in a chemical system at equilibrium, and explain why there are no changes in the concentrations of reactants and products despite these changes.
22. Given a balanced equation for a reversible chemical reaction, write its equilibrium constant, K_C , expression with the reactants and products described in terms of concentrations.
23. Given a balanced equation for a reversible chemical reaction that involves at least one gaseous substance, write its equilibrium constant, K_P , expression with the reactants and products described in terms of gas pressures.
24. Given a balanced equation for a reversible chemical change and gas pressures for reactants and products at equilibrium, calculate the reaction's K_P .
25. Given an equilibrium constant for a reversible chemical reaction, predict whether the reaction favors reactants, products, or neither.
26. Explain why pure solids and liquids are left out of equilibrium constant expressions for heterogeneous equilibria.
27. Explain why increased temperature drives a reversible chemical reaction in the endothermic direction.
28. Explain why increased temperature increases the equilibrium constant for a reversible chemical change that has an endothermic forward reaction and why increased temperature decreases the equilibrium constant for a change that has an exothermic forward reaction.
29. Explain why some exothermic chemical reactions are run at high temperature despite the fact that the ratio of products to reactants will be lower at equilibrium.

Section 14.4 Disruption of Equilibrium

30. Explain why an increase in the concentration of a reactant in a reversible reaction at equilibrium will disrupt the equilibrium and shift the system toward more products.
31. Explain why a decrease in the concentration of a product in a reversible reaction at equilibrium will disrupt the equilibrium and shift the system toward more products.

32. Given a complete, balanced equation for a reversible chemical reaction at equilibrium and being told whether it is endothermic or exothermic, predict whether the following changes would shift the system toward more products, more reactants, or neither: adding reactant, adding product, removing reactant, removing product, increasing temperature, decreasing temperature, or adding catalyst.
33. Explain your answers for the previous objective in terms of Le Chatelier's principle and in terms of the effect of the changes on the forward and reverse reaction rates.
34. Explain why a catalyst has no effect on equilibrium concentrations for a reversible reaction.

-
1. Describe what you visualize occurring inside a container of oxygen gas, O_2 , at room temperature and pressure.
 2. Write the word in each blank that best fits the definition.
 - a. _____ is the capacity to do work.
 - b. _____ is the capacity to do work due to the motion of an object.
 - c. A(n) _____ change is a change that absorbs energy.
 - d. A(n) _____ change is a change that releases energy.
 - e. _____ is the energy associated with the random motion of particles.
 - f. _____ is energy that is transferred from a region of higher temperature to a region of lower temperature due to the collisions of particles.
 - g. A(n) _____ change is a change that leads to *heat* energy being evolved from the system to the surroundings.
 - h. A(n) _____ change is a change that leads the system to absorb *heat* energy from the surroundings.
 - i. A(n) _____ is a substance that speeds a chemical reaction without being permanently altered itself.
 3. When the temperature of the air changes from $62\text{ }^\circ\text{C}$ at 4:00 A.M. to $84\text{ }^\circ\text{C}$ at noon on a summer's day, does the average kinetic energy of the particles in the air increase, decrease, or stay the same?
 4. Explain why it takes energy to break an O–O bond in an O_3 molecule.
 5. Explain why energy is released when two oxygen atoms come together to form an O_2 molecule.
 6. Explain why some chemical reactions release heat to their surroundings.
 7. Explain why some chemical reactions absorb heat from their surroundings.
 8. What are the general characteristics of any dynamic equilibrium system?

