

SECTION	STUDENT ACTIVITIES/FEATURES	TEACHER'S RESOURCE PACKAGE
<p>19.1 Rates of Reaction</p> <p>Objectives</p> <ul style="list-style-type: none"> ▶ Explain what is meant by the rate of a chemical reaction ▶ Using collision theory, explain how the rate of a chemical reaction is influenced by the reaction conditions 	<p>Discover It! <i>Temperature and Reaction Rates</i>, p. 532</p> <p>Link to Auto Shop <i>Auto Body Repair</i>, p. 538</p>	<p>Review Module (Chapters 17–20)</p> <ul style="list-style-type: none"> ▶ Section Review 19.1 ▶ Practice Problems ▶ Quizzes <p>Laboratory Manual</p> <ul style="list-style-type: none"> ▶ Experiment 34: <i>Factors Affecting Reaction Rates</i> ▶ Experiment 35: <i>A Clock Reaction</i> <p>Laboratory Practical 19-1</p> <p>Small-Scale Chemistry Lab Manual, Experiment 24: <i>Factors Affecting the Rate of a Chemical Reaction</i></p>
<p>19.2 Reversible Reactions and Equilibrium</p> <p>Objectives</p> <ul style="list-style-type: none"> ▶ Predict changes in the equilibrium position due to changes in concentration, temperature, and pressure ▶ Write the equilibrium-constant expression for a reaction and calculate its value from experimental data 	<p>Sample Problems 19-1 through 19-4</p>	<p>Review Module</p> <ul style="list-style-type: none"> ▶ Section Review 19.2 ▶ Practice Problems ▶ Quizzes <p>Laboratory Manual, Experiment 36: <i>Disturbing Equilibrium</i></p> <p>Small-Scale Chemistry Lab Manual, Experiment 25: <i>Le Châtelier's Principle and Chemical Equilibrium</i></p>
<p>19.3 Determining Whether a Reaction Will Occur</p> <p>Objectives</p> <ul style="list-style-type: none"> ▶ Define entropy and free energy, and characterize reactions as spontaneous or nonspontaneous ▶ Describe how heat change and entropy change determine the spontaneity of a reaction 	<p>Mini Lab <i>Does Steel Burn?</i> p. 556</p> <p>Small-Scale Lab <i>Enthalpy and Entropy</i>, p. 557</p>	<p>Review Module</p> <ul style="list-style-type: none"> ▶ Section Review 19.3 ▶ Practice Problems ▶ Interpreting Graphics 19-1 ▶ Quizzes <p>Laboratory Recordsheets 19-1 and 19-2</p>
<p>19.4 Calculating Entropy and Free Energy</p> <p>Objectives</p> <ul style="list-style-type: none"> ▶ Calculate the standard entropy changes that accompany chemical and physical processes ▶ Calculate the free-energy changes that accompany chemical and physical processes 	<p>CHEMath <i>Balancing Equations</i>, p. 559</p> <p>Link to Geology <i>Weathering of Rocks</i>, p. 562</p> <p>Sample Problems 19-5 through 19-8</p>	<p>Review Module</p> <ul style="list-style-type: none"> ▶ Section Review 19.4 ▶ Practice Problems ▶ Interpreting Graphics 19-2 ▶ Quizzes
<p>19.5 The Progress of Chemical Reactions</p> <p>Objectives</p> <ul style="list-style-type: none"> ▶ Interpret experimental rate data to deduce the rate laws for simple chemical reactions ▶ Given an energy diagram for a reaction, analyze the mechanism for the reaction 	<p>Sample Problem 19-9</p> <p>Chemistry Serving . . . the Consumer <i>Don't Let Good Food Go Bad</i>, p. 570</p> <p>Chemistry in Careers <i>FDA Inspector</i>, p. 570</p>	<p>Review Module</p> <ul style="list-style-type: none"> ▶ Section Review 19.5 ▶ Practice Problems ▶ Vocabulary Review 19 ▶ Chapter 19 Tests and Quizzes <p>Solutions Manual for Chapter Reviews</p> <p>Graphing Calculator Problems</p>

PLANNING GUIDE *continued*

TECHNOLOGY RESOURCES

Internet Connections

Within this chapter, you will see the chemSURF logo. If you and your students have access to the Internet, the following URL address will provide various Internet connections that are related to topics and features presented in this chapter.

<http://www.chemsurf.com>



You can also find relevant chapter material at The Chemistry Place address:

<http://www.chemplace.com>

CD-ROMs

Chem ASAP! CD-ROM

- ▶ Chapter 19

ResourcePro CD-ROM

- ▶ Chapter 19

Assessment Resources CD-ROM

Videodiscs and Videotapes

Chemistry Alive! Videodisc

- ▶ Grain Elevator Explosion
- ▶ Oscillating Clock

Small-Scale Lab Video and Videodisc

- ▶ #19: Equilibrium and Kinetics

Overhead Transparencies

- ▶ #63: Collision Theory
- ▶ #64: Activation Energy and Catalysts
- ▶ #65: Reversible Reactions and Equilibrium
- ▶ #66: Entropy
- ▶ #67: Heat, Entropy, and Free Energy

ASSESSMENT

Student Edition

- ▶ Section Reviews 19.1–19.5
- ▶ Chapter 19 Review, pp. 571–574
- ▶ Alternative Assessment, p. 575

Teacher's Resource Package

- Review Module (Chap. 17–20)
- ▶ Vocabulary Review
- ▶ Chapter 19 Test A and Test B
- ▶ Chapter 19 Quizzes

Technology

- Chem ASAP! CD-ROM
- ▶ Assessment 19.1–19.5
- Assessment Resources CD-ROM
- ▶ Chapter 19 Tests

PLANNING FOR ACTIVITIES

STUDENT EDITION

Discover It! p. 532

- ▶ masking tape
- ▶ plastic cups
- ▶ hot and cold tap water
- ▶ ice
- ▶ thermometers
- ▶ effervescent antacid tablets
- ▶ clocks or watches with second hand
- ▶ graph paper
- ▶ pens or pencils

Mini Lab p. 556

- ▶ steel wool pads
- ▶ tissue paper
- ▶ tongs
- ▶ Bunsen burners
- ▶ heat-resistant pads
- ▶ pencils
- ▶ paper

Small-Scale Lab, p. 557

- ▶ alcohol thermometers
- ▶ 1-oz plastic cups
- ▶ NaCl(s), NH₄Cl(s), CaCl₂(s)
- ▶ plastic spoons
- ▶ crushed ice
- ▶ water

TEACHER'S EDITION

Teacher Demo, p. 536

- ▶ 5 mL of ethanoic acid
- ▶ 5 mL of isoamyl alcohol
- ▶ two test tubes
- ▶ granules of anhydrous calcium sulfate
- ▶ concentrated sulfuric acid
- ▶ boiling water bath

Teacher Demo, p. 537

- ▶ cornstarch
- ▶ water glass
- ▶ match
- ▶ Bunsen burner
- ▶ spatula
- ▶ goggles
- ▶ Plexiglas shield

Teacher Demo, p. 541

- ▶ sulfuric acid
- ▶ two test tubes
- ▶ anhydrous calcium sulfate

Teacher Demo, p. 544

- ▶ fume hood
- ▶ small amount (3 g or less) of copper turnings
- ▶ test tube
- ▶ 10 mL of 6M nitric acid
- ▶ one-hole stopper fitted with a glass delivery tube and rubber hose
- ▶ two Pyrex test tubes
- ▶ stoppers
- ▶ ice bath
- ▶ warm water bath

Teacher Demo, p. 552

- ▶ block of ice
- ▶ beaker
- ▶ water
- ▶ heat source

Teacher Demo, p. 562

- ▶ 0.1M solution of KMnO₄ in 0.1M HCl
- ▶ 1000-mL beaker
- ▶ thermometer
- ▶ graduated cylinder
- ▶ 20 mL of 30% H₂O₂
- ▶ watch glass
- ▶ glowing splint

19.1

RATES OF REACTION

SECTION REVIEW

Objectives

- Explain what is meant by the rate of a chemical reaction
- Using collision theory, explain how the rate of a chemical reaction is influenced by the reaction conditions

Key Terms

- rates
- collision theory
- activation energy
- activated complex
- transition state
- catalyst
- inhibitor

Part A Completion

Use this completion exercise to check your understanding of the concepts and terms that are introduced in this section. Each blank can be completed with a term, short phrase, or number.

- _____ 1 _____ measure the speed of any change that occurs within a time interval. Collision theory states that particles _____ 2 _____ when they collide, provided that they have enough _____ 3 _____.
- The rate at which a chemical reaction occurs is determined by an _____ 4 _____ energy barrier. The activation energy is the _____ 5 _____ energy that reactants must have to go to _____ 6 _____. The higher the activation energy barrier, the _____ 7 _____ the reaction. Chemists help reactants overcome the activation barrier in a number of ways.
- Two effective methods are to increase the _____ 8 _____ at which the reaction is done or use a _____ 9 _____. Rates of reaction can also be increased by _____ 10 _____ the concentration of reactants.
1. _____
2. _____
3. _____
4. _____
5. _____
6. _____
7. _____
8. _____
9. _____
10. _____

Part B True-False

Classify each of these statements as always true, AT; sometimes true, ST; or never true, NT.

- _____ 11. An increase in temperature will generally increase the rate of a reaction.
- _____ 12. A catalyst is considered as a reactant in a chemical reaction.

- _____ 13. The speed of a reaction can be increased by increasing reactant concentration or decreasing particle size.
- _____ 14. An enzyme is a biological catalyst.

Part C Matching

Match each description in Column B to the correct term in Column A.

Column A

- _____ 15. rate
- _____ 16. collision theory
- _____ 17. activation energy
- _____ 18. transition state
- _____ 19. catalyst
- _____ 20. inhibitor

Column B

- a. synonym for an activated complex
- b. speed of a change that occurs over time
- c. substance that interferes with the action of a catalyst
- d. Particles can react to form products when they collide, provided they have enough kinetic energy.
- e. substance that increases the rate of a reaction without being used up
- f. minimum energy particles must have in order to react

Part D Questions and Problems

Answer the following question and solve the following problem in the space provided.

21. An ice machine can produce 120 kg of ice in 24 hours. Express the rate of ice production in kg/hr.
22. Which of the following will increase the rate of a reaction?
- a. increase particle size
 - b. increase temperature
 - c. decrease concentration
 - d. add a catalyst

19.2

REVERSIBLE REACTIONS AND EQUILIBRIUM

SECTION REVIEW

Objectives

- Predict changes in the equilibrium position due to changes in concentration, temperature, and pressure
- Write the equilibrium-constant expression for a reaction and calculate its value from experimental data

Key Terms

- reversible reactions
- chemical equilibrium
- equilibrium position
- Le Châtelier's principle
- equilibrium constant (K_{eq})

Key Equation

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

When $aA + bB \rightleftharpoons cC + dD$

Part A Completion

Use this completion exercise to check your understanding of the concepts and terms that are introduced in this section. Each blank can be completed with a term, short phrase, or number.

In principle, all reactions are 1. That is, reactants go to 2 in the 3 direction and products go to 4 in the 5 direction.

The point at which the rate of conversion of 6 to 7 and vice versa is equal is the position of 8. The 9 of a reversible reaction, K_{eq} , is useful for determining the position of equilibrium. It is essentially a measure of the 10 of products to reactants at equilibrium. The direction of change in the position of equilibrium may be predicted by applying 11 principle.

- _____
- _____
- _____
- _____
- _____
- _____
- _____
- _____
- _____
- _____
- _____

Part B True-False

Classify each of these statements as always true, AT; sometimes true, ST; or never true, NT.

- _____ 12. The concentrations of reactants and products in a system at dynamic equilibrium are always changing.
- _____ 13. A change in the pressure on a system can cause a shift in the equilibrium position.
- _____ 14. For a chemical equilibrium to be established, the chemical reaction must be irreversible.
- _____ 15. The K_{eq} for a certain reaction was 2×10^{-7} . For this reaction at equilibrium, the concentration of the reactants is greater than the concentration of the products.

