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18 Reaction Rates and Equilibrium

Big idea

CHEMICAL REACTIONS MATTER AND ENERGY

18.1 Rates of Reaction

For students using the Foundation edition, assign problem 4–9, 11, 12, 14, and 18.

Essential Understanding Collision theory explains why some reactions happen faster than others.

Lesson Summary

Describing Reaction Rates The rate of a reaction is determined by the number of effective collisions per unit of time.

- Collision theory states particles must collide for a reaction to occur.
- Activation energy is the minimum amount of kinetic energy colliding particles must have for a reaction to occur.

Factors Affecting Reaction Rates Temperature, concentration, surface area, and catalysts affect the rate of reaction.

- Temperature change affects reaction rate by changing the speed of the colliding particle.
- Concentration and particle size affect reaction rate by controlling the number of particles and the surface area available for collisions.
- A catalyst speeds up a reaction without being used up in the reaction.

After reading Lesson 18.1, answer the following questions.

Describing Reaction Rates

1. How are rates of chemical change expressed?

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

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

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

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

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

ineffective collision *effective collision*

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

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

   a. reactants

   b. activated complex

   c. products

7. Circle the letter of the term that completes the sentence correctly. The minimum amount of energy that particles must have in order to react is called the _____.

   a. kinetic energy

   b. activation energy

   c. potential energy

   d. collision energy

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

9. Circle the letter of the term that best describes the lifetime of an activated complex.

   a. 10^{-15} s

   b. 10^{13} s

   c. 10^{-13} s

   d. 10^{-1} s

10. Why is an activated complex sometimes called the transition state?

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

Factors Affecting Reaction Rates

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

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

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13. What happens when you put more reacting particles into a fixed volume?

The concentration of reactants increases, the collision frequency increases, and, therefore, the reaction rate increases.

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

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

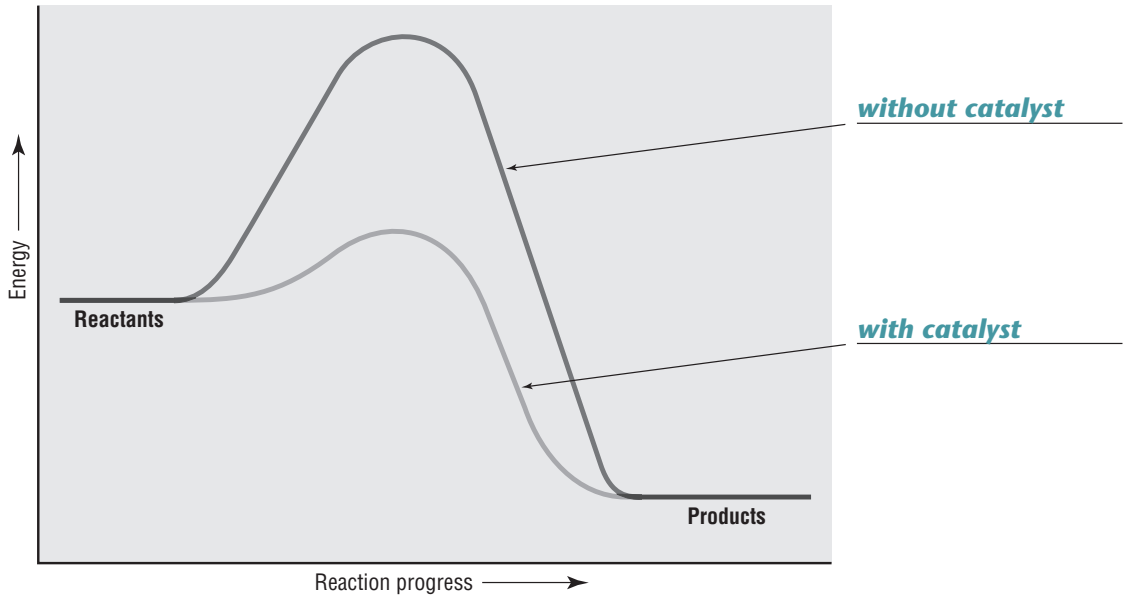
One way is to dissolve the solid; another way is to grind the solid into a fine powder.

