Chapter 9

Reaction rates and equilibrium

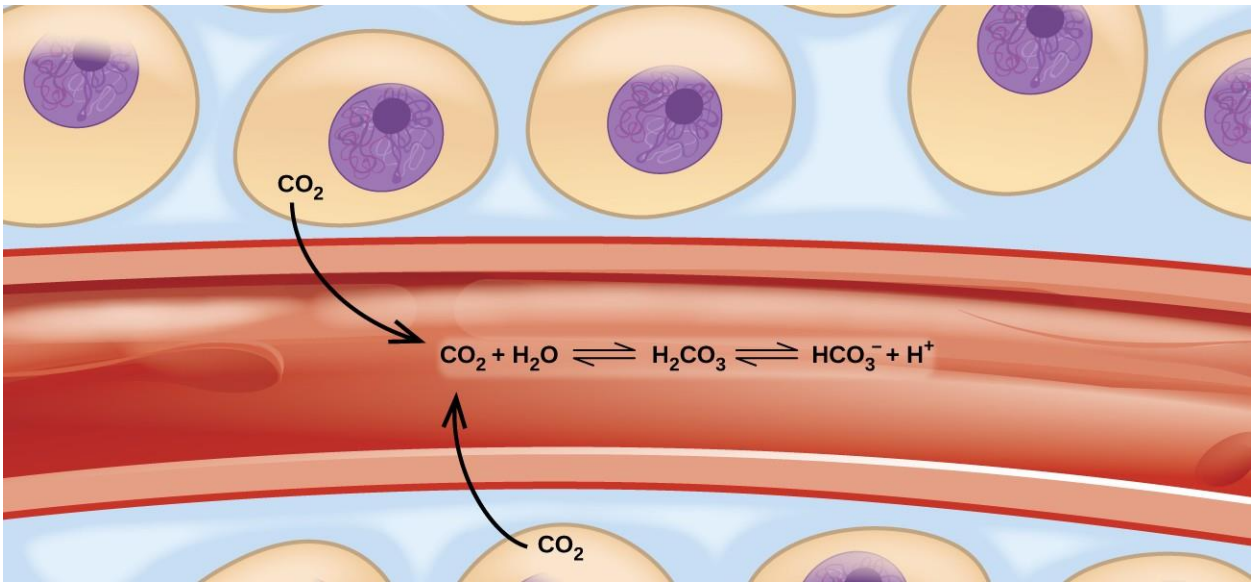


Figure 9.1 Movement of carbon dioxide through tissues and blood cells involves several equilibrium reactions.

Chapter Outline

9.1 Chemical Reaction Rates

9.2 Factors Affecting Reaction Rates

9.3 Collision Theory

9.4 Catalysis

9.5 Chemical Equilibria

9.6 Equilibrium Constants

9.7 Shifting Equilibria: Le Châtelier's Principle

Introduction

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. When planning to run a chemical reaction, we should ask at least two questions. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" A reaction that takes 50 years to produce a product is about as useful as one that never gives a product at all. A third question is often asked when investigating reactions in greater detail: "What specific molecular-level processes take place as the reaction occurs?" Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled. In this chapter, we will examine the factors that influence the rates of chemical reactions, the mechanisms by which reactions proceed, and the quantitative techniques used to determine and describe the rate at which reactions occur. In addition, reactions can

occur in both directions simultaneously (reactants to products and products to reactants) and eventually reach a state of balance. These balanced two-way reactions occur all around and even in us. For example, they occur in our blood, where the reaction between carbon dioxide and water forms carbonic acid (H_2CO_3) (**Figure 9.1**). Human physiology is adapted to the amount of ionized products produced by this reaction (HCO_3^- and H^+). This chapter provides a thorough introduction to the essential aspects of chemical equilibria.

9.1 Chemical Reaction Rates

By the end of this section, you will be able to:

- Define chemical reaction rate

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The **rate of reaction** is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

Chemistry in Everyday Life Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (**Figure 9.2**). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations. The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

$$C_6H_{12}O_6 + O_2 \xrightarrow[\text{Catalyst}]{} C_6H_{10}O_6 + H_2O_2$$

$$2H_2O_2 + 2I^- \xrightarrow[\text{Catalyst}]{} I_2 + 2H_2O + O_2$$

The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change. The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it is (a *false-*

negative result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.

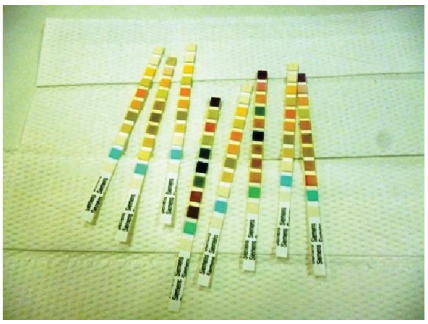


Figure 9.2 Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)

9.2 Factors Affecting Reaction Rates

By the end of this section, you will be able to:

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

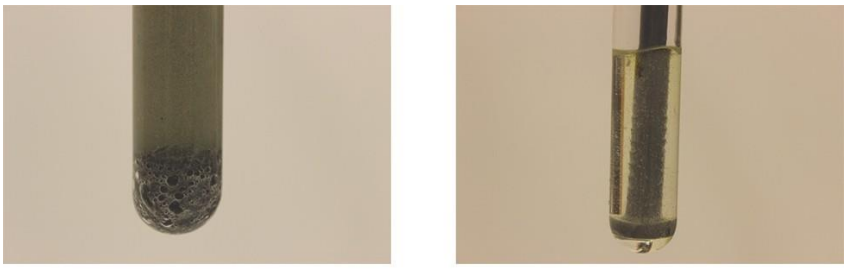
The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. We can identify four factors that affect the rates of chemical reactions: the chemical nature of the reacting substances, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

The State of Subdivision of the Reactants

Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. Hence, the rate of a reaction between two phases depends to a great extent on the surface contact between them. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus, a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid. For example, large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly (**Figure 9.3**). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



(a) (b)

Figure 9.3 (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total surface area: $2Fe(s) + 6HCl(aq) \longrightarrow 2FeCl_3(aq) + 3H_2(g)$. (b) An iron nail reacts more slowly.

Link to Learning

Watch **this video (http://openstaxcollege.org/l/16cesium)** to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10 °C will approximately double the rate of a reaction in a homogeneous system.

Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($CaCO_3$) deteriorates because of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (**Figure 9.4**). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$SO_2(g) + H_2O(g) \longrightarrow H_2SO_3(aq)$$

Calcium carbonate reacts with sulfurous acid as follows:

$$CaCO_3(s) + H_2SO_3(aq) \longrightarrow CaSO_3(aq) + CO_2(g) + H_2O(l)$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air.

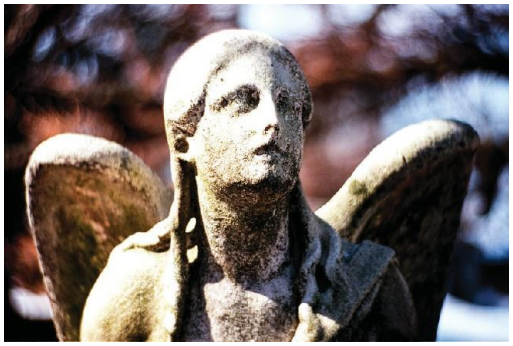


Figure 9.4 Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, thermal expansion and contraction. But, pollutants like sulfur dioxide accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs faster. (credit: James P Fisher III)

Link to Learning

Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this **video (http://openstaxcollege.org/l/**

The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide's decomposition. But, without any catalyst (like in the bottle in the medicine cabinet) complete decomposition can take months. A **catalyst** is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Activation energy is the minimum amount of energy required for a chemical reaction to proceed in the forward direction. A catalyst increases the reaction rate by providing an alternative pathway or mechanism for the reaction to follow (**Figure 9.5**).