Part C Matching

Match each description in Column B to the correct term in Column A.

Column A	Column B
_____ 16. reversible reactions	a. state of balance in which forward and reverse reactions take place at the same rate
_____ 17. chemical equilibrium	b. measurement of the amount of solute that is dissolved in a given quantity of solvent
_____ 18. equilibrium position	c. relative concentrations of reactants and products of a reaction that has reached equilibrium
_____ 19. Le Châtelier's principle	d. When stress is applied to a system at equilibrium, the system changes to relieve the stress.
_____ 20. equilibrium constant	e. reaction in which conversion of reactants to products and products to reactants occur simultaneously
_____ 21. concentration	f. ratio of product concentrations to reactant concentrations with each raised to a power given by the number of moles of the substance in the balanced equation

Part D Questions and Problems

Solve the following problem in the space provided. Show your work.



Calculate K_{eq} for this reaction if the equilibrium concentrations are:
 $[\text{SO}_2] = 0.42\text{M}$, $[\text{O}_2] = 0.21\text{M}$, $[\text{SO}_3] = 0.072\text{M}$

19.3

DETERMINING WHETHER A REACTION WILL OCCUR

SECTION REVIEW

Objectives

- Define entropy and free energy, and characterize reactions as spontaneous or nonspontaneous
- Describe how heat change and entropy change determine the spontaneity of a reaction

Key Terms

- free energy
- entropy
- spontaneous reactions
- law of disorder
- nonspontaneous reactions

Part A Completion

Use this completion exercise to check your understanding of the concepts and terms that are introduced in this section. Each blank can be completed with a term, short phrase, or number.

Reactions that actually occur as written are called 1 1. _____
 reactions. Equations for other reactions may be written, but the 2. _____
 reactions are 2. All spontaneous reactions release 3 3. _____
 that becomes available to do 4. This energy is called 4. _____
5. 5. _____

It is the natural tendency for all things to go to lower 6 6. _____
 and toward 7 disorder. In addition to the change in heat 7. _____
 content, 8 is a factor that determines whether a reaction 8. _____
 will be spontaneous. 9. _____

Entropy is a measure of the 9 of a system. The 10. _____
10 states that processes move in the direction of 11 11. _____
 disorder.

Part B True-False

Classify each of these statements as always true, AT; sometimes true, ST; or never true, NT.

_____ 12 An exothermic reaction is a spontaneous reaction.

- _____ 13. When a sandwich is eaten and digested, its entropy increases.
- _____ 14. Some spontaneous reactions appear to be nonspontaneous because their rate of reaction is slow.
- _____ 15. Spontaneous reactions release free energy.
- _____ 16. Entropy will increase in a spontaneous reaction.

Part C Matching

Match each description in Column B to the correct term in Column A.

Column A	Column B
_____ 17. free energy	a. measure of the disorder of a system
_____ 18. spontaneous reactions	b. energy in a reaction that is available to do work
_____ 19. nonspontaneous reactions	c. It is the natural tendency of systems to move in the direction of maximum disorder.
_____ 20. entropy	d. reactions that do not give products under the specified conditions
_____ 21. law of disorder	e. reactions that favor formation of products under the specified conditions

Part D Questions and Problems

Complete the following question and solve the following problem in the space provided.

22. In each of the following pairs, choose the system with the higher entropy.
- a. a heap of loose stamps or stamps in an album _____
 - b. ice cubes in their tray or ice cubes in a bucket _____
 - c. 10 mL of water at 100 °C or 10 mL of steam at 100 °C _____
 - d. the people watching the parade or a parade _____
23. Which combination of factors will always give a spontaneous reaction?
- a. heat absorbed, entropy increases
 - b. heat released, entropy increases
 - c. heat released, entropy decreases
 - d. heat absorbed, entropy decreases
24. Which combination described in question 23 will never give a spontaneous reaction?

19.4

CALCULATING ENTROPY AND FREE ENERGY

SECTION REVIEW

Objectives

- Calculate the standard entropy changes that accompany chemical and physical processes
- Calculate the free-energy changes that accompany chemical and physical processes

Key Terms

- standard entropy (S^0)
- Gibbs free-energy change (ΔG)

Key Equations

- $\Delta S^0 = S^0(\text{products}) - S^0(\text{reactants})$
- $\Delta G = \Delta H - T\Delta S$
- $\Delta G^0 = \Delta G_f^0(\text{products}) - \Delta G_f^0(\text{reactants})$

Part A Completion

Use this completion exercise to check your understanding of the concepts and terms that are introduced in this section. Each blank can be completed with a term, short phrase, or number.

- S is the symbol for 1, which is a qualitative measure of 1. _____
 disorder. The 2 of a substance is designated as S^0 at 25 °C 2. _____
 and 101.3 kPa. 3. _____
- The standard entropy change in a reaction can be calculated 4. _____
 by subtracting S^0 of the 3 from S^0 of the 4. 5. _____
- Energy from a reaction that is available to do work is called the 6. _____
5, or ΔG . This quantity can be calculated when the entropy 7. _____
 change and 6 change are known. 8. _____
- ΔG for a reaction can also be calculated using free energy of 9. _____
7. Thus ΔG^0 can be obtained by subtracting ΔG_f^0 of the
8 from ΔG_f^0 of the 9.

Part B True-False

Classify each of these statements as always true, AT; sometimes true, ST; or never true, NT.

- _____ 10. Spontaneous processes provide energy for work.
- _____ 11. A reaction with a negative ΔH is spontaneous.
- _____ 12. Substances have negative entropies below 0 °C.
- _____ 13. The higher the temperature, the more likely a reaction will be spontaneous.

Part C Matching

Match each description in Column B to the correct term in Column A.

Column A

- _____ 14. standard entropy
- _____ 15. Gibbs free-energy change
- _____ 16. enthalpy
- _____ 17. spontaneous reaction

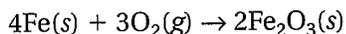
Column B

- a. the amount of heat a substance has at a given temperature and pressure
- b. maximum amount of energy that can be coupled to another process to do work
- c. a reaction known to give the products as written in a balanced equation at the specified conditions
- d. entropy of a substance in its stable state at 25 °C and 1 atm

Part D Questions and Problems

Complete the following question and solve the following problem in the space provided.

18. Using the information found in Table 19.2 of your text, calculate the change in entropy for the following reaction.



19. The reaction $\text{A} + 2\text{B} \rightarrow 3\text{C}$ has a ΔH^0 of -163 kJ/mol and a ΔS^0 of $-0.51 \text{ kJ/(K} \times \text{mol)}$ at 25 °C. Is this reaction spontaneous?

19.5

THE PROGRESS OF CHEMICAL REACTIONS

SECTION REVIEW

Objectives

- Interpret experimental rate data to deduce the rate laws for simple chemical reactions
- Given an energy diagram for a reaction, analyze the mechanism for the reaction

Key Terms

- rate law
- elementary reaction
- specific rate constant
- reaction mechanism
- first-order reaction
- intermediate

Part A Completion

Use this completion exercise to check your understanding of the concepts and terms that are introduced in this section. Each blank can be completed with a term, short phrase, or number.

The 1 of a reaction is dependent in part on the 2 of the reactants. An equation that relates reaction rate to reactant concentration is called a 3. In a rate law equation, K is known as the 4.

1. _____

3. _____

4. _____

5. _____

The power to which a reaction concentration is raised is called the 5 of the reaction. A reaction whose rate is proportional to the concentration of one reactant is called a 6 reaction.

6. _____

7. _____

8. _____

A reaction that is first order for each of two reactants is 7 overall. The actual kinetic order of a reaction is determined by 8.

9. _____

10. _____

A single step reaction is called an 9. A series of elementary reactions combine to form the 10 of a complex reaction.

Part B True-False

Classify each of these statements as always true, AT; sometimes true, ST; or never true, NT.

- _____ 11. The rate order of a reaction can be determined from the balanced equation.
- _____ 12. There is at least one intermediate product in a chemical reaction.
- _____ 13. There is at least one activated complex in a chemical reaction.
- _____ 14. An elementary reaction is a one-step reaction.

Part C Matching

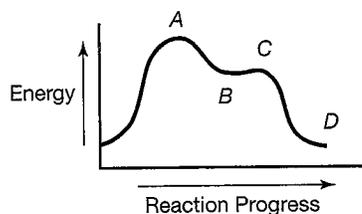
Match each description in Column B to the correct term in Column A.

Column A	Column B
_____ 15. rate law	a. a single-step reaction
_____ 16. specific rate constant	b. reaction in which the rate is directly proportional to the concentration of one reactant
_____ 17. first-order reaction	c. a product of a reaction that becomes a reactant in another reaction
_____ 18. elementary reaction	d. expression relating the rate of a reaction to the concentration of the reactants
_____ 19. reaction mechanism	e. series of elementary reactions that take place during a complex reaction
_____ 20. intermediate product	f. proportionality constant relating the concentrations of reactants to the reaction rate

Part D Questions and Problems

Complete the following question and solve the following problem in the space provided.

21. Below is the reaction progress curve for a complex reaction. Describe the reaction represented by the curve (number of steps and the significance of points A, B, C, and D).



19

REACTION RATES AND EQUILIBRIUM**PRACTICE PROBLEMS**

In your notebook, solve the following problems.

SECTION 19.1 RATES OF REACTION

- List three ways that reaction rates can generally be increased.
- Ethyl acetate ($C_4H_8O_2$) reacts with a solution of sodium hydroxide (NaOH) in water to form sodium acetate ($C_2H_3O_2Na$) and ethyl alcohol (C_2H_6O). Suppose at $25^\circ C$ two moles of ethyl acetate react completely in four hours. How would you express the rate of reaction?
- How would the following actions likely change the rate of the reaction in problem 2?
 - the temperature is lowered to $4^\circ C$.
 - the concentration of sodium hydroxide in water is increased.
- Ethyl acetate and water are not miscible; thus, the reaction in problem 2 only occurs at the interface of the two liquids. What would be the effect on the reaction rate of adding a solvent to make the reaction homogeneous?

SECTION 19.2 REVERSIBLE REACTIONS AND EQUILIBRIUM

- Write the expression for the equilibrium constant for this reaction:

$$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$$
- Calculate the equilibrium constant for the reaction in problem 1 if the equilibrium concentrations are $[N_2O_5] = 0.50 \text{ mol/L}$, $[NO_2] = 0.80 \text{ mol/L}$, $[O_2] = 0.20 \text{ mol/L}$.
- How would the equilibrium position for the equation in problem 1 be affected by
 - an addition of O_2 to the reaction vessel?
 - a decrease in the pressure?

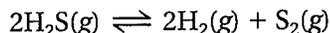
- The equilibrium constant for the reaction of nitrogen dioxide to form dinitrogen tetroxide is 5.6.

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

In a one-liter container, the amount of N_2O_4 , at equilibrium, is 0.66 mol. What is the equilibrium concentration of NO_2 ?

- Write the equilibrium constant expression for each of the following reactions.
 - $4NO(g) + 2O_2(g) \rightleftharpoons 2N_2O_4(g)$
 - $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$
 - $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
 - $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
- What effect would an increase in pressure have on the equilibrium position of each reaction in problem 5?

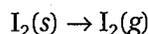
7. Which value of K_{eq} indicates most favorably for product formation, $K_{\text{eq}} = 1 \times 10^{12}$, $K_{\text{eq}} = 1.5$, or $K_{\text{eq}} = 5.6 \times 10^{-4}$?
8. Hydrogen sulfide gas decomposes into its elements and establishes an equilibrium at 1400 °C.



A liter of this gas mixture contains 0.18 mol H_2S , 0.014 mol H_2 , and 0.035 mol S_2 . Calculate the equilibrium constant, K_{eq} , for this reaction.