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

17. What does a catalyst do?

A catalyst speeds up a reaction and permits it to proceed at a lower energy than is normally required. A catalyst lowers the activation energy.

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



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

19. What does the graph show about the effect of a catalyst on the rate of a reaction?

The catalyst lowers the activation energy and, thus, the amount of energy required by the system.

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

The catalyst is often written above the yield arrow in the equation.

21. A(n) *inhibitor* is a substance that interferes with the action of a catalyst.

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18.2 The Progress of Chemical Reactions

For students using the Foundation edition, assign problems 1, 4, 6, 8.

Essential Understanding The rate of a reaction depends on the concentrations of the reactants, and is limited by the slowest step in a sequence of steps.

Lesson Summary

Rate Laws Rate laws express reaction rate in terms of the concentrations of the reactants.

- The specific rate constant, k, times the concentration of a reactant equals the reaction rate.
- In a first-order reaction, reaction rate depends on the concentration of only one reactant.
- In a higher-order reaction, reaction rate depends on the concentrations of more than one reactant.

Order	Reaction	Rate
first-order	$A \rightarrow B$	$k[A]$
higher-order	$aA + bB \rightarrow cC + dD$	$k[A]^a[B]^b$

Reaction Mechanisms Most reactions occur in more than one step, with the speed of the reaction determined by the speed of the slowest step.

- In elementary reactions, reactants form products in a single step.
- Most reactions take place in several steps, each step being an elementary reaction.
- In a multi-step reaction, the rate of the slowest step determines the rate of the reaction.

After reading Lesson 18.2, answer the following questions.

Rate Laws

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

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

   The constant is a proportionality constant relating the concentrations of reactants to the rate of the reaction.

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

4. In a first-order reaction, the reaction rate is directly proportional to the concentration of _____.

   a. two or more reactants

   b. both reactants and products

   c. only one reactant

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5. How do you determine the reaction mechanism of a reaction?

The reaction mechanism must be determined by experiment.

Reaction Mechanisms

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

7. What is a reaction progress curve?

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

8. Is the following sentence true or false? A reaction mechanism includes all of the elementary reactions of a complex reaction. *true*

9. What is an intermediate of a reaction?

It is a product of one step in the reaction mechanism that becomes a reactant in the next step in the reaction.

10. What determines the rate of a multi-step chemical reaction?

The rate of a multi-step reaction is determined by the rate of the slowest step.

11. Look at Figure 18.11. What is one difference between this graph and the chemical equation for this reaction?

The graph shows that the reaction proceeds through five steps; the chemical equation sums up the five steps into what appears to be one step.

18.3 Reversible Reactions and Equilibrium

For students using the Foundation edition, assign problems 1–5, 7, 9, 15, and 16.

Essential Understanding All reactions are reversible. Reactants go to products in the forward direction. Products go to reactants in the reverse direction.

Reading Strategy

Cause and Effect A cause and effect chart is a useful tool when you want to describe how, when, or why one event causes another. As you read, draw a cause and effect chart that shows the relationship between stresses on a chemical system at equilibrium and the shift in the equilibrium of the system.

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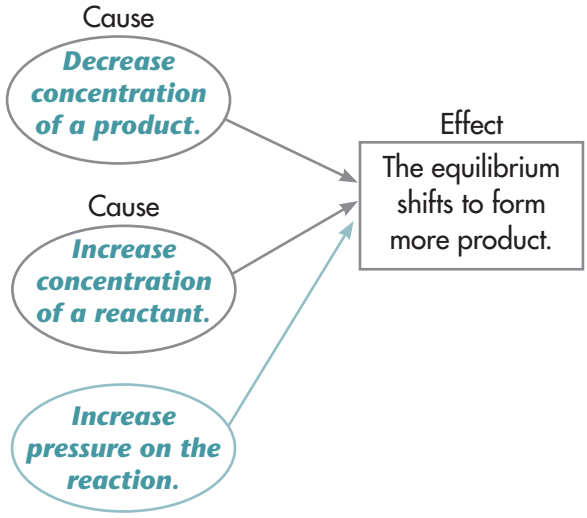
As you read Lesson 18.3, use the cause and effect chart below. List two changes in concentration that result in a shift in equilibrium toward more product.



