Chapter 18: Reaction Rates and Equilibrium

18.1 Rates of Reaction

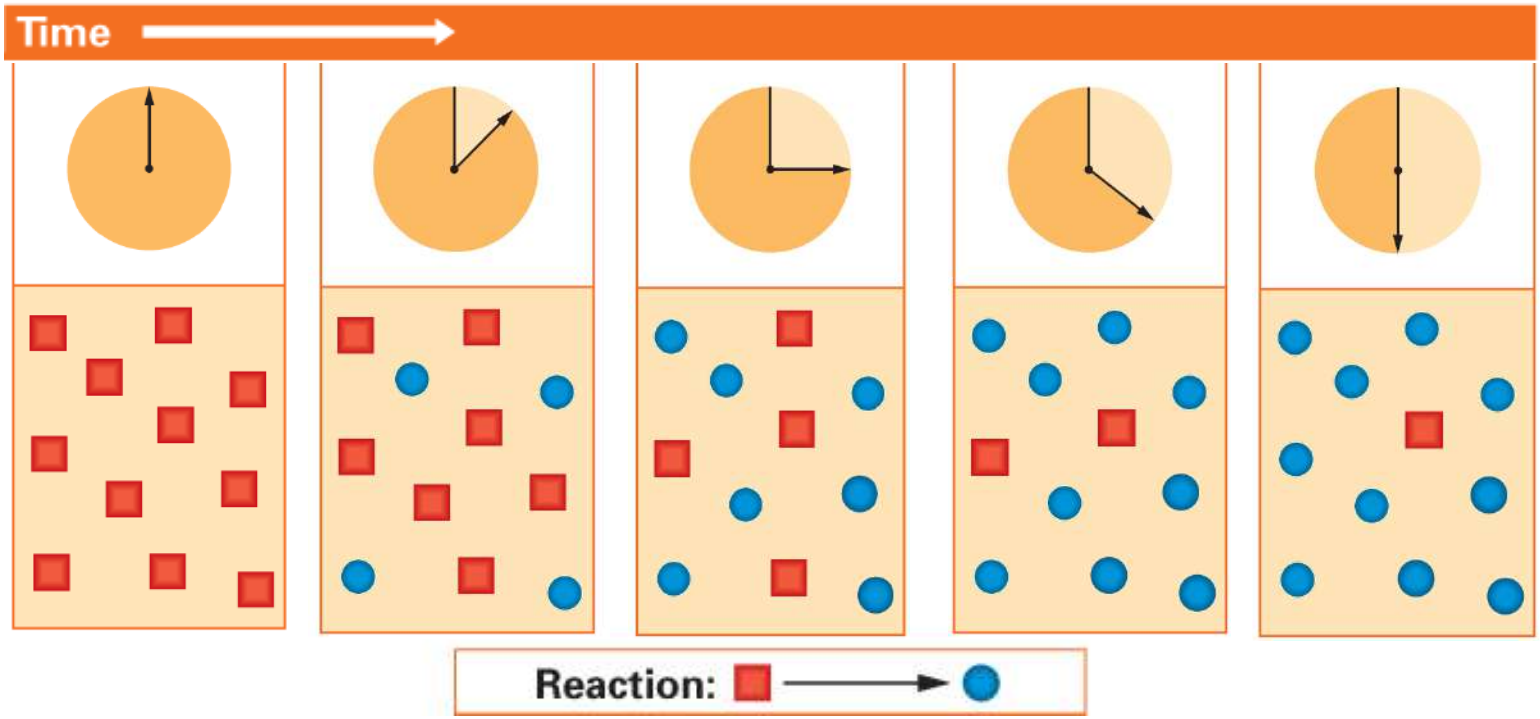
Collision Theory

- In chemistry, the rate of chemical change, or the reaction rate, is usually expressed as the amount of reactant changing per unit time.

Collision Theory

- A **rate** is a measure of the speed of any change that occurs within an interval of time.

- Rates of chemical reactions are often measured as a change in the number of moles during an interval of time.



Collision Theory

Average Reaction Rate Equation

- Avg rxn rate = $\frac{-\Delta[\text{reactant}]}{\Delta t}$

$\Delta[\text{reactant}]$ is the change in concentration of reactant

Δt is the change in time

Example

- In a reaction between butyl chloride (C_4H_9Cl) and water, the concentration of C_4H_9Cl is 0.220 M at the beginning of the reaction. At 4.00 s, the concentration is 0.100 M. Calculate the average reaction rate.

Practice

Time (s)	$[H_2]$ (M)	$[Cl_2]$ (M)	[HCl] (M)
0.00	0.030	0.050	0.000
4.00	0.020	0.040	