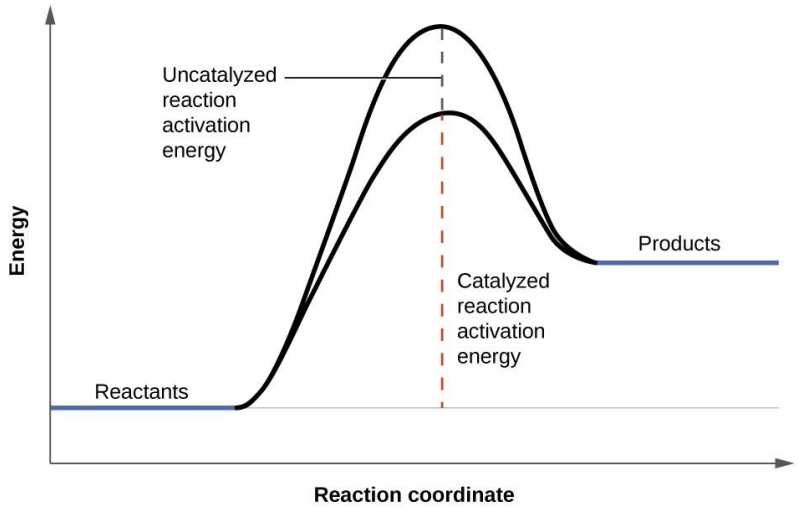


Figure 9.5 The presence of a catalyst increases the rate of a reaction by lowering its activation energy

Link to Learning

Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the **PhET Reactions & Rates interactive (http://openstaxcollege.org/l/16PHETreaction)** to explore how temperature, concentration, and the nature of the reactants affect reaction rates.

9.3 Collision Theory

By the end of this section, you will be able to:

- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- Define the concept of activation energy

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates. **Collision theory** is based on the following postulates:

1. The rate of a reaction is proportional to the rate of reactant collisions:

$$reaction\ rate\ \propto = \frac{\#\ collisions}{time}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:

$$2\ CO(g) + O_2(g) \longrightarrow 2\ CO_2(g)$$

Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. If carbon monoxide and oxygen are present in sufficient quantity, the reaction is spontaneous at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$CO(g) + O_2(g) \longrightarrow CO_2(g) + O(g)$$

Although there are many different possible orientations the two molecules can have relative to each other, consider

the two presented in **Figure 9.6**. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms (O=C=O). This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.

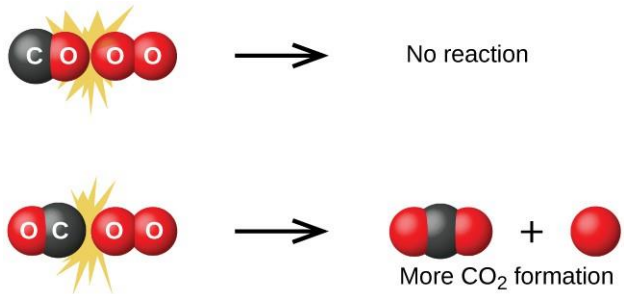


Figure 9.6 Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. In addition to a proper orientation, the collision must also occur with sufficient energy to result in product formation. When reactant species collide with both proper orientation and adequate energy, they combine to form an unstable species called an **activated complex** or a **transition state**. As an example, **Figure 9.7** depicts the structure of possible transitions states in the reaction between CO and O_2 to form CO_2.

Figure 9.7 Possible transition states (activated complexes) for carbon monoxide reacting with oxygen to form carbon

O=C···O=O

O···C···O=O

O=C···O···O

dioxide. Solid lines represent covalent bonds, while dotted lines represent unstable orbital overlaps that may, or may not, become covalent bonds as product is formed. In the first two examples in this figure, the O=O double bond is not impacted; therefore, carbon dioxide cannot form. The third proposed transition state will result in the formation of carbon dioxide if the third "extra" oxygen atom separates from the rest of the molecule.

In most circumstances, it is impossible to isolate or identify a transition state or activated complex. In the reaction between carbon monoxide and oxygen to form carbon dioxide, activated complexes have only been observed spectroscopically in systems that utilize a heterogeneous catalyst. The gas-phase reaction occurs too rapidly to isolate any such chemical compound. Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

Activation Energy

The minimum energy necessary to form a product during a collision between reactants is called the **activation energy (E_a)**. The kinetic energy of reactant molecules plays an important role in a reaction because the energy necessary to form a product is provided by a collision of a reactant molecule with another reactant molecule. (In single-reactant reactions, activation energy may be provided by a collision of the reactant molecule with the wall of the reaction vessel or with molecules of an inert contaminant.) If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly: Only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, the fraction of molecules possessing the necessary kinetic energy will be large; most collisions between molecules will result in reaction, and the reaction will occur rapidly.

$A + B \longrightarrow C + D$

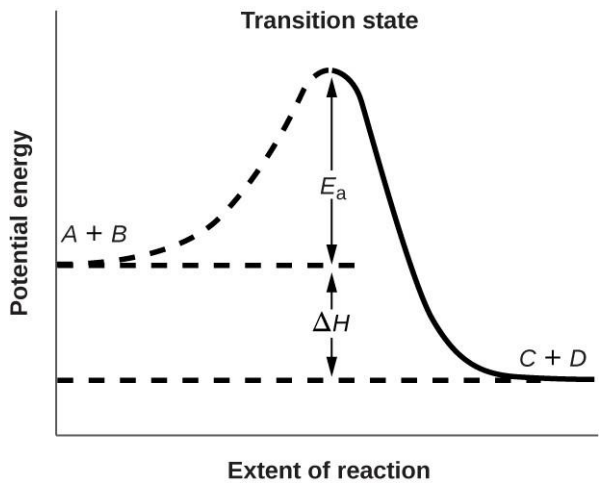


Figure 9.8 This graph shows the potential energy relationships for the reaction $A + B \longrightarrow C + D$. The dashed portion of the curve represents the energy of the system with a molecule of *A* and a molecule of *B* present, and the solid portion represents the energy of the system with a molecule of *C* and a molecule of *D* present. The activation energy for the forward reaction is represented by E_a. The activation energy for the reverse reaction is greater than that for the forward reaction by an amount equal to ΔH. The curve's peak represents the transition state.

Figure 9.8 shows that the energy of the transition state is higher than that of the reactants *A* and *B* by an amount equal to E_a, the activation energy. Thus, the sum of the kinetic energies of *A* and *B* must be equal to or greater than E_a to reach the transition state. After the transition state has been reached, and as *C* and *D* begin to form, the system loses energy until its total energy is lower than that of the initial mixture. This lost energy is transferred to other molecules, giving them enough energy to reach the transition state. The forward reaction (that between molecules *A* and *B*) therefore tends to take place readily once the reaction has started. In **Figure 9.8**, ΔH represents the difference in enthalpy between the reactants (*A* and *B*) and the products (*C* and *D*). At one extreme, the system does not contain enough energy for collisions to overcome the activation barrier. In such cases, no reaction occurs. At the other extreme, the system has so much energy that every collision with the correct orientation can overcome the activation barrier, causing the reaction to proceed. In such cases, the reaction is nearly instantaneous. An increase in temperature has the

same effect as a decrease in activation energy.

9.4 Catalysis

By the end of this section, you will be able to:

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

We have seen that the rate of many reactions can be accelerated by catalysts. A catalyst speeds up the rate of a reaction by lowering the activation energy; in addition, the catalyst is regenerated in the process. Several reactions that are energetically favorable in the absence of a catalyst only occur at a reasonable rate when a catalyst is present. One example is hydrogenation, a process used in food industries to convert unsaturated fats to saturated fats. A comparison of the reaction coordinate diagrams (also known as energy diagrams) for catalyzed and uncatalyzed hydrogenation of a simple hydrocarbon molecule is shown in **Figure 9.9**.

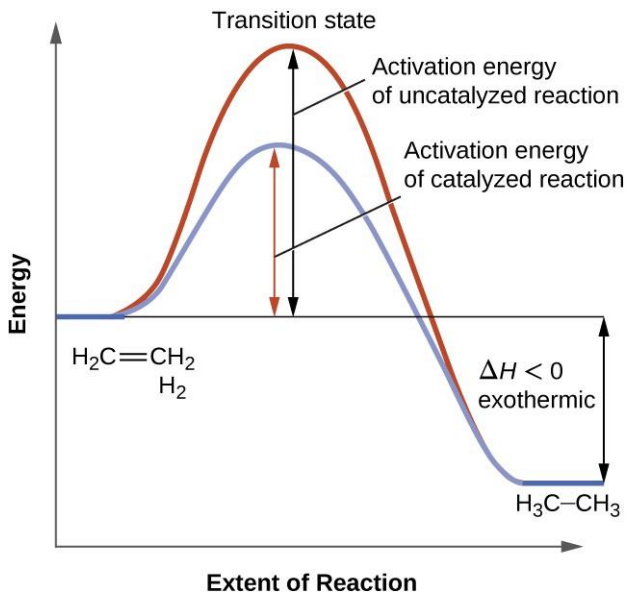


Figure 9.9 This graph compares the reaction coordinates for catalyzed and uncatalyzed alkene hydrogenation.