EXTENSION Add another cause to the cause and effect chart that shows how a change in pressure results in more product in this reaction: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$.

Lesson Summary

Reversible Reactions A reversible reaction is a chemical reaction that does not go to completion and can occur in both the forward and reverse directions.

- During a reversible reaction, reactants form from products at the same time products form from reactants.
- When forward and reverse reactions occur at the same rate, equilibrium exists.

Factors Affecting Equilibrium: Le Châtelier's Principle Any stress on an equilibrium causes the equilibrium to shift in the direction that releases the stress.

- A change in concentration of any reactant or product will shift the equilibrium.
- Changing the temperature of an equilibrium causes the equilibrium to shift.
- Changes in pressure or volume change the equilibrium of reactions that involve gases.

Stresses and Their Effects on Equilibrium

Stress		Shift
Reactant concentration	increase	right
Reactant concentration	decrease	left
Product concentration	increase	left
Product concentration	decrease	right
Temperature	increase	left
Temperature	decrease	right
Pressure	increase	toward side with fewer moles of gas
Volume	decrease	toward side with fewer moles of gas

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Equilibrium Constants Equilibrium constants can be used to calculate concentrations and solubilities.

- An equilibrium constant is the ratio of product concentrations to reactant concentrations at equilibrium.
- The equilibrium constant is represented by K_{eq}.
- When the equilibrium constant is greater than one, formation of products is favored. When it is less than one, formation of reactants is favored.

BUILD Math Skills

Significant Figures Significant figures are important because they tell us how precise our data really is. Using significant figures in science ensures that everyone understands the *precision* of the measurements. Remember, significant digits apply only to measurements. They do not apply to pure numbers or definitions, such as 60 s/min.

How to Determine Significant Figures in a Number

Step 1 Does your number have a decimal point? If it does not have a decimal point, go to Step 2. If it does have a decimal point, go to Step 3.

Step 2 Counting significant figures with no decimal point: start at the right-hand side of the number. Begin going to the left until you reach a non-zero number. Once you reach a non-zero number, that number and all other numbers to the left of it (including zeros) count as significant figures.

Step 3 Counting significant figures with a decimal point: start at the left-hand side of the number. Begin going to the right until you reach a non-zero number. Once you reach a non-zero number, that number and all other numbers to the right of it (including zeros) count as significant figures.

Sample Problem How many significant figures are in 23500?

There's no decimal, so start at the right and move left. → 23500

Move left until you reach a non-zero number. Five is the first non-zero number. → 23500