- For the reaction $H_2 + Cl_2 \rightarrow 2\ HCl$

a) Calculate the average reaction rate with respect to H_2; with respect to Cl_2

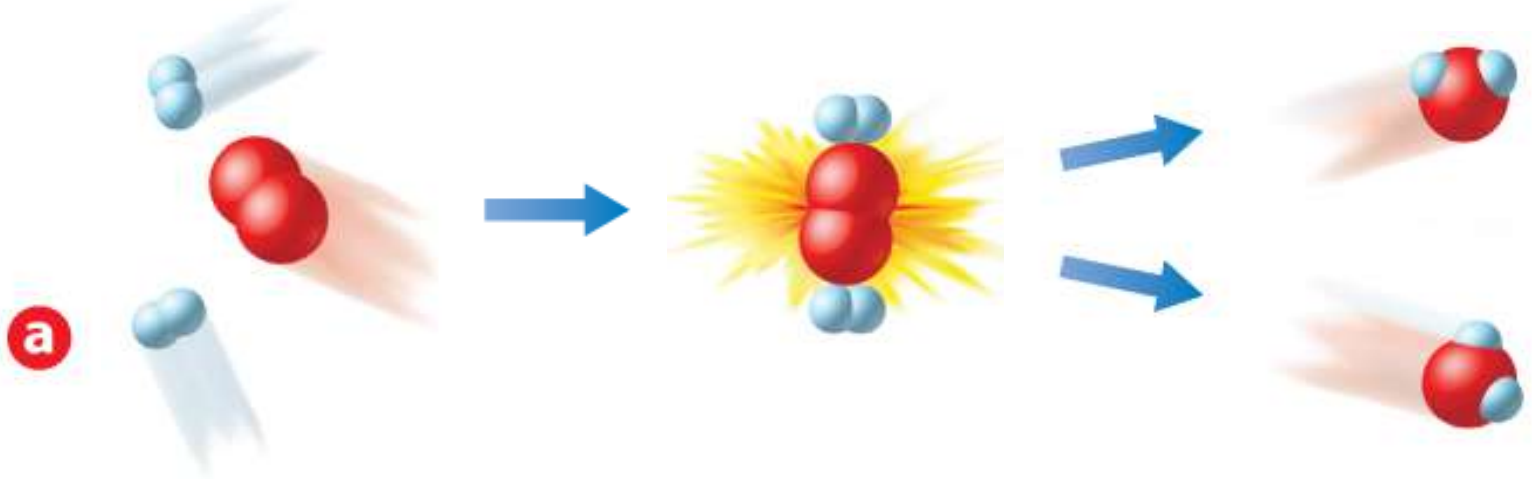
b) If the average reaction rate is 0.0050 mol/L·s HCl, what concentration of HCl would be present after 4.00 s?

Collision Theory

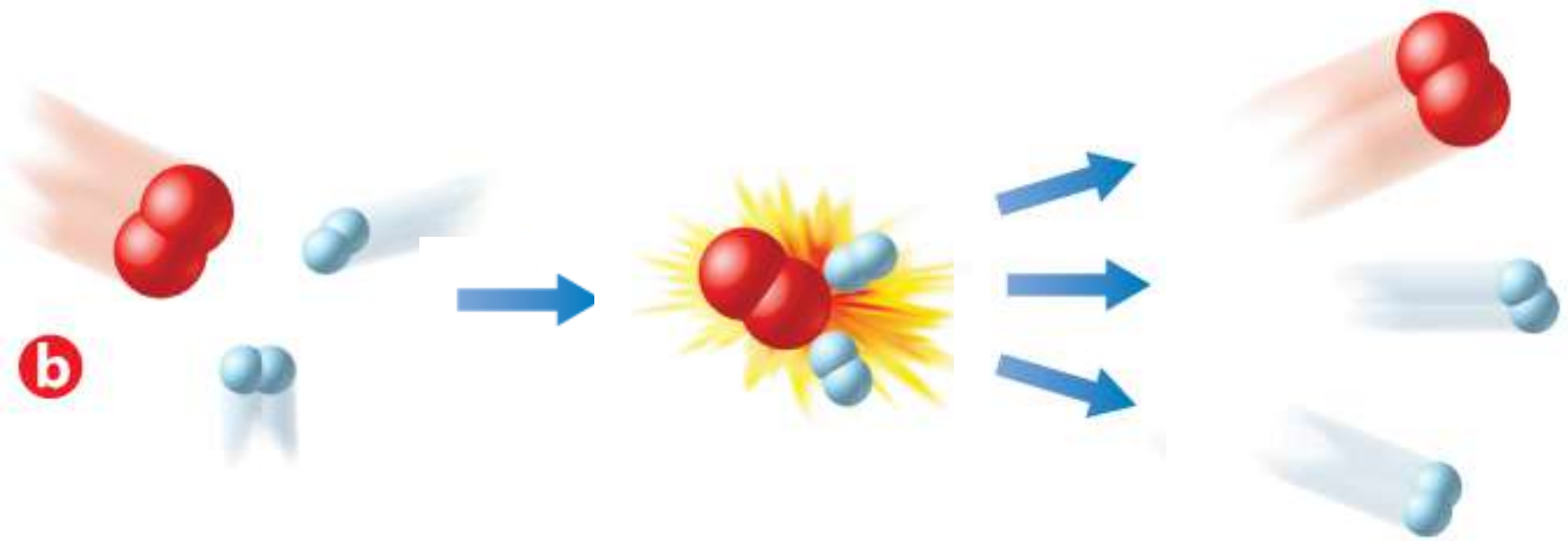
- According to **collision theory**, atoms, ions, and molecules can react to form products when they collide with one another, provided that the colliding particles have enough kinetic energy.