SECTION 19.3 DETERMINING WHETHER A REACTION WILL OCCUR

1. When gently warmed, the element iodine will sublime:



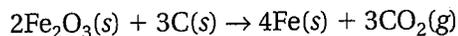
Is this process accompanied by an increase or decrease in entropy?

2. Is there an increase or decrease in entropy when air is cooled and liquefied (changed from a gas to a liquid)?
3. Is the degree of disorder increasing or decreasing in these reactions?
- $\text{H}_2(g) + \text{Br}_2(l) \rightarrow 2\text{HBr}(g)$
 - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) \rightarrow \text{CuSO}_4(s) + 5\text{H}_2\text{O}(g)$
 - $2\text{XeO}_3(s) \rightarrow 2\text{Xe}(g) + 3\text{O}_2(g)$
4. Classify each of these systems as always spontaneous (A), never spontaneous (N), or depends on the relative magnitude of the heat and entropy changes (D).
- entropy decreases, heat is released
 - entropy decreases, heat is absorbed
 - entropy increases, heat is absorbed
 - entropy increases, heat is released

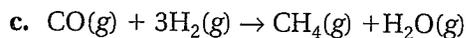
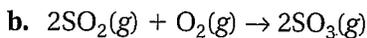
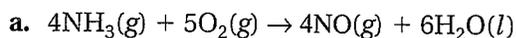
SECTION 19.4 CALCULATING ENTROPY AND FREE ENERGY

For problems 1–4, calculate the standard entropy change associated with each reaction. Refer to table 19.2 in your textbook.

- $2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$
- $2\text{H}_2\text{O}(g) + 2\text{Cl}_2(g) \rightarrow 4\text{HCl}(g) + \text{O}_2(g)$
- $\text{I}_2(g) \rightarrow \text{I}_2(s)$
- $2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$
- A reaction is endothermic (positive ΔH) and has a positive entropy. Would this reaction more likely be spontaneous at high or low temperatures? Explain.
- A reaction has a ΔS of $-122 \text{ J}/(\text{K} \times \text{mol})$ and a ΔH of $-78 \text{ kJ}/\text{mol}$. Is this reaction spontaneous at 285 °C?
- Calculate the standard free energy change for the reaction between iron(III) oxide and carbon (graphite). Refer to Table 19.4 in your textbook.



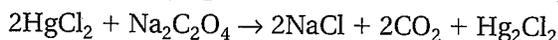
8. Calculate the ΔG° of each of these reactions. Indicate whether each reaction is spontaneous or nonspontaneous at 25°C. Refer to Table 19.4 in your textbook.



SECTION 19.5 THE PROGRESS OF CHEMICAL REACTIONS

1. A first order reaction has an initial reaction rate of 2.4 mol/(L × s). What is the rate when one-eighth the starting materials remain?

2. It has been experimentally determined that the rate law for the reaction between mercury(II) chloride and sodium oxalate is third-order overall and first-order with respect to HgCl_2 . Write the rate law for this equation.



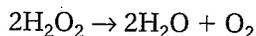
3. A certain combination reaction gave the following data. What is the rate law for this reaction?



Initial concentration (mol/L)		Initial rate (mol/L × s)
[J]	[K]	Reaction of J
0.30	0.50	0.080
0.60	0.50	0.160
0.60	0.25	0.080

4. Iodide ion catalyzes the decomposition of hydrogen peroxide. The reaction is first-order in H_2O_2 . What is the value of the rate constant, k , if the initial rate is 0.00842 mol/(L × s)?

The initial concentration of H_2O_2 is 0.500 mol/L.

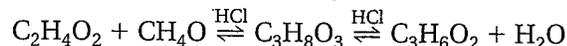


5. A proposed reaction mechanism has two intermediates. How many elementary reactions are there in this mechanism?

6. The reaction $\text{A} + \text{B} \rightarrow \text{C}$ is first order in A and B, second order overall. Complete the following table:

Initial concentration (mol/L)		Initial rate (mol/L × s)
[A]	[B]	
0.50	0.50	0.020
0.50		0.040
0.25	1.0	

7. The condensation of acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) with methanol (CH_4O) to form methyl acetate ($\text{C}_3\text{H}_6\text{O}_2$) and water is catalyzed by HCl



a. How many elementary reactions are there in this condensation?

b. Write the formula for the reaction intermediate(s).

c. Write the rate law for this condensation

19

INTERPRETING GRAPHICS

USE WITH SECTIONS 19.3 AND 19.4

<p>A</p> <p>Heat released (favorable)</p> <p>Entropy increase (favorable)</p> <p>Reaction spontaneous</p>	
<p>B</p> <p>Entropy increase (favorable)</p> <p>Heat absorbed (unfavorable)</p> <p>Reaction spontaneous</p>	
<p>C</p> <p>Heat released (favorable)</p> <p>Entropy decrease (unfavorable)</p> <p>Reaction spontaneous</p>	
	<p>D</p> <p>Heat absorbed (unfavorable)</p> <p>Entropy increase (favorable)</p> <p>Reaction nonspontaneous</p>
	<p>E</p> <p>Entropy decrease (unfavorable)</p> <p>Heat released (favorable)</p> <p>Reaction nonspontaneous</p>
	<p>F</p> <p>Heat absorbed (unfavorable)</p> <p>Entropy decrease (unfavorable)</p> <p>Reaction nonspontaneous</p>

The lettered diagrams on the previous page are from Figure 19.20 in your textbook. Use them to answer the following questions.

1. For each example, state whether ΔG is positive or negative.

a. _____

b. _____

c. _____

d. _____

e. _____

f. _____

2. For each example; state whether ΔH is positive or negative.

a. _____

b. _____

c. _____

d. _____

e. _____

f. _____

3. For Example B, is $|T\Delta S|$ greater or less than $|\Delta G|$?

4. For Example D, is $|T\Delta S|$ greater or less than $|\Delta G|$?

5. Which example would provide the most energy for work?

6. Could Example D be made to be spontaneous by an increase in temperature?

19**VOCABULARY REVIEW**

Match the correct vocabulary term to each numbered statement. Write the letter of the correct term on the line provided.

Column A

- _____ 1. the disorder of a system
- _____ 2. a substance that interferes with the action of a catalyst
- _____ 3. reactions that favor the formation of products at the specified conditions
- _____ 4. the minimum energy colliding particles must have in order to react
- _____ 5. a substance that increases the rate of a reaction without being used up in the reaction
- _____ 6. the arrangement of atoms at the peak of the activation-energy barrier
- _____ 7. a reaction in which the rate is directly proportional to the concentration of one of the reactants
- _____ 8. energy that is available to do work
- _____ 9. when the forward and reverse reactions are taking place at the same rate
- _____ 10. the ratio of product concentrations to reactant concentrations, with each concentration raised to a power given by the number of moles of that substance in the balanced equation

Column B

- a. activation energy
- b. catalyst
- c. chemical equilibrium
- d. free energy
- e. entropy
- f. activated complex
- g. inhibitor
- h. equilibrium constant
- i. spontaneous reactions
- j. first-order reaction

19**REACTION RATES AND EQUILIBRIUM**

Quiz for CHAPTER 19

Write the letter of the best answer in the blank.

- _____ 1. At chemical equilibrium, the rates of the forward reaction and reverse reactions are: 19.2
a. equal to 0. c. at a maximum.
b. equal to each other. d. at a minimum.
- _____ 2. A catalyst works by: 19.1
a. changing the pressure of the system.
b. changing the temperature of the reactants.
c. shifting the equilibrium position toward the products.
d. lowering the activation energy barrier.
- _____ 3. The rate of a chemical reaction normally: 19.1
a. increases as reactant concentration increases.
b. is slowed down by a catalyst.
c. decreases as temperature increases.
d. decreases as reactant concentration increases.
- _____ 4. Activation energy is: 19.1
a. heat released or absorbed in a reaction.
b. the minimum energy colliding particles must have in order to react.
c. the energy given off when reactants collide.
d. generally very high for a reaction that takes place rapidly.
- _____ 5. Spontaneous reactions: 19.3
a. are always exothermic.
b. always take place at a rapid rate.
c. always result in increased disorder of the system.
d. naturally favor the formation of products.
- _____ 6. On a cold day, water vapor condenses to form frost. This represents an: 19.3
a. entropy increase and enthalpy increase.
b. entropy increase and enthalpy decrease.
c. entropy decrease and enthalpy increase.
d. entropy decrease and enthalpy decrease.

Classify each of these statements as always true, AT; sometimes true, ST; or never true, NT.

- _____ 7. The value of K_{eq} for a spontaneous reaction is much less than 1. 19.3
- _____ 8. The standard entropy, S^0 , of a liquid or solid is the entropy at 25° C and 101.3 kPa. 19.4
- _____ 9. The Gibbs free energy for a spontaneous process is negative. 19.4
- _____ 10. In a first-order reaction involving several reactants, the reaction rate is directly proportional to the concentration of each of the reactants. 19.5

19**REACTION RATES AND EQUILIBRIUM****CHAPTER TEST A****A. Matching**

Match each description in Column B with the correct term in Column A. Write the letter of the correct definition in the space provided.

Column A	Column B
_____ 1. activated complex	a. the number of particles that react in a given time to form products
_____ 2. reaction rate	b. energy available to do work
_____ 3. Le Châtelier's principle	c. favoring the formation of products
_____ 4. spontaneous	d. the minimum energy colliding particles must have in order to react
_____ 5. elementary reaction	e. when the forward and reverse reactions take place at the same rate
_____ 6. chemical equilibrium	f. a substance that interferes with the action of a catalyst
_____ 7. entropy	g. reactants are converted to products in a single step
_____ 8. activation energy	h. the measure of disorder
_____ 9. inhibitor	i. the arrangement of atoms at the peak of the activation energy barrier
_____ 10. free energy	j. If a stress is applied to a system in dynamic equilibrium, the system changes to relieve the stress.

B. Multiple Choice

Write the letter of the best answer in the blank.

- _____ 11. In which of the following physical states does a given substance have the highest entropy?
- a. solid
 - b. gas
 - c. liquid
 - d. all of the above
- _____ 12. A reaction that requires free energy:
- a. must be endothermic.
 - b. is nonspontaneous.
 - c. must correspond to a decrease in entropy.
 - d. is spontaneous.

- _____ 13. The two factors that determine whether a reaction is spontaneous or nonspontaneous are:
- entropy and disorder.
 - entropy and enthalpy change.
 - electron configuration and energy change.
 - energy and the heat of reaction.
- _____ 14. In which of these systems is the entropy decreasing?
- air escaping from a tire
 - snow melting
 - salt dissolving in water
 - a gas condensing to a liquid
- _____ 15. All spontaneous processes:
- are exothermic.
 - are endothermic
 - involve an increase in entropy.
 - release free energy.
- _____ 16. If a catalyst is used in a reaction:
- the energy of activation increases.
 - the reaction rate does not change.
 - the reaction rate increases.
 - the equilibrium shifts.
- _____ 17. Which of the following affects the rate of a chemical reaction?
- the presence of a catalyst
 - the temperature
 - the concentration of reactants
 - all of the above
- _____ 18. What is the expression for K_{eq} for this reaction?
- $$2\text{H}_2\text{O}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$$
- $K_{\text{eq}} = \frac{[\text{2H}_2\text{O}]}{[\text{H}_2] \times [\text{O}_2]}$
 - $K_{\text{eq}} = \frac{[\text{H}_2]^2 \times [\text{O}_2]}{[\text{H}_2\text{O}]^2}$
 - $K_{\text{eq}} = \frac{[\text{2H}_2] \times [\text{O}_2]}{[\text{2H}_2\text{O}]}$
 - $K_{\text{eq}} = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2 \times [\text{O}_2]}$
- _____ 19. In an equilibrium reaction with a K_{eq} of 1×10^8
- reactants are favored.
 - reaction is nonspontaneous.
 - products are favored.
 - reaction is exothermic.
- _____ 20. What is the effect of adding more CO_2 to the following equilibrium reaction?
- $$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$$
- More H_2CO_3 is produced.
 - More H_2O is produced.
 - The equilibrium is pushed in the direction of reactants.
 - no change
- _____ 21. Doing which of the following generally increases the entropy of a substance?
- freezing it
 - dissolving it in water
 - condensing it
 - all of the above
- _____ 22. The K_{eq} of a reaction is 4×10^{-7} . At equilibrium:
- the reactants are favored.
 - the products are favored.
 - the reactants and products are present in equal amounts.
 - the rate of the reverse reaction is much greater than the rate of the forward reaction.