Key Ideas

Complete the following statements by writing one of these words or phrases in each blank.

activated complex	kilojoules per mole, kJ/mol
alternative pathway	larger
balanced	lower activation energy
change	minimum
close to each other	moles per liter
collide	more quickly
collision	negative
coefficient	net
disrupts	new bonds
endergonic	no effect
endergonic reaction	old bonds
equal	orientation
equal to	phase
equilibrium constant	positive
exergonic	pressures
fraction	products
greater than	reactants
heterogeneous	released
homogeneous	shorter
increases	toward products
K_p	transition state

9. At a certain stage in the progress of a reaction, bond breaking and bond making are of equal importance. In other words, the energy necessary for bond breaking is _____ by the energy supplied by bond making. At this turning point, the particles involved in the reaction are joined in a structure known as the activated complex, or _____.
10. As a reaction continues beyond the activated complex, the energy released in bond making becomes greater than the energy necessary for bond breaking, and energy is _____.
11. In a chemical reaction, the _____ energy necessary for reaching the activated complex and proceeding to products is called the activation energy. Only the collisions that provide a net kinetic energy _____ or _____ the activation energy can lead to products.
12. The energies associated with chemical reactions are usually described in terms of _____. If the energy is released, the value is described with a(n) _____ sign.
13. The energies associated with endergonic (or endothermic) changes are described with _____ values.

14. Collision theory stipulates that three requirements must be met before a reaction between two particles is likely to take place. The reactant particles must _____. The _____ must provide at least the minimum energy necessary to produce the _____. The _____ of the colliding particles must favor the formation of the activated complex, in which the new bond or bonds are able to form as the old bond or bonds break.
15. Because the formation of the _____ provides some of the energy necessary to break the _____, the making and breaking of bonds must occur more or less simultaneously. This is possible only when the particles collide in such a way that the bond-forming atoms are _____.
16. In general, increased temperature _____ the rate of chemical reactions.
17. Increased temperature means an increase in the average kinetic energy of the collisions between the particles in a system. This leads to an increase in the _____ of the collisions that have enough energy to reach the activated complex (the activation energy).
18. Increasing the concentration of one or both reactants will lead to _____ distances between reactant particles and to their occupying a larger percentage of the volume. Therefore, more collisions can be expected to occur per second.
19. One of the ways in which catalysts accelerate chemical reactions is by providing a(n) _____ between reactants and products that has a(n) _____.
20. If the reactants and the catalyst are all in the same state (all gases or all in solution) the catalyst is a(n) _____ catalyst.
21. If the catalyst is not in the same state as the reactants, the catalyst is called a(n) _____ catalyst.
22. In a dynamic equilibrium for a reversible chemical reaction, the forward and reverse reaction rates are _____, so although reactants and products are constantly changing back and forth, there is no _____ change in the amount of either.
23. The extent to which reversible reactions proceed toward products before reaching equilibrium can be described with a(n) _____, which is derived from the ratio of the concentrations of products to the concentrations of reactants at equilibrium. For homogeneous equilibria, the concentrations of all reactants and products can be described in _____, and the concentration of each is raised to a power equal to its _____ in a balanced equation for the reaction.
24. Gases in equilibrium constant expressions are often described with _____ instead of concentrations (mol/L). When an equilibrium constant is derived from gas pressures, we represent it with the symbol _____.
25. The _____ a value for K , the farther the reaction shifts toward products before the rates of the forward and reverse reactions become equal and the concentrations of reactants and products stop changing.
26. When the reactants and products for a reversible reaction are not all in the same _____ (gas, liquid, solid, or aqueous), the equilibrium is called a heterogeneous equilibrium.

27. Changing temperature always causes a shift in equilibrium systems—sometimes toward more products and sometimes toward more _____.
28. Increased temperature increases the rate of both the forward and the reverse reactions, but it increases the rate of the _____ reaction more than it increases the rate of the _____ reaction. Therefore, increasing the temperature of a chemical system at equilibrium will disrupt the balance of the forward and reverse rates of reaction and shift the system in the direction of the _____.
29. If the forward reaction in a reversible reaction is endergonic, increased temperature will shift the system toward more _____.
30. The increase of one or more reactants shifts a system initially at equilibrium _____.
31. Le Chatelier's principle states that if a system at equilibrium is altered in a way that _____ the equilibrium, the system will shift in such a way as to counter the _____.
32. The presence of a catalyst has _____ on the equilibrium concentrations of reactants and products. Catalysts speed both the forward and reverse rates to the same degree. The system will reach equilibrium _____, but the ratio of the concentrations of products to reactants—and thus the value of the equilibrium constant—is unchanged.