Collision Theory

- **Effective Collision**

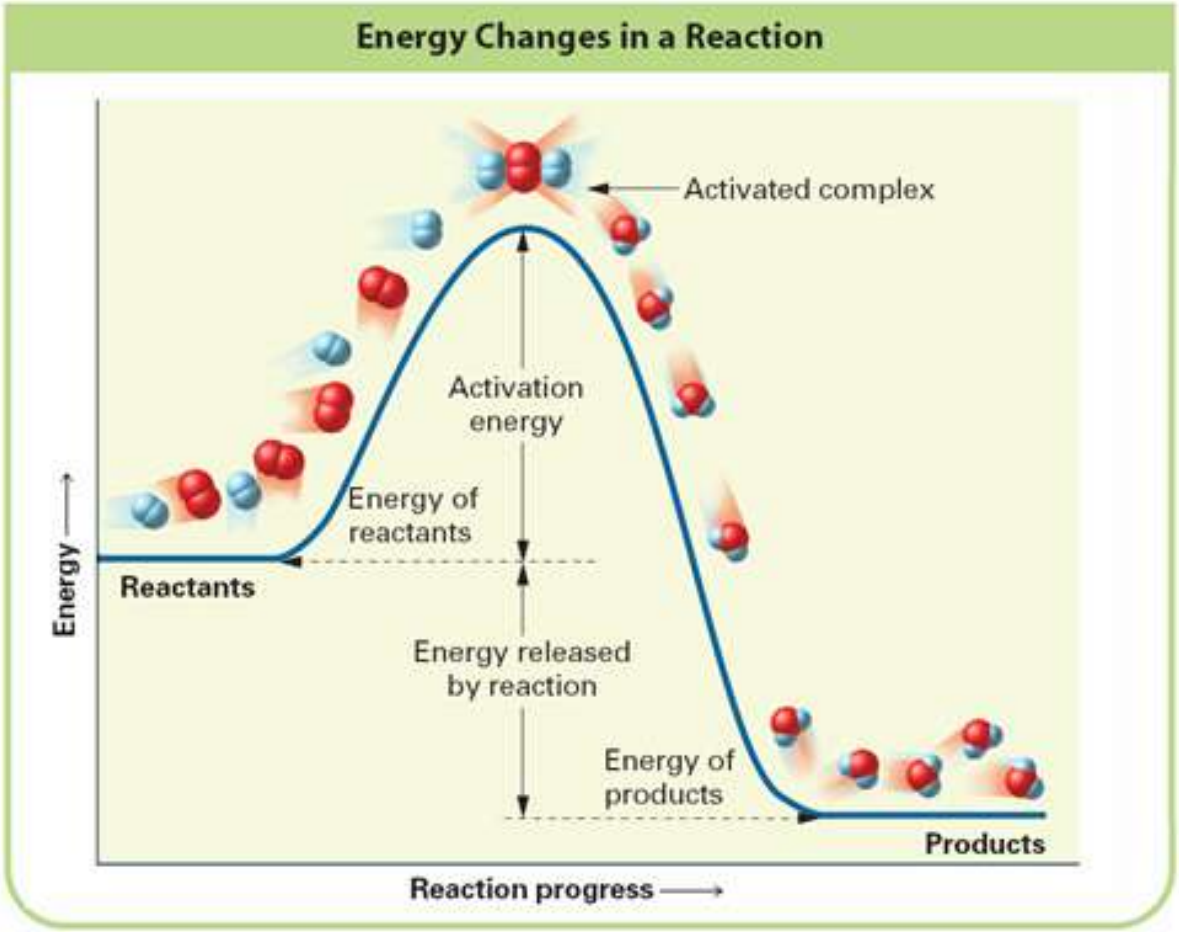


Collision Theory – Ineffective Collision



Collision Theory

- The minimum energy that colliding particles must have in order to react is called the **activation energy**.



Collision Theory

- An **activated complex** is an unstable arrangement of atoms that forms momentarily at the peak of the activation-energy barrier.
- The activated complex is sometimes called the **transition state.**

Factors Affecting Reaction Rates

- The rate of a chemical reaction depends upon temperature, concentration, particle size, and the use of a catalyst.

Temperature

- Storing foods in a refrigerator keeps them fresh longer. Low temperatures slow microbial action.