D. Essay

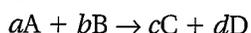
Write a short essay for the following.

27. Characterize spontaneous and nonspontaneous reactions. Then explain why a spontaneous reaction may appear to be nonspontaneous.

E. Additional Problems

Solve the following problems in the space provided. Show your work.

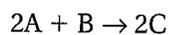
28. The rate law for the following reaction is: $\text{Rate} = k[\text{A}]^a \times [\text{B}]^b$.



From the data in the following chart, find the kinetic order of the reaction with respect to A and B, as well as the overall order.

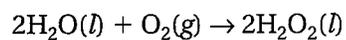
Initial concentration of A (mol/L)	Initial concentration of B (mol/L)	Initial Rate [mol/(L × s)]
0.50	0.05	2×10^{-3}
0.10	0.05	4×10^{-3}
0.20	0.05	8×10^{-3}
0.01	0.05	1×10^{-3}
0.01	0.10	8×10^{-3}
0.01	0.20	64×10^{-3}

29. The following reaction has an H^0 of 53 kJ/mol and a S^0 of 0.070 kJ/(K × mol) at 25 °C.



Is this reaction spontaneous? (Calculate ΔG .)

30. What is the standard change in entropy for the following reaction when all reactants are in the specified states?



Standard entropies S° in $\text{J}/(\text{K} \times \text{mol})$:

$$\text{H}_2\text{O}(l) = 69.94, \text{H}_2\text{O}_2(l) = 92.0, \text{O}_2(g) = 205.0$$

19

REACTION RATES AND EQUILIBRIUM

CHAPTER TEST B

A. Matching

Match each term in Column B with the correct description in Column A. Write the letter of the correct term in the blank provided.

Column A

- _____ 1. when the forward and reverse reactions are taking place at the same rate
- _____ 2. Things move in the direction of maximum disorder or randomness.
- _____ 3. the minimum energy colliding particles must have in order to react
- _____ 4. the ratio of product concentrations to reactant concentrations, with each concentration raised to a power given by the number of moles of that substance in the balanced equation
- _____ 5. a substance that increases the rate of a reaction without being used up itself in the reaction
- _____ 6. the disorder of a system
- _____ 7. Atoms, ions, and molecules can form a chemical bond between them when they collide, provided the particles have enough kinetic energy.
- _____ 8. energy that is available to do work
- _____ 9. the arrangement of atoms at the peak of the activation energy barrier
- _____ 10. If a stress is applied to a system in a dynamic equilibrium, the system changes to relieve the stress.

Column B

- a. Le Châtelier's principle
- b. activated complex
- c. entropy
- d. collision theory
- e. free energy
- f. catalyst
- g. law of disorder
- h. activation energy
- i. equilibrium constant
- j. chemical equilibrium

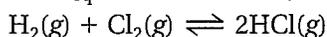
B. Multiple Choice

Choose the best answer and write its letter in the blank.

- _____ 11. According to the collision theory, in order for a chemical reaction to occur, the reactant atoms must:
- make contact with each other.
 - have a minimum level of kinetic energy.
 - form an activated complex.
 - all of these

- _____ 12. In general, increasing temperature causes the rate of most chemical reactions to:
- increase.
 - decrease.
 - remain the same.
 - vary unpredictably.
- _____ 13. Which of the following is true concerning the impact of increasing temperature on reaction rates?
- The number of collisions between reactant atoms is increased.
 - The energy of each reactant atom is increased.
 - The percentage of collisions with sufficient energy to cross the activation energy barrier is increased.
 - all of these
- _____ 14. What would decrease the rate of most chemical reactions?
- increasing the concentration of reactant atoms
 - increase the size of the reactant particles
 - adding an appropriate catalyst
 - all of these
- _____ 15. Catalysts alter the rate of a chemical reaction by:
- increasing the number of collisions between reactant atoms.
 - increasing the kinetic energy of each reactant atom.
 - lowering the activation energy barrier.
 - being consumed in the reaction.
- _____ 16. Which of the following is true concerning a reaction that has reached chemical equilibrium?
- The forward reaction is occurring faster than the reverse reaction.
 - The reverse reaction is occurring faster than the forward reaction.
 - The forward reaction is occurring as fast as the reverse reaction.
 - The mass of products is equal to the mass of reactants.
- _____ 17. Given the following system at equilibrium:
- $$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
- what would be the effect of removing $\text{NH}_3(\text{g})$ as it is formed?
- The equilibrium would shift to the left.
 - More $\text{N}_2(\text{g})$ would be produced.
 - More $\text{H}_2(\text{g})$ would be produced.
 - The equilibrium would shift to the right.
- _____ 18. Given the following system at equilibrium:
- $$\text{H}_2\text{O}(\text{l}) + \text{heat} \rightleftharpoons \text{H}_2\text{O}(\text{g})$$
- how would a decrease in temperature affect the system?
- The equilibrium would shift to the right.
 - More $\text{H}_2\text{O}(\text{l})$ would be produced.
 - More $\text{H}_2\text{O}(\text{g})$ would be produced.
 - The levels of reactants and products would remain the same.
- _____ 19. Which of the following would increase the yield of $\text{CO}(\text{g})$ in the following equilibrium system?
- $$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) + \text{heat} \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$$
- decreasing temperature
 - increasing pressure
 - adding $\text{H}_2(\text{g})$
 - adding $\text{H}_2\text{O}(\text{g})$

- _____ 20. Spontaneous reactions:
- favor the formation of products.
 - give substantial amounts of reactants at equilibrium.
 - absorb free energy.
 - have high reaction rates.
- _____ 21. Which of the following has the greatest entropy?
- ice
 - water
 - steam
 - cannot be predicted
- _____ 22. The type of reaction most likely to be spontaneous is one in which:
- both heat content and entropy are decreased.
 - heat content is decreased, while entropy is increased.
 - both heat content and entropy are increased.
 - heat content is increased, while entropy is decreased.
- _____ 23. The expression for K_{eq} for the following reaction is:



- $K_{eq} = \frac{[\text{H}_2] \times [\text{Cl}_2]}{[2\text{HCl}]}$
- $K_{eq} = \frac{[2\text{HCl}]}{[\text{H}_2] \times [\text{Cl}_2]}$
- $K_{eq} = \frac{[\text{HCl}]^2}{[\text{H}_2] \times [\text{Cl}_2]}$
- $K_{eq} = \frac{[\text{H}_2] \times [\text{Cl}_2]}{[\text{HCl}]^2}$

- _____ 24. If the equilibrium concentrations for the system in question 24 are as follows, find the value of K_{eq} :

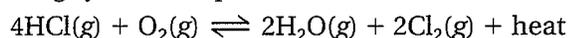
$$[\text{H}_2] = 0.450 \text{ mol/L}, [\text{Cl}_2] = 0.450 \text{ mol/L}, [\text{HCl}] = 6.25 \text{ mol/L}$$

- 1.62×10^{-2}
- 193
- 5.18×10^{-3}
- 61.7

C. Problems

Solve the following problems in the space provided. Show your work.

25. Given the following system at equilibrium:



determine the effect of each of the following changes on the equilibrium position of the system (shifts right or left) and on the amount of $\text{Cl}_2(\text{g})$ that would result (increases or decreases):

	Equilibrium Position	Amount of $\text{Cl}_2(\text{g})$
a. increasing temperature		
b. decreasing pressure		
c. adding $\text{O}_2(\text{g})$		
d. removing $\text{H}_2\text{O}(\text{g})$		
e. increasing pressure		
f. adding $\text{H}_2\text{O}(\text{g})$		

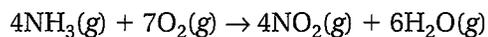
26. At equilibrium, the concentrations of the components of the reaction in problem 25 are as follows:

$$[\text{HCl}] = 1.2 \times 10^{-3} \text{ mol/L}, [\text{O}_2] = 3.8 \times 10^{-4} \text{ mol/L},$$

$$[\text{H}_2\text{O}] = 5.8 \times 10^{-2} \text{ mol/L}, \text{ and } [\text{Cl}_2] = 5.8 \times 10^{-2} \text{ mol/L}$$

Determine the value of K_{eq} for this system.

27. Calculate the standard entropy change, ΔS° , that occurs in the following reaction at 25 °C and 101.3 kPa.



Standard entropies S° (J/K \times mol):

$$S^\circ \text{ for } \text{NH}_3(\text{g}) = 192.5$$

$$S^\circ \text{ for } \text{O}_2(\text{g}) = 205.0$$

$$S^\circ \text{ for } \text{NO}_2(\text{g}) = 240.5$$

$$S^\circ \text{ for } \text{H}_2\text{O}(\text{g}) = 188.7$$

D. Essay

Write short essays for the following.

28. Explain how and why an equilibrium system reacts to each of the following stresses:

a. the addition of more reactant

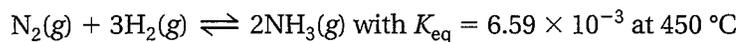
b. an increase in temperature

c. an increase in pressure (for a gaseous system with an unequal number of molecules)

E. Additional Problems

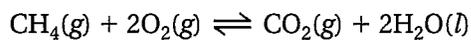
Solve the following problems in the space provided. Show your work.

29. Given:



If $[\text{NH}_3] = 1.23 \times 10^{-4} \text{ mol/L}$ and $[\text{H}_2] = 2.75 \times 10^{-6} \text{ mol/L}$ at equilibrium, what is the concentration of N_2 at equilibrium?