Chapter Problems

Section 14.1 Collision Theory: A Model for the Reaction Process

33. Assume that the following reaction is a single-step reaction in which one of the O–O bonds in O_3 is broken and a new N–O bond is formed. The heat of reaction is -226 kJ/mol.



OBJECTIVE 2

- a. With reference to collision theory, describe the general process that takes place as this reaction moves from reactants to products.

OBJECTIVE 11

- b. List the three requirements that must be met before a reaction between $NO(g)$ and $O_3(g)$ is likely to take place.

OBJECTIVE 3

- c. Explain why $NO(g)$ and $O_3(g)$ must collide before a reaction can take place.

OBJECTIVE 4

- d. Explain why it is usually necessary for the new N–O bonds to form at the same time as the O–O bonds are broken.
- e. Draw a rough sketch of the activated complex. (You do not need to show bond angles. Be sure to show the bond that is breaking and the bond that is being formed.)

OBJECTIVE 6

- f. Explain why a collision between $NO(g)$ and $O_3(g)$ must have a certain minimum energy (activation energy) in order to proceed to products.

OBJECTIVE 7

- g. The activation energy for this reaction is 132 kJ/mol. Draw an energy diagram for this reaction, showing the relative energies of the reactants, the activated complex, and the products. Using arrows show the activation energy and heat of reaction.

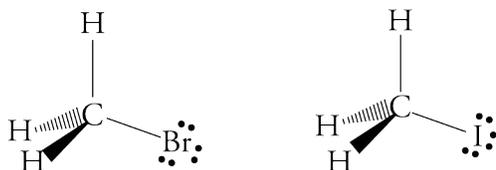
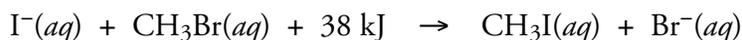
OBJECTIVES 5 & 8

- h. Is this reaction exothermic or endothermic?

OBJECTIVE 10

- i. Explain why $NO(g)$ and $O_3(g)$ molecules must collide with the correct orientation if a reaction between them is going to be likely to take place.

34. Assume that the following reaction is a single step reaction in which a C–Br bond is broken as the C–I bond is formed. The heat of reaction is +38 kJ/mol.



- With reference to collision theory, describe the general process that takes place as this reaction moves from reactants to products. OBJECTIVE 2
- List the three requirements that must be met before a reaction between I^{-} and CH_3Br is likely to take place. OBJECTIVE 11
- Explain why an I^{-} ion and a CH_3Br molecule must collide before a reaction can take place. OBJECTIVE 3
- Explain why, in the process of this reaction, it is usually necessary for the new C–I bonds to form at the same time as the C–Br bonds are broken. OBJECTIVE 4
- Draw a rough sketch of the activated complex. (You do not need to show bond angles. Be sure to show the bond that is breaking and the bond that is being formed.)
- Explain why a collision between an I^{-} ion and a CH_3Br molecule must have a certain minimum energy (activation energy) in order to proceed to products. OBJECTIVE 6
- The activation energy for this reaction is 76 kJ/mol. Draw an energy diagram for this reaction, showing the relative energies of the reactants, the activated complex, and the products. Using arrows show the activation energy and heat of reaction. OBJECTIVE 7
- Is this reaction exothermic or endothermic? OBJECTIVES 5 & 8
- Explain why an I^{-} ion and a CH_3Br molecule must collide with the correct orientation if a reaction between them is going to be likely to take place. OBJECTIVE 10