Increasing temperature increases reaction rate

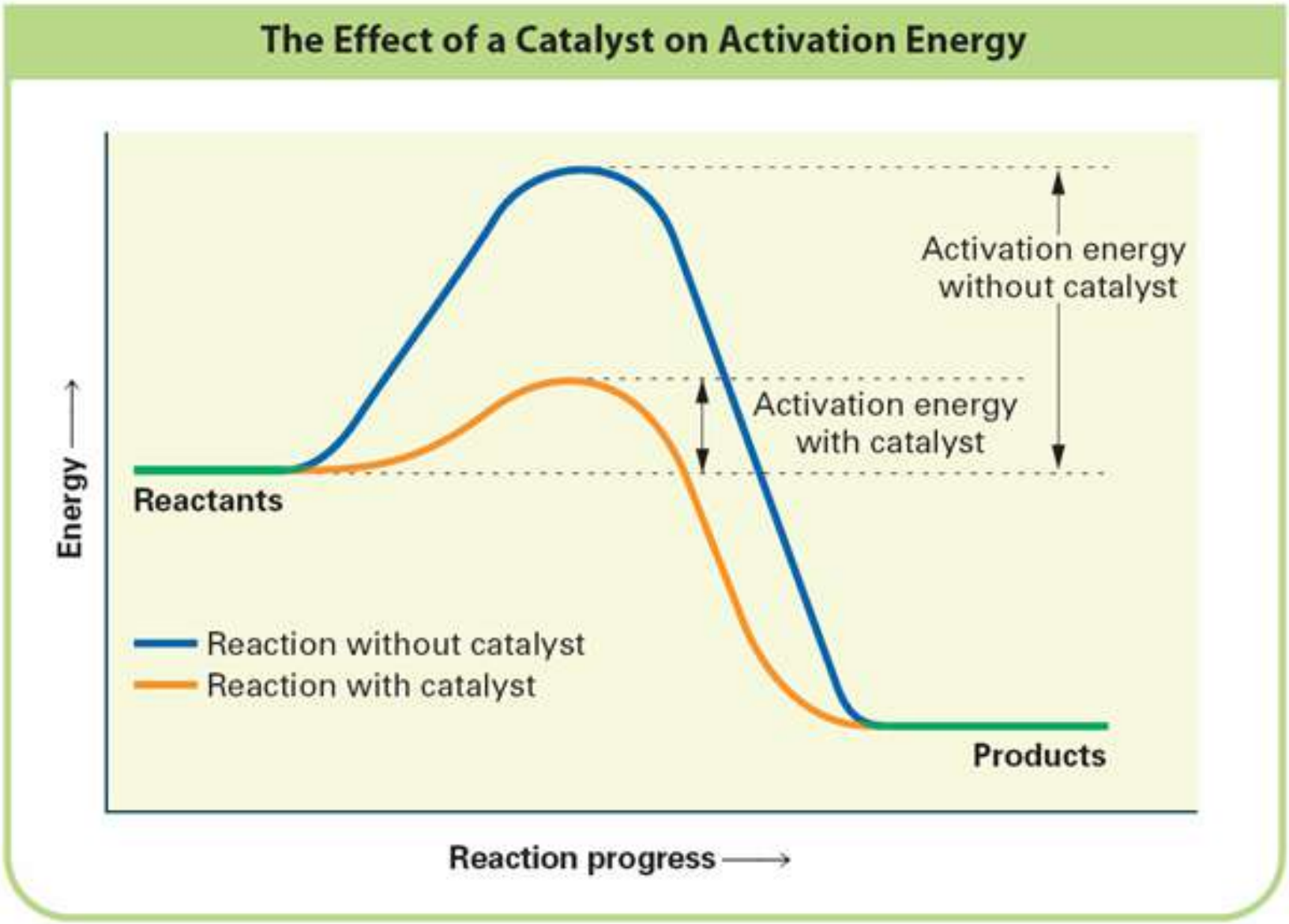
Concentration

- Increasing concentration increases the reaction rate

Particle Size

- A smaller particle size (greater surface area) increases the reaction rate

⑩Catalysts


The Effect of a Catalyst on Activation Energy
Activation energy without catalyst
Activation energy with catalyst
Energy
Reactants
Reaction without catalyst
Reaction with catalyst
Products
Reaction progress

Catalysts

- Increase the reaction rate by lowering the activation energy

- An **inhibitor** is a substance that interferes with the action of a catalyst. Antioxidants and antimicrobials used in drying fruits and preserving fruit juices slow the action of microbes and limit contact with air.

18.1 Section Quiz.

- 1. The units below that would be appropriate to measure the rate of a chemical reaction is

  a) mol/s.

  b) mol/L.

  c) kJ/mol.

  d) h/mol.

18.1 Section Quiz.

- 2. In a chemical reaction, the energy of reactants is always

  a) greater than the energy of the products.

  b) more than the activation energy.

  c) less than the activation energy.

  d) less than the energy of the products.

18.1 Section Quiz.

- 3. An increase in which one of the following will NOT increase the reaction rate?

  a) temperature

  b) concentration of reactants

  c) total mass of reactants

  d) surface area of reactants

18.1 Section Quiz.

- 4. A catalyst works because it

  a) lowers the activation energy.

  b) increases the temperature.

  c) is permanently changed in a reaction.

  d) supplies energy to a reaction.

18.2 Reversible Reactions and Equlibrium

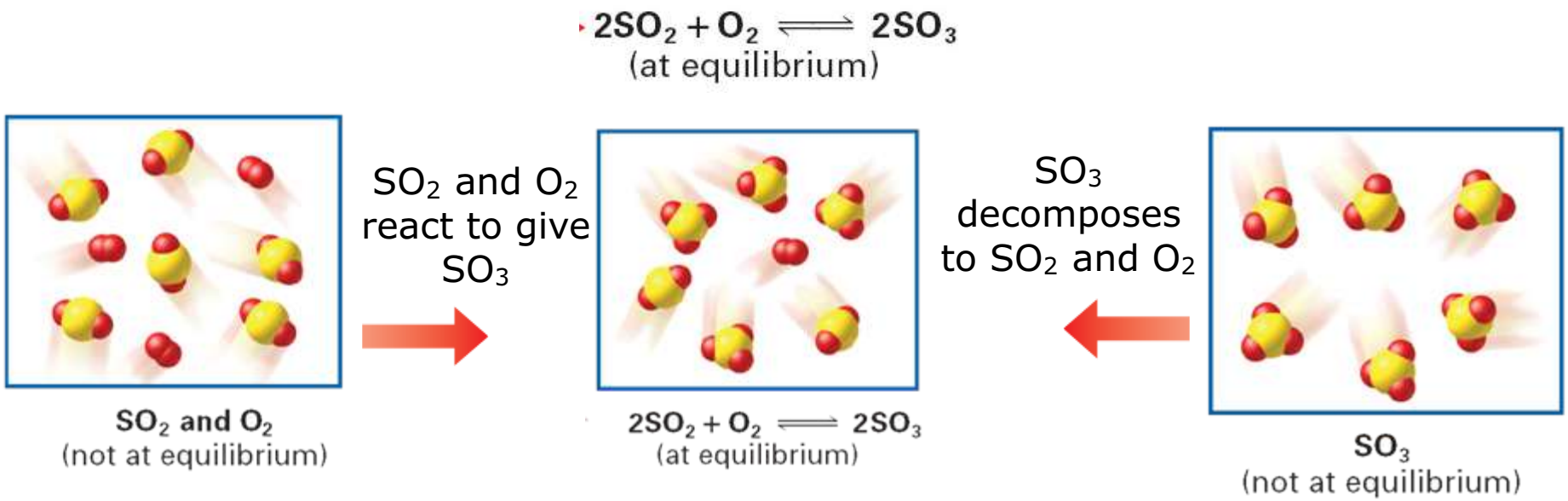
Reversible Reactions

- At chemical equilibrium, no net change occurs in the actual amounts of the components of the system.