30. Determine whether the following reaction is spontaneous by using the ΔG_f° for the reactants and products.



$$\Delta G_f^\circ \text{ for } \text{CH}_4(\text{g}) = -50.79 \text{ kJ/mol}$$

$$\Delta G_f^\circ \text{ for } \text{O}_2(\text{g}) = 0.00 \text{ kJ/mol}$$

$$\Delta G_f^\circ \text{ for } \text{CO}_2(\text{g}) = -394.4 \text{ kJ/mol}$$

$$\Delta G_f^\circ \text{ for } \text{H}_2\text{O}(\text{l}) = -237.2 \text{ kJ/mol}$$

31. Based on the values given below, calculate ΔG° and determine whether the reaction is spontaneous.

$$\Delta H^\circ = -85.2 \text{ kJ/mol}, T = 127 \text{ }^\circ\text{C}, \Delta S^\circ = 0.125 \text{ kJ/K} \times \text{mol}$$

SECTION	STUDENT ACTIVITIES/FEATURES	TEACHER'S RESOURCE PACKAGE
<p>19.1 Rates of Reaction</p> <p>Objectives</p> <ul style="list-style-type: none"> ▶ Explain what is meant by the rate of a chemical reaction ▶ Using collision theory, explain how the rate of a chemical reaction is influenced by the reaction conditions 	<p>Discover It! <i>Temperature and Reaction Rates</i>, p. 532</p> <p>Link to Auto Shop <i>Auto Body Repair</i>, p. 538</p>	<p>Review Module (Chapters 17–20)</p> <ul style="list-style-type: none"> ▶ Section Review 19.1 ▶ Practice Problems ▶ Quizzes <p>Laboratory Manual</p> <ul style="list-style-type: none"> ▶ Experiment 34: <i>Factors Affecting Reaction Rates</i> ▶ Experiment 35: <i>A Clock Reaction</i> <p>Laboratory Practical 19-1</p> <p>Small-Scale Chemistry Lab Manual, Experiment 24: <i>Factors Affecting the Rate of a Chemical Reaction</i></p>
<p>19.2 Reversible Reactions and Equilibrium</p> <p>Objectives</p> <ul style="list-style-type: none"> ▶ Predict changes in the equilibrium position due to changes in concentration, temperature, and pressure ▶ Write the equilibrium-constant expression for a reaction and calculate its value from experimental data 	<p>Sample Problems 19-1 through 19-4</p>	<p>Review Module</p> <ul style="list-style-type: none"> ▶ Section Review 19.2 ▶ Practice Problems ▶ Quizzes <p>Laboratory Manual, Experiment 36: <i>Disturbing Equilibrium</i></p> <p>Small-Scale Chemistry Lab Manual, Experiment 25: <i>Le Châtelier's Principle and Chemical Equilibrium</i></p>
<p>19.3 Determining Whether a Reaction Will Occur</p> <p>Objectives</p> <ul style="list-style-type: none"> ▶ Define entropy and free energy, and characterize reactions as spontaneous or nonspontaneous ▶ Describe how heat change and entropy change determine the spontaneity of a reaction 	<p>Mini Lab <i>Does Steel Burn?</i> p. 556</p> <p>Small-Scale Lab <i>Enthalpy and Entropy</i>, p. 557</p>	<p>Review Module</p> <ul style="list-style-type: none"> ▶ Section Review 19.3 ▶ Practice Problems ▶ Interpreting Graphics 19-1 ▶ Quizzes <p>Laboratory Recordsheets 19-1 and 19-2</p>
<p>19.4 Calculating Entropy and Free Energy</p> <p>Objectives</p> <ul style="list-style-type: none"> ▶ Calculate the standard entropy changes that accompany chemical and physical processes ▶ Calculate the free-energy changes that accompany chemical and physical processes 	<p>CHEMath <i>Balancing Equations</i>, p. 559</p> <p>Link to Geology <i>Weathering of Rocks</i>, p. 562</p> <p>Sample Problems 19-5 through 19-8</p>	<p>Review Module</p> <ul style="list-style-type: none"> ▶ Section Review 19.4 ▶ Practice Problems ▶ Interpreting Graphics 19-2 ▶ Quizzes
<p>19.5 The Progress of Chemical Reactions</p> <p>Objectives</p> <ul style="list-style-type: none"> ▶ Interpret experimental rate data to deduce the rate laws for simple chemical reactions ▶ Given an energy diagram for a reaction, analyze the mechanism for the reaction 	<p>Sample Problem 19-9</p> <p>Chemistry Serving . . . the Consumer <i>Don't Let Good Food Go Bad</i>, p. 570</p> <p>Chemistry in Careers <i>FDA Inspector</i>, p. 570</p>	<p>Review Module</p> <ul style="list-style-type: none"> ▶ Section Review 19.5 ▶ Practice Problems ▶ Vocabulary Review 19 ▶ Chapter 19 Tests and Quizzes <p>Solutions Manual for Chapter Reviews</p> <p>Graphing Calculator Problems</p>

PLANNING GUIDE *continued*

TECHNOLOGY RESOURCES

Internet Connections

Within this chapter, you will see the chemSURF logo. If you and your students have access to the Internet, the following URL address will provide various Internet connections that are related to topics and features presented in this chapter.

<http://www.chemsurf.com>



You can also find relevant chapter material at **The Chemistry Place** address:

<http://www.chemplace.com>

CD-ROMs

Chem ASAP! CD-ROM

- ▶ Chapter 19

ResourcePro CD-ROM

- ▶ Chapter 19

Assessment Resources CD-ROM

Videodiscs and Videotapes

Chemistry Alive! Videodisc

- ▶ Grain Elevator Explosion
- ▶ Oscillating Clock

Small-Scale Lab Video and Videodisc

- ▶ #19: Equilibrium and Kinetics

Overhead Transparencies

- ▶ #63: Collision Theory
- ▶ #64: Activation Energy and Catalysts
- ▶ #65: Reversible Reactions and Equilibrium
- ▶ #66: Entropy
- ▶ #67: Heat, Entropy, and Free Energy

ASSESSMENT

Student Edition

- ▶ Section Reviews 19.1–19.5
- ▶ Chapter 19 Review, pp. 571–574
- ▶ Alternative Assessment, p. 575

Technology

- Chem ASAP! CD-ROM
- ▶ Assessment 19.1–19.5
- Assessment Resources CD-ROM
- ▶ Chapter 19 Tests

Teacher's Resource Package

- Review Module (Chap. 17–20)
- ▶ Vocabulary Review
- ▶ Chapter 19 Test A and Test B
- ▶ Chapter 19 Quizzes

PLANNING FOR ACTIVITIES

STUDENT EDITION

Discover It! p. 532

- ▶ masking tape
- ▶ plastic cups
- ▶ hot and cold tap water
- ▶ ice
- ▶ thermometers
- ▶ effervescent antacid tablets
- ▶ clocks or watches with second hand
- ▶ graph paper
- ▶ pens or pencils

Mini Lab p. 556

- ▶ steel wool pads
- ▶ tissue paper
- ▶ tongs
- ▶ Bunsen burners
- ▶ heat-resistant pads
- ▶ pencils
- ▶ paper

Small-Scale Lab, p. 557

- ▶ alcohol thermometers
- ▶ 1-oz plastic cups
- ▶ NaCl(s), NH₄Cl(s), CaCl₂(s)
- ▶ plastic spoons
- ▶ crushed ice
- ▶ water

TEACHER'S EDITION

Teacher Demo, p. 536

- ▶ 5 mL of ethanoic acid
- ▶ 5 mL of isoamyl alcohol
- ▶ two test tubes
- ▶ granules of anhydrous calcium sulfate
- ▶ concentrated sulfuric acid
- ▶ boiling water bath

Teacher Demo, p. 537

- ▶ cornstarch
- ▶ water glass
- ▶ match
- ▶ Bunsen burner
- ▶ spatula
- ▶ goggles
- ▶ Plexiglas shield

Teacher Demo, p. 541

- ▶ sulfuric acid
- ▶ two test tubes
- ▶ anhydrous calcium sulfate

Teacher Demo, p. 544

- ▶ fume hood
- ▶ small amount (3 g or less) of copper turnings
- ▶ test tube
- ▶ 10 mL of 6M nitric acid
- ▶ one-hole stopper fitted with a glass delivery tube and rubber hose
- ▶ two Pyrex test tubes
- ▶ stoppers
- ▶ ice bath
- ▶ warm water bath

Teacher Demo, p. 552

- ▶ block of ice
- ▶ beaker
- ▶ water
- ▶ heat source

Teacher Demo, p. 562

- ▶ 0.1M solution of KMnO₄ in 0.1M HCl
- ▶ 1000-mL beaker
- ▶ thermometer
- ▶ graduated cylinder
- ▶ 20 mL of 30% H₂O₂
- ▶ watch glass
- ▶ glowing splint

19.1

RATES OF REACTION

SECTION REVIEW

Objectives

- Explain what is meant by the rate of a chemical reaction
- Using collision theory, explain how the rate of a chemical reaction is influenced by the reaction conditions

Key Terms

- rates
- collision theory
- activation energy
- activated complex
- transition state
- catalyst
- inhibitor

Part A Completion

Use this completion exercise to check your understanding of the concepts and terms that are introduced in this section. Each blank can be completed with a term, short phrase, or number.

- _____ 1 _____ measure the speed of any change that occurs within a time interval. Collision theory states that particles _____ 2 _____ when they collide, provided that they have enough _____ 3 _____.
- The rate at which a chemical reaction occurs is determined by an _____ 4 _____ energy barrier. The activation energy is the _____ 5 _____ energy that reactants must have to go to _____ 6 _____. The higher the activation energy barrier, the _____ 7 _____ the reaction. Chemists help reactants overcome the activation barrier in a number of ways.
- Two effective methods are to increase the _____ 8 _____ at which the reaction is done or use a _____ 9 _____. Rates of reaction can also be increased by _____ 10 _____ the concentration of reactants.
1. _____
2. _____
3. _____
4. _____
5. _____
6. _____
7. _____
8. _____
9. _____
10. _____

Part B True-False

Classify each of these statements as always true, AT; sometimes true, ST; or never true, NT.

- _____ 11. An increase in temperature will generally increase the rate of a reaction.
- _____ 12. A catalyst is considered as a reactant in a chemical reaction.

- _____ 13. The speed of a reaction can be increased by increasing reactant concentration or decreasing particle size.
- _____ 14. An enzyme is a biological catalyst.

Part C Matching

Match each description in Column B to the correct term in Column A.

Column A

- _____ 15. rate
- _____ 16. collision theory
- _____ 17. activation energy
- _____ 18. transition state
- _____ 19. catalyst
- _____ 20. inhibitor

Column B

- a. synonym for an activated complex
- b. speed of a change that occurs over time
- c. substance that interferes with the action of a catalyst
- d. Particles can react to form products when they collide, provided they have enough kinetic energy.
- e. substance that increases the rate of a reaction without being used up
- f. minimum energy particles must have in order to react

Part D Questions and Problems

Answer the following question and solve the following problem in the space provided.

21. An ice machine can produce 120 kg of ice in 24 hours. Express the rate of ice production in kg/hr.
22. Which of the following will increase the rate of a reaction?
- increase particle size
 - increase temperature
 - decrease concentration
 - add a catalyst

19.2

REVERSIBLE REACTIONS AND EQUILIBRIUM

SECTION REVIEW

Objectives

- Predict changes in the equilibrium position due to changes in concentration, temperature, and pressure
- Write the equilibrium-constant expression for a reaction and calculate its value from experimental data

Key Terms

- reversible reactions
- chemical equilibrium
- equilibrium position
- Le Châtelier's principle
- equilibrium constant (K_{eq})

Key Equation

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

When $aA + bB \rightleftharpoons cC + dD$

Part A Completion

Use this completion exercise to check your understanding of the concepts and terms that are introduced in this section. Each blank can be completed with a term, short phrase, or number.

- In principle, all reactions are 1. That is, reactants go to 2 in the 3 direction and products go to 4 in the 5 direction.
- The point at which the rate of conversion of 6 to 7 and vice versa is equal is the position of 8. The 9 of a reversible reaction, K_{eq} , is useful for determining the position of equilibrium. It is essentially a measure of the 10 of products to reactants at equilibrium. The direction of change in the position of equilibrium may be predicted by applying 11 principle.
1. _____
 2. _____
 3. _____
 4. _____
 5. _____
 6. _____
 7. _____
 8. _____
 9. _____
 10. _____
 11. _____

Part B True-False

Classify each of these statements as always true, AT; sometimes true, ST; or never true, NT.

- _____ 12. The concentrations of reactants and products in a system at dynamic equilibrium are always changing.
- _____ 13. A change in the pressure on a system can cause a shift in the equilibrium position.
- _____ 14. For a chemical equilibrium to be established, the chemical reaction must be irreversible.
- _____ 15. The K_{eq} for a certain reaction was 2×10^{-7} . For this reaction at equilibrium, the concentration of the reactants is greater than the concentration of the products.

Part C Matching

Match each description in Column B to the correct term in Column A.

Column A	Column B
_____ 16. reversible reactions	a. state of balance in which forward and reverse reactions take place at the same rate
_____ 17. chemical equilibrium	b. measurement of the amount of solute that is dissolved in a given quantity of solvent
_____ 18. equilibrium position	c. relative concentrations of reactants and products of a reaction that has reached equilibrium
_____ 19. Le Châtelier's principle	d. When stress is applied to a system at equilibrium, the system changes to relieve the stress.
_____ 20. equilibrium constant	e. reaction in which conversion of reactants to products and products to reactants occur simultaneously
_____ 21. concentration	f. ratio of product concentrations to reactant concentrations with each raised to a power given by the number of moles of the substance in the balanced equation

Part D Questions and Problems

Solve the following problem in the space provided. Show your work.