All numbers to the left are significant. → 23500 or three significant figures

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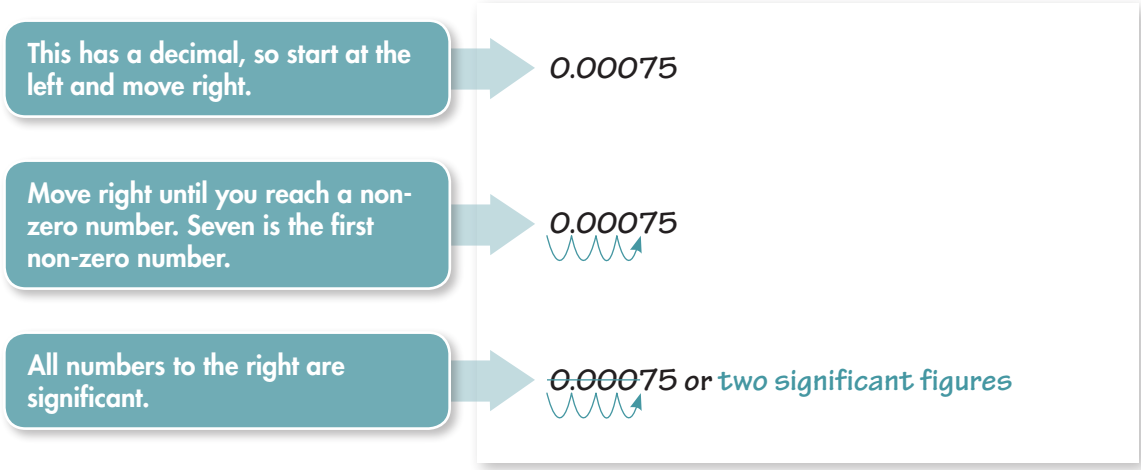
Sample Problem How many significant figures are in 0.00075?



Now it's your turn to identify significant figures in the numbers below.

1. 0.0145009 *6 significant figures: 145009*
2. 34.9 *all numbers are significant*
3. 600.0 *4 significant figures: 6000*
4. 200.000 *all numbers are significant*

Significant Figures in Calculations

Multiplication or Division The number of significant figures in the answer is the same as that in the quantity with the *smallest* number of significant figures.

For example, suppose you divide 25.624 grams by 25 mL. The answer should have only 2 significant figures because 25 mL has the *smallest* number of significant figures. The answer is 1.0 g/mL, not 1.0000 g/mL or 1.000 g/mL.

Addition and Subtraction The number of decimal places in the answer is equal to the number of decimal places in the quantity with the *smallest number of decimal places*.

For example, suppose you add 14.16 + 3.2. You get 17.36, but this is not the final answer. Since the smallest number of decimal places is 1, you have to round to get only 1 decimal place. The correct answer is 17.4.

Now it's your turn to do some calculations with significant figures. Be sure that each answer is expressed to the correct number of significant figures.

5. 46.6 kg + 5.72 kg = *52.3 kg*
6. 4.62 × 0.19 = *88*

For questions 7–9, write the final answer and explain your reasoning.

7. 22.37 cm × 3.10 cm × 85.75 cm = 5946.50525 cm^3

5950 cm^3; the answer can only show 3 significant digits because that is the least number of significant digits in the original problem. 5946.50525 shows 9 significant digits, so we must round to the tens place in order to show only 3 significant digits.

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8. 91.68 mL − 19.1 mL = 72.50 mL

72.5 mL; the answer can only show 3 significant figures because that is the smallest number of decimal places in the original problem. 72.50 has 4 significant figures, so we have to drop the 0 to show only 3 significant figures.

9. 1.473 ÷ 2.6 = 0.5665

0.57; the result is the same as the least number of significant figures in the original problem. 1.473 has 4 significant figures and 2.6 has only 2 significant figures, so the result will have 2 significant figures. 0.5665 was rounded up to 0.57 from 0.5665 because the number to the right of the last significant figure was greater than 5.

After reading Lesson 18.3, answer the following questions.

Reversible Reactions

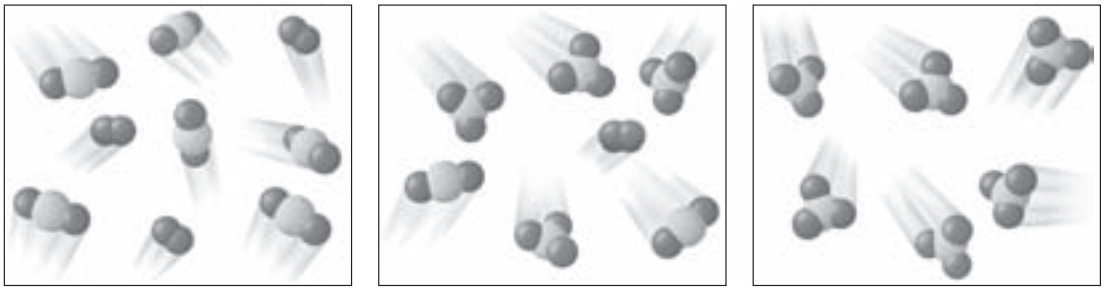
10. What happens in a reversible reaction?