Reversible Reactions

- A **reversible reaction** is one in which the conversion of reactants to products and the conversion of products to reactants occur simultaneously.

Reversible Reactions



At equilibrium, all three types of molecules are present.

Reversible Reactions

- When the rates of the forward and reverse reactions are equal, the reaction has reached a state of balance called **chemical equilibrium**.

Factors Affecting Equilibrium: Le Châtelier's Principle

- The French chemist Le Châtelier proposed what has come to be called **Le Châtelier's principle**: If a stress is applied to a system in dynamic equilibrium, the system changes in a way that relieves the stress.

Concentration

- If you increase the concentration of reactants, you make more products (shift right)
- If you add more product, you make more reactant (shift left)
- If you remove product, you make more product (shift right)

Temperature

- An increase in temperature shifts in the direction that absorbs heat
- Ex: in an exothermic reaction heat is a product so increases temp. forms reactants; removing heat would shift right to form products

Pressure

- An increase in pressure shifts to the side with fewer moles of gas

Conceptual Problem 18.1

Applying Le Châtelier's Principle

What effect do each of the following changes have on the equilibrium position for this reversible reaction?

$$PCl_5(g) + \text{heat} \rightleftharpoons PCl_3(g) + Cl_2(g)$$

a. addition of Cl_2

b. increase in pressure

c. removal of heat

d. removal of PCl_3 as it is formed

for Conceptual Problem 18.1

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

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

a. lowering the temperature

b. increasing the pressure

c. removing hydrogen

d. adding water vapor

$N_2O_{4(g)} + 58\ kJ \leftrightarrow 2NO_{2(g)}$

- Addition of heat
- Decrease in pressure
- Addition of NO_2
- Removal of N_2O_4

Equilibrium Constants

- 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.

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

Equilibrium Constants

- A value of K_{eq} greater than 1 means that products are favored over reactants; a value of K_{eq} less than 1 means that reactants are favored over products.

Write Equilibrium Expressions for:

- $H_2(g) + I_2(g) \leftrightarrow 2\ HI(g)$
- $N_{2(g)} + O_2(g) \leftrightarrow 2\ NO(g)$
- $2\ SO_3(g) \leftrightarrow 2\ SO_2(g) + O_2(g)$

Practice Problem 18.1

Expressing and Calculating K_{eq}

The colorless gas dinitrogen tetroxide (N_2O_4) and the dark brown gas nitrogen dioxide (NO_2) exist in equilibrium with each other.

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

A liter of a gas mixture at equilibrium at 10°C contains 0.0045 mol of N_2O_4 and 0.030 mol of NO_2. Write the expression for the equilibrium constant and calculate the equilibrium constant (K_{eq}) for the reaction.

for Sample Problem 18.1

7. The reversible reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

produces ammonia, which is a fertilizer. 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.

Practice Problem 18.2

Finding the Equilibrium Constant

One mol of colorless hydrogen gas and 1.00 mol of violet iodine vapor are sealed in a 1-L flask and allowed to react at 450°C. At equilibrium, 1.56 mol of colorless hydrogen iodide is present, together with some of the reactant gases. Calculate K_{eq} for the reaction.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

9. 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: $N_2 = 0.50$ mol, $O_2 = 0.50$ mol, and NO = 0.020 mol. Calculate K_{eq} for the reaction.

Practice

- The reaction $COCl_2(g) \leftrightarrow CO(g) + Cl_2(g)$ reaches equilibrium at 900 K. K_{eq} is 8.2×10^{-2} . If the equilibrium concentrations of CO and Cl_2 are 0.150 M, what is the equilibrium concentration of $COCl_2$?

Practice

- At 1405 K, hydrogen sulfide decomposes to form hydrogen gas and diatomic sulfur. The equilibrium constant for the reaction is 2.27×10^{-3}. What is the concentration of hydrogen gas if $[S_2] = 0.0540$ mol/L and $[H_2S] = 0.184$ mol/L?

Practice

- K_{eq} = 10.5 for the equilibrium $CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$
- A) Calculate [CO] when $[H_2]$ = 0.933 M and $[CH_3OH]$ = 1.32 M
- B) Calculate $[H_2]$ when [CO] = 1.09 M and $[CH_3OH]$ = 0.325 M
- C) Calculate $[CH_3OH]$ when $[H_2]$ = 0.0661 M and [CO] = 3.85 M

18.2 Section Quiz.

- 1. In a reaction at equilibrium, reactants and products
  - a) decrease in concentration.
  - b) form at equal rates.
  - c) have equal concentrations.
  - d) have stopped reacting.

18.2 Section Quiz.

- 2. In the reaction $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$, increasing the pressure on the reaction would cause

  a) the amount of NO to increase.

  b) the amount of NO_2 to increase.

  c) nothing to happen.

  d) the amount of O_2 to increase.