Catalysts function by providing an alternate reaction mechanism that has a lower activation energy than would be found in the absence of the catalyst. In some cases, the catalyzed mechanism may include additional steps, as depicted in the reaction diagrams shown in **Figure 9.10**. This lower activation energy results in an increase in rate. Note that a catalyst decreases the activation energy for both the forward and the reverse reactions and hence *accelerates both the forward and the reverse reactions*. Consequently, the presence of a catalyst will permit a system to reach equilibrium more quickly, but it has no effect on the position of the equilibrium as reflected in the value of its equilibrium constant (see the later part of this chapter on chemical equilibrium).

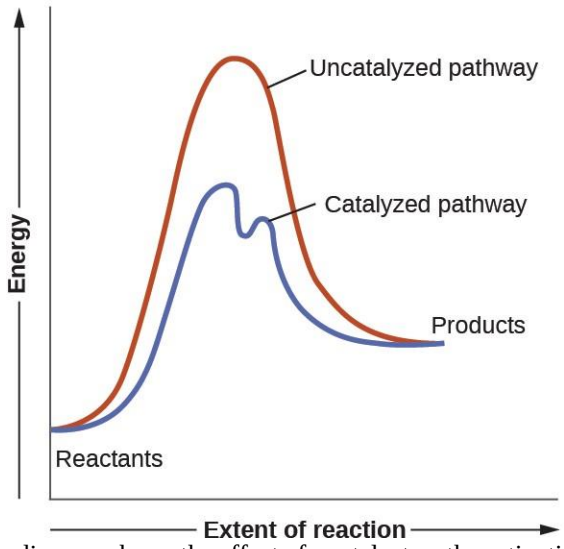
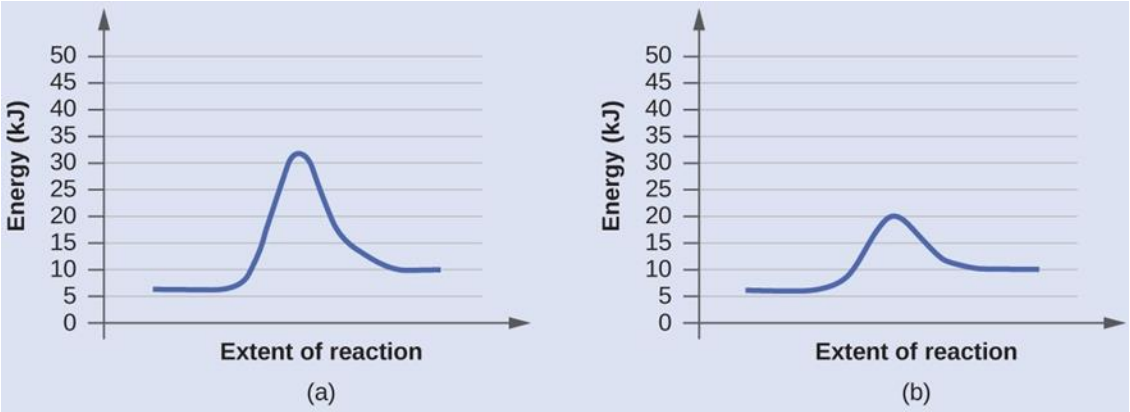


Figure 9.10 This potential energy diagram shows the effect of a catalyst on the activation energy. The catalyst provides a different reaction path with a lower activation energy. As shown, the catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Example 9.1

Using Reaction Diagrams to Compare Catalyzed Reactions: The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Identify which diagram suggests the presence of a catalyst, and determine the activation energy for the catalyzed reaction:



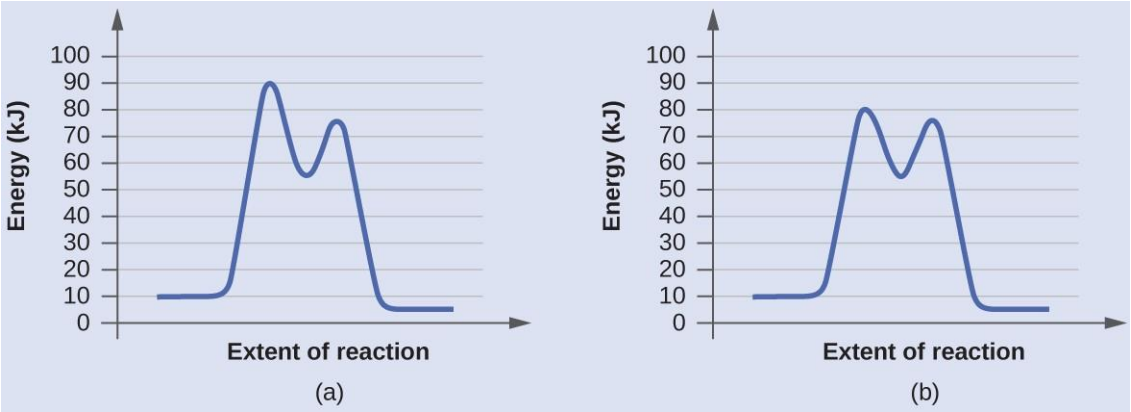
Solution:

A catalyst does not affect the energy of reactant or product, so those aspects of the diagrams can be ignored; they are, as we would expect, identical in that respect. There is, however, a noticeable difference in the transition state, which is distinctly lower in diagram (b) than it is in (a). This indicates the use of a catalyst in diagram (b). The activation energy is the difference between the energy of the starting reagents and the transition state—a maximum on the reaction coordinate diagram. The reagents are at 6 kJ and the transition state is at 20 kJ, so the activation energy can be calculated as follows:

$E_a = 20\ \text{kJ} - 6\ \text{kJ} = 14\ \text{kJ}$

Check Your Learning

Determine which of the two diagrams here (both for the same reaction) involves a catalyst, and identify the activation energy for the catalyzed reaction:



Answer: Diagram (b) is a catalyzed reaction with an activation energy of about 70 kJ.

How Sciences Interconnect

Glucose-6-Phosphate Dehydrogenase Deficiency

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in **Figure 9.11**, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

Figure 9.11 Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD

deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.

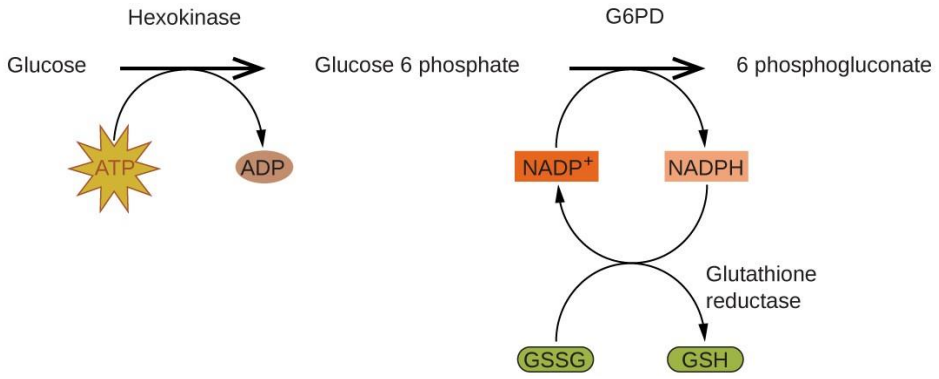


Figure 9.12 In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

Chemistry in Everyday: Life Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. Catalytic converters take advantage of all five factors that affect the speed of chemical reactions to ensure that exhaust emissions are as safe as possible.

By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (**Figure 9.13**).

