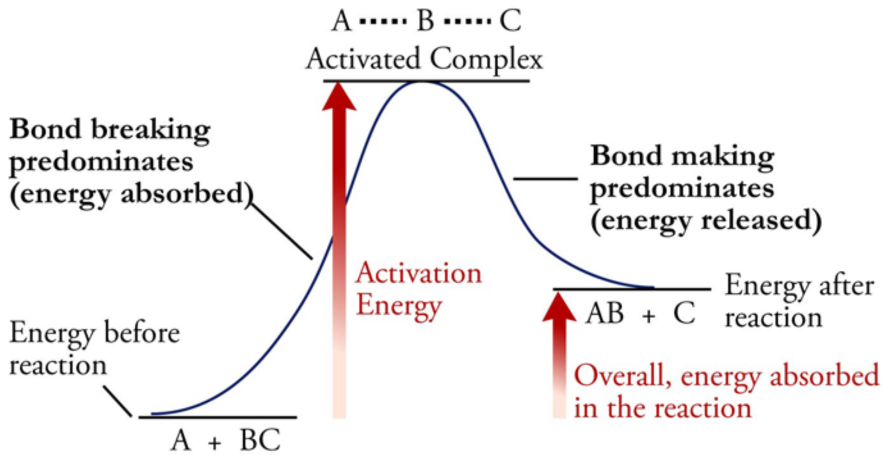
Chapter 14 - The Process of Chemical Reactions



Section Goals and Introductions

Section 14.1 Collision Theory: A Model for the Reaction Process

Goals

- *To describe a model, called collision theory, that helps us to visualize the process of many chemical reactions.*
- *To use collision theory to explain why not all collisions between possible reactants lead to products.*
- *To use collision theory to explain why possible reactants must collide with an energy equal to or above a certain amount to have the possibility of reacting and forming products.*
- *To show how the energy changes in chemical reactions can be described with diagrams.*
- *To use collision theory to explain why possible reactants must collide with a specific orientation to have the possibility of reacting and forming products.*

Once again, this chapter emphasizes that if you develop the ability to visualize changes on the particle level, it will help you understand and explain many different things. This section introduces you to a model for chemical change that is called collision theory, which helps you explain the factors that affect the rates of chemical reactions. These factors are described in Section 14.2.

Section 14.2 Rates of Chemical Reactions

Goals

- *To show how rates of chemical reactions are described.*
- *To explain why increased temperature increases the rates of most chemical reactions.*
- *To explain why increased concentration of reactants increases the rates of chemical reactions.*
- *To describe how catalysts increase the rates of certain chemical reactions.*

This section shows how collision theory helps you explain the factors that affect rates of chemical changes. These factors include amounts of reactants and products, temperature, and catalysts.

Section 14.3 Reversible Reactions and Chemical Equilibrium

Goals

- *To explain why chemical reactions that are reversible come to a dynamic equilibrium with equal forward and reverse rates of reaction.*
- *To show what equilibrium constants are and how they can be determined.*
- *To describe how equilibrium constants can be used to show the relative amounts of reactants and products in the system at equilibrium.*
- *To explain the effect of temperature on equilibrium systems and equilibrium constants.*

This section takes the basic ideas of dynamic equilibrium introduced in Chapter 12 and applies them to reversible chemical changes. This is a very important topic, so plan to spend some extra time on this section, if necessary. You will also learn how equilibrium constants are used to describe the relative amounts of reactants and products for a chemical reaction at equilibrium, and you will learn how these values can be calculated. Finally, you will learn more about the effect of temperature on chemical changes. See the three related sections on our Web site:

Internet: Calculating Concentrations and Gas Pressures

Internet: pH and pH Calculations

Internet: Weak Acids and Equilibrium Constants

Section 14.4 Disruption of Equilibrium

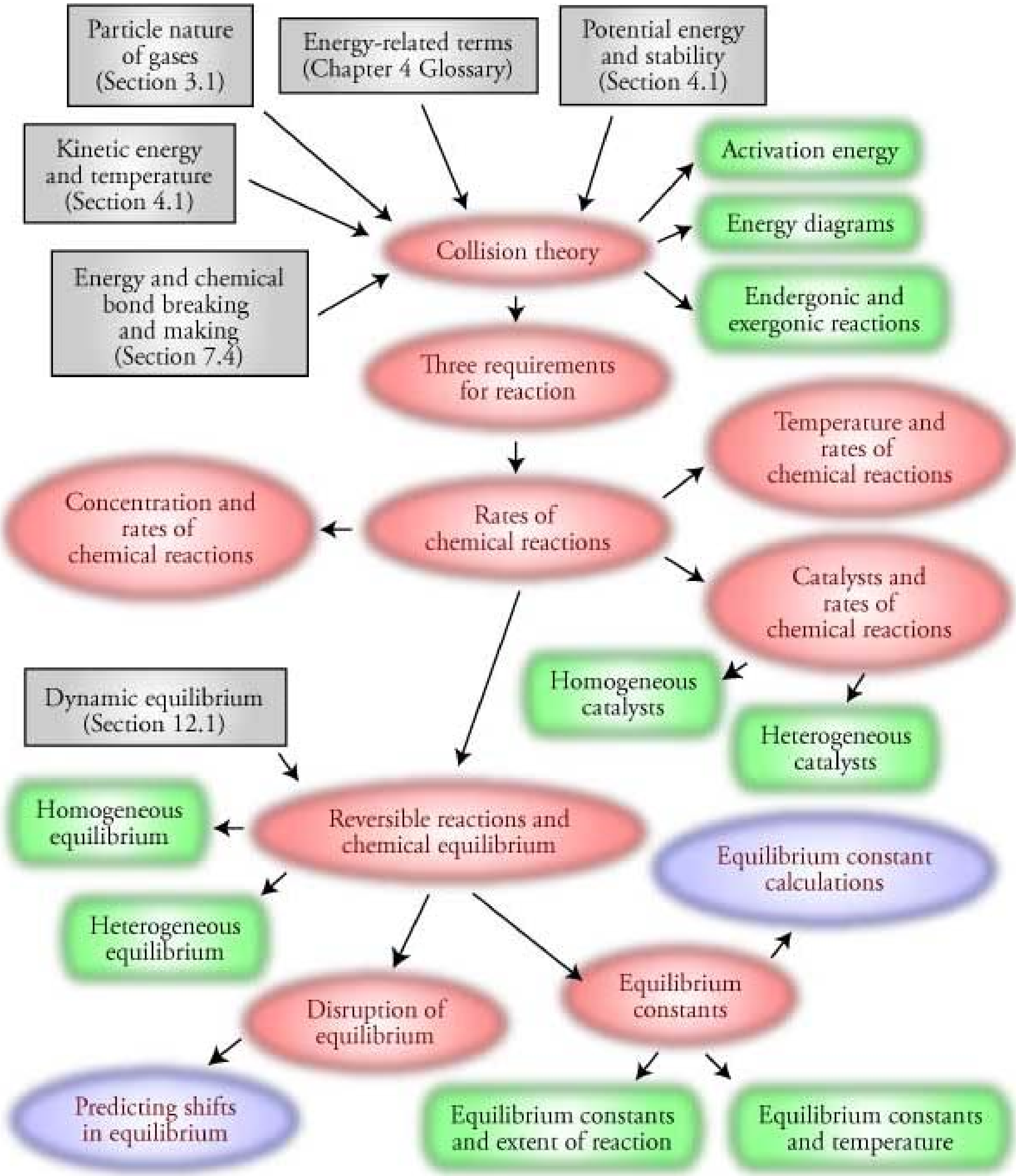
Goal: To describe how equilibrium systems can be disrupted and show you how to predict whether certain changes on a system at equilibrium will lead to more products, more reactants, or neither.

Although the concept of chemical equilibrium is very important, many reversible reactions in nature never form equilibrium systems. This section's description of the ways that equilibrium systems can be disrupted will help you to understand why this is true. The ability to predict the effects of changes on equilibrium systems will help you understand the ways that research and industrial chemists create conditions for their chemical reactions that maximize the rate at which desirable reactions move to products and minimize that rate at which undesirable reactions take place.

See the section on our Web site that provides information on Changing Volumes and Gas Phase Equilibrium.

Internet: Changing Volume and Gas Phase Equilibrium

Chapter 14 Map



Chapter Checklist

- ☐ Read the Review Skills section. If there is any skill mentioned that you have not yet mastered, review the material on that topic before reading this chapter.
- ☐ Read the chapter quickly before the lecture that describes it.
- ☐ Attend class meetings, take notes, and participate in class discussions.
- ☐ Work the Chapter Exercises, perhaps using the Chapter Examples as guides.
- ☐ Study the Chapter Glossary and test yourself on our Web site:

    Internet: Glossary Quiz
- ☐ Study all of the Chapter Objectives. You might want to write a description of how you will meet each objective.
- ☐ This chapter has logic sequences in Figures 14.11, 14.13, 14.15, 14.22, and 14.25. Convince yourself that each of the statements in these sequences logically leads to the next statement.
- ☐ To get a review of the most important topics in the chapter, fill in the blanks in the Key Ideas section.
- ☐ Work all of the selected problems at the end of the chapter, and check your answers with the solutions provided in this chapter of the study guide.
- ☐ Ask for help if you need it.