18.2 Section Quiz.

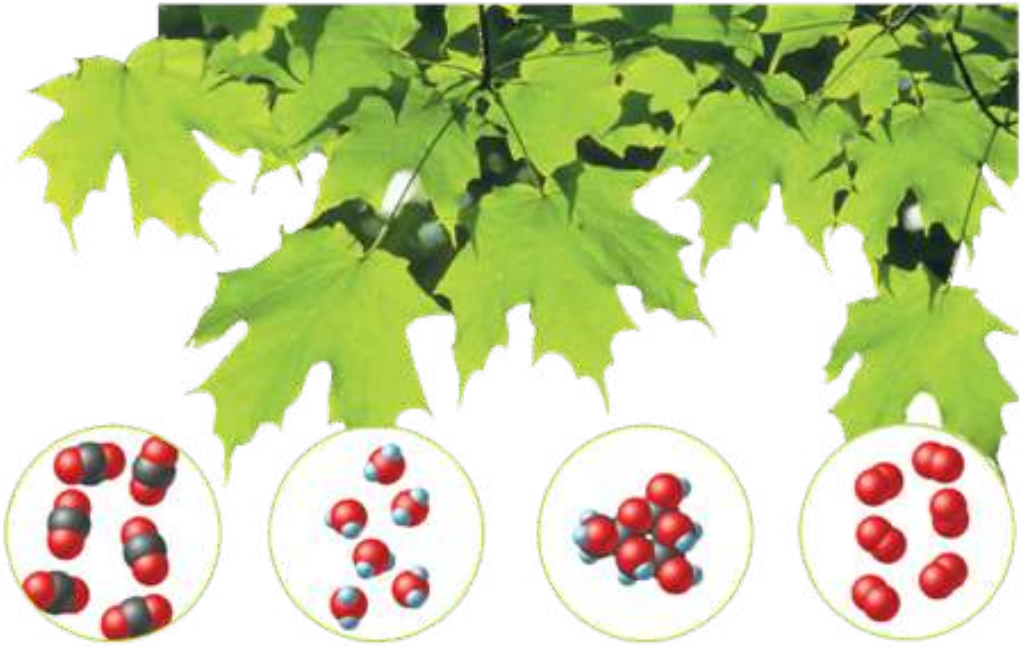
- 3. For the following reaction, $K_{eq} = 1$.
  - $A(g) + B(g) \rightarrow C(g) + D(g)$
    Therefore, at equilibrium
  - a) [C] = [A].
    b) [A][B] = 0.
    c) [AB] = [CD] = 1.
    d) [A][B] = [C][D].

18.4 Entropy and Free Energy

Free Energy and Spontaneous Reactions

- A **spontaneous reaction** occurs naturally and favors the formation of products at the specified conditions.

- A **nonspontaneous reaction** is a reaction that does not favor the formation of products at the specified conditions.



$$6CO_2 + 6H_2O \xrightarrow{\text{light energy}} C_6H_{12}O_6 + 6O_2$$

Photosynthesis is a nonspontaneous reaction that requires an input of energy.

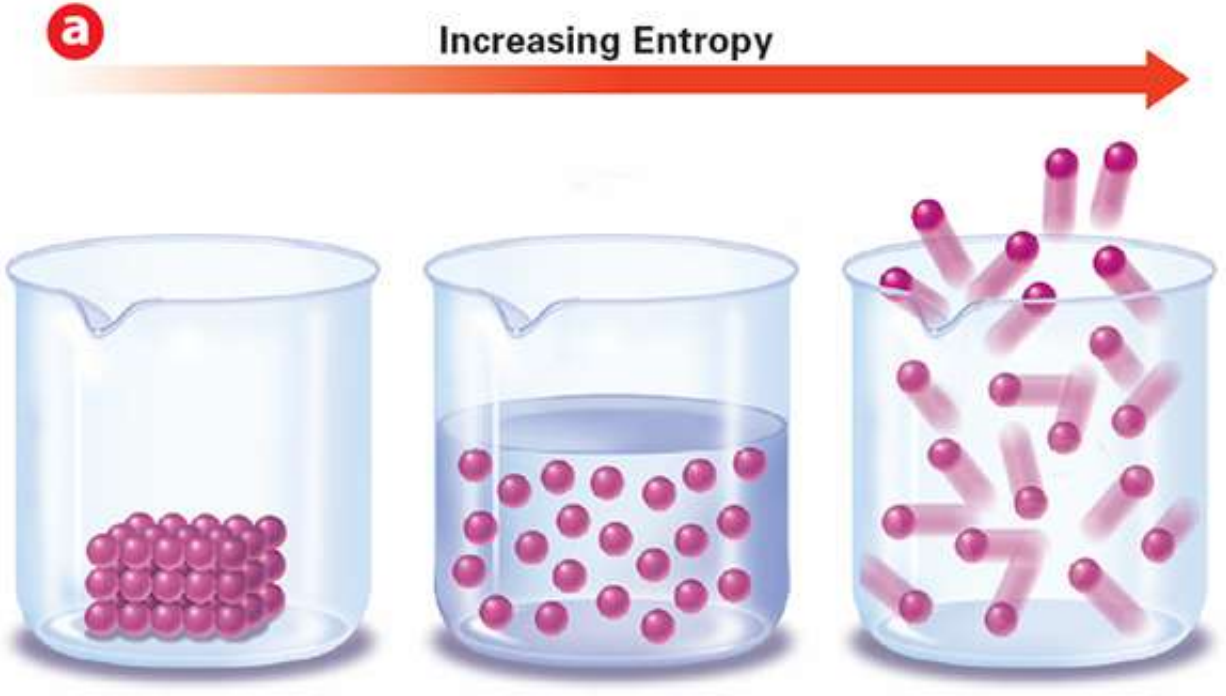
Free Energy and Spontaneous Reactions

- Spontaneous reactions produce substantial amounts of products at equilibrium and release free energy.
- Free energy **is energy that is available to do work.**

