SECTION 18.1 RATES OF REACTION (pages 541–547)

This section explains what is meant by the rate of a chemical reaction. It also uses collision theory to show how the rate of a chemical reaction is influenced by the reaction conditions.

Collision Theory (pages 541–544)

1. How are rates of chemical change expressed?

   Rates of chemical change are usually expressed as the amount of reactant changing per unit time.

2. Look at Figure 18.3 on page 542. In a typical reaction, as time passes, the amount of reactant decreases and the amount of product increases.

3. What does collision theory say about the energies of atoms, ions, or molecules reacting to form products when they collide?

   Collision theory states that the particles must have enough kinetic energy when they collide to form products.

4. Look at the figures below. One shows a collision that results in the formation of product. Label it effective collision. Label the other collision ineffective collision.

   ineffective collision       effective collision

5. Is the following sentence true or false? Particles lacking the necessary kinetic energy to react bounce apart unchanged when they collide. _____ true

6. Look at Figure 18.5 on page 543. Which arrangement of atoms contains the least amount of energy?

   a. reactants
   b. activated complex
   c. products
CHAPTER 18, Reaction Rates and Equilibrium (continued)

7. Circle the letter of the term that completes the sentence correctly. The minimum amount of energy that particles must have in order to react is called the _______.
   a. kinetic energy  c. potential energy
   b. activation energy  d. collision energy

8. An activated complex is the arrangement of atoms at the peak of the activation-energy barrier.

9. Circle the letter of the term that best describes the lifetime of an activated complex.
   a. $10^{-15}$ s  b. $10^{13}$ s  c. $10^{-13}$ s  d. $10^{-1}$ s

10. Why is an activated complex sometimes called the transition state?
    It is called the transition state because an activated complex is unstable and is as likely to re-form reactants as it is to form products.

Factors Affecting Reaction Rates (pages 545–547)

11. Changes in the rate of chemical reactions depend on conditions such as temperature, concentration, and particle size.

12. The main effect of increasing the temperature of a chemical reaction is to increase the number of particles that have enough kinetic energy to react when they collide.

13. What happens when you put more reacting particles into a fixed volume?
    The concentration of reactants increases, the collision frequency increases, and, therefore, the reaction rate increases.

14. Is the following sentence true or false? The smaller the particle size, the larger the surface area of a given mass of particles. true

15. What are some ways to increase the surface area of solid reactants?
    One way is to dissolve the solid; another way is to grind the solid into a fine powder.

16. A catalyst is a substance that increases the rate of a reaction without being used up itself during the reaction.

17. What does a catalyst do? A catalyst permits reactions to proceed at a lower energy than is normally required. A catalyst lowers the activation energy.
Chapter 18 Reaction Rates and Equilibrium

18. Label each curve as with catalyst or without catalyst.

19. What does the graph show about the effect of a catalyst on the rate of a reaction? The catalyst lowers the activation energy and, thus, the amount of energy required by the system.

20. In a chemical equation, how do you show that catalysts are not consumed or chemically altered during a reaction? The catalyst is often written above the yield arrow in the equation.

21. A(n) inhibitor is a substance that interferes with the action of a catalyst.
SECTION 18.2 REVERSIBLE REACTIONS AND EQUILIBRIUM (pages 549–559)

This section shows you how to predict changes in the equilibrium position due to changes in concentration, temperature, and pressure. It teaches you how to write the equilibrium-constant expression for a reaction and calculate its value from experimental data.

**Reversible Reactions (pages 549–551)**

1. What happens in reversible reactions? In reversible reactions, two opposite reactions occur simultaneously.

2. Is the following sentence true or false? Chemical equilibrium is a state in which the forward and reverse reactions take place at different rates. False

3. The equilibrium position of a reaction is given by the relative concentrations of the system’s components at equilibrium.

4. Fill in the missing labels on the diagram below with either the words at equilibrium or not at equilibrium. At equilibrium, how many types of molecules are present in the mixture? 3

   ![Diagram](SO_2 and O_2, 2SO_2 + O_2 ⇌ 2SO_3)

5. Use Figure 18.10 on page 550 to answer these questions.

   a. Which graph, left or right, shows an initial concentration of 100% SO_3 and no SO_2? Right

   b. Compare the initial concentrations of the substances shown in the other graph. There is twice as much SO_2 as O_2 and no SO_3.

   c. What is the favored substance at equilibrium? How can you tell? SO_3, because it has the greatest concentration at equilibrium.