In a reversible reaction, the reaction occurs in both directions at the same time so that both reactants and products are being produced.

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

12. The equilibrium position of a reaction is given by the relative *concentrations* of the system's components at equilibrium.

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



SO_2 and O_2 → $2SO_2 + O_2 \rightleftharpoons 2SO_3$ ← SO_3

not at equilibrium *at equilibrium* *not at equilibrium*

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14. Use Figure 18.13 to answer these questions.

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

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

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

Factors Affecting Equilibrium: Le Châtelier's Principle

15. What is Le Châtelier's principle?

Le Châtelier's principle states that if a stress is applied to a system in dynamic equilibrium, the system changes to relieve the stress.

16. Circle the letters of the terms that complete the sentence correctly. Stresses that upset the equilibrium of a chemical system include changes in _____.

(**a.**) concentration
b. the amount of catalyst
(**c.**) pressure
(**d.**) temperature

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

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

19. How does increasing pressure affect a chemical system?

An increase in pressure results in a shift in the equilibrium position that favors the formation of a smaller number of molecules of gas.

20. Decreasing the pressure on the system shown in Figure 18.16 results in a shift of equilibrium to favor *the reactants*.

Equilibrium Constants

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

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

The exponents are the coefficients from the balanced chemical equation.

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

The square brackets indicate the concentrations of substances in moles per liter (mol/L).

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

25. A value of K_{eq} greater than one means that ***products*** are favored over ***reactants*** . A value of K_{eq} less than one means that ***reactants*** are favored over ***products*** .

18.4 Solubility Equilibrium

For students using the Foundation edition, assign problems 2–5.

Essential Understanding Equilibrium between ions in solution and undissolved compounds reflect the solubility of an ionic compound.

Lesson Summary

The Solubility Product Constant

The solubility product constant of an ionic compound reflects the number of ions the compound forms in solution.

- Even ionic compounds that appear to be insoluble produce some ions in solution.
- The solubility product constant, K_{sp}, reflects only the concentrations of the dissolved ions raised to the power that is the coefficient of that ion in the equation.

$$K_{sp} = [A^+]^a[B^-]^b$$

The Common Ion Effect

The common ion effect is a shift in equilibrium that happens because the concentration of an ion that is part of the equilibrium is changed.

- A common ion is an ion that is found in more than one compound in solution.
- The addition of a common ion to a solution reduces the solubility of the dissolved compound.
- A precipitate forms if the concentration of two ions in solution is greater than the K_{sp} for the compound formed from the ions.

After reading Lesson 18.4, answer the following questions.

The Solubility Product Constant

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

The solubility product constant equals the product of the concentration of the ions, each raised to a power equal to the coefficient of the ion in the dissociation equation.

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

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

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

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The Common Ion Effect

4. A common ion is an ion that is present in both ***ionic compounds*** in a solution.

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

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

18.5 Entropy and Free Energy

For students using the Foundation edition, assign problems 1–3, 8–14, 18–19, 21.

Essential Understanding Whether a reaction occurs spontaneously depends on heat changes involved in the reaction and the randomness of the particles involved.

Lesson Summary

Free Energy and Spontaneous Reactions

Spontaneous reactions occur naturally and release free energy.

- Free energy is energy available to do work.
- In a reversible reaction, the favored reaction is considered to be the spontaneous reaction.

Entropy

Entropy measures the degree of disorder, or randomness, of a system.

- According to the law of disorder, systems naturally move in the direction of maximum disorder.
- Reactions are favored if entropy increases in the reaction.