Entropy

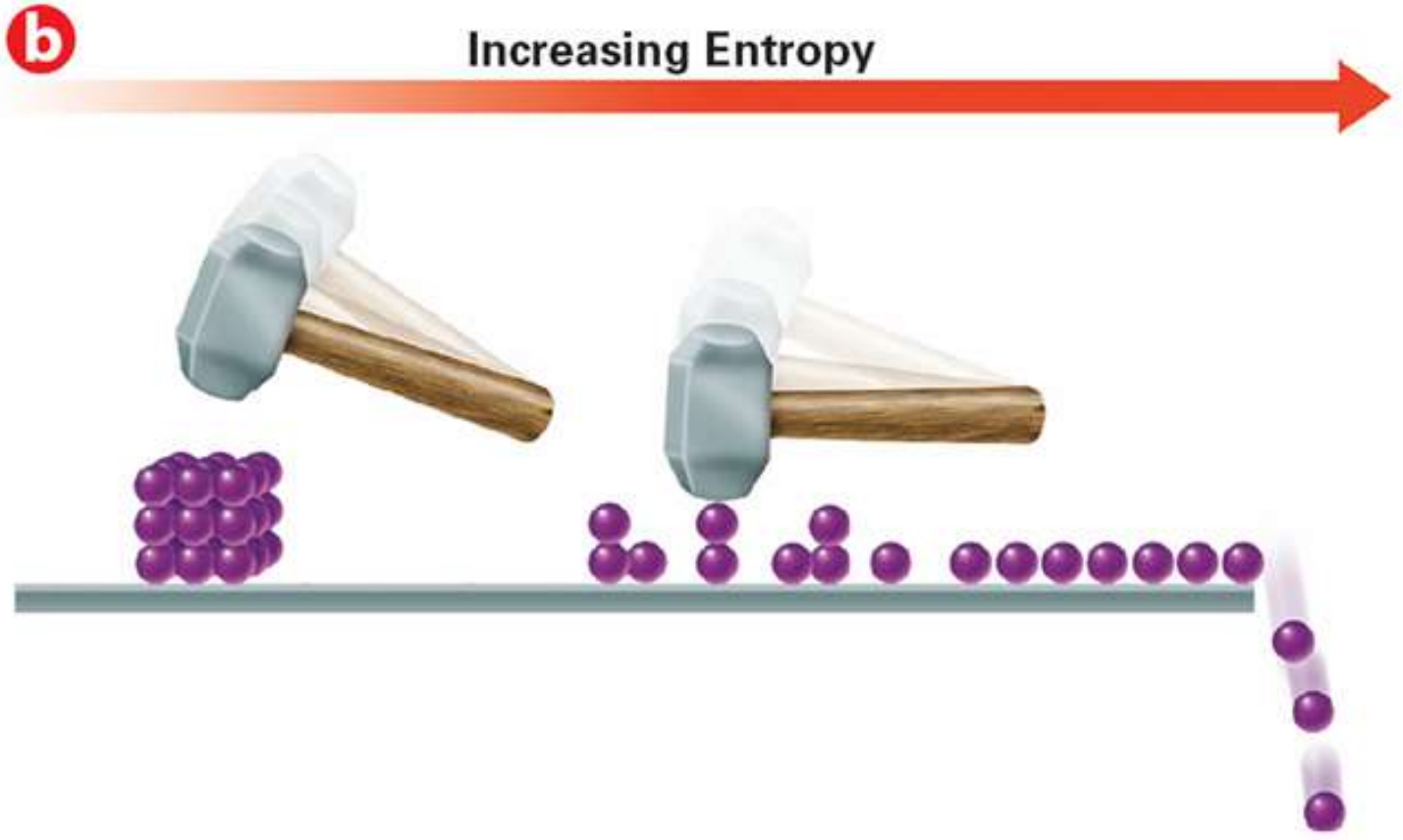
- **Entropy** is a measure of the disorder of a system.
  - Physical and chemical systems attain the lowest possible energy.
  - The **law of disorder** states that the natural tendency is for systems to move in the direction of maximum disorder or randomness.

- For a given substance, the entropy of the gas is greater than the entropy of the liquid or the solid. Similarly, the entropy of the liquid is greater than that of the solid.