Calculate K_{eq} for this reaction if the equilibrium concentrations are:
 $[\text{SO}_2] = 0.42\text{M}$, $[\text{O}_2] = 0.21\text{M}$, $[\text{SO}_3] = 0.072\text{M}$

19.3

DETERMINING WHETHER A REACTION WILL OCCUR

SECTION REVIEW

Objectives

- Define entropy and free energy, and characterize reactions as spontaneous or nonspontaneous
- Describe how heat change and entropy change determine the spontaneity of a reaction

Key Terms

- free energy
- entropy
- spontaneous reactions
- law of disorder
- nonspontaneous reactions

Part A Completion

Use this completion exercise to check your understanding of the concepts and terms that are introduced in this section. Each blank can be completed with a term, short phrase, or number.

Reactions that actually occur as written are called 1 1. _____
 reactions. Equations for other reactions may be written, but the 2. _____
 reactions are 2. All spontaneous reactions release 3 3. _____
 that becomes available to do 4. This energy is called 4. _____
5. 5. _____
 It is the natural tendency for all things to go to lower 6 6. _____
 and toward 7 disorder. In addition to the change in heat 7. _____
 content, 8 is a factor that determines whether a reaction 8. _____
 will be spontaneous. 9. _____
 Entropy is a measure of the 9 of a system. The 10. _____
10 states that processes move in the direction of 11 11. _____
 disorder.

Part B True-False

Classify each of these statements as always true, AT; sometimes true, ST; or never true, NT.

12 An exothermic reaction is a spontaneous reaction.

- _____ 13. When a sandwich is eaten and digested, its entropy increases.
- _____ 14. Some spontaneous reactions appear to be nonspontaneous because their rate of reaction is slow.
- _____ 15. Spontaneous reactions release free energy.
- _____ 16. Entropy will increase in a spontaneous reaction.

Part C Matching

Match each description in Column B to the correct term in Column A.

Column A	Column B
_____ 17. free energy	a. measure of the disorder of a system
_____ 18. spontaneous reactions	b. energy in a reaction that is available to do work
_____ 19. nonspontaneous reactions	c. It is the natural tendency of systems to move in the direction of maximum disorder.
_____ 20. entropy	d. reactions that do not give products under the specified conditions
_____ 21. law of disorder	e. reactions that favor formation of products under the specified conditions

Part D Questions and Problems

Complete the following question and solve the following problem in the space provided.

22. In each of the following pairs, choose the system with the higher entropy.
- a. a heap of loose stamps or stamps in an album _____
 - b. ice cubes in their tray or ice cubes in a bucket _____
 - c. 10 mL of water at 100 °C or 10 mL of steam at 100 °C _____
 - d. the people watching the parade or a parade _____
23. Which combination of factors will always give a spontaneous reaction?
- a. heat absorbed, entropy increases
 - b. heat released, entropy increases
 - c. heat released, entropy decreases
 - d. heat absorbed, entropy decreases
24. Which combination described in question 23 will never give a spontaneous reaction?

19.4

CALCULATING ENTROPY AND FREE ENERGY

SECTION REVIEW

Objectives

- Calculate the standard entropy changes that accompany chemical and physical processes
- Calculate the free-energy changes that accompany chemical and physical processes

Key Terms

- standard entropy (S^0)
- Gibbs free-energy change (ΔG)

Key Equations

- $\Delta S^0 = S^0(\text{products}) - S^0(\text{reactants})$
- $\Delta G = \Delta H - T\Delta S$
- $\Delta G^0 = \Delta G_f^0(\text{products}) - \Delta G_f^0(\text{reactants})$

Part A Completion

Use this completion exercise to check your understanding of the concepts and terms that are introduced in this section. Each blank can be completed with a term, short phrase, or number.

S is the symbol for 1, which is a qualitative measure of 1. _____
 disorder. The 2 of a substance is designated as S^0 at 25 °C 2. _____
 and 101.3 kPa. 3. _____

The standard entropy change in a reaction can be calculated 4. _____
 by subtracting S^0 of the 3 from S^0 of the 4. 5. _____

Energy from a reaction that is available to do work is called the 6. _____
5, or ΔG . This quantity can be calculated when the entropy 7. _____
 change and 6 change are known. 8. _____

ΔG for a reaction can also be calculated using free energy of 9. _____
7. Thus ΔG^0 can be obtained by subtracting ΔG_f^0 of the _____
8 from ΔG_f^0 of the 9.

Part B True-False

Classify each of these statements as always true, AT; sometimes true, ST; or never true, NT.

- _____ 10. Spontaneous processes provide energy for work.
- _____ 11. A reaction with a negative ΔH is spontaneous.
- _____ 12. Substances have negative entropies below 0 °C.
- _____ 13. The higher the temperature, the more likely a reaction will be spontaneous.

Part C Matching

Match each description in Column B to the correct term in Column A.

Column A

- _____ 14. standard entropy
- _____ 15. Gibbs free-energy change
- _____ 16. enthalpy
- _____ 17. spontaneous reaction

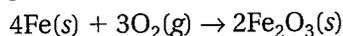
Column B

- a. the amount of heat a substance has at a given temperature and pressure
- b. maximum amount of energy that can be coupled to another process to do work
- c. a reaction known to give the products as written in a balanced equation at the specified conditions
- d. entropy of a substance in its stable state at 25 °C and 1 atm

Part D Questions and Problems

Complete the following question and solve the following problem in the space provided.

18. Using the information found in Table 19.2 of your text, calculate the change in entropy for the following reaction.



19. The reaction $\text{A} + 2\text{B} \rightarrow 3\text{C}$ has a ΔH^0 of -163 kJ/mol and a ΔS^0 of $-0.51 \text{ kJ}/(\text{K} \times \text{mol})$ at 25 °C. Is this reaction spontaneous?

19.5

THE PROGRESS OF CHEMICAL REACTIONS

SECTION REVIEW

Objectives

- Interpret experimental rate data to deduce the rate laws for simple chemical reactions
- Given an energy diagram for a reaction, analyze the mechanism for the reaction

Key Terms

- rate law
- specific rate constant
- first-order reaction
- elementary reaction
- reaction mechanism
- intermediate

Part A Completion

Use this completion exercise to check your understanding of the concepts and terms that are introduced in this section. Each blank can be completed with a term, short phrase, or number.

The 1 of a reaction is dependent in part on the 2 of the reactants. An equation that relates reaction rate to reactant concentration is called a 3. In a rate law equation, K is known as the 4.

1. _____

3. _____

4. _____

5. _____

The power to which a reaction concentration is raised is called the 5 of the reaction. A reaction whose rate is proportional to the concentration of one reactant is called a 6 reaction.

6. _____

7. _____

8. _____

A reaction that is first order for each of two reactants is 7 overall. The actual kinetic order of a reaction is determined by 8.

9. _____

10. _____

A single step reaction is called an 9. A series of elementary reactions combine to form the 10 of a complex reaction.

Part B True-False

Classify each of these statements as always true, AT; sometimes true, ST; or never true, NT.

- _____ 11. The rate order of a reaction can be determined from the balanced equation.
- _____ 12. There is at least one intermediate product in a chemical reaction.
- _____ 13. There is at least one activated complex in a chemical reaction.
- _____ 14. An elementary reaction is a one-step reaction.

Part C Matching

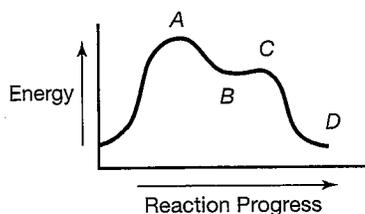
Match each description in Column B to the correct term in Column A.

Column A	Column B
_____ 15. rate law	a. a single-step reaction
_____ 16. specific rate constant	b. reaction in which the rate is directly proportional to the concentration of one reactant
_____ 17. first-order reaction	c. a product of a reaction that becomes a reactant in another reaction
_____ 18. elementary reaction	d. expression relating the rate of a reaction to the concentration of the reactants
_____ 19. reaction mechanism	e. series of elementary reactions that take place during a complex reaction
_____ 20. intermediate product	f. proportionality constant relating the concentrations of reactants to the reaction rate

Part D Questions and Problems

Complete the following question and solve the following problem in the space provided.

21. Below is the reaction progress curve for a complex reaction. Describe the reaction represented by the curve (number of steps and the significance of points A, B, C, and D).



19

REACTION RATES AND EQUILIBRIUM

PRACTICE PROBLEMS

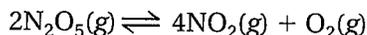
In your notebook, solve the following problems.

SECTION 19.1 RATES OF REACTION

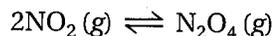
- List three ways that reaction rates can generally be increased.
- Ethyl acetate ($C_4H_8O_2$) reacts with a solution of sodium hydroxide (NaOH) in water to form sodium acetate ($C_2H_3O_2Na$) and ethyl alcohol (C_2H_6O). Suppose at 25 °C two moles of ethyl acetate react completely in four hours. How would you express the rate of reaction?
- How would the following actions likely change the rate of the reaction in problem 2?
 - the temperature is lowered to 4 °C.
 - the concentration of sodium hydroxide in water is increased.
- Ethyl acetate and water are not miscible; thus, the reaction in problem 2 only occurs at the interface of the two liquids. What would be the effect on the reaction rate of adding a solvent to make the reaction homogeneous?

SECTION 19.2 REVERSIBLE REACTIONS AND EQUILIBRIUM

- Write the expression for the equilibrium constant for this reaction:



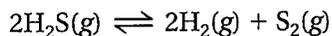
- Calculate the equilibrium constant for the reaction in problem 1 if the equilibrium concentrations are $[N_2O_5] = 0.50 \text{ mol/L}$, $[NO_2] = 0.80 \text{ mol/L}$, $[O_2] = 0.20 \text{ mol/L}$.
- How would the equilibrium position for the equation in problem 1 be affected by
 - an addition of O_2 to the reaction vessel?
 - a decrease in the pressure?
- The equilibrium constant for the reaction of nitrogen dioxide to form dinitrogen tetroxide is 5.6.



In a one-liter container, the amount of N_2O_4 , at equilibrium, is 0.66 mol. What is the equilibrium concentration of NO_2 ?

- Write the equilibrium constant expression for each of the following reactions.
 - $4NO(g) + 2O_2(g) \rightleftharpoons 2N_2O_4(g)$
 - $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$
 - $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
 - $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
- What effect would an increase in pressure have on the equilibrium position of each reaction in problem 5?

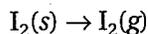
7. Which value of K_{eq} indicates most favorably for product formation, $K_{\text{eq}} = 1 \times 10^{12}$, $K_{\text{eq}} = 1.5$, or $K_{\text{eq}} = 5.6 \times 10^{-4}$?
8. Hydrogen sulfide gas decomposes into its elements and establishes an equilibrium at 1400 °C.



A liter of this gas mixture contains 0.18 mol H_2S , 0.014 mol H_2 , and 0.035 mol S_2 . Calculate the equilibrium constant, K_{eq} , for this reaction.

SECTION 19.3 DETERMINING WHETHER A REACTION WILL OCCUR

1. When gently warmed, the element iodine will sublime:



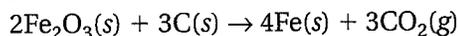
Is this process accompanied by an increase or decrease in entropy?