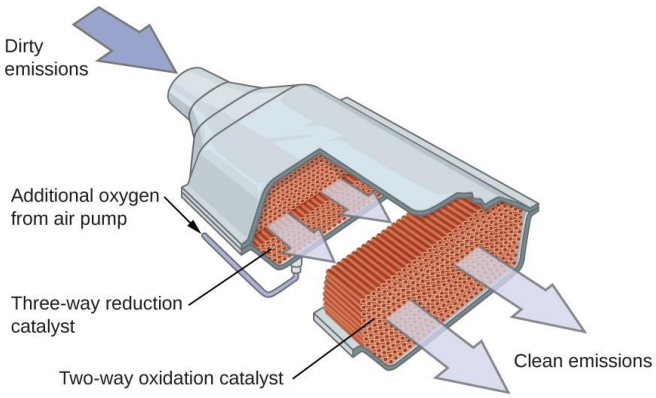


Figure 9.13 A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion of nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

$$2NO_2(g) \longrightarrow N_2(g) + 2O_2(g)$$

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

To be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

Link to Learning

The University of California at Davis' "ChemWiki" provides a **thorough explanation (http://openstaxcollege.org/l/16catconvert)** of how catalytic converters work.

How Sciences Interconnect: Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in **Table 9.1**.

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Table 9.1 Classes of Enzymes and Their Functions

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (**Figure 9.14**).

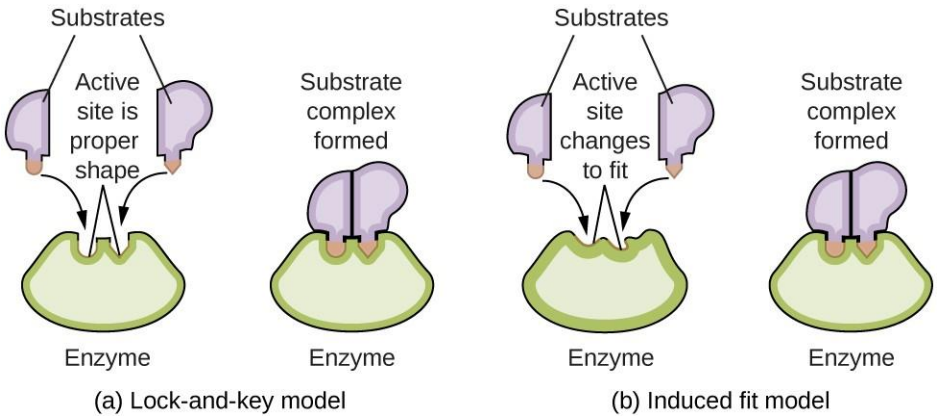


Figure 9.14 (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape to bond with the substrate.

Example 9.2

Conditions that increase or decrease rate of Reaction: For the following reactions, state whether the indicated change in conditions would increase or decrease the rate of the reaction. Explain why.

a. $Zn(s) + 2HCl \longrightarrow ZnCl_2(aq) + H_2(g)$

More HCl is added to the reaction.

b. $I_2(s) + H_2(g) \longrightarrow 2\ HI(g)$

The temperature is decreased from 100°C to 25°C.

c. $2CH_3CH_2OH + O_2 \longrightarrow 2CH_3CHO + 2\ H_2O$

A catalyst is added.

Solution:

a. The reaction rate increases because the concentration of one of the reactant was increased.

b. The reaction rate decreased because the temperature is lowered. At low temperatures, molecules have less kinetic energy, so there are fewer collisions between them.

c. The reaction rate increases because a catalyst has been added. The catalyst lowers the activation energy.

Check Your Learning

Acetylene gas reacts with oxygen and burns at high temperature in an acetylene torch. How would each of the following change the rate of this reaction?

$2\ C_2H_2(g) + 5\ O_2(g) \longrightarrow 4\ CO_2(g) + 2\ H_2O(l)$

a. Adding oxygen

b. Decreasing the amount of acetylene (C_2H_2)

c. Increasing the temperature

d. Adding a catalyst

Answer: a. increases rate; b. decreases the rate; c. increases the rate; d. increases the rate

9.5 Chemical Equilibria

By the end of this section, you will be able to:

- Describe the nature of equilibrium systems and explain the dynamic nature of a chemical equilibrium

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions. In a chemical **equilibrium**, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium. A mixture of reactants and products is found at equilibrium. For example, when we place a sample of dinitrogen tetroxide (N_2O_4, a colorless gas) in a glass tube, it forms nitrogen dioxide (NO_2, a brown gas) by the reaction the color becomes darker as N_2O_4 is converted to NO_2. When the system reaches equilibrium, both N_2O_4 and NO_2 are present (**Figure 9.15**).

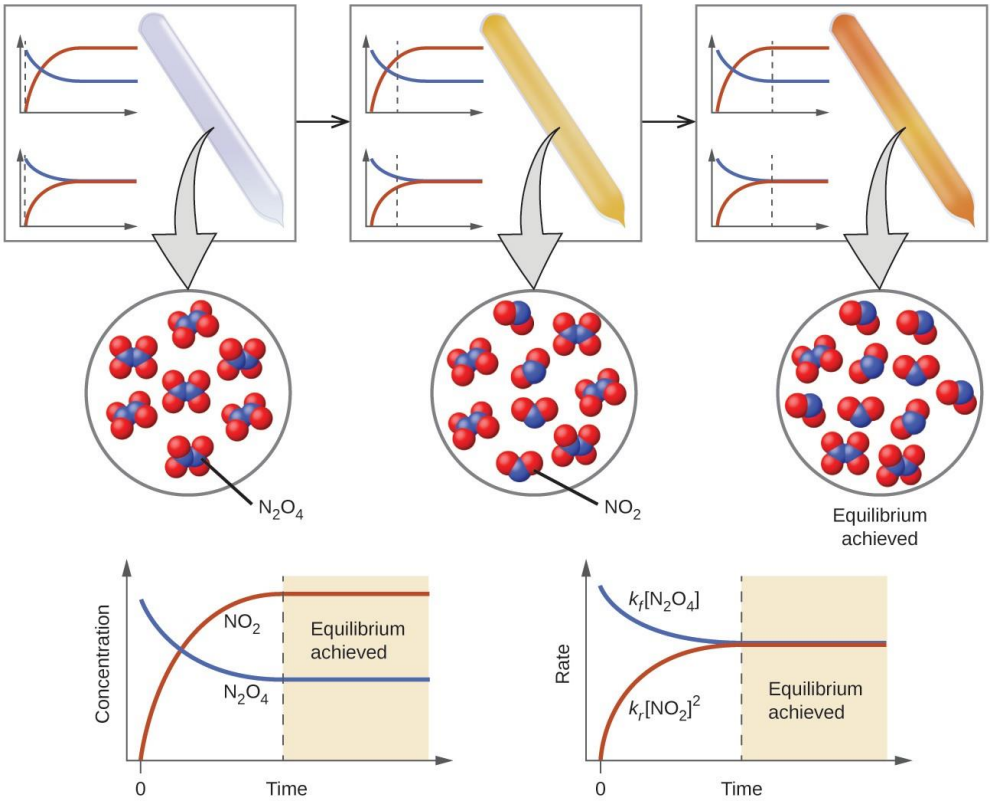


Figure 9.15 A mixture of NO_2 and N_2O_4 moves toward equilibrium. Colorless N_2O_4 reacts to form brown NO_2. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of NO_2.

The formation of NO_2 from N_2O_4 is a **reversible reaction**, which is identified by the equilibrium arrow (⇌). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from

reactants to products. Many other reactions, such as the formation of NO_2 from N_2O_4, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can N_2O_4 decompose to form NO_2, but the NO_2 produced can react to form N_2O_4. As soon as the forward reaction produces any NO_2, the reverse reaction begins and NO_2 starts to react to form N_2O_4. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. *Chemical equilibrium is a dynamic process*: as with the jugglers below, the numbers of clubs in the air remains constant, yet there is a flux back and forth between them (**Figure 9.16**).

