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18 REACTION RATES AND EQUILIBRIUM

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?

_____

_____

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

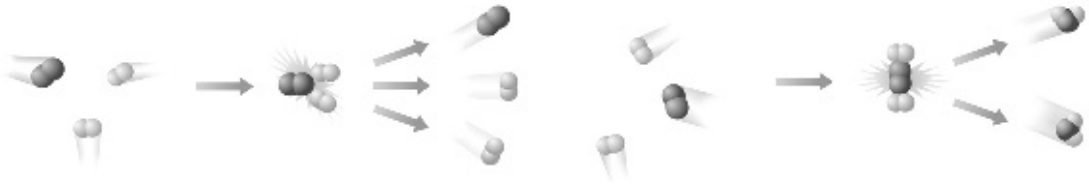
3. What does collision theory say about the energies of atoms, ions, or molecules reacting to form products when they collide?

_____

_____

_____

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.*



_____ _____

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

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

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 _____ 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?

_____

_____

▶ Factors Affecting Reaction Rates (pages 545–547)

11. Changes in the rate of chemical reactions depend on conditions such as _____ .

12. The main effect of increasing the temperature of a chemical reaction is to _____ 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?

_____

_____

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

15. What are some ways to increase the surface area of solid reactants?

_____

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

17. What does a catalyst do? _____

_____

_____

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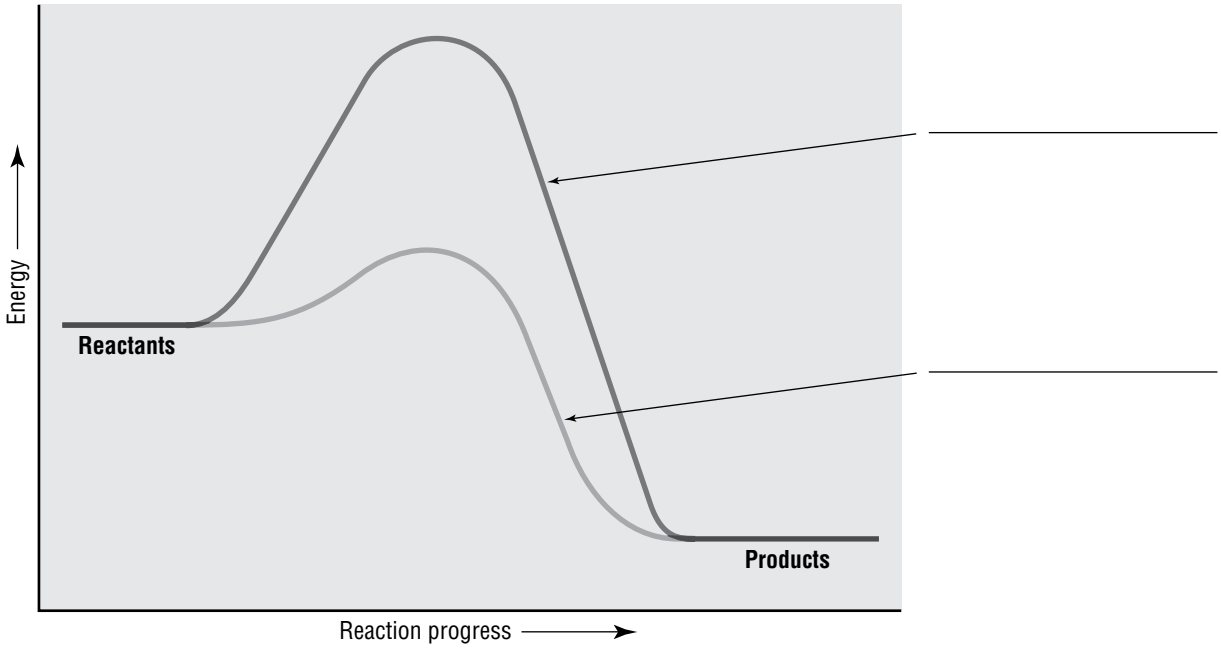
The graph below shows the reaction rate of the same reaction with and without a catalyst. Use it to help you answer Questions 18 and 19.