Web Resources

Internet: Calculating Concentrations and Gas Pressures
Internet: pH and pH Calculations
Internet: Weak Acids and Equilibrium Constants
Internet: Changing Volume and Gas Phase Equilibrium
Internet: Glossary Quiz

Exercises Key

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. *(Objs 24 & 25)*

$$2H_2S(g) + 3O_2(g) \rightleftharpoons 2SO_2(g) + 2H_2O(g)$$

$$K_C = \frac{[SO_2]^2[H_2O]^2}{[H_2S]^2[O_2]^3} \qquad K_P = \frac{P_{SO_2}{}^2\, P_{H_2O}{}^2}{P_{H_2S}{}^2\, P_{O_2}{}^3}$$

Exercise 14.2 – Equilibrium Constant Calculation: 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 °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 °C? *(Obj 26)*

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

$$K_P = \frac{P_{C_2H_5OH}}{P_{C_2H_4}\ P_{H_2O}} = \frac{0.11\,\text{atm}}{0.35\,\text{atm}\,(0.75\,\text{atm})} = \mathbf{0.42\ 1/atm\ \ or\ 0.42}$$

Exercise 14.3 – Predicting the Extent of Reaction: Using the information in Table 14.1, predict whether each of the following reversible reactions favors reactants, products, or neither at 25 °C. *(Obj 27)*

a. This reaction is partially responsible for the release of pollutants from automobiles.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

According to Table 14.1, the K_P for this reaction is 2.2×10^{12}, so it **favors products.**

b. The $NO_2(g)$ molecules formed in the reaction in part (a) can combine to form N_2O_4.

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

According to Table 14.1, the K_P for this reaction is 6.7. **Neither** *reactants nor products are favored.*

Exercise 14.4 – Writing Equilibrium Constants for Heterogeneous Equilibria: The following equation describes one of the steps in the purification of titanium dioxide, which is used as a white pigment in paints. Liquid titanium(IV) chloride reacts with oxygen gas to form solid titanium oxide and chlorine gas. Write K_C and K_P expressions for this reaction. *(Objs 24 & 25)*

$$TiCl_4(l) + O_2(g) \rightleftharpoons TiO_2(s) + 2Cl_2(g)$$

$$K_C = \frac{[Cl_2]^2}{[O_2]} \qquad K_P = \frac{{P_{Cl_2}}^2}{P_{O_2}}$$

Exercise 14.5 – Predicting the Effect of Disruptions on Equilibrium: 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 700-900 °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 to neither. Explain each answer in two ways: (1) by applying Le Châtelier's principle and (2) by describing the effect of the change on the forward and reverse reaction rates. *(Objs 40- 42 & 44- 46)*

$$3NO_2(g) + H_2O(g) \underset{\substack{750\text{-}920\ °C \\ 5\text{-}8\ atm}}{\overset{Rh/Pt}{\rightleftharpoons}} 2HNO_3(g) + NO(g) + 37.6\ kJ$$

a. The concentration of H_2O is increased by the addition of more H_2O.
   - *(1) Using Le Châtelier's Principle, we predict that the system will* **shift to more products** *to partially counteract the increase in H_2O.*
   - *(2) The increase in the concentration of water vapor speeds the forward reaction without initially affecting the rate of the reverse reaction. The equilibrium is disrupted, and the system* **shifts to more products** *because the forward rate is greater than the reverse rate.*

b. The concentration of NO_2 is decreased.
   - *(1) Using Le Châtelier's Principle, we predict that the system will* **shift to more reactants** *to partially counteract the decrease in NO_2.*
   - *(2) The decrease in the concentration of $NO_2(g)$ slows the forward reaction without initially affecting the rate of the reverse reaction. The equilibrium is disrupted, and the system* **shifts toward more reactants** *because the reverse rate is greater than the forward rate.*

c. The concentration of $HNO_3(g)$ is decreased by removing the nitric acid as it forms.
   - *(1) Using Le Châtelier's Principle, we predict that the system will* **shift to more products** *to partially counteract the decrease in HNO_3.*
   - *(2) The decrease in the concentration of $HNO_3(g)$ slows the reverse reaction without initially affecting the rate of the forward reaction. The equilibrium is disrupted, and the system* **shifts toward more products** *because the forward rate is greater than the reverse rate.*

d. The temperature is decreased from 1000 °C to 800 °C.
   - *(1) Using Le Châtelier's Principle, we predict that the system shifts in the exothermic direction to partially counteract the decrease in temperature. As the system* **shifts toward more products**, *energy is released, and the temperature increases.*
   - *(2) The decreased temperature decreases the rates of both the forward and reverse reactions, but it has a greater effect on the endothermic reaction. Because the forward reaction is exothermic, the reverse reaction must be endothermic. Therefore, the reverse reaction is slowed more than the forward reaction. The system* **shifts toward more products** *because the forward rate becomes greater than the reverse rate.*

e. The Rh/Pt catalyst is added to the equilibrium system.
   - *(1) Le Châtelier's Principle does not apply here.*
   - *(2) The catalyst speeds both 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.*

Review Questions Key

1. Describe what you visualize occurring inside a container of oxygen gas, O_2, at room temperature and pressure.

   The gas is composed of O_2 molecules that are moving constantly in the container. For a typical gas, the average distance between particles is about ten times the diameter of each particle. This leads to the gas particles themselves taking up only about 0.1% of the total volume. The other 99.9% of the total volume is empty space. According to our model, each O_2 molecule moves freely in a straight-line path until it collides with another O_2 molecule or one of the walls of the container. The particles are moving fast enough to break any attraction that might form between them, so after two particles collide, they bounce off each other and continue on alone. Due to collisions, each particle is constantly speeding up and slowing down, but its average velocity stays constant as long as the temperature stays constant.