Figure 9.16 These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in **Figure 9.15**.We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, **Figure 9.15** shows the reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in **Figure 9.15**, the rate of the forward reaction

$$N_2O_4(g) \longrightarrow 2NO_2(g)$$

is equal to the rate of the backward reaction

$$2NO_2(g) \longrightarrow N_2O_4(g)$$

Chemistry in Everyday Life: Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804; mostly known today for his role in the discovery and identification of oxygen) discovered a method of infusing water with carbon dioxide to make carbonated water. In 1772, Priestly published a paper entitled "Impregnating Water with Fixed Air." The paper describes dripping oil of vitriol (today we call this sulfuric acid, but what a great way to describe sulfuric acid: "oil of vitriol" literally means "liquid nastiness") onto chalk (calcium carbonate). The resulting CO_2 falls into the container of water beneath the vessel in which the initial reaction takes place; agitation helps the gaseous CO_2 mix into the liquid water.

$$H_2SO_4(l) + CaCO_3(s) \longrightarrow CO_2(g) + H_2O(l) + CaSO_4(aq)$$

Carbon dioxide is slightly soluble in water. There is an equilibrium reaction that occurs as the carbon dioxide reacts with the water to form carbonic acid (H_2CO_3). Since carbonic acid is a weak acid, it can dissociate into protons (H^+) and hydrogen carbonate ions (HCO_3^-).

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

Today, CO_2 can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the CO_2 gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase CO_2 and dissolved or aqueous CO_2 to shift, lowering the concentration of CO_2 in the soft drink. Less CO_2 dissolved in the liquid leads to carbonic acid decomposing to dissolved CO_2 and H_2O. The lowered carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the CO_2 bubbles up out of the beverage, releasing the gas into the air (**Figure 9.17**). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of the reactants remain. This results in a soft drink with a much-lowered CO_2 concentration, often referred to as "flat."

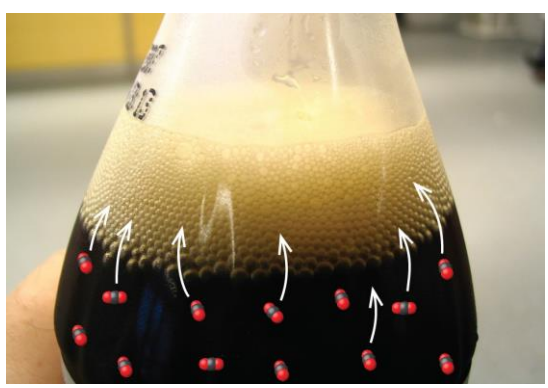


Figure 9.17 When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by "D Coetzee"/Flickr).

9.6 Equilibrium Constants

By the end of this section, you will be able to:

- Derive reaction quotients from chemical equations

- Calculate values of reaction quotients and equilibrium constants, using concentrations
- Use algebra to perform various types of equilibrium calculations
- Relate the magnitude of an equilibrium constant to properties of the chemical system

Now that we have a symbol (⇌) to designate reversible reactions, we will need a way to express mathematically how the amounts of reactants and products affect the equilibrium of the system. A general equation for a reversible reaction may be written as follows:

$mA + nB + \rightleftharpoons xC + yD$

We can write the **reaction quotient (*Q*)** for this equation. When evaluated using concentrations, it is called Q_c. We use brackets to indicate molar concentrations of reactants and products.

$$Q_C = \frac{[C]^X[D]^Y}{[A]^m[B]^n}$$

The reaction quotient is equal to the molar concentrations of the products of the chemical equation (multiplied together) over the reactants (also multiplied together), with each concentration raised to the power of the coefficient of that substance in the balanced chemical equation. For example, the reaction quotient for the reversible reaction: $2NO_2(g) \rightleftharpoons N_2O_4(g)$ is given by this expression:

$$Q_C = \frac{[N_2O_4]}{[NO_2]^2}$$

Example 9.3

Writing Reaction Quotient Expressions: Write the expression for the reaction quotient for each of the following reactions:

(a) $3O_2(g) \rightleftharpoons 2O_3(g)$

(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(c) $BaSO_3(s) \rightleftharpoons BaO(s) + SO_3(g)$

Solution:

(a) $Q_C = \frac{[O_3]^2}{[O_2]^3}$

(b) $Q_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(c) $Q_c = [SO_3]$

Check Your Learning

Write the expression for the reaction quotient for each of the following reactions:

(a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(b) $C_4H_8(g) \rightleftharpoons 2C_2H_4(g)$

(c) $2C_4H_{10}(g) + 13O_2(g) \rightleftharpoons 8CO_2(g) + 10H_2O(g)$

Answer: (a) $Q_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$; (b) $Q_C = \frac{C_2H_4}{[C_4H_8]}$; (c) $Q_C = \frac{[CO_2]^8[H_2O]^{10}}{[C_4H_{10}]^2\,[O_2]}$

The numeric value of Q_c for a given reaction varies; it depends on the concentrations of products and reactants present at the time when Q_c is determined. When pure reactants are mixed, Q_c is initially zero because there are no products present at that point. As the reaction proceeds, the value of Q_c increases as the concentrations of the products increase and the concentrations of the reactants simultaneously decrease (**Figure 9.18**). When the reaction reaches equilibrium, the value of the reaction quotient no longer changes because the concentrations no longer change.

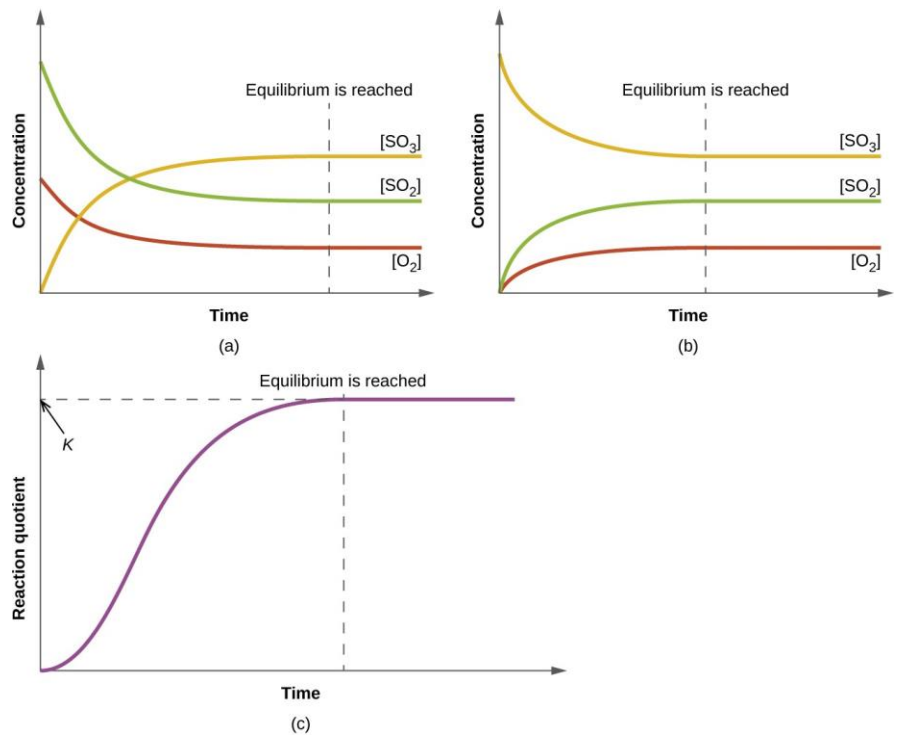


Figure 9.18 (a) The change in the concentrations of reactants and products is depicted as the $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$ reaction approaches equilibrium. (b) The change in concentrations of reactants and products is depicted as the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g)+O_2(g)$ approaches equilibrium. (c) The graph shows the change in the value of the reaction quotient as the reaction approaches equilibrium.

When a mixture of reactants and products of a reaction reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the **equilibrium constant (*K*)** of the reaction at that temperature. As for the reaction quotient, when evaluated in terms of concentrations, it is noted as K_c.

That a reaction quotient always assumes the same value at equilibrium can be expressed as:

$$Q_C \; at \; equilibrium = K_C = \frac{[C]^X[D]^Y}{[A]^m[B]^n}$$

This equation is a mathematical statement of the **law of mass action**: When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value. Please note that the concentration can also be expressed in partial pressures if the chemicals are in gaseous states.