**Factors Affecting Equilibrium: Le Châtelier’s Principle (pages 552–555)**

6. What is Le Châtelier’s principle? Le Châtelier’s principle states that if a stress is applied to a system in dynamic equilibrium, the system changes to relieve the stress.
7. Circle the letters of the terms that complete the sentence correctly. Stresses that upset the equilibrium of a chemical system include changes in ________.
   a. concentration  c. pressure
   b. the amount of catalyst  d. temperature

8. When you add a product to a reversible chemical reaction, the reaction is always pushed in the direction of _______ reactants _______. When you remove a product, the reaction is pulled in the direction of _______ products _______.

9. Is the following sentence true or false? Increasing the temperature of a chemical reaction causes the equilibrium position of a reaction to shift in the direction that absorbs heat. _______ true _______.

10. How does increasing pressure affect a chemical system? _______ An increase in pressure results in a shift in the equilibrium position that favors the formation of a smaller volume of gas. _______.

11. Decreasing the pressure on the system shown in Figure 18.13 on page 554 results in a shift of equilibrium to favor _______ the reactants _______.

**Equilibrium Constants (pages 556–559)**

12. The equilibrium constant \( K_{eq} \) is the ratio of _______ product concentrations to _______ reactant concentrations at equilibrium, with each concentration raised to a power equal to the number of _______ moles _______ of that substance in the balanced chemical equation.

13. What are the exponents in the equilibrium-constant expression?
   The exponents are the coefficients from the balanced chemical equation.

14. What do the square brackets indicate in the equilibrium-constant expression?
   The square brackets indicate the concentrations of substances in moles per liter (mol/L).

15. Is the following sentence true or false? The value of \( K_{eq} \) for a reaction depends on the temperature. _______ true _______.

16. A value of \( K_{eq} \) greater than 1 means that _______ products _______ are favored over _______ reactants _______. A value of \( K_{eq} \) less than 1 means that _______ reactants _______ are favored over _______ products _______.
CHAPTER 18, Reaction Rates and Equilibrium (continued)

SECTION 18.3 SOLUBILITY EQUILIBRIUM (pages 560–565)
This section explains how to calculate the solubility product constant of a slightly soluble salt.

► The Solubility Product Constant (pages 560–562)

1. What is the solubility product constant \( (K_{sp}) \)?

   The solubility product constant equals the product of the concentration terms each raised to the power of the coefficient of the substance in the dissociation equation.

2. Look at Table 18.1 on page 561. Which ionic compounds are exceptions to the general insolubility of carbonates, phosphates, and sulfites?

   Compounds of the alkali metals and of ammonium ions are exceptions.

3. Look at Table 18.2 on page 562. Which salt is more soluble in water, silver bromide \( (\text{AgBr}) \) or silver chromate \( (\text{Ag}_2\text{CrO}_4) \)?

   silver chromate

► The Common Ion Effect (pages 563–565)

4. A common ion is an ion that is common to both __________ salts in a solution.

5. Is the following sentence true or false? The raising of the solubility of a substance by the addition of a common ion is called the common ion effect.

   false

6. A solubility product can be used to predict whether a __________ will form when solutions are mixed.

SECTION 18.4 ENTROPY AND FREE ENERGY (pages 566–573)
This section defines entropy and free energy, and characterizes reactions as spontaneous or nonspontaneous. It also describes how heat change and entropy change determine the spontaneity of a reaction.

► Free Energy and Spontaneous Reactions (pages 566–568)

1. Free energy is energy that is available to do __________ .

2. Is the following sentence true or false? All processes can be made 100% efficient.

   false
3. Make a concept map about balanced chemical reactions.

**Balanced Chemical Reactions**

- Reactions that **actually** occur
- Reactions that tend not to occur

4. Spontaneous reactions are reactions that occur naturally and that favor the formation of **products** at the specified conditions.