2. Write in each blank the word that best fits the definition.
   a. **Energy** is the capacity to do work.
   b. **Kinetic energy** is the capacity to do work due to the motion of an object.
   c. A(n) **endergonic** change is a change that absorbs energy.
   d. A(n) **exergonic** change is a change that releases energy.
   e. **Thermal energy** is the energy associated with the random motion of particles.
   f. **Heat** is thermal energy that is transferred from a region of higher temperature to a region of lower temperature as a result of the collisions of particles.
   g. A(n) **exothermic** change is a change that leads to *heat* energy being evolved from the system to the surroundings.
   h. A(n) **endothermic** change is a change that leads the system to absorb *heat* energy from the surroundings.
   i. A(n) **catalyst** is a substance that speeds a chemical reaction without being permanently altered itself.

3. When the temperature of the air changes from 62 °C at 4:00 A.M. to 84 °C at noon on a summer day, does the average kinetic energy of the particles in the air increase, decrease, or stay the same?

   Increased temperature means **increased average kinetic energy**.

4. Explain why it takes energy to break an O–O bond in an O_3 molecule.

   Separate atoms are less stable, and therefore, higher potential energy than atoms in a bond. The Law of Conservation of Energy states that energy cannot be created or destroyed, so energy must be added to the system. It always takes energy to break attractions between particles.

5. Explain why energy is released when two oxygen atoms come together to form an O_2 molecule.

   Atoms in a bond are more stable, and therefore, lower potential energy. The Law of Conservation of Energy states that energy cannot be created or destroyed, so energy is released from the system. Energy is always released when new attractions between particles are formed.

6. Explain why some chemical reactions *release heat* to their surroundings.

   If the bonds in the products are stronger and lower potential energy than in the reactants, energy will be released from the system. If the energy released is due to the conversion of potential energy to kinetic energy, the temperature of the products will be higher than the original reactants. The higher temperature products are able to transfer heat to the surroundings, and the temperature of the surroundings increases.

7. Explain why some chemical reactions *absorb heat* from their surroundings.

   If the bonds in the products are weaker and higher potential energy than in the reactants, energy must be absorbed. If the energy absorbed is due to the conversion of kinetic energy to potential energy, the temperature of the products will be lower than the original reactants. The lower temperature products are able to absorb heat from the surroundings, and the temperature of the surroundings decreases.

8. What are the general characteristics of any dynamic equilibrium system?

   The system must have two opposing changes, from state A to state B and from state B to state A. For a dynamic equilibrium to exist, the rates of the two opposing changes must be equal, so there are constant changes between state A and state B but no net change in the components of the system.

Key Ideas Answers

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 **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**.
11. 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.
13. The energies associated with endergonic (or endothermic) changes are described with **positive** values.
15. 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**.
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 **fraction** of the collisions that have enough energy to reach the activated complex (the activation energy).
19. One of the ways in which catalysts accelerate chemical reactions is by providing a(n) **alternative pathway** between reactants and products that has a(n) **lower activation energy**.

21. If the catalyst is not in the same state as the reactants, the catalyst is called a(n) **heterogeneous** catalyst.
23. The extent to which reversible reactions proceed toward products before reaching equilibrium can be described with a(n) **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.
25. 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.
27. Changing temperature always causes a shift in equilibrium systems—sometimes toward more products and sometimes toward more **reactants**.
29. If the forward reaction in a reversible reaction is endergonic, increased temperature will shift the system toward more **products**.
31. Le Châtelier's 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**.

Problems Key

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.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) + 226\text{ kJ}$$

a. With reference to collision theory, describe the general process that takes place as this reaction moves from reactants to products. *(Obj 2)*

NO and O_3 molecules are constantly moving in the container, sometimes with a high velocity and sometimes more slowly. The particles are constantly colliding, changing their direction of motion, and speeding up or slowing down. If the molecules collide in a way that puts the nitrogen atom in NO near one of the outer oxygen atoms in O_3, one of the O–O bonds in the O_3 molecule begins to break, and a new bond between one of the oxygen atoms in the ozone molecule and the nitrogen atom in NO begins to form. If the collision yields enough energy to reach the activated complex, it proceeds on to products. If the molecules do not have the correct orientation, or if they do not have enough energy, they separate without a reaction taking place.

b. List the three requirements that must be met before a reaction between NO(*g*) and O_3(*g*) is likely to take place. *(Obj 11)*

NO and O_3 molecules must collide, they must collide with the correct orientation to form an N–O bond at the same time that an O–O bond is broken, and they must have the minimum energy necessary to reach the activated complex (the activation energy).