Example 9.4

Calculation of an Equilibrium Constant: Calculate the equilibrium constant (K) for the following reaction at 25°C given the following equilibrium concentrations 0.01 M H_2, 0.01 M N_2, and 1.8 M NH_3.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Solution:

Step 1: Write the equilibrium expression

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Step 2: Substitute equilibrium (molar) concentration and calculate Kc.

$$K_C = \frac{[1.8]^2}{[0.010][0.010]^3} = 3.2\ x10^8$$

Check Your Learning

Calculate the equilibrium constant for the following reaction:

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

if at equilibrium the concentrations are:

Cl_2	1.0M
NO	0.030 M
NOCl	0.023 M

Answer: 1.7

Example 9.5

Calculation of a Missing Equilibrium Concentration: If we know the equilibrium constant for a reaction and know the concentrations at equilibrium of all reactants and products except one, we can calculate the missing concentration. Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the equilibrium constant for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, is 4.1×10^{-4}. Calculate the equilibrium concentration of NO(*g*) in air at 1 atm pressure and 2000 °C. The equilibrium concentrations of N_2 and O_2 at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

Solution:

We are given all the equilibrium concentrations except that of NO. Thus, we can solve for the missing equilibrium concentration by rearranging the equation for the equilibrium constant.

$$K_C = \frac{[NO]^2}{[N_2][O_2]}$$

$$[NO]^2 = K_C[N_2][O]$$

$$[NO] = \sqrt{K_C[N_2][O_2]}$$

$$= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

$$= \sqrt{1.31 * 10^{-7}}$$

$$= 3.6 * 10^{-4}$$

Thus [NO] is 3.6 × 10−4 mol/L at equilibrium under these conditions.

We can check our answer by substituting all equilibrium concentrations into the equilibrium expression for the reaction quotient to see whether it is equal to the equilibrium constant.

$$K_C = \frac{[NO]^2}{[N_2][O_2]} = \frac{(3.6 * 10^{-4})^2}{(0.036)(0.0089)}$$

$$K_C = 4.0 * 10^{-4}$$

The answer checks; our calculated value gives the equilibrium constant within the error associated with the significant figures in the problem.

Check Your Learning

The equilibrium constant for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 *M* and 2.09 *M*, respectively.

Answer: 1.53 M

Ethanol can be produced by reacting ethylene (C_2H_4) with water vapor. At 327°C, the Kc = 9 x 10^3.

$C_2H_4(g) + H_2O(g) \leftrightarrows C_2H_5OH(g)$

If an equilibrium mixture has concentrations of $[C_2H_4]$ = 0.20 M and $[H_2O]$ = 0.15 M, what is the equilibrium concentration of ethanol.

Answer: 207 M

Example 9.6

Magnitude of Equilibrium Constant: The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A large value for K_c indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K_c—much less than 1—indicates that equilibrium is attained when only a small proportion of the reactants have been converted into products. Indicate whether each of the following equilibrium mixtures contains mostly products or mostly reactants:

a. $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ Kc= $1x10^{-14}$

b. $CO(g) + O_2(g) \rightleftharpoons CO_2(g)$ Kc= $2x10^{11}$

Solution:

a. When a reaction has a small equilibrium constant, the equilibrium mixture contains mostly reactants and few products.

b. When a reaction has a large equilibrium constant, the equilibrium mixture contains mostly products and few reactants.

9.7 Shifting Equilibria: Le Châtelier's Principle

By the end of this section, you will be able to:

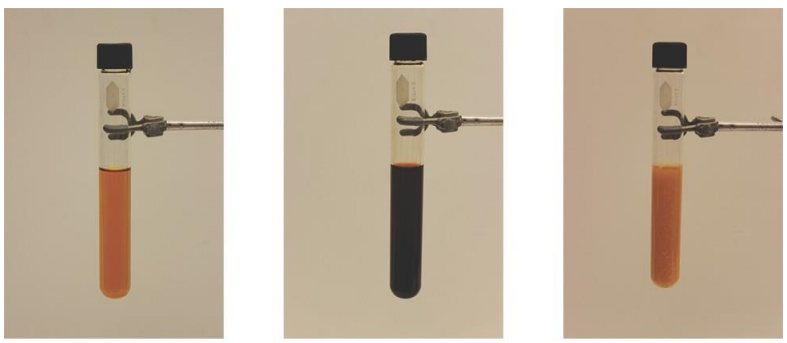
- Describe the ways in which an equilibrium system can be stressed and predict the response of a stressed equilibrium using Le Châtelier's principle

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We next address what happens when a system at equilibrium is disturbed. If a system at equilibrium is subjected to a perturbance or **stress** (such as a change in concentration) the **position of equilibrium** changes. To re-establish equilibrium, the system will either shift toward the products or the reactants until equilibrium is established. This process is described by **Le Châtelier's principle**: When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance.

Effect of Change in Concentration on Equilibrium

A chemical system at equilibrium can be temporarily shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

Reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants) causes a stress on the system $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$, **Figure 9.19**. As a consequence, Le Châtelier's principle leads us to predict that the equilibrium will shift to the left and the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.



(a) (b) (c)

Figure 9.19 (a) The test tube contains 0.1 *M* Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$. (c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN^- as the white solid AgSCN. $Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)$. The decrease in the SCN^- concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the $Fe(SCN)^{2+}$. (credit: modification of work by Mark Ott)

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_c = 50.0 \text{ at } 400\,°C$$

If H_2 is introduced into the system, the reaction will shift to the right so that a new equilibrium is reached. We have stressed this system by introducing additional H_2. The stress is relieved, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

Link to Learning

Check out this **link (http://openstaxcollege.org/l/16equichange)** to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Châtelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\mathrm{NO}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO}(g)$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Temperature on Equilibrium

A change in temperature changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a reactant or product and applying Le Châtelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad \Delta H = -9.4\,\text{kJ}\,(\text{exothermic})$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) + \text{heat}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = 57.20\,\text{kJ}$$

The positive ΔH value tells us that the reaction is endothermic and could be written with heat as a reactant

$$\text{heat} + N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

Link to Learning

This interactive **animation (http://openstaxcollege.org/l/16chatelier)** allows you to apply Le Châtelier's principle to predict the effects of changes in concentration, pressure, and temperature on reactant and product concentrations.

Catalysts Do Not Affect Equilibrium

As we learned during our study of reaction rates, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays

an important role in the production of fertilizers, explosives, plastics, dyes, fibers, and the steel industry. It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood. To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure. Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H = -92.2 \text{ kJ}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature. Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly. In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (Figure 9.20).

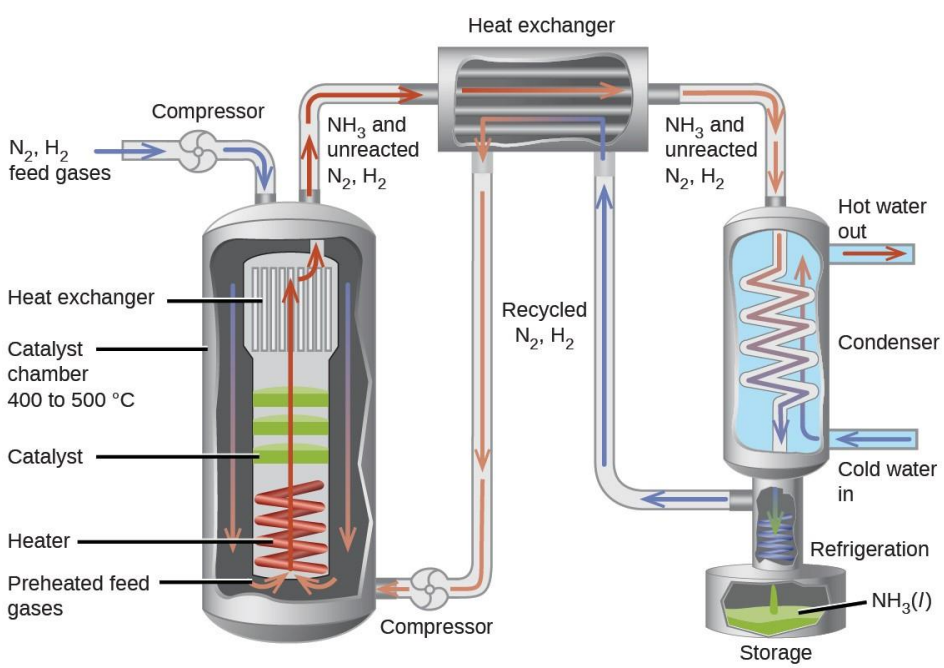


Figure 9.20 Commercial production of ammonia requires heavy equipment to handle the high temperatures and

pressures required. This schematic outlines the design of an ammonia plant.

