Chapter 18: Reaction Rates and Equilibrium

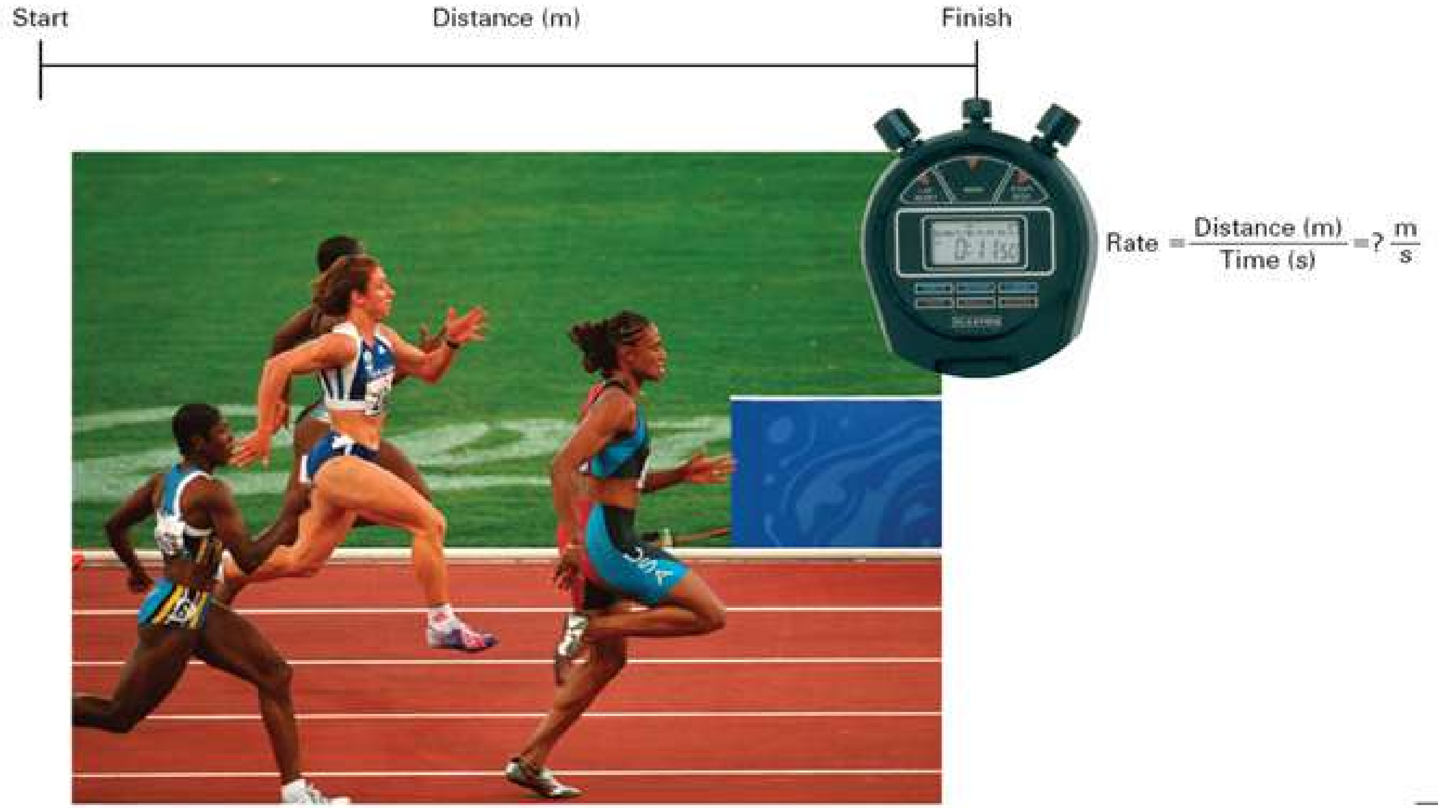
18.1 Rates of Reaction

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.