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? _____

_____

20. In a chemical equation, how do you show that catalysts are not consumed or chemically altered during a reaction? _____

_____

21. A(n) _____ 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)

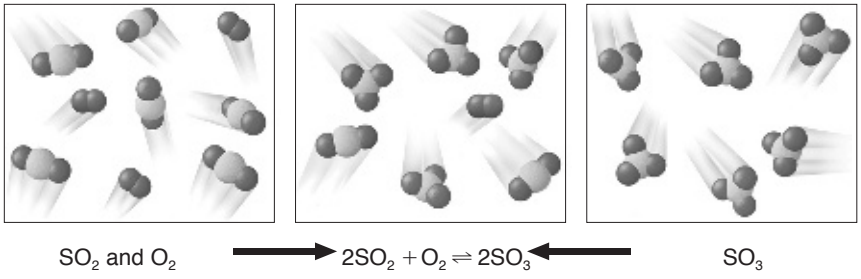
1. What happens in reversible reactions? _____

_____

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. _____

3. The equilibrium position of a reaction is given by the relative _____ 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? _____



_____ _____ _____

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? _____

b. Compare the initial concentrations of the substances shown in the other graph.

_____

c. What is the favored substance at equilibrium? How can you tell?

_____

▶ Factors Affecting Equilibrium: Le Châtelier's Principle (pages 552–555)

6. What is Le Châtelier's principle? _____

_____

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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 _____ . When you remove a product, the reaction is pulled in the direction of _____ .

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. _____

10. How does increasing pressure affect a chemical system? _____

_____

_____

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

▶ Equilibrium Constants (pages 556–559)

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

13. What are the exponents in the equilibrium-constant expression?

_____

14. What do the square brackets indicate in the equilibrium-constant expression?

_____

_____

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

16. A value of K_{eq} greater than 1 means that _____ are favored over _____ . A value of K_{eq} less than 1 means that _____ are favored over _____ .

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})?

_____

_____

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

_____

3. Look at Table 18.2 on page 562. Which salt is more soluble in water, silver bromide (AgBr) or silver chromate (Ag_2CrO_4)? _____

▶ The Common Ion Effect (pages 563–565)

4. A common ion is an ion that is common to both _____ 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. _____

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. _____

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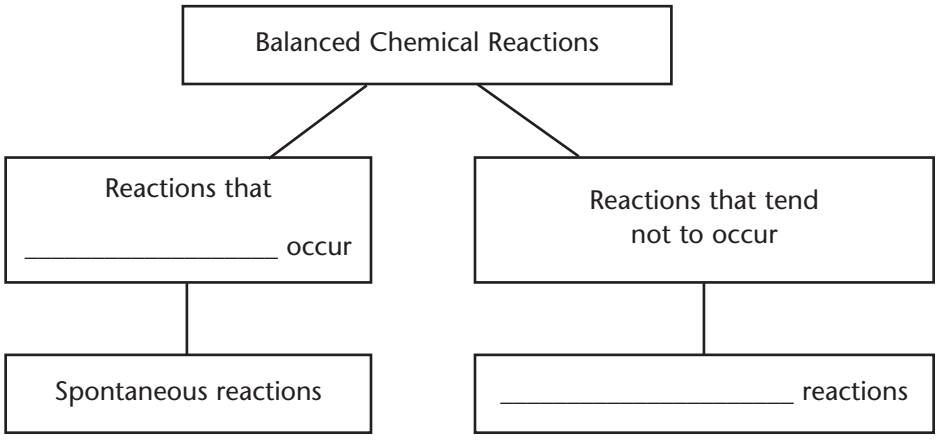
3. Make a concept map about balanced chemical reactions.



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

5. Describe four spontaneous reactions mentioned in this section.

a. _____

b. _____

c. _____

d. _____

6. What are nonspontaneous reactions?

_____

_____

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

▶ Entropy (pages 568–570)

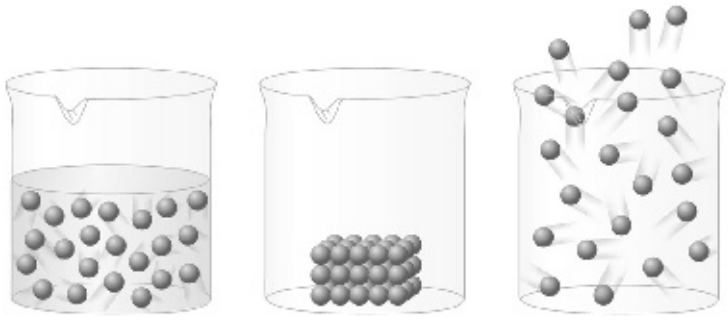
8. Some factor other than _____ change must help determine whether a physical or chemical process is spontaneous.