2. Is there an increase or decrease in entropy when air is cooled and liquefied (changed from a gas to a liquid)?
3. Is the degree of disorder increasing or decreasing in these reactions?
- $\text{H}_2(\text{g}) + \text{Br}_2(\text{l}) \rightarrow 2\text{HBr}(\text{g})$
 - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightarrow \text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{g})$
 - $2\text{XeO}_3(\text{s}) \rightarrow 2\text{Xe}(\text{g}) + 3\text{O}_2(\text{g})$
4. Classify each of these systems as always spontaneous (A), never spontaneous (N), or depends on the relative magnitude of the heat and entropy changes (D).
- entropy decreases, heat is released
 - entropy decreases, heat is absorbed
 - entropy increases, heat is absorbed
 - entropy increases, heat is released

SECTION 19.4 CALCULATING ENTROPY AND FREE ENERGY

For problems 1–4, calculate the standard entropy change associated with each reaction. Refer to table 19.2 in your textbook.

- $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
- $2\text{H}_2\text{O}(\text{g}) + 2\text{Cl}_2(\text{g}) \rightarrow 4\text{HCl}(\text{g}) + \text{O}_2(\text{g})$
- $\text{I}_2(\text{g}) \rightarrow \text{I}_2(\text{s})$
- $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$
- A reaction is endothermic (positive ΔH) and has a positive entropy. Would this reaction more likely be spontaneous at high or low temperatures? Explain.
- A reaction has a ΔS of $-122 \text{ J}/(\text{K} \times \text{mol})$ and a ΔH of $-78 \text{ kJ}/\text{mol}$. Is this reaction spontaneous at 285 °C?
- Calculate the standard free energy change for the reaction between iron(III) oxide and carbon (graphite). Refer to Table 19.4 in your textbook.

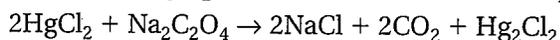


8. Calculate the ΔG° of each of these reactions. Indicate whether each reaction is spontaneous or nonspontaneous at 25°C. Refer to Table 19.4 in your textbook.

- $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$
- $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$
- $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$

SECTION 19.5 THE PROGRESS OF CHEMICAL REACTIONS

- A first order reaction has an initial reaction rate of 2.4 mol/(L × s). What is the rate when one-eighth the starting materials remain?
- It has been experimentally determined that the rate law for the reaction between mercury(II) chloride and sodium oxalate is third-order overall and first-order with respect to HgCl_2 . Write the rate law for this equation.



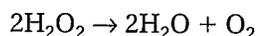
- A certain combination reaction gave the following data. What is the rate law for this reaction?



Initial concentration (mol/L)		Initial rate (mol/L × s)
[J]	[K]	Reaction of J
0.30	0.50	0.080
0.60	0.50	0.160
0.60	0.25	0.080

- Iodide ion catalyzes the decomposition of hydrogen peroxide. The reaction is first-order in H_2O_2 . What is the value of the rate constant, k , if the initial rate is 0.00842 mol/(L × s)?

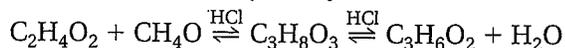
The initial concentration of H_2O_2 is 0.500 mol/L.



- A proposed reaction mechanism has two intermediates. How many elementary reactions are there in this mechanism?
- The reaction $\text{A} + \text{B} \rightarrow \text{C}$ is first order in A and B, second order overall. Complete the following table:

Initial concentration (mol/L)		Initial rate (mol/L × s)
[A]	[B]	
0.50	0.50	0.020
0.50		0.040
0.25	1.0	

- The condensation of acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) with methanol (CH_4O) to form methyl acetate ($\text{C}_3\text{H}_6\text{O}_2$) and water is catalyzed by HCl



- How many elementary reactions are there in this condensation?
- Write the formula for the reaction intermediate(s).
- Write the rate law for this condensation

19

INTERPRETING GRAPHICS

USE WITH SECTIONS 19.3 AND 19.4

<p>A</p> <p>Heat released (favorable)</p> <p>Entropy increase (favorable)</p> <p>Reaction spontaneous</p>	
<p>B</p> <p>Entropy increase (favorable)</p> <p>Heat absorbed (unfavorable)</p> <p>Reaction spontaneous</p>	
<p>C</p> <p>Heat released (favorable)</p> <p>Entropy decrease (unfavorable)</p> <p>Reaction spontaneous</p>	
	<p>D</p> <p>Heat absorbed (unfavorable)</p> <p>Entropy increase (favorable)</p> <p>Reaction nonspontaneous</p>
	<p>E</p> <p>Entropy decrease (unfavorable)</p> <p>Heat released (favorable)</p> <p>Reaction nonspontaneous</p>
	<p>F</p> <p>Heat absorbed (unfavorable)</p> <p>Entropy decrease (unfavorable)</p> <p>Reaction nonspontaneous</p>

The lettered diagrams on the previous page are from Figure 19.20 in your textbook. Use them to answer the following questions.

1. For each example, state whether ΔG is positive or negative.

a. _____

b. _____

c. _____

d. _____

e. _____

f. _____

2. For each example; state whether ΔH is positive or negative.

a. _____

b. _____

c. _____

d. _____

e. _____

f. _____

3. For Example B, is $|T\Delta S|$ greater or less than $|\Delta G|$?

4. For Example D, is $|T\Delta S|$ greater or less than $|\Delta G|$?

5. Which example would provide the most energy for work?

6. Could Example D be made to be spontaneous by an increase in temperature?

19

VOCABULARY REVIEW

Match the correct vocabulary term to each numbered statement. Write the letter of the correct term on the line provided.

Column A

- _____ 1. the disorder of a system
- _____ 2. a substance that interferes with the action of a catalyst
- _____ 3. reactions that favor the formation of products at the specified conditions
- _____ 4. the minimum energy colliding particles must have in order to react
- _____ 5. a substance that increases the rate of a reaction without being used up in the reaction
- _____ 6. the arrangement of atoms at the peak of the activation-energy barrier
- _____ 7. a reaction in which the rate is directly proportional to the concentration of one of the reactants
- _____ 8. energy that is available to do work
- _____ 9. when the forward and reverse reactions are taking place at the same rate
- _____ 10. the ratio of product concentrations to reactant concentrations, with each concentration raised to a power given by the number of moles of that substance in the balanced equation

Column B

- a. activation energy
- b. catalyst
- c. chemical equilibrium
- d. free energy
- e. entropy
- f. activated complex
- g. inhibitor
- h. equilibrium constant
- i. spontaneous reactions
- j. first-order reaction

19

REACTION RATES AND EQUILIBRIUM

Quiz for CHAPTER 19

Write the letter of the best answer in the blank.

- _____ 1. At chemical equilibrium, the rates of the forward reaction and reverse reactions are: 19.2
a. equal to 0. c. at a maximum.
b. equal to each other. d. at a minimum.
- _____ 2. A catalyst works by: 19.1
a. changing the pressure of the system.
b. changing the temperature of the reactants.
c. shifting the equilibrium position toward the products.
d. lowering the activation energy barrier.
- _____ 3. The rate of a chemical reaction normally: 19.1
a. increases as reactant concentration increases.
b. is slowed down by a catalyst.
c. decreases as temperature increases.
d. decreases as reactant concentration increases.
- _____ 4. Activation energy is: 19.1
a. heat released or absorbed in a reaction.
b. the minimum energy colliding particles must have in order to react.
c. the energy given off when reactants collide.
d. generally very high for a reaction that takes place rapidly.
- _____ 5. Spontaneous reactions: 19.3
a. are always exothermic.
b. always take place at a rapid rate.
c. always result in increased disorder of the system.
d. naturally favor the formation of products.
- _____ 6. On a cold day, water vapor condenses to form frost. This represents an: 19.3
a. entropy increase and enthalpy increase.
b. entropy increase and enthalpy decrease.
c. entropy decrease and enthalpy increase.
d. entropy decrease and enthalpy decrease.

Classify each of these statements as always true, AT; sometimes true, ST; or never true, NT.

- _____ 7. The value of K_{eq} for a spontaneous reaction is much less than 1. 19.3
- _____ 8. The standard entropy, S^0 , of a liquid or solid is the entropy at 25° C and 101.3 kPa. 19.4
- _____ 9. The Gibbs free energy for a spontaneous process is negative. 19.4
- _____ 10. In a first-order reaction involving several reactants, the reaction rate is directly proportional to the concentration of each of the reactants. 19.5

19**REACTION RATES AND EQUILIBRIUM****CHAPTER TEST A****A. Matching**

Match each description in Column B with the correct term in Column A. Write the letter of the correct definition in the space provided.

Column A	Column B
_____ 1. activated complex	a. the number of particles that react in a given time to form products
_____ 2. reaction rate	b. energy available to do work
_____ 3. Le Châtelier's principle	c. favoring the formation of products
_____ 4. spontaneous	d. the minimum energy colliding particles must have in order to react
_____ 5. elementary reaction	e. when the forward and reverse reactions take place at the same rate
_____ 6. chemical equilibrium	f. a substance that interferes with the action of a catalyst
_____ 7. entropy	g. reactants are converted to products in a single step
_____ 8. activation energy	h. the measure of disorder
_____ 9. inhibitor	i. the arrangement of atoms at the peak of the activation energy barrier
_____ 10. free energy	j. If a stress is applied to a system in dynamic equilibrium, the system changes to relieve the stress.

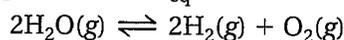
B. Multiple Choice

Write the letter of the best answer in the blank.

- _____ 11. In which of the following physical states does a given substance have the highest entropy?
- a. solid
 - b. gas
 - c. liquid
 - d. all of the above
- _____ 12. A reaction that requires free energy:
- a. must be endothermic.
 - b. is nonspontaneous.
 - c. must correspond to a decrease in entropy.
 - d. is spontaneous.

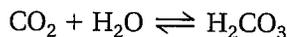
- _____ 13. The two factors that determine whether a reaction is spontaneous or nonspontaneous are:
- a. entropy and disorder.
 - b. entropy and enthalpy change.
 - c. electron configuration and energy change.
 - d. energy and the heat of reaction.
- _____ 14. In which of these systems is the entropy decreasing?
- a. air escaping from a tire
 - b. snow melting
 - c. salt dissolving in water
 - d. a gas condensing to a liquid
- _____ 15. All spontaneous processes:
- a. are exothermic.
 - b. are endothermic
 - c. involve an increase in entropy.
 - d. release free energy.
- _____ 16. If a catalyst is used in a reaction:
- a. the energy of activation increases.
 - b. the reaction rate does not change.
 - c. the reaction rate increases.
 - d. the equilibrium shifts.
- _____ 17. Which of the following affects the rate of a chemical reaction?
- a. the presence of a catalyst
 - b. the temperature
 - c. the concentration of reactants
 - d. all of the above

- _____ 18. What is the expression for K_{eq} for this reaction?



- a. $K_{eq} = \frac{[\text{2H}_2\text{O}]}{[\text{H}_2] \times [\text{O}_2]}$
 - b. $K_{eq} = \frac{[\text{H}_2]^2 \times [\text{O}_2]}{[\text{H}_2\text{O}]^2}$
 - c. $K_{eq} = \frac{[\text{2H}_2] \times [\text{O}_2]}{[\text{2H}_2\text{O}]}$
 - d. $K_{eq} = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2 \times [\text{O}_2]}$
- _____ 19. In an equilibrium reaction with a K_{eq} of 1×10^8
- a. reactants are favored.
 - b. reaction is nonspontaneous.
 - c. products are favored.
 - d. reaction is exothermic.

- _____ 20. What is the effect of adding more CO_2 to the following equilibrium reaction?



- a. More H_2CO_3 is produced.
 - b. More H_2O is produced.
 - c. The equilibrium is pushed in the direction of reactants.
 - d. no change
- _____ 21. Doing which of the following generally increases the entropy of a substance?
- a. freezing it
 - b. dissolving it in water
 - c. condensing it
 - d. all of the above

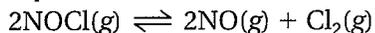
- _____ 22. The K_{eq} of a reaction is 4×10^{-7} . At equilibrium:
- a. the reactants are favored.
 - b. the products are favored.
 - c. the reactants and products are present in equal amounts.
 - d. the rate of the reverse reaction is much greater than the rate of the forward reaction.