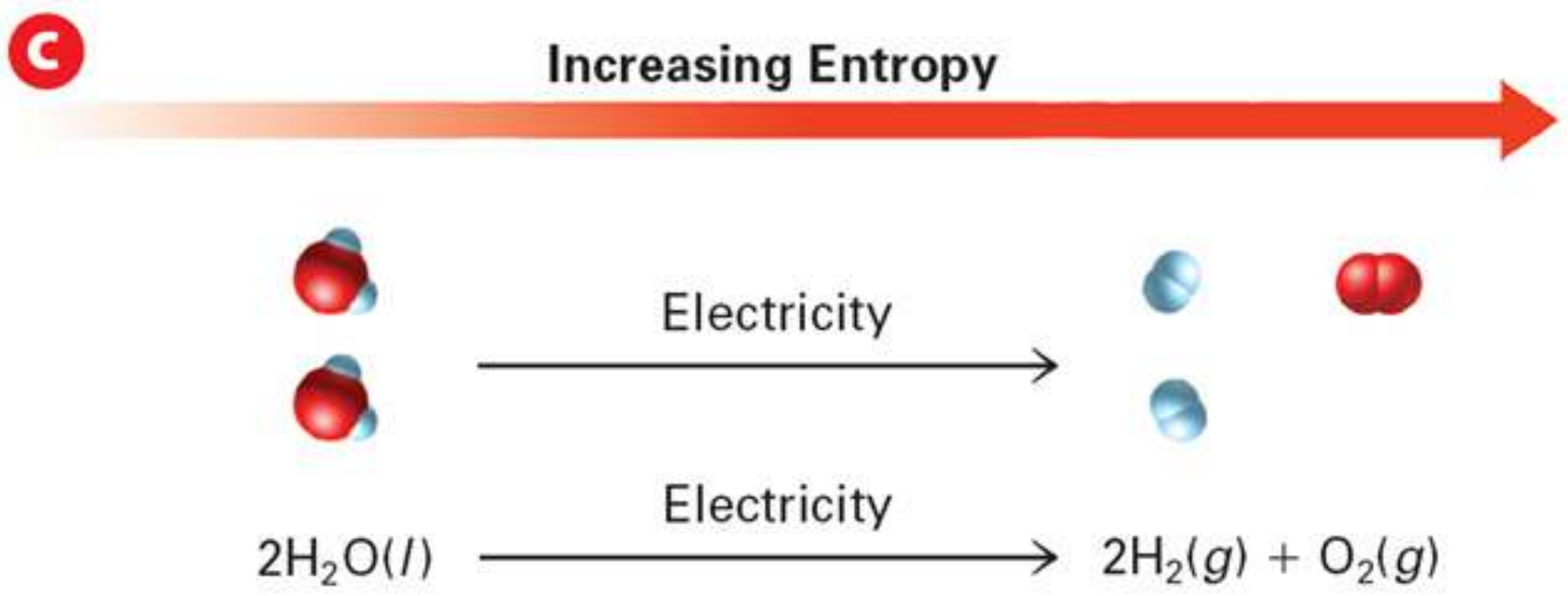


Entropy

- Entropy increases when a substance is divided into parts.

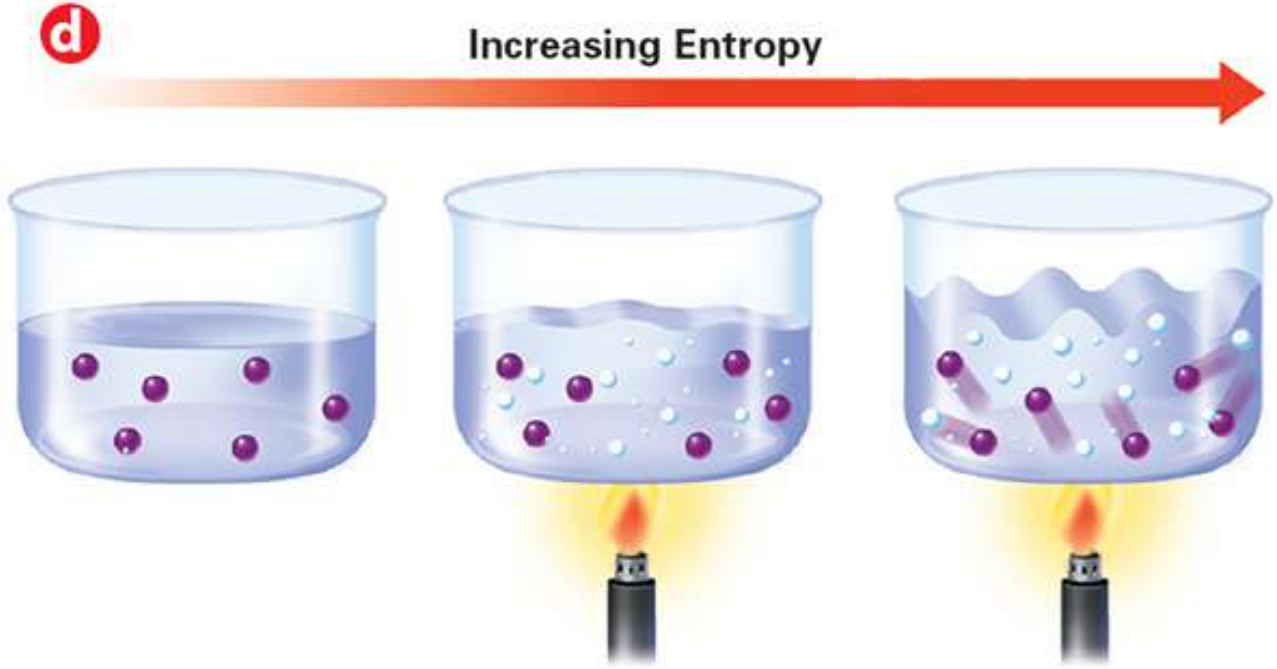


- Entropy tends to increase in chemical reactions in which the total number of product molecules is greater than the total number of reactant molecules.



Electrolysis of water

- Entropy tends to increase when temperature increases. As the temperature increases, the molecules move faster and faster, which increases the disorder.



Practice

- Predict the sign of ΔS:

a) $ClF(g) + F_2(g) \rightarrow ClF(g)$

b) $NH_3(g) \rightarrow NH_3(aq)$

c) $CH_3OH(l) \rightarrow CH_3OH(aq)$

d) $C_{10}H_8(l) \rightarrow C_{10}H_8(s)$

18.4 Section Quiz.

1. Free energy from a reaction is the amount of energy that is
   - absorbed by an entropy decrease.
   - equal to the enthalpy change.
   - wasted as heat.
   - available to do work.

18.4 Section Quiz.

- 2. Which of the following involves a decrease in entropy?
  - Natural gas burns.
  - A liquid freezes.
  - Dry ice sublimes.
  - Water evaporates.