Example 9.7

Predict the effect: Glucose is completely oxidized to CO_2 in our bodies in an exothermic reaction:

$C_6H_{12}O_6(aq) + 6O_2(g) \rightleftharpoons 6\,CO_2(g) + 6H_2O(g)$

Predict the effect (shift right, shift left, or no effect) of:

a. increasing and decreasing body temperature

b. increasing the amount of glucose, we eat

c. exhaling carbon dioxide

d. a catalyst is added

Solution:

a. Since the reaction is exothermic, heat is a product, when body temperature increases the reaction shifts to the left when body temperature decreases the reaction shift to the right.

b. Increasing a reactant, glucose, shifts the equilibrium to the right

c. Decreasing a product, CO_2, shifts the equilibrium to the right

d. Adding a catalyst has no effect on the position of equilibrium

A link to health (modified from MIT OpenCourseWare)

Hemoglobin (Hb) is an oxygen transport protein and there are approximately 300 million hemoglobin molecules per red blood cell. The reaction of hemoglobin with oxygen to form oxyhemoglobin (HbO_2) is a reversible reaction that can be represented by the following equation:

$$Hb + O_2 \rightleftharpoons HbO_2$$

Hemoglobin oxygen oxyhemoglobin

When blood circulates to the lungs, where the concentration of oxygen is high, the equilibrium shifts to the right to produce more oxyhemoglobin. When blood reaches the muscle and other oxygen-starved tissues, where the concentration of oxygen is much lower, the equilibrium shifts to the left releasing oxygen, which becomes available to the cells. The free hemoglobin returns to the lungs where the process is repeated.

At a high altitude of 3km the partial pressure of oxygen is only about 0.14 atm, compared to 0.2 atm at sea level. According to Le Châtelier's principle, the equilibrium would shift to the left. Without adequate oxygen being delivered to the tissues a person tends to feel light-headed or develops hypoxia (oxygen deprivation). To compensate to people living at high altitude the body produces more hemoglobin, which pushes the reaction towards products, resulting in more highly oxygenated blood, the body makes more Hb which results in shifting the equilibrium towards formation of the products

$$Hb + O_2 \rightleftharpoons HbO_2$$

Key Terms

activation energy (E_a) energy necessary for a reaction to take place

catalyst substance that increases the rate of a reaction without itself being consumed by the reaction

collision theory model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

equilibrium constant (K) value of the reaction quotient for a system at equilibrium

equilibrium in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

K_c equilibrium constant for reactions based on concentrations of reactants and products

Le Châtelier's principle when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

rate of reaction measure of the speed at which a chemical reaction takes place, change in the amount of a reactant or product per unit time

reaction quotient (Q) ratio of the product of molar concentrations of the products to that of the reactants, each concentration being raised to the power equal to the coefficient in the equation

reversible reaction chemical reaction that can proceed in both the forward and reverse directions under given conditions

stress change to a reaction's conditions that may cause a shift in the equilibrium

Key Equations

- $Q = \frac{[C]^X[D]^Y}{[A]^m[B]^n}$ $\quad$ $where\ mA + nB \rightleftharpoons XC + YD$

Summary

9.1 Chemical Reaction Rates

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction.

9.2 Factors Affecting Reaction Rates

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway that causes the activation energy of the reaction to decrease.

9.3 Collision Theory

Chemical reactions require collisions between reactant species. These reactant collisions must be of proper orientation

and sufficient energy in order to result in product formation. Collision theory provides a simple but effective explanation for the effect of many experimental parameters on reaction rates. The Arrhenius equation describes the relation between a reaction's rate constant and its activation energy, temperature, and dependence on collision orientation.

9.4 Catalysis

Catalysts affect the rate of a chemical reaction by altering its mechanism to provide a lower activation energy. Catalysts can be homogenous (in the same phase as the reactants) or heterogeneous (a different phase than the reactants).

9.5 Chemical Equilibria

A reaction is at equilibrium when the amounts of reactants or products no longer change. Chemical equilibrium is a dynamic process, meaning the rate of formation of products by the forward reaction is equal to the rate at which the products re-form reactants by the reverse reaction.

9.6 Equilibrium Constants

For any reaction that is at equilibrium, the reaction quotient Q is equal to the equilibrium constant K for the reaction. If a reactant or product is a pure solid, a pure liquid, or the solvent in a dilute solution, the concentration of this component does not appear in the expression for the equilibrium constant. At equilibrium, the values of the concentrations of the reactants and products are constant. Their particular values may vary depending on conditions, but the value of the reaction quotient will always equal K (K_c when using concentrations or K_P when using partial pressures).

9.7 Shifting Equilibria: Le Châtelier's Principle

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Châtelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/ increase in gas	pressure decreases	toward side with fewer moles of gas	none

pressure			
increase in volume/ decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Table 9.2 Effects of Disturbances of Equilibrium and *K*

Exercises

9.1 Chemical Reaction Rates

1. Define the rate of reactions.
2. What is activation energy?
3. What is the relationship between the activation energy and the rate of a reaction?
4. Complete the sentence: A catalyst increase the rate of a chemical reaction by ?

9.2 Factors Affecting Reaction Rates

1. Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

2. Explain why an egg cooks more slowly in boiling water in Denver than in New York City. (Hint: Consider the effect of temperature on reaction rate and the effect of pressure on boiling point.)

3. Go to the PhET Reactions & Rates (http://openstaxcollege.org/l/16PHETreaction) interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red plunger to release the atom and observe the results. Then, click on "Reload Launcher" and change to "Angled shot" to see the difference.

(a) What happens when the angle of the collision is changed?

(b) Explain how this is relevant to rate of reaction.

4. In the PhET Reactions & Rates (http://openstaxcollege.org/l/16PHETreaction) interactive, use the "Many Collisions" tab to observe how multiple atoms and molecules interact under varying conditions. Select a molecule to pump into the chamber. Set the initial temperature and select the current amounts of each reactant. Select "Show bonds" under Options. How is the rate of the reaction affected by concentration and temperature?

5. In the PhET Reactions & Rates (http://openstaxcollege.org/l/16PHETreaction) interactive, on the Many Collisions tab, set up a simulation with 15 molecules of A and 10 molecules of BC. Select "Show Bonds" under Options.

(a) Leave the Initial Temperature at the default setting. Observe the reaction. Is the rate of reaction fast or

slow?

(b) Click "Pause" and then "Reset All," and then enter 15 molecules of A and 10 molecules of BC once again. Select "Show Bonds" under Options. This time increase the initial temperature until, on the graph, the total average energy line is completely above the potential energy curve. Describe what happens to the reaction.

9.3 Collision Theory

1. What happens when reacting molecules collide with sufficient energy but don't have proper orientation?
2. Explain why the reaction rate increase as concentration of reactant increases.
3. Explain what happens to the number of collisions when the temperature of a reaction is decreased.

9.4 Catalysis

1. Account for the increase in reaction rate brought about by a catalyst.
2. Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as CCl_2F_2, catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:

$$O_3 \xrightarrow{\text{sunlight}} O_2 + O$$

$$O_3 + Cl \longrightarrow O_2 + ClO$$

$$ClO + O \longrightarrow Cl + O_2$$

(a) Explain why chlorine atoms are catalysts in the gas-phase transformation:

$$2O_3 \longrightarrow 3O_2$$

(b) Nitric oxide is also involved in the decomposition of ozone by the mechanism:

$$O_3 \xrightarrow{\text{sunlight}} O_2 + O$$

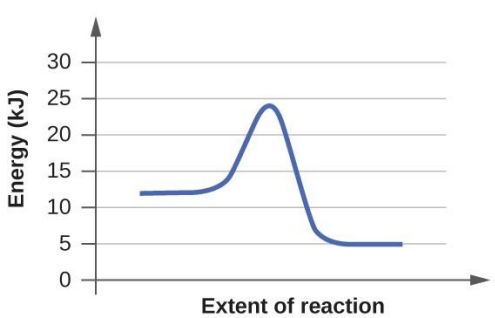
$$O_3 + NO \longrightarrow NO_2 + O_2$$

$$NO_2 + O \longrightarrow NO + O_2$$

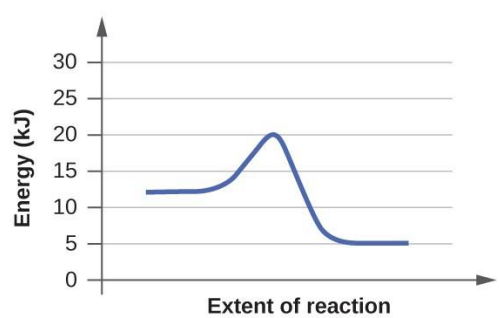
Is NO a catalyst for the decomposition? Explain your answer.