Enthalpy and Entropy

Enthalpy and entropy together determine whether a reaction is spontaneous.

- A reaction is spontaneous if heat is released and entropy increases.
- A reaction is nonspontaneous if heat is absorbed and entropy decreases.
- If the change in either entropy or enthalpy is favorable and the other change is not, the size of each change must be known to determine if the reaction is spontaneous.

Free Energy Change

Free energy change is calculated from enthalpy change, entropy change, and temperature.

- Free energy change equals enthalpy change minus the product of the temperature and the entropy change.

$$\Delta G = \Delta H - T\Delta S$$

- When free energy change is negative, a reaction is spontaneous.
- A change in temperature can make a formerly nonspontaneous reaction spontaneous.

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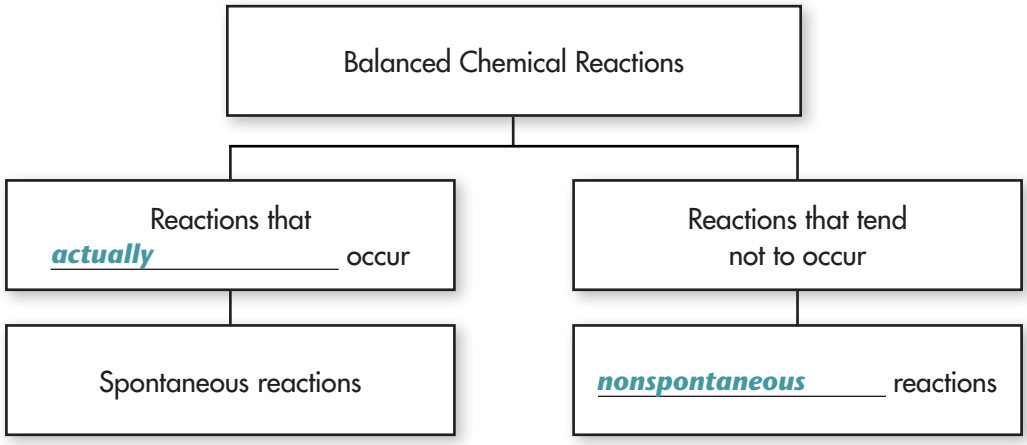
After reading Lesson 18.5, answer the following questions.

Free Energy and Spontaneous Reactions

1. Free energy is energy that is available to do ***work*** .
2. Is the following sentence true or false? A process can be made 100% efficient. ***false***
3. Make a concept map about balanced chemical reactions.



4. Spontaneous reactions are reactions that occur naturally and that favor the formation of ***products*** at the specified conditions.
5. Describe four spontaneous reactions mentioned in this section.
   a. ***exploding fireworks***
   b. ***the decomposition of carbonic acid in water***
   c. ***the reaction of aqueous solutions of $Cd(NO_3)_2$ and Na_2S to produce solid CdS***
   d. ***sugar and oxygen to produce carbon dioxide and water***
6. What are nonspontaneous reactions?
   Nonspontaneous reactions are reactions that do not favor the formation of products at the specified conditions.
7. Is the following sentence true or false? Some reactions that are non-spontaneous at one set of conditions may be spontaneous at other conditions. ***true***

Entropy

8. Some factor other than ***heat or enthalpy*** change must help determine whether a physical or chemical process is spontaneous.
9. What is entropy? ***Entropy is the measure of the disorder of a system.***
10. The law of disorder states that processes move in the direction of ***maximum*** disorder or randomness.

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

12. Number the diagrams below from 1 to 3 to show the increasing entropy of the system. Diagram 1 should show the least amount of entropy.

2 ***1*** ***3***

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

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

Enthalpy and Entropy

15. What determines whether a reaction is spontaneous?

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

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

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

Free Energy Change

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

19. The Gibbs free-energy change (ΔG) is an indication as to whether a process is ***spontaneous*** at a given temperature.