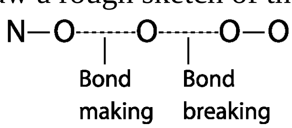
c. Explain why NO(*g*) and O_3(*g*) must collide before a reaction can take place. *(Obj 3)*

The collision brings the atoms that will form the new bonds close, and the net kinetic energy in the collision provides the energy necessary to reach the activated complex and proceed to products.

d. Explain why it is usually necessary for the new N–O bonds to form at the same time that the O–O bonds are broken. *(Obj 4)*

It takes a significant amount of energy to break O–O bonds, and collisions between particles are not likely to provide enough. As N–O bonds form, they release energy, so the formation of the new bonds can provide energy to supplement the energy provided by the collisions. The sum of the energy of collision and the energy released in bond formation is more likely to provide enough energy for the reaction.

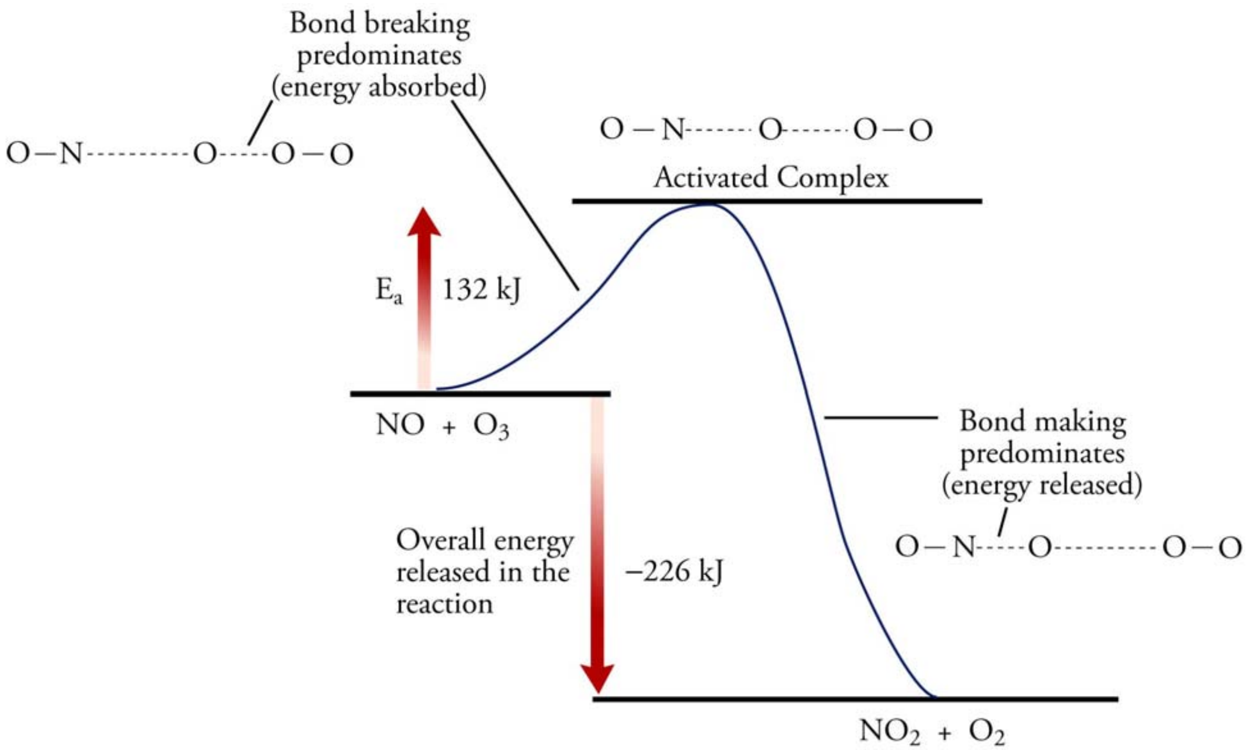
e. Draw a rough sketch of the activated complex.



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. *(Obj 5)*

In the initial stage of the reaction, the energy released in bond making is less than the energy absorbed by bond breaking. Therefore, energy must be available from the colliding particles to allow the reaction to proceed. At some point in the change, the energy released in bond formation becomes equal to the energy absorbed in bond breaking. If the colliding particles have enough energy to reach this point (in other words, if they have the activation energy), the reaction proceeds to products.

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. *(Obj 7)*



h. Is this reaction exothermic or endothermic? *(Objs 6 & 8)*

The negative sign for the heat of reaction shows that energy is released overall, so the reaction is **exothermic**.

i. Explain why NO(*g*) and O_3(*g*) molecules must collide with the correct orientation if a reaction between them is likely to take place. *(Obj 10)*

For a reaction to be likely, new bonds must be made at the same time as other bonds are broken. Therefore, the nitrogen atom in NO must collide with one of the outer oxygen atoms in O_3.