Section 14.2 Rates of Chemical Reactions

35. Consider the following general reaction for which gases A and B are mixed in a constant volume container.



What happens to the rate of this reaction when

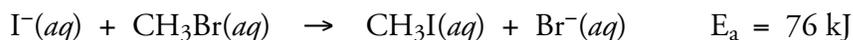
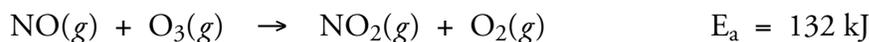
- more gas A is added to the container?
 - the temperature is decreased?
 - a catalyst is added that lowers the activation energy?
36. Consider the following general reaction for which gases A and B are mixed in a constant volume container.



What happens to the rate of this reaction when

- gas B is removed from the container?
- the temperature is increased?

37. The reactions listed below are run at the same temperature. The activation energy for the first reaction is 132 kJ/mol. The activation energy for the second reaction is 76 kJ/mol. In which of these reactions would a higher fraction of collisions between reactants have the minimum energy necessary to react (the activation energy)? Explain your answer.



38. Consider the following reaction.

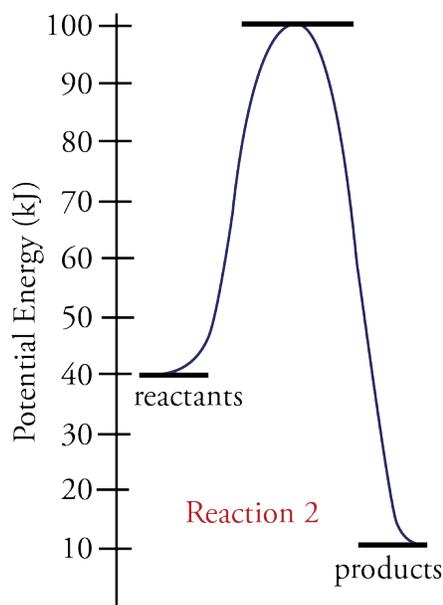
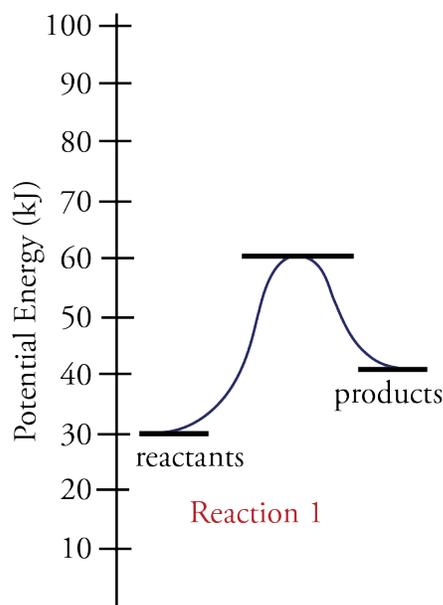


- Explain why increased temperature increases the rate of reaction.
- Will an increase in the concentration of $\text{NO}(g)$ increase, decrease, or not affect the rate of the reaction? Explain your answer.

OBJECTIVE 12

OBJECTIVE 13

39. Two reactions can be described by the energy diagrams below. What is the approximate activation energy for each reaction? Which reaction is exothermic and which is endothermic?



40. If both systems described by the energy diagrams in the previous problem are at the same temperature, if the concentrations of initial reactants are equivalent for each reaction, and if the orientation requirements for each reaction are about the same, which of these reactions would you expect to have the greatest forward reaction rate? Why?

OBJECTIVE 14

41. Explain why chlorine atoms speed the conversion of ozone molecules, O_3 , and oxygen atoms, O , to oxygen molecules, O_2 .

OBJECTIVE 15

42. Write a general explanation for why the rate of a catalyzed reaction would be expected to be greater than the rate of the same reaction without the catalyst.