5. Describe four spontaneous reactions mentioned in this section.
   a. **exploding fireworks**
   b. **the decomposition of carbonic acid in water**
   c. **the reaction of aqueous solutions of Cd(NO₃)₂ and Na₂S to produce solid CdS**
   d. **sugar and oxygen to produce carbon dioxide and water**

6. What are nonspontaneous reactions?
   
   **Nonspontaneous reactions are reactions that do not favor the formation of products at the specified conditions.**

7. Is the following sentence true or false? Some reactions that are nonspontaneous at one set of conditions may be spontaneous at other conditions. **true**

**Entropy (pages 568–570)**

8. Some factor other than **heat** change must help determine whether a physical or chemical process is spontaneous.

9. What is entropy? **Entropy is the measure of the disorder of a system.**

10. The law of disorder states that processes move in the direction of **maximum** disorder or randomness.

11. Is the following sentence true or false? Entropy decreases when a substance is divided into parts. **false**
12. Number the diagrams below from 1 to 3 to show the increasing entropy of the system. Diagram 1 should show the least amount of entropy.

- Liquid
- Solid
- Gas

13. Does entropy tend to increase or decrease in chemical reactions in which the total number of product molecules is greater than the total number of reactant molecules? **entropy increases**

14. Entropy tends to **increase** when temperature increases.

**Heat, Entropy, and Free Energy (pages 571–572)**

15. What determines whether a reaction is spontaneous?

   The size and direction of heat (enthalpy) changes and entropy changes together determine whether a reaction is spontaneous.

16. Why is an exothermic reaction accompanied by an increase in entropy considered a spontaneous reaction? **because both factors are favorable**

17. Is the following sentence true or false? A nonspontaneous reaction, one in which the products are not favored, has heat changes, entropy changes, or both working against it. **true**

18. What is the symbol for a change in entropy? **ΔS**

**Gibbs Free-Energy (pages 572–573)**

19. The Gibbs free-energy change (ΔG) is the maximum amount of energy that can be coupled to another process to do useful **work**.

20. What is the equation used to calculate the Gibbs free-energy change?

   \[ ΔG = ΔH - TΔS \]

   where \( ΔH \) is the change in enthalpy, \( ΔS \) is the change in entropy, and temperature \( (T) \) is in kelvins.
21. The numerical value of $\Delta G$ is _____ negative _____ in spontaneous processes because the system loses free energy; the numerical value of $\Delta G$ is _____ positive _____ in nonspontaneous processes because the system requires that work be expended to make them go forward at the specified conditions.

**Reading Skill Practice**

Writing a summary can help you remember the information you have read. When you write a summary, include only the most important points. Write a summary of the information under the heading *Gibbs Free-Energy*, pages 572–573. Your summary should be shorter than the text on which it is based. Do your work on a separate sheet of paper.

Students’ summaries should include the definition of the highlighted term *Gibbs free-energy change*, as well as an explanation of the free-energy equation and the meaning of each term.

**SECTION 18.5 THE PROGRESS OF CHEMICAL REACTIONS**

This section describes how to use experimental rate data to deduce the rate laws for simple chemical reactions. It also shows how to analyze the mechanism for a reaction from an energy diagram.

**Rate Laws**

1. What is a one-step reaction? **It is a reaction with only one activated complex** _______ between the reactants and the products. _______

2. Is the following sentence true or false? A rate law is an expression relating the rate of a reaction to the concentration of products. _______ false _______

3. What is a specific rate constant ($k$) for a reaction? **The constant is a proportionality constant relating the concentrations of reactants to the rate of the reaction.** _______

4. The _____ order _____ of a reaction is the power to which the concentration of a reactant must be raised to give the experimentally observed relationship between concentration and rate. _______

5. In a first-order reaction, the reaction rate is directly proportional to the concentration of ______. _______
   a. two or more reactants
   b. both reactants and products
   c. only one reactant
6. How do you determine the actual kinetic order of a reaction?
   The actual kinetic order must be determined by experiment.

7. What is a reaction progress curve? A reaction progress curve is a graph of all the energy changes that occur as reactants are converted to products.