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.

$$A(g) + B(g) \rightarrow C(g) + D(g)$$

What happens to the rate of this reaction when

a. more gas A is added to the container?

Increased concentration of reactant A leads to increased rate of collision between A and B and therefore leads to **increased rate of reaction**.

b. the temperature is decreased?

Decreased temperature leads to decreased average kinetic energy of collisions between A and B. This leads to a decrease in the percentage of collisions with the *minimum energy necessary for the reaction and therefore leads to* **decreased rate of reaction**.

c. a catalyst is added that lowers the activation energy?

With a lower activation energy, there is a greater percentage of collisions with the minimum energy necessary for the reaction and therefore an **increased rate of reaction**.

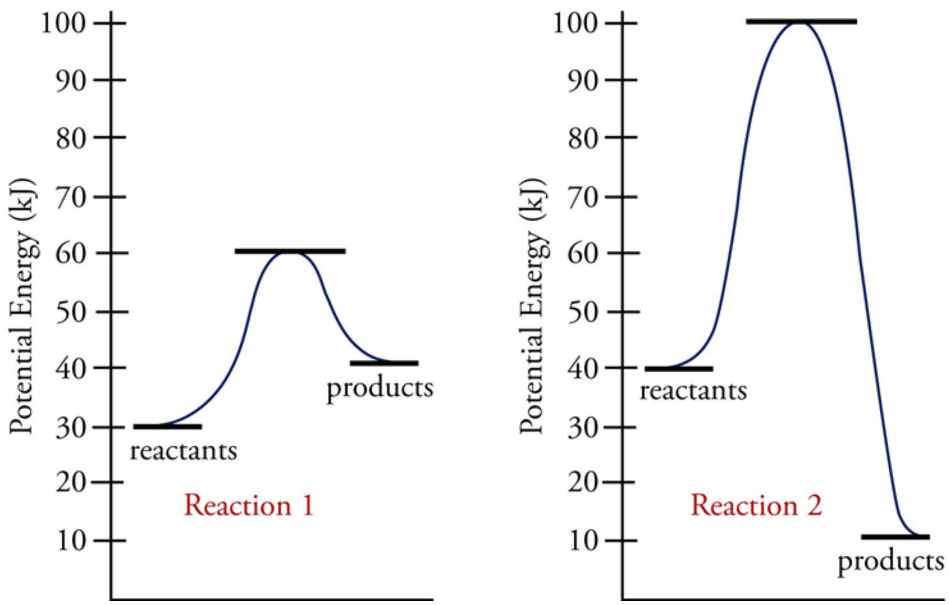
37. The reactions listed below are run at the same temperature. The activation energy for the first reaction is 132 kJ/mol. The activation energy for the second reaction is 76 kJ/mol. In which of these reactions would a higher fraction of collisions between reactants have the minimum energy necessary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

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$ Activation energy = 132 kJ

$I^-(aq) + CH_3Br(aq) \rightarrow CH_3I(aq) + Br^-(aq)$ Activation energy = 76 kJ

At a particular temperature, the lower the activation energy is, the higher the percentage of collisions with at least that energy or more will be. Thus the **second reaction** *would have the higher fraction of collisions with the activation energy.*

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?



The approximate activation energy for reaction 1 is 30 kJ and for reaction 2 is 60 kJ. Reaction 1 is endothermic, and reaction 2 is exothermic.

41. Explain why chlorine atoms speed the conversion of ozone molecules, O_3, and oxygen atoms, O, into oxygen molecules, O_2. *(Obj 14)*

In part, chlorine atoms are a threat to the ozone layer just because they provide another pathway for the conversion of O_3 and O to O_2, but there is another reason. 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 reach 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. The uncatalyzed reaction has an activation energy of 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. Thus a much higher fraction of the collisions have the minimum energy necessary to react for the catalyzed reaction than for the direct reaction between O_3 and O. Thus a much greater fraction of the collisions has the minimum energy necessary for the reaction to proceed for the catalyzed reaction than for the uncatalyzed reaction. Figures 14.14 and 14.15 of the textbook illustrate this.

43. Using the proposed mechanism for the conversion of NO(*g*) into N_2(*g*) and O_2(*g*) as an example, write a description of the four steps thought to occur in heterogeneous catalysis. (Obj 16)

Step 1: *The reactants (NO molecules) collide with the surface of the catalyst where they bind to the catalyst. This step is called adsorption. The bonds within the reactant molecules are weakened or even broken as the reactants are adsorbed. (N–O bonds are broken.)*

Step 2: *The adsorbed particles (separate N and O atoms) move over the surface of the catalyst.*

Step 3: *The adsorbed particles combine to form products (N_2 and O_2).*

Step 4: *The products (N_2 and O_2) leave the catalyst.*

See Figure 14.16 of the textbook.