Average Reaction Rate Equation

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

Δ[reactant] is the change in concentration of reactant

Δ*t* 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

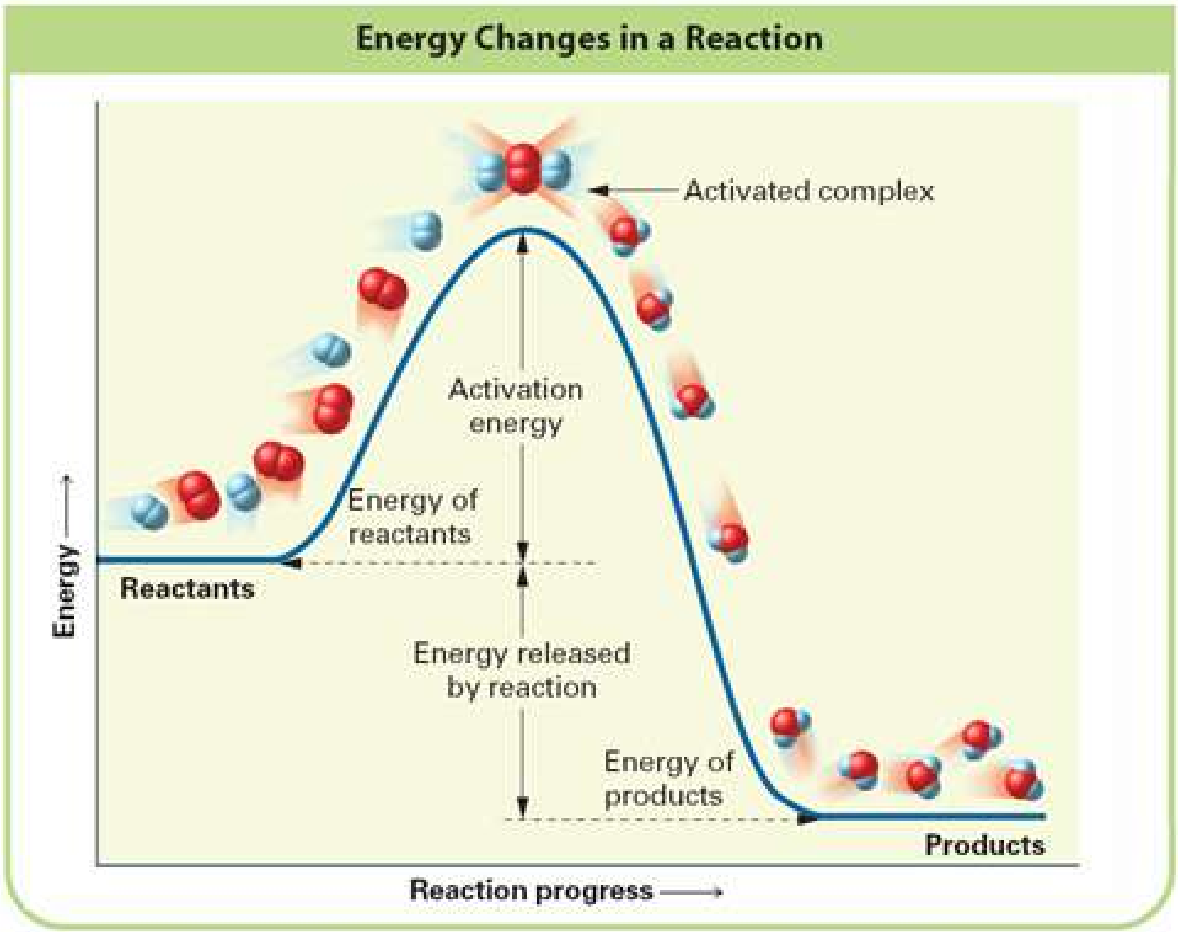
b) If the average reaction rate is 0.0050 mol/L·s HCl, what concentration of HCl would be present after 4.00 s?

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

- 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

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

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

Reversible Reactions

- When the rates of the forward and reverse reactions are equal, the reaction has reached a state of balance called **chemical equilibrium**.
- The relative concentrations of the reactants and products at equilibrium constitute the **equilibrium position** of a reaction.

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. Changing which of the following would NOT affect the equilibrium position of a chemical reaction?
  - a) concentration of a reactant only
  - b) concentration of a product only
  - c) temperature only
  - d) volume only

18.2 Section Quiz.

- 4. 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].