3. For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

(a)

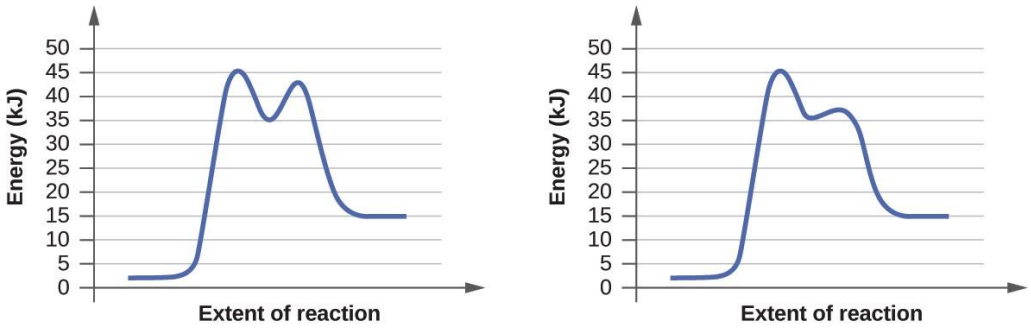


(a)



(b)

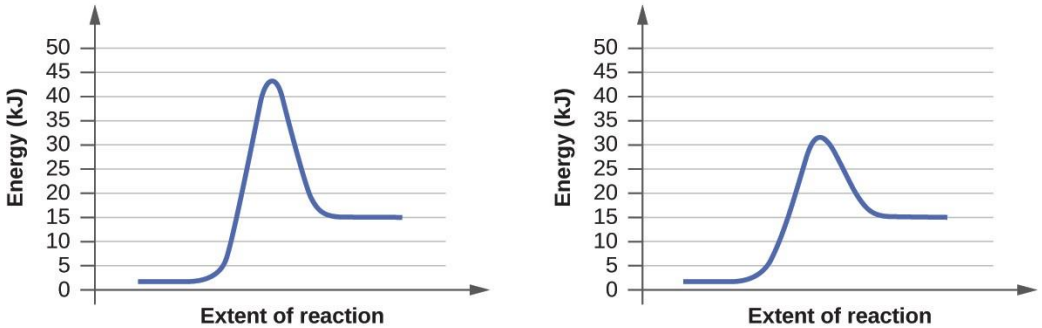
(b)



(a) (b)

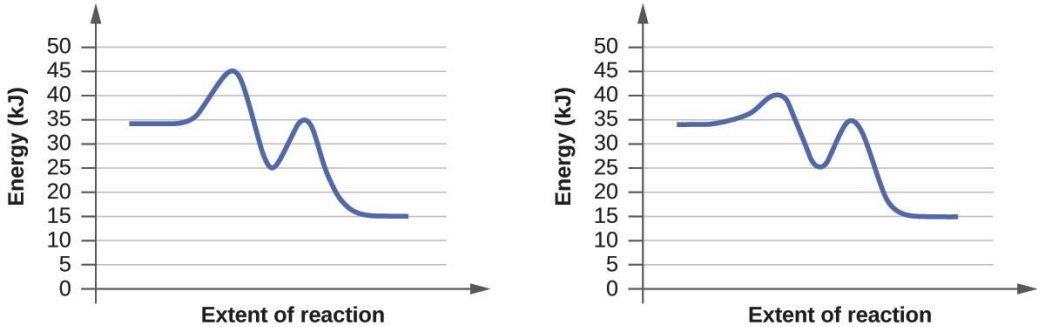
4. For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

(a)



(a) (b)

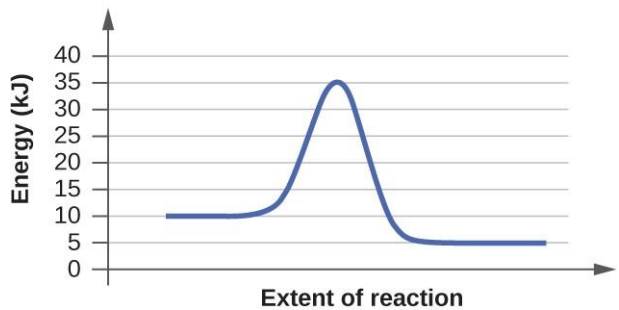
(b)



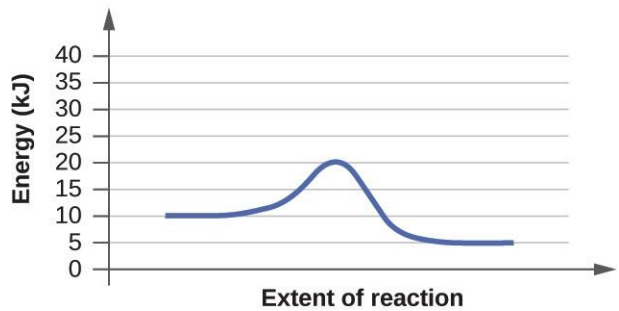
(a) (b)

5. For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)



6. Based on the diagrams in **Exercise 5** above, which of the reactions has the fastest rate? Which has the slowest rate?

9.5 Chemical Equilibrium

1. What does it mean to describe a reaction as "reversible"?
2. When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?
3. If a reaction is reversible, when can it be said to have reached equilibrium?
4. Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?
5. If the concentrations of products and reactants are equal, is the system at equilibrium?
6. If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?

$2NO_2(g) \rightleftharpoons N_2O_4(g)$

9.6 Equilibrium Constants

1. Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

(a) $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(c) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(f) $Br_2(g) \rightleftharpoons 2Br(g)$

(g) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

(h) $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$

2. What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 *M* H_2, 1.15 *M* N_2, and 4.12×10^{-1} *M* NH_3.

3. Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?

4. A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature.

5. Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400 °C established the concentration of N_2 to be 1.2 *M* and the concentration of H_2 to be 0.24 *M*.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_C = 0.50 \text{ at } 400\,^\circ\text{C}$

Calculate the equilibrium molar concentration of NH_3.

6. Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00−L flask at 448 °C.

$H_2 + I_2 \rightleftharpoons 2HI \qquad K_C = 50.2 \text{ at } 448\,^\circ\text{C}$

7. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \longrightarrow C_6H_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

9.7 Shifting equilibria: Le châtelier's Principle

1. Explain how to recognize the conditions under which changes in pressure would affect systems at equilibrium.

2. What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

3. The following reaction occurs when a burner on a gas stove is lit:

$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

4. Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:

$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g) \qquad \Delta H = 95\text{kJ}$

5. The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the

concentration of H^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

$$HbO_2(aq) + H^+(aq) + CO_2(g) \rightleftharpoons CO_2 - Hb - H^+ + O_2(g)$$

(a) Write the equilibrium constant expression for this reaction.

(b) Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

6. How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $\Delta H = 92\text{kJ}$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = 181\text{kJ}$

(c) $2O_3(g) \rightleftharpoons 3O_2(g)$ $\Delta H = -285\text{kJ}$

(d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92.2\text{kJ}$

7. Nitrogen and oxygen react at high temperatures.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = 181\text{kJ}$

(b) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?

(c) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?

(d) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?

(e) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?

(f) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?

(g) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?

8. Consider the equilibrium

$$4NO_2(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 7O_2(g)$$

(a) What is the expression for the equilibrium constant (K_c) of the reaction?

(b) If the reaction were at equilibrium, how would a decrease in pressure (from an increase in the volume of the reaction vessel) affect the position of equilibrium shift right, shift left, no effect??