Section 14.3 Reversible Reactions and Chemical Equilibrium

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. a solution of the weak acid acetic acid, $HC_2H_3O_2$ (Chapter 6)

Acetic acid molecules react with water to form hydronium ions and acetate ions, and at the same time, hydronium ions react with acetate ions to return to acetic acid molecules and water.

$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

b. pure liquid in a closed container (Chapter 12)

Liquids evaporate to form vapor at a rate that is balanced by the return of vapor to liquid.

c. a closed bottle of carbonated water with 4 atm of CO_2 in the gas space above the liquid (Chapter 13)

Carbon dioxide escapes from the solution at a rate that is balanced by the return of CO_2 to the solution.

47. Two gases, A and B, are added to an empty container. They react in the following reversible reaction.

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

a. 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?

The forward reaction rate is at its peak when A and B are first mixed. Because A and B concentrations are diminishing as they form C and D, the rate of the forward reaction declines steadily until equilibrium is reached.

b. 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?

The reverse reaction rate is at its peak when the reaction reaches equilibrium. Because C and D concentrations are increasing as they form from A and B, the rate of the reverse reaction increases steadily until equilibrium is reached.

49. Assume that in the following reversible reaction both the forward and the reverse reactions take place in a single step.

$$I^-(aq) + CH_3Br(aq) \rightleftharpoons CH_3I(aq) + Br^-(aq)$$

a. 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. *(Obj 20)*

When I^- ions and CH_3Br molecules are added to a container, they begin to collide and react. As the reaction proceeds, the concentrations of I^- and CH_3Br diminish, so the rate of the forward reaction decreases. Initially, there are no CH_3I molecules or Br^- ions in the container, so the rate of the reverse reaction is initially zero. As the concentrations of CH_3I and Br^- 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 (I^- and CH_3Br) will steadily decrease, and the concentrations of products (CH_3I and Br^-) will constantly increase. This leads to a decrease in the forward rate of the reaction and an increase in the rate of the reverse reaction. This continues until the two rates become equal. At this point, our system has reached a dynamic equilibrium.

b. 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. *(Obj 21)*

In a dynamic equilibrium for reversible chemical reactions, the forward and reverse reaction rates are equal, so although there are constant changes between reactants and products, there is no net change in the amounts of each. I^- and CH_3Br are constantly reacting to form CH_3I and Br^-, but CH_3I and Br^- are reacting to reform CH_3Br and I^- at the same rate. Thus there is no net change in the amounts of $I^{□}$, CH_3Br, CH_3I, or Br^-.

50. Write K_C and K_P expressions for each of the following equations. *(Objs 22 & 23)*

a. $2CH_4(g) \rightleftharpoons C_2H_2(g) + 3H_2(g)$

$$K_C = \frac{[C_2H_2][H_2]^3}{[CH_4]^2} \qquad K_P = \frac{P_{C_2H_2}\, P_{H_2}^3}{P_{CH_4}^2}$$

b. $2N_2O(g) + O_2(g) \rightleftharpoons 4NO(g)$

$$K_C = \frac{[NO]^4}{[N_2O]^2[O_2]} \qquad K_P = \frac{P_{NO}^4}{P_{N_2O}^2\, P_{O_2}}$$

c. $Sb_2S_3(s) + 3H_2(g) \rightleftharpoons 2Sb(s) + 3H_2S(g)$

$$K_C = \frac{[H_2S]^3}{[H_2]^3} \qquad K_P = \frac{P_{H_2S}^3}{P_{H_2}^3}$$

52. A mixture of nitrogen dioxide and dinitrogen tetroxide is allowed to come to equilibrium at 30 °C, and the gases partial pressures are found to be 1.69 atm N_2O_4 and 0.60 atm NO_2. *(Obj 24)*

a. On the basis of these data, what is K_P for the following equation?

$NO_2(g) \rightleftharpoons ½N_2O_4(g)$

$$K_P = \frac{P_{N_2O_4}^{1/2}}{P_{NO_2}} = \frac{(1.69)^{1/2}}{0.60} = \mathbf{2.2}$$

b. On the basis of these data, what is K_P for the following equation?

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

$$K_P = \frac{P_{N_2O_4}}{P_{NO_2}^2} = \frac{1.69}{(0.60)^2} = \mathbf{4.7}$$

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.

Changing temperature leads to a change in the value for an equilibrium constant. (Because K_P for this reaction decreases with increasing temperature, the reaction must be exothermic.)