OBJECTIVE 16

43. Using the proposed mechanism for the conversion of $\text{NO}(g)$ to $\text{N}_2(g)$ and $\text{O}_2(g)$ as an example, write a description of the four steps thought to occur in heterogeneous catalysis.

Section 14.3 Reversible Reactions and Chemical Equilibrium

44. Reversible chemical reactions lead to dynamic equilibrium states. What is dynamic about these states? Why are they called equilibrium states?
45. Equilibrium systems have two opposing rates of change that are equal. For each of the following equilibrium systems that were mentioned in earlier chapters, describe what is changing in the two opposing rates.
- a solution of the weak acid acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$ (Chapter 6)
 - pure liquid in a closed container (Chapter 12)
 - a closed bottle of carbonated water with 4 atm of CO_2 in the gas space above the liquid (Chapter 13)
46. Equilibrium systems have two opposing rates of change that are equal. For each of the following equilibrium systems that were mentioned in earlier chapters, describe what is changing in the two opposing rates.
- a solution of the weak base ammonia, NH_3 (Chapter 8)
 - saturated solution of table salt, NaCl , with excess solid NaCl (Chapter 13)
47. Two gases, A and B, are added to an empty container. They react in the following reversible reaction.
- $$\text{A}(g) + \text{B}(g) \rightleftharpoons \text{C}(g) + \text{D}(g)$$
- When is the forward reaction rate greatest: (1) when A and B are first mixed, (2) when the reaction reaches equilibrium, or (3) sometime between these two events?
 - When is the reverse reaction rate greatest: (1) when A and B are first mixed, (2) when the reaction reaches equilibrium, or (3) sometime between these two events?
48. Assume that in the following reversible reaction both the forward and the reverse reactions take place in a single step.
- $$\text{NO}(g) + \text{O}_3(g) \rightleftharpoons \text{NO}_2(g) + \text{O}_2(g)$$
- Describe the changes that take place in the reaction vessel from the time when $\text{NO}(g)$ and $\text{O}_3(g)$ are first added to the container until a dynamic equilibrium is reached (including the changes in concentrations of reactants and products and the changes in the forward and reverse reaction rates).
49. Assume that in the following reversible reaction both the forward and the reverse reactions take place in a single step.
- $$\text{I}^-(aq) + \text{CH}_3\text{Br}(aq) \rightleftharpoons \text{CH}_3\text{I}(aq) + \text{Br}^-(aq)$$
- With reference to the changing forward and reverse reaction rates, explain why this reaction moves toward a dynamic equilibrium with equal forward and reverse reaction rates.
 - Describe the changes that take place once the reaction reaches an equilibrium state. Are there changes in the concentrations of reactants and products at equilibrium? Explain your answer.
50. Write K_C and K_P expressions for each of the following equations.
- $2\text{CH}_4(g) \rightleftharpoons \text{C}_2\text{H}_2(g) + 3\text{H}_2(g)$
 - $2\text{N}_2\text{O}(g) + \text{O}_2(g) \rightleftharpoons 4\text{NO}(g)$
 - $\text{Sb}_2\text{S}_3(s) + 3\text{H}_2(g) \rightleftharpoons 2\text{Sb}(s) + 3\text{H}_2\text{S}(g)$

OBJECTIVE 17

OBJECTIVE 17

OBJECTIVE 17

OBJECTIVE 18

OBJECTIVE 19

OBJECTIVE 20

OBJECTIVE 21

OBJECTIVE 22

OBJECTIVE 23

OBJECTIVE 22

51. Write K_C and K_P expressions for each of the following equations.

OBJECTIVE 23

- a. $4\text{CuO}(s) \rightleftharpoons 2\text{Cu}_2\text{O}(s) + \text{O}_2(g)$
 b. $\text{CH}_4(g) + 4\text{Cl}_2(g) \rightleftharpoons \text{CCl}_4(l) + 4\text{HCl}(g)$
 c. $2\text{H}_2\text{S}(g) + \text{CH}_4(g) \rightleftharpoons \text{CS}_2(g) + 4\text{H}_2(g)$

OBJECTIVE 24

52. A mixture of nitrogen dioxide and dinitrogen tetroxide are allowed to come to equilibrium at 30°C , and their partial pressures are found to be $1.69\text{ atm N}_2\text{O}_4$ and 0.60 atm NO_2 .