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

$\Delta G = \Delta H - T\Delta S$, where ΔH is the change in enthalpy, ΔS is the change in entropy, and temperature (T) is in kelvins.

21. The numerical value of ΔG is ***negative*** in spontaneous processes because the system loses free energy; the numerical value of ΔG is ***positive*** in nonspontaneous processes because the system requires that work be expended to make them go forward at the specified conditions.

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Guided Practice Problems

Show that the unit of k for a first-order reaction is a reciprocal unit of time, such as a reciprocal second (s^{-1}). Begin with the expression Rate $= k$[A].

1. Analyze

Plan a problem-solving strategy. The definition of the reaction rate is the change in concentration of a reactant per unit of time. So using a unit, "concentration," for the numerator and "time" for the denominator, the reaction rate has units [concentration/time]. Use this knowledge algebraically to show the unit for k.

2. Solve

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

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

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

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

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

Answer the following questions about Practice Problem 17.

How is the equilibrium position of this reaction affected by the following changes?

$$C(s) + H_2O(g) + \text{heat} \rightleftharpoons CO(g) + H_2(g)$$

a. lowering the temperature

b. increasing the pressure

c. removing hydrogen

d. adding water vapor

1. Analyze

Identify the relevant concepts. According to Le Châtelier's principle, the equilibrium position will shift in a direction that minimizes the imposed stress.

2. Solve

Apply the concepts to this problem. Use Le Châtelier's principle to analyze the shift in the system effected by each stress.

a. ***Lowering the temperature will shift the equilibrium to the left to produce heat.***

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

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

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

Answer the following questions about Practice Problem 18.

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

1. Analyze

List the knowns and the unknown.

Knowns

$[H_2] = 0.15$ mol/L

$[N_2] = 0.25$ mol/L

$[NH_3] = 0.10$ mol/L

$K_{eq}(\text{algebraic}) = \dfrac{[NH_3]^2}{[N_2] \times [H_2]^3}$

Unknown

$K_{eq}(\text{numerical}) = ?$

2. Calculate

Solve for the unknowns.

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

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

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

$$= 11.85$$

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Answer the following questions about Practice Problem 20.

Suppose the following system reaches equilibrium.

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

Analysis of the equilibrium mixture in a 1-L flask gives the following results: 0.50 mol of N_2, 0.50 mol of O_2, 0.020 mol of NO. Calculate K_{eq} for the reaction.

1. Analyze

List the knowns and the unknowns.

Knowns

$[N_2] =$ ***0.50 mol/L***

$[O_2] =$ ***0.50 mol/L***

$[NO] = 0.020$ mol/L

Unknown

$K_{eq} = ?$

2. Calculate

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

$$K_{eq} = \frac{[NO]^2}{[N_2] \times [O_2]}$$

Substitute the known values in the expression.

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

Solve. Write your answer in scientific notation.

$$K_{eq} = 0.0016 = \boxed{1.6 \times 10^{-3}}$$

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Answer the following questions about Practice Problem 32.

What is the concentration of calcium ions in a saturated calcium carbonate solution at 25°C ? Use the K_{sp} value for calcium carbonate from Table 18.2.

1. Analyze

List the knowns and the unknown.

Knowns

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

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

$CaCO_3 = Ca^{2+} + CO_3^{2-}$

Unknown

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

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

2. Calculate

Solve for the unknown.

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

Make a substitution based on the equilibrium condition stated above:

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

Now solve for the unknown:

$[Ca^{2+}] = 6.7 \times 10^{-5}\ M$

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Answer the following questions about Practice Problem 33.

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

1. Analyze

List the knowns and the unknown.

Knowns

$K_{sp} = 8 \times 10^{-19}$

moles of $Fe(NO_3)_2 = 0.04$ mol

volume of solution = 1.0 L

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

$K_{sp} = [Fe^{2+}] \times [S^{2-}]$

Unknown

$[S^{2-}] = ?$ M

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

2. Calculate

Solve for the unknown.