8. A(n) _______ elementary _______ reaction is one in which reactants are converted to products in a single step.

9. Is the following sentence true or false? A reaction mechanism includes some of the elementary reactions of a complex reaction. _______ false _______

10. What is an intermediate product of a reaction?
    It is a product of one step in the reaction mechanism that becomes a reactant in the next step in the reaction.

11. Look at Figure 18.28 on page 578. What is one difference between this graph and the chemical equation for this reaction? The graph shows that the reaction proceeds through five steps; the chemical equation sums up the five steps into what appears to be one step.
GUIDED PRACTICE PROBLEMS

GUIDED PRACTICE PROBLEM 6 (page 555)

6. How is the equilibrium position of this reaction affected by the following changes?
   \[ C(s) + H_2O(g) + \text{heat} \rightleftharpoons CO(g) + H_2(g) \]
   a. lowering the temperature
   b. increasing the pressure
   c. removing hydrogen
   d. adding water vapor

Analyze

Step 1. Plan a problem-solving strategy.
a-d Use Le Châtelier's principle to analyze the shift in the system effected by each stress.

Solve

Step 2. Apply the problem-solving strategy.
a. Lowering the temperature will shift the equilibrium to the left to produce heat.

b. Increasing the pressure will shift equilibrium to the left because fewer gas molecules are on the reactant side.

c. Removing hydrogen will shift the equilibrium to the right so the system will create more hydrogen gas.

d. Increasing the amount of water vapor will shift the equilibrium position to the right because there is an increase in a reactant.

Evaluate

Step 3. Does the result make sense?
The answers follow Le Châtelier's principle.
GUIDED PRACTICE PROBLEM 7 (page 557)

7. The reaction \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \) produces ammonia. At equilibrium, a 1-L flask contains 0.15 mol \( \text{H}_2 \), 0.25 mol \( \text{N}_2 \), and 0.10 mol \( \text{NH}_3 \). Calculate \( K_{eq} \) for the reaction.

### Analyze

**Step 1.** List the knowns and the unknown.

**Knowns**

- \( [\text{H}_2] = 0.15 \text{ mol/L} \)
- \( [\text{N}_2] = 0.25 \text{ mol/L} \)
- \( [\text{NH}_3] = 0.10 \text{ mol/L} \)

**Unknown**

- \( K_{eq} \) (algebraic) = \( \frac{[\text{NH}_3]^2}{[\text{N}_2] \times [\text{H}_2]^3} \)

### Calculate

**Step 2.** Solve for the unknowns.

Use the concentrations given and the coefficients from the balanced equation to determine \( K_{eq} \):

\[
K_{eq} = \frac{[\text{NH}_3]^2}{[\text{N}_2] \times [\text{H}_2]^3}
\]

\[
= \frac{0.10^2}{0.25 \times 0.15^3}
\]

\[
= \frac{12}{0.1125} = 108
\]
GUIDED PRACTICE PROBLEM 9 (page 558)

9. Suppose the following system reaches equilibrium.

\[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \]

An analysis of the equilibrium mixture in a 1-L flask gives the following results: nitrogen, 0.50 mol; oxygen, 0.50 mol; nitrogen monoxide, 0.020 mol. Calculate \( K_{eq} \) for the reaction.

---

**Step 1.** List the known values and the unknowns.

<table>
<thead>
<tr>
<th>Known</th>
<th>Unknown</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{N}_2]) = 0.50 \text{ mol/L}</td>
<td>( K_{eq} ) = ?</td>
</tr>
<tr>
<td>([\text{O}_2]) = 0.50 \text{ mol/L}</td>
<td></td>
</tr>
<tr>
<td>([\text{NO}]) = 0.020 \text{ mol/L}</td>
<td></td>
</tr>
</tbody>
</table>

**Step 2.** Write the \( K_{eq} \) for the reaction. It should have three variables.

\[ K_{eq} = \frac{[\text{NO}]^2}{[\text{N}_2] \times [\text{O}_2]} \]

**Step 3.** Substitute the known values in the expression.

\[ K_{eq} = \frac{(0.020 \text{ mol/L})^2}{0.50 \text{ mol/L} \times 0.50 \text{ mol/L}} \]