18.3 Solubility Equilibrium

The Solubility Product Constant

- The solubility product constant (K_{sp}), equals the product of the concentrations of the ions, each raised to a power equal to the coefficient of the ion in the dissociation equation.
    - The smaller the numerical value, the lower the solubility of the compound.

Table 18.1

Solubilities of Ionic Compounds in Water		
Compounds	**Solubility**	**Exceptions**
Salts of Group 1A metals and ammonia	Soluble	Some lithium compounds
Ethanoates, nitrates, chlorates, and perchlorates	Soluble	Few exceptions
Sulfates	Soluble	Compounds of Pb, Ag, Hg, Ba, Sr, and Ca
Chlorides, bromides, and iodides	Soluble	Compounds of Ag and some compounds of Hg and Pb
Sulfides and hydroxides	Most are insoluble	Alkali metal sulfides and hydroxides are soluble. Compounds of Ba, Sr, and Ca are slightly soluble.
Carbonates, phosphates, and sulfites	Insoluble	Compounds of the alkali metals and of ammonium ions

Table 18.2

Solubility Product Constants (K_{sp}) at 25°C

Salt	K_{sp}	Salt	K_{sp}	Salt	K_{sp}
Halides		**Sulfates**		**Hydroxides**	
$AgCl$	1.8×10^{-10}	$PbSO_4$	6.3×10^{-7}	$Al(OH)_3$	3.0×10^{-34}
$AgBr$	5.0×10^{-13}	$BaSO_4$	1.1×10^{-10}	$Zn(OH)_2$	3.0×10^{-16}
AgI	8.3×10^{-17}	$CaSO_4$	2.4×10^{-5}	$Ca(OH)_2$	6.5×10^{-6}
$PbCl_2$	1.7×10^{-5}	**Sulfides**		$Mg(OH)_2$	7.1×10^{-12}
$PbBr_2$	2.1×10^{-6}	NiS	4.0×10^{-20}	$Fe(OH)_2$	7.9×10^{-16}
PbI_2	7.9×10^{-9}	CuS	8.0×10^{-37}	**Carbonates**	
PbF_2	3.6×10^{-8}	Ag_2S	8.0×10^{-51}	$CaCO_3$	4.5×10^{-9}
CaF_2	3.9×10^{-11}	ZnS	3.0×10^{-23}	$SrCO_3$	9.3×10^{-10}
Chromates		FeS	8.0×10^{-19}	$ZnCO_3$	1.0×10^{-10}
$PbCrO_4$	1.8×10^{-14}	CdS	1.0×10^{-27}	Ag_2CO_3	8.1×10^{-12}
Ag_2CrO_4	1.2×10^{-12}	PbS	3.0×10^{-28}	$BaCO_3$	5.0×10^{-9}

Sample Problem 18.3

Finding the Ion Concentrations in a Saturated Solution

What is the concentration of lead ions and chromate ions in a saturated lead chromate solution at 25°C? ($K_{sp} = 1.8 \times 10^{-14}$)

for Sample Problem 18.3

17. Lead(II) sulfide (PbS) has a K_{sp} of 3.0×10^{-28}. What is the concentration of lead(II) ions in a saturated solution of PbS?

Practice

- Calculate the solubility in mol/L of copper(II) carbonate. $K_{sp} = 2.5 \times 10^{-10}$ at 298 K.
- The K_{sp} of lead (II) carbonate is 7.40×10^{-14} at 298 K. What is the solubility of lead carbonate in g/L?

Example

- Magnesium hydroxide is a white solid obtained from seawater and used in many medications. Determine the hydroxide ion concentration in a saturated solution of $Mg(OH)_2$ at 298 K.

$K_{sp} = 5.6 \times 10^{-12}$

Practice

- 1) Calculate $[Ag^+]$ in a solution of AgBr ($K_{sp} = 5.4 \times 10^{-13}$)
- 2) Calculate $[F^-]$ in a solution of CaF_2 ($K_{sp} = 3.5 \times 10^{-11}$)
- 3) Calculate the solubility