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

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

Rearranging for x gives the result:

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

So $[S^{2-}] =$ ***2×10^{-17} M***

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Apply the Big idea

Use the Reaction Mechanism to answer questions 1–5.

Reaction Mechanism		
Step 1 *fast*	**Step 2** *slow*	**Step 3** *fast*
A + B ⟶ C	A + D ⟶ E	C + E ⟶ F

1. What is the overall balanced equation? ***2A + B + D → F***
2. The highest activation energy is in which step? ***step 2***
3. What is the rate law for this reaction mechanism? rate = ***k[A][D]***
4. Which letters, if any, represent intermediates in the reaction mechanism shown?
   C and E
5. What term describes step 2, the slowest step in the reaction mechanism?
   rate determining step

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18 Self-Check Activity

For Questions 1–11, complete each statement by writing the correct word or words. If you need help, you can go online.

18.1 Rates of Reaction

1. Reaction rate is usually expressed as the change in concentration of ***reactant*** per unit time.
2. Temperature, particle size, ***concentration***, and the use of a catalyst can affect reaction rate.

18.2 The Progress of Chemical Reactions

3. The value of *k*, which represents the ***specific rate constant***, is large when products form quickly and small when reactants form quickly.
4. Two or more ***elementary*** reactions make up most chemical reactions.

18.3 Reversible Reactions and Equilibrium

5. At equilibrium, both the forward and the reverse reactions continue, but the ***concentrations*** of the reactants stay the same.
6. Stresses that upset chemical equilibrium include changes in concentration, ***temperature***, and pressure.

18.4 Solubility Equilibrium

7. Compounds that have low solubility have ***small*** solubility product constants.
8. A(n) ***precipitate*** forms if the product of the concentrations of two ions in a mixture is greater than the K_{sp} of the compound the ions form.

18.5 Entropy and Free Energy

9. ***Spontaneous*** reactions release free energy and produce large amounts of products.
10. A reaction is spontaneous based on the size and direction of entropy changes and ***enthalpy*** changes.
11. When the value of ΔG is ***negative***, a process is spontaneous.

If You Have Trouble With…											
Question	1	2	3	4	5	6	7	8	9	10	11
See Page	543	546	552	555	558	560	570	572	576	580	582

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Review Key Equations

Match items in column A to those in column B.

Column A

E **1.** $k\,[A]$

B **2.** $k\,[A]^a[B]^b$

C **3.** $\dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

A **4.** $[A]^a[B]^b$

D **5.** $\Delta H - T\Delta S$

Column B

A. K_{sp}, the solubility product constant

B. the rate of a higher-order reaction

C. K_{eq}, the equilibrium constant

D. ΔG, change in free energy

E. the rate of a first-order reaction

Review Vocabulary

Each cell has a vocabulary term from the chapter. Write how you'll remember the definition of each term on the table. A few have been done for you.

rate *change per time*	inhibitor *stops catalyst, slows reaction*	activation energy *energy needed to react*	entropy *measure of disorder*	activated complex *unstable, momentary transition arrangement of atoms*	
rate law *rate of reaction, rate = k[A]*	specific rate constant *large if quick reaction, small if slow*	first-order reaction A → B	elementary reaction *one step*	reaction mechanism *several reactions before done*	intermediate product of step 1 is reactant in step 2
reversible reaction ⟷	chemical equilibrium *forward equals backward*	equilibrium position *how much of each at equilibrium*	equilibrium constant *ratio of [product] to [reactant]*	Le Châtelier's principle *system reacts to lower stress*	
solubility product constant *K_{sp} = [A]^a × [B]^b for ions in a salt*		common ion effect *+ common ion, ↓ solubility of compound*	common ion *an ion common to both compounds*	nonspontaneous reaction *products not favored, it won't happen*	
free energy *energy available (free) to do work*	spontaneous reaction happens naturally	collision theory *high energy crashes form products*	law of disorder *systems move to disorder*		