- a. Based on this data, what is K_P for the following equation?
 $\text{NO}_2(g) \rightleftharpoons \frac{1}{2}\text{N}_2\text{O}_4(g)$
 b. Based on this data, what is K_P for the equation below?
 $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$
 c. Table 14.1 lists the K_P for the equation in part (b) as 6.7 at 25°C . Explain why your answer to part (b) is not 6.7.

OBJECTIVE 24

53. A mixture of nitrogen gas, hydrogen gas, and ammonia gas are allowed to come to equilibrium at 200°C , and their partial pressures are found to be 0.61 atm N_2 , 1.1 atm H_2 , and 0.52 atm NH_3 .

- a. Based on this data, what is K_P for the following equation?
 $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$
 b. Based on this data, what is K_P for the equation below?
 $\frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g) \rightleftharpoons \text{NH}_3(g)$

OBJECTIVE 25

54. Predict whether each of the following reactions favor reactants, products, or neither at the temperature for which the equilibrium constant is given.

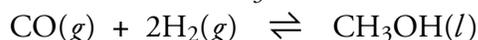
- a. $\text{CH}_3\text{OH}(g) + \text{CO}(g) \rightleftharpoons \text{CH}_3\text{CO}_2\text{H}(g)$ $K_P = 1.2 \times 10^{-22}$ at 25°C
 b. $\text{CH}_4(g) + 4\text{Cl}_2(g) \rightleftharpoons \text{CCl}_4(g) + 4\text{HCl}(g)$ $K_P = 3.3 \times 10^{68}$ at 25°C
 c. $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$ $K_P = 0.20$ at 600°C

OBJECTIVE 25

55. Predict whether each of the following reactions favor reactants, products, or neither at the temperature for which the equilibrium constant is given.

- a. $2\text{COF}_2(g) \rightleftharpoons \text{CO}_2(g) + \text{CF}_4(g)$ $K_P = 2$ at 1000°C
 b. $\frac{1}{8}\text{S}_8(s) + \text{O}_2(g) \rightleftharpoons \text{SO}_2(g)$ $K_P = 4.2 \times 10^{52}$ at 25°C
 c. $\text{C}_2\text{H}_6(g) \rightleftharpoons \text{C}_2\text{H}_4(g) + \text{H}_2(g)$ $K_P = 1.2 \times 10^{-18}$ at 25°C

OBJECTIVE 22

56. Write the K_C expression for the following equation. Explain why the concentration of CH_3OH is left out of the expression.

OBJECTIVE 22

57. Write the K_C expression for the following equation. Explain why the concentration of NH_4HS is left out of the expression.

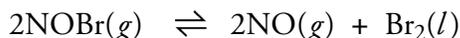
OBJECTIVE 26

58. Ethylene, C_2H_4 , is one of the organic substances found in the air we breathe.It reacts with ozone in an endothermic reaction to form formaldehyde, CH_2O , which is one of the substances in smoggy air that cause eye irritation.

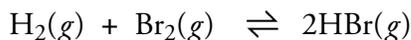
- a. Why does the forward reaction take place more rapidly in Los Angeles than in a wilderness area of Montana with the same air temperature?
 b. For a variety of reasons, natural systems rarely reach equilibrium, but if this reaction was run in the laboratory, would increased temperature for the reaction at equilibrium shift the reaction to more reactants or more products?



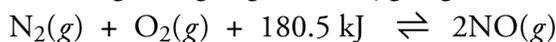
59. When the temperature of an equilibrium system for the following reaction is increased, the reaction shifts toward more products. Is the reaction endothermic or exothermic?