- _____ 23. Two opposing reactions ($A + B \rightleftharpoons C + D$) occurring simultaneously at the same rate is an example of:
- a. reversibility.
 - b. chemical equilibrium.
 - c. neither a nor b
 - d. both a and b

C. Problems

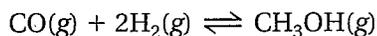
Solve the following problems in the space provided. Show your work.

24. Calculate the value of K_{eq} for this reaction at equilibrium.



An analysis of the equilibrium mixture in a 1-L flask gives the following results: NOCl, 0.30 mol; NO, 1.2 mol; Cl_2 , 0.60 mol.

25. Carbon monoxide and hydrogen are combined in the commercial preparation of methyl alcohol.



At a certain set of conditions, the equilibrium mixture contains 0.020 mol/L of CO, 0.60 mol/L of H_2 , and the equilibrium constant is $2.2 \times 10^2 \text{ L}^2/\text{mol}^2$. What is the concentration of CH_3OH in the equilibrium mixture?

26. Predict the changes in the equilibrium position for this reaction when the following changes are made:



- a. decrease the concentration of C;
- b. add more heat;
- c. increase the concentration of A;
- d. increase the pressure.

In each case, state whether the change causes a shift that favors the formation of reactants or of products.

- a. _____
- b. _____
- c. _____
- d. _____

D. Essay

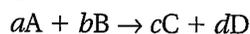
Write a short essay for the following.

27. Characterize spontaneous and nonspontaneous reactions. Then explain why a spontaneous reaction may appear to be nonspontaneous.

E. Additional Problems

Solve the following problems in the space provided. Show your work.

28. The rate law for the following reaction is: $\text{Rate} = k[\text{A}]^a \times [\text{B}]^b$.



From the data in the following chart, find the kinetic order of the reaction with respect to A and B, as well as the overall order.

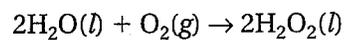
Initial concentration of A (mol/L)	Initial concentration of B (mol/L)	Initial Rate [mol/(L × s)]
0.50	0.05	2×10^{-3}
0.10	0.05	4×10^{-3}
0.20	0.05	8×10^{-3}
0.01	0.05	1×10^{-3}
0.01	0.10	8×10^{-3}
0.01	0.20	64×10^{-3}

29. The following reaction has an H^0 of 53 kJ/mol and a S^0 of 0.070 kJ/(K × mol) at 25 °C.



Is this reaction spontaneous? (Calculate ΔG .)

30. What is the standard change in entropy for the following reaction when all reactants are in the specified states?



Standard entropies S° in $\text{J}/(\text{K} \times \text{mol})$:

$\text{H}_2\text{O}(l) = 69.94$, $\text{H}_2\text{O}_2(l) = 92.0$, $\text{O}_2(g) = 205.0$

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REACTION RATES AND EQUILIBRIUM

CHAPTER TEST B

A. Matching

Match each term in Column B with the correct description in Column A. Write the letter of the correct term in the blank provided.

Column A

- _____ 1. when the forward and reverse reactions are taking place at the same rate
- _____ 2. Things move in the direction of maximum disorder or randomness.
- _____ 3. the minimum energy colliding particles must have in order to react
- _____ 4. the ratio of product concentrations to reactant concentrations, with each concentration raised to a power given by the number of moles of that substance in the balanced equation
- _____ 5. a substance that increases the rate of a reaction without being used up itself in the reaction
- _____ 6. the disorder of a system
- _____ 7. Atoms, ions, and molecules can form a chemical bond between them when they collide, provided the particles have enough kinetic energy.
- _____ 8. energy that is available to do work
- _____ 9. the arrangement of atoms at the peak of the activation energy barrier
- _____ 10. If a stress is applied to a system in a dynamic equilibrium, the system changes to relieve the stress.

Column B

- a. Le Châtelier's principle
- b. activated complex
- c. entropy
- d. collision theory
- e. free energy
- f. catalyst
- g. law of disorder
- h. activation energy
- i. equilibrium constant
- j. chemical equilibrium

B. Multiple Choice

Choose the best answer and write its letter in the blank.

- _____ 11. According to the collision theory, in order for a chemical reaction to occur, the reactant atoms must:
- make contact with each other.
 - have a minimum level of kinetic energy.
 - form an activated complex.
 - all of these

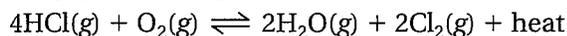
- _____ 12. In general, increasing temperature causes the rate of most chemical reactions to:
- increase.
 - decrease.
 - remain the same.
 - vary unpredictably.
- _____ 13. Which of the following is true concerning the impact of increasing temperature on reaction rates?
- The number of collisions between reactant atoms is increased.
 - The energy of each reactant atom is increased.
 - The percentage of collisions with sufficient energy to cross the activation energy barrier is increased.
 - all of these
- _____ 14. What would decrease the rate of most chemical reactions?
- increasing the concentration of reactant atoms
 - increase the size of the reactant particles
 - adding an appropriate catalyst
 - all of these
- _____ 15. Catalysts alter the rate of a chemical reaction by:
- increasing the number of collisions between reactant atoms.
 - increasing the kinetic energy of each reactant atom.
 - lowering the activation energy barrier.
 - being consumed in the reaction.
- _____ 16. Which of the following is true concerning a reaction that has reached chemical equilibrium?
- The forward reaction is occurring faster than the reverse reaction.
 - The reverse reaction is occurring faster than the forward reaction.
 - The forward reaction is occurring as fast as the reverse reaction.
 - The mass of products is equal to the mass of reactants.
- _____ 17. Given the following system at equilibrium:
- $$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
- what would be the effect of removing $\text{NH}_3(\text{g})$ as it is formed?
- The equilibrium would shift to the left.
 - More $\text{N}_2(\text{g})$ would be produced.
 - More $\text{H}_2(\text{g})$ would be produced.
 - The equilibrium would shift to the right.
- _____ 18. Given the following system at equilibrium:
- $$\text{H}_2\text{O}(\text{l}) + \text{heat} \rightleftharpoons \text{H}_2\text{O}(\text{g})$$
- how would a decrease in temperature affect the system?
- The equilibrium would shift to the right.
 - More $\text{H}_2\text{O}(\text{l})$ would be produced.
 - More $\text{H}_2\text{O}(\text{g})$ would be produced.
 - The levels of reactants and products would remain the same.
- _____ 19. Which of the following would increase the yield of $\text{CO}(\text{g})$ in the following equilibrium system?
- $$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) + \text{heat} \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$$
- decreasing temperature
 - increasing pressure
 - adding $\text{H}_2(\text{g})$
 - adding $\text{H}_2\text{O}(\text{g})$

- _____ 20. Spontaneous reactions:
- favor the formation of products.
 - give substantial amounts of reactants at equilibrium.
 - absorb free energy.
 - have high reaction rates.
- _____ 21. Which of the following has the greatest entropy?
- ice
 - water
 - steam
 - cannot be predicted
- _____ 22. The type of reaction most likely to be spontaneous is one in which:
- both heat content and entropy are decreased.
 - heat content is decreased, while entropy is increased.
 - both heat content and entropy are increased.
 - heat content is increased, while entropy is decreased.
- _____ 23. The expression for K_{eq} for the following reaction is:
- $$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$$
- $K_{eq} = \frac{[\text{H}_2] \times [\text{Cl}_2]}{[2\text{HCl}]}$
 - $K_{eq} = \frac{[2\text{HCl}]}{[\text{H}_2] \times [\text{Cl}_2]}$
 - $K_{eq} = \frac{[\text{HCl}]^2}{[\text{H}_2] \times [\text{Cl}_2]}$
 - $K_{eq} = \frac{[\text{H}_2] \times [\text{Cl}_2]}{[\text{HCl}]^2}$
- _____ 24. If the equilibrium concentrations for the system in question 24 are as follows, find the value of K_{eq} :
- $[\text{H}_2] = 0.450 \text{ mol/L}$, $[\text{Cl}_2] = 0.450 \text{ mol/L}$, $[\text{HCl}] = 6.25 \text{ mol/L}$
- 1.62×10^{-2}
 - 193
 - 5.18×10^{-3}
 - 61.7

C. Problems

Solve the following problems in the space provided. Show your work.

25. Given the following system at equilibrium:



determine the effect of each of the following changes on the equilibrium position of the system (shifts right or left) and on the amount of $\text{Cl}_2(\text{g})$ that would result (increases or decreases):

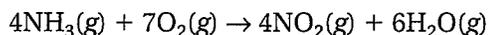
	Equilibrium Position	Amount of $\text{Cl}_2(\text{g})$
a. increasing temperature		
b. decreasing pressure		
c. adding $\text{O}_2(\text{g})$		
d. removing $\text{H}_2\text{O}(\text{g})$		
e. increasing pressure		
f. adding $\text{H}_2\text{O}(\text{g})$		

26. At equilibrium, the concentrations of the components of the reaction in problem 25 are as follows:

$$[\text{HCl}] = 1.2 \times 10^{-3} \text{ mol/L}, [\text{O}_2] = 3.8 \times 10^{-4} \text{ mol/L},$$
$$[\text{H}_2\text{O}] = 5.8 \times 10^{-2} \text{ mol/L}, \text{ and } [\text{Cl}_2] = 5.8 \times 10^{-2} \text{ mol/L}$$

Determine the value of K_{eq} for this system.

27. Calculate the standard entropy change, ΔS° , that occurs in the following reaction at 25 °C and 101.3 kPa.



Standard entropies S° (J/K \times mol):

$$S^\circ \text{ for } \text{NH}_3(\text{g}) = 192.5$$

$$S^\circ \text{ for } \text{O}_2(\text{g}) = 205.0$$

$$S^\circ \text{ for } \text{NO}_2(\text{g}) = 240.5$$

$$S^\circ \text{ for } \text{H}_2\text{O}(\text{g}) = 188.7$$

D. Essay

Write short essays for the following.

28. Explain how and why an equilibrium system reacts to each of the following stresses:

a. the addition of more reactant

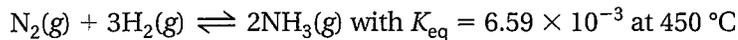
b. an increase in temperature

c. an increase in pressure (for a gaseous system with an unequal number of molecules)

E. Additional Problems

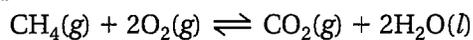
Solve the following problems in the space provided. Show your work.

29. Given:



If $[\text{NH}_3] = 1.23 \times 10^{-4} \text{ mol/L}$ and $[\text{H}_2] = 2.75 \times 10^{-6} \text{ mol/L}$ at equilibrium, what is the concentration of N_2 at equilibrium?

30. Determine whether the following reaction is spontaneous by using the ΔG_f° for the reactants and products.



$$\Delta G_f^\circ \text{ for } \text{CH}_4(\text{g}) = -50.79 \text{ kJ/mol}$$

$$\Delta G_f^\circ \text{ for } \text{O}_2(\text{g}) = 0.00 \text{ kJ/mol}$$

$$\Delta G_f^\circ \text{ for } \text{CO}_2(\text{g}) = -394.4 \text{ kJ/mol}$$

$$\Delta G_f^\circ \text{ for } \text{H}_2\text{O}(\text{l}) = -237.2 \text{ kJ/mol}$$

31. Based on the values given below, calculate ΔG° and determine whether the reaction is spontaneous.

$$\Delta H^\circ = -85.2 \text{ kJ/mol}, T = 127 \text{ }^\circ\text{C}, \Delta S^\circ = 0.125 \text{ kJ/K} \times \text{mol}$$