54. Predict whether each of the following reactions favors reactants, products, or neither at the temperature for which the equilibrium constant is given. *(Obj 25)*

a. $CH_3OH(g) + CO(g) \rightleftharpoons CH_3CO_2H(g)$ $K_P = 1.2 \times 10^{-22}$ at 25 °C

$K_P < 10^{-2}$ so reactants favored

b. $CH_4(g) + 4Cl_2(g) \rightleftharpoons CCl_4(g) + 4HCl(g)$ $K_P = 3.3 \times 10^{68}$ at 25 °C

$K_P > 10^2$ so products favored

c. $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$ $K_P = 0.20$ at 600 °C

$10^{-2} < K_P < 10^2$ so neither favored

56. Write the K_C expression for the following equation. Explain why the concentration of CH_3OH is left out of the expression. *(Objs 22 & 26)*

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(l)$$

$$K_C = \frac{1}{[CO][H_2]^2}$$

If the number of moles of $CH_3OH(l)$ in the container is doubled, its volume doubles too, leaving the concentration (mol/L) of the methanol constant. Increasing or decreasing the total volume of the container will not change the volume occupied by the liquid methanol, so the concentration (mol/L) of the $CH_3OH(l)$ also remains constant with changes in the volume of the container. The constant concentration of methanol can be incorporated into the equilibrium constant itself and left out of the equilibrium constant expression.

$$K' = \frac{[CH_3OH]}{[CO][H_2]^2} \qquad \frac{K'}{[CH_3OH]} = \frac{1}{[CO][H_2]^2} = K_C$$

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.

$$2C_2H_4(g) + 2O_3(g) + \text{energy} \rightleftharpoons 4CH_2O(g) + O_2(g)$$

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?

Los Angeles has a much higher ozone concentration than in the Montana wilderness.

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?

Toward more products *(Increased temperature favors the endothermic direction of reversible reactions.)*

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?

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

Increased temperature favors the endothermic direction of reversible reactions, so this reaction is endothermic in the reverse direction and **exothermic** *in the forward direction.*

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 wakeup 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?

$$(NH_4)_2CO_3(s) + \text{energy} \rightleftharpoons 2NH_3(g) + CO_2(g) + H_2O(g)$$

Increased temperature will drive this endothermic reaction toward products, so warming the smelling salt container in your hands will increase the amount of ammonia released.

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 mole of CH_2O formed, so the reaction is exothermic.

$$2CH_3OH(g) + O_2(g) \rightleftharpoons 2CH_2O(g) + 2H_2O(g)$$

   a. Increased temperature drives the reaction toward reactants and lowers the value for the equilibrium constant. Explain why this is true. *(Objs 27 & 28)*

      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, changing 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. Because this reaction is exothermic in the forward direction, it must be endothermic in the reverse direction. Increased temperature shifts the system toward more reactants, decreasing the ratio of products to reactants and, therefore, decreasing the equilibrium constant.

   b. 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. *(Obj 29)*

      To maximize the percent yield at equilibrium, 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. In this case, it is best to run the reaction at high temperature to get to equilibrium quickly. (The unreacted methanol can be recycled back into the original reaction vessel after the formaldehyde has been removed from the product mixture.)

Section 14.4 Disruption of Equilibrium

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 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 to neither. Explain each answer in two ways: (1) by applying Le Châtelier's principle and (2) by describing the effect of the change on the forward and reverse reaction rates. *(Objs 30-33)*

$$2NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2(s) + H_2O(g) + 135.7\text{ kJ}$$

   a. 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 NH_3 to CO_2 is 3:1.)

      - *Using Le Châtelier's Principle, we predict that the system will* **shift to more products** *to partially counteract the increase in NH_3.*
      - *The increase in the concentration of ammonia speeds the forward reaction without initially affecting the rate of the reverse reaction. The equilibrium is*

disrupted, and the system **shifts to more products** *because the forward rate is greater than the reverse rate.*

b. The concentration of $H_2O(g)$ is decreased by removing water vapor.

- *Using Le Châtelier's Principle, we predict that the system will* **shift to more products** *to partially counteract the decrease in* H_2O.
- *The decrease in the concentration of* $H_2O(g)$ *slows the reverse reaction without initially affecting the rate of the forward reaction. The equilibrium is disrupted, and the system* **shifts toward more products** *because the forward rate is greater than the reverse rate.*

c. 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.)

- *Using Le Châtelier'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.*

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.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) + 9.4\text{ kJ}$$

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?

The **addition of either H_2 or I_2 (or both)** *would increase the concentrations of reactants, increasing the rate of collision between them, increasing the forward rate, and shifting the system toward more product.*

Lower temperature favors the exothermic direction of the reaction, so **lower temperature** *would shift this reaction to a higher percentage of products at equilibrium.*

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.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

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.)

a. The concentration of $COCl_2$ after the system has shifted to come to a new equilibrium.

The system will shift toward products, which leads to **increased $COCl_2$**.

b. The concentration of Cl_2 after the system has shifted to come to a new equilibrium.

The system will shift toward products, which leads to **decreased Cl_2**.

c. The equilibrium constant for the reaction.

Equilibrium constants are unaffected by reactant and product concentrations, so the **equilibrium constant remains the same**.