60. When the temperature of an equilibrium system for the following reaction is increased, the reaction shifts toward more reactants. Is the reaction endothermic or exothermic?



61. A lightning bolt creates a large quantity of nitrogen monoxide in its path by combining nitrogen gas and oxygen gas.



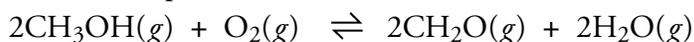
- Explain why lightning increases the amount of $\text{NO}(g)$ produced by this reaction. (Hint: Lightning generates a lot of heat.)
 - Would increased temperature increase or decrease the equilibrium constant for this reaction?
62. Assume that you are picking up a few extra dollars to pay for textbooks by acting as a trainer's assistant for a heavyweight boxer. One of your jobs is to wave smelling salts under the nose of the fighter to clear his head between rounds. The smelling salts are ammonium carbonate, which decomposes in the following reaction to yield ammonia. The ammonia does the wake up job. Suppose the fighter gets a particularly nasty punch to the head and needs an extra jolt to be brought back to his senses. How could you shift the following equilibrium to the right to yield more ammonia?



63. Ethylene, C_2H_4 , used to make polyethylene plastics, can be made from ethane, C_2H_6 , one of the components of natural gas. The heat of reaction for the decomposition of ethane gas into ethylene gas and hydrogen gas is 136.94 kJ per mole of C_2H_4 formed, so it is endothermic. The reaction is run at high temperature, in part because at 800-900 °C, the equilibrium constant for the reaction is much higher, indicating that a higher percentage of products forms at this temperature. Explain why increased temperature drives this reversible chemical reaction in the endergonic direction and why this leads to an increase in the equilibrium constant for the reaction.



64. Formaldehyde, CH_2O , is one of the components of embalming fluids and has been used to make foam insulation and plywood. It can be made from methanol, CH_3OH (often called wood alcohol). The heat of reaction for the combination of gaseous methanol and oxygen gas to form gaseous formaldehyde and water vapor is -199.32 kJ per mol of CH_2O formed, so the reaction is exothermic.



- Increased temperature drives the reaction toward reactants and lowers the value for the equilibrium constant. Explain why this is true.
- This reaction is run by the chemical industry at 450-900 °C, even though the equilibrium ratio of product to reactant concentrations is lower than at room temperature. Explain why this exothermic chemical reaction is run at high temperature despite this fact.



OBJECTIVE 27

OBJECTIVE 28

OBJECTIVE 27

OBJECTIVE 28

OBJECTIVE 29

65. Is the equilibrium constant for a particular reaction dependent on
- the initial concentration of reactants?
 - the initial concentration of products?
 - the temperature for the reaction?

Section 14.4 Disruption of Equilibrium

OBJECTIVE 30

OBJECTIVE 31

OBJECTIVE 32

OBJECTIVE 33

- 66.** Urea, NH_2CONH_2 , is an important substance in the production of fertilizers. The equation shown below describes an industrial reaction that produces urea. The heat of the reaction is -135.7 kJ per mole of urea formed. Predict whether each of the following changes in the equilibrium system will shift the system to more products, to more reactants, or neither. Explain each answer in two ways, (1) by applying Le Chatelier's principle and (2) by describing the effect of the change on the forward and reverse reaction rates.



- The concentration of NH_3 is increased by the addition of more NH_3 . (In the industrial production of urea, an excess of ammonia is added so that the ratio of $\text{NH}_3:\text{CO}_2$ is 3:1.)
- The concentration of $\text{H}_2\text{O}(g)$ is decreased by removing water vapor.
- The temperature is increased from 25°C to 190°C . (In the industrial production of urea, ammonia and carbon dioxide are heated to 190°C .)