9. What is entropy? _____

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

11. Is the following sentence true or false? Entropy decreases when a substance is divided into parts. _____

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? _____

14. Entropy tends to _____ when temperature increases.

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

15. What determines whether a reaction is spontaneous?

_____

_____

16. Why is an exothermic reaction accompanied by an increase in entropy considered a spontaneous reaction? _____

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. _____

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

▶ 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 _____ .

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

_____

_____

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21. The numerical value of ΔG is _____ in spontaneous processes because the system loses free energy; the numerical value of ΔG is _____ 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.

SECTION 18.5 THE PROGRESS OF CHEMICAL REACTIONS (pages 575–579)

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 (pages 575–577)

1. What is a one-step reaction? _____

_____

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. _____

3. What is a specific rate constant (k) for a reaction? _____

_____

4. The _____ 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?

_____

▶ Reaction Mechanisms (page 578)

7. What is a reaction progress curve? _____

_____

8. A(n) _____ 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. _____

10. What is an intermediate product of a reaction?

_____

_____

11. Look at Figure 18.28 on page 578. What is one difference between this graph and the chemical equation for this reaction?

_____

_____

_____

_____

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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. _____

_____

b. _____

_____

c. _____

_____

d. _____

_____

Evaluate

Step 3. Does the result make sense?

_____

GUIDED PRACTICE PROBLEM 7 (page 557)

7. The reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ produces ammonia. At equilibrium, a 1-L flask contains 0.15 mol H_2, 0.25 mol N_2, and 0.10 mol NH_3. Calculate K_{eq} for the reaction.

Analyze

Step 1. List the knowns and the unknown.
Knowns

_____

_____

_____

_____

Unknown

_____

Calculate

Step 2. Solve for the unknowns.
Use the concentrations given and the coefficients from the balanced equation to determine K_{eq}:

$$K_{eq} = \frac{[NH_3]^2}{[N_2] \times [H_2]^3}$$

$$= \frac{0.10^2}{0.25 \times 0.15^3} = 11.85$$

= _____

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GUIDED PRACTICE PROBLEM 9 (page 558)

9. Suppose the following system reaches equilibrium.

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

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.

Known

$[N_2] =$ _____

$[O_2] =$ _____

$[NO] = 0.020$ mol/L

Unknown

$K_{eq} = ?$

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

$K_{eq} =$ _____

Step 3. Substitute the known values in the expression.

$$K_{eq} = \frac{(\square \text{ mol/L})^2}{\square \text{ mol/L} \times \square \text{ mol/L}}$$

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

$K_{eq} = 0.0016 = \square$

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

_____

_____

_____

Unknown

_____

At equilibrium $[Ca^{2+}] = [CO_3^{2-}]$. This fact will be used to solve for the unknown.

Calculate

Step 2. Solve for the unknown.

$K_{sp} = [Ca^{2+}] \times [CO_3^{2-}]$

Make a substitution based on the equilibrium condition stated above:

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

Now solve for the unknown:

$[Ca^{2+}] =$ _____

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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 8×10^{-19}.

Analyze

Step 1. List the knowns and the unknown.
Knowns

_____

_____

_____

_____

_____

Unknown

_____

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

Calculate

Step 2. Solve for the unknown.
Because K_{sp} is very small, simplify by assuming $x << 0.04$, and becomes negligible. Thus $[Fe^{2+}]$ is approximately equal to 0.04 *M*.

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

Rearranging for x gives the result:

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

So $[S^{2-}] =$ _____

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}).

Analyze

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.

$$\frac{\text{A}}{\text{t}} = k \times [\text{A}]$$

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

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

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

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

Evaluate

Step 3. Does the result make sense?

_____

_____