**Step 4.** Solve. Write your answer in scientific notation.

\[ K_{eq} = 0.0016 = 1.6 \times 10^{-3} \]
CHAPTER 18, Reaction Rates and Equilibrium  (continued)

GUIDED PRACTICE PROBLEM 18 (page 562)

18. What is the concentration of calcium ions in a saturated calcium carbonate solution at 25°C? \( (K_{sp} = 4.5 \times 10^{-9}) \)

**Analyze**

**Step 1.** List the knowns and the unknown.

**Knowns**

\[ \text{Knowns} \]

\[ K_{sp} = 4.5 \times 10^{-9} \]

\[ K_{sp} = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] \]

\[ \text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-} \]

**Unknown**

\[ [\text{Ca}^{2+}] = ? \]

At equilibrium \([\text{Ca}^{2+}] = [\text{CO}_3^{2-}]\). This fact will be used to solve for the unknown.

**Calculate**

**Step 2.** Solve for the unknown.

\[ K_{sp} = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] \]

Make a substitution based on the equilibrium condition stated above:

\[ K_{sp} = [\text{Ca}^{2+}] \times [\text{Ca}^{2+}] = [\text{Ca}^{2+}]^2 = 4.5 \times 10^{-9} \]

Now solve for the unknown:

\[ [\text{Ca}^{2+}] = \frac{4.5 \times 10^{-9}}{1} = 6.7 \times 10^{-5} \text{ M} \]
GUIDED PRACTICE PROBLEM 19 (page 564)

19. What is the concentration of sulfide ion in a 1.0-L solution of iron(II) sulfide to which 0.04 mol of iron(II) nitrate is added? The $K_{sp}$ of FeS is $8 \times 10^{-19}$.

**Analyze**

**Step 1.** List the knowns and the unknown.

**Knowns**
- $K_{sp} = 8 \times 10^{-19}$
- moles of Fe(NO$_3$)$_2$ = 0.04 mol
- volume of solution = 1.0 L

**FeS $\rightleftharpoons$ Fe$^{2+}$ + S$^{2-}$**

**Unknown**
- $[S^{2-}] = ? \text{ M}$

Let $x = [S^{2-}]$ so that $x + 0.04 = [\text{Fe}^{2+}]$

**Calculate**

**Step 2.** Solve for the unknown.

Because $K_{sp}$ is very small, simplify by assuming $x \ll 0.04$, and becomes negligible. Thus $[\text{Fe}^{2+}]$ is approximately equal to 0.04 M.

Solve for $x$ in the equation: $K_{sp} = [\text{Fe}^{2+}] \times [S^{2-}] = [\text{Fe}^{2+}] \times x = 8 \times 10^{-19}$

Rearranging for $x$ gives the result:

$$x = \frac{8 \times 10^{-19}}{[\text{Fe}^{2+}]} = \frac{8 \times 10^{-19}}{0.04 \text{ mol}} = 2 \times 10^{-17} \text{ M}$$

So $[S^{2-}] = 2 \times 10^{-17} \text{ M}$
GUIDED PRACTICE PROBLEM 36 (page 577)

36. Show that the unit of $k$ for a first-order reaction is a reciprocal unit of time, such as a reciprocal second ($s^{-1}$).

**Analyse**

**Step 1.** Plan a problem-solving strategy

The definition of the reaction rate is the change in concentration of a substance per change in time. So using a unit, “concentration” for the numerator and “time” for the denominator, the reaction rate has units [concentration/time].

Use this knowledge algebraically to show the unit for $k$.

**Solve**

**Step 2.** Apply the problem solving strategy.

Because the change in concentration per unit time is proportional to the initial concentration, setting up an equation with units will show this proportionality.

\[
\frac{[\text{concentration}]}{[\text{time}]} = k \times \frac{[\text{concentration}]}{[\text{time}]}
\]

Canceling the unit “concentration” from both sides of the equation gives the result:

\[
\frac{1}{[\text{time}]} = k
\]

The unit of $k$ is [time]$^{-1}$

**Evaluate**

**Step 3.** Does the result make sense?

Units can be treated just as algebraic variables in equations, making dimensional analysis a useful problem-solving tool.