OBJECTIVE 30

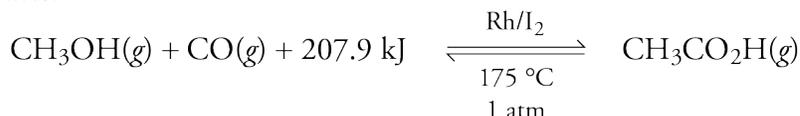
OBJECTIVE 31

OBJECTIVE 32

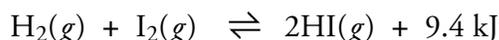
OBJECTIVE 33

OBJECTIVE 34

- 67.** Acetic acid, which is used to make many important compounds, is produced from methanol and carbon monoxide (which are themselves both derived from methane in natural gas) by a process called the Monsanto process. The endothermic reaction is run over a rhodium and iodine catalyst at 175°C and 1 atm of pressure. Predict whether each of the following changes in the equilibrium system will shift the system to more products, to more reactants, or neither. Explain each answer in two ways, (1) by applying Le Chatelier's principle and (2) by describing the effect of the change on the forward and reverse reaction rates.

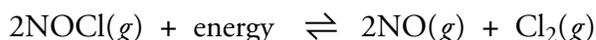


- The concentration of CO is increased by the addition of more CO .
 - The concentration of CH_3OH is decreased.
 - The concentration of $\text{CH}_3\text{CO}_2\text{H}(g)$ is decreased by removing the acetic acid as it forms.
 - The temperature is decreased from 300°C to 175°C .
 - The Rh/I_2 catalyst is added to the equilibrium system.
- 68.** Hydriodic acid, which is used to make pharmaceuticals, is made from hydrogen iodide. The hydrogen iodide is made from hydrogen gas and iodine gas in the following exothermic reaction.



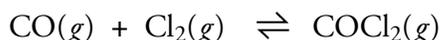
What changes could you make for this reaction at equilibrium to shift the reaction to the right and maximize the concentration of hydrogen iodide in the final product mixture?

69. Nitrosyl chloride is used to make synthetic detergents. It decomposes to form nitrogen monoxide and chlorine gas.



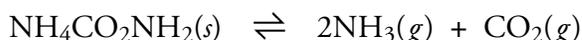
Without directly changing the concentration of NOCl, what changes could you make for this reaction at equilibrium to shift the reaction to the left and minimize the decomposition of the NOCl?

70. Phosgene gas, COCl_2 , which is a very toxic substance used to make pesticides and herbicides, is made by passing carbon monoxide gas and chlorine gas over solid carbon, which acts as a catalyst.



If the carbon monoxide concentration is increased by adding CO to an equilibrium system of this reaction, what effect, if any, does it have on the following? (Assume constant temperature.)

- The concentration of COCl_2 after the system has shifted to come to a new equilibrium.
 - The concentration of Cl_2 after the system has shifted to come to a new equilibrium.
 - The equilibrium constant for the reaction.
71. The fertilizer ammonium carbamate decomposes in the following reaction.



If the ammonia concentration is increased by adding NH_3 to an equilibrium system of this reaction, what effect, if any, does it have on the following? (Assume constant temperature.)

- The concentration of CO_2 after the system has shifted to come to a new equilibrium.
- The equilibrium constant for the reaction.

Discussion Problems

72. Illustrate the following characteristics of a reversible chemical change by developing an analogy based on a new college library.
- When reactants are first added to a container, the rate of the forward reaction is at a peak, and it decreases steadily with time.
 - If there are no products initially, the rate of the reverse reaction is zero at the instant that reactants are added to the container, but the reverse rate of change increases steadily as the reaction proceeds.
 - At some point, the forward and reverse rates become equal, and if the system is not disrupted, the rates will remain equal. This leads to a constant amount of reactants and products.
 - The addition of one or more of the reactants to a system at equilibrium will drive the system to produce more products.
 - The removal of one or more of the products from a system at equilibrium will also drive the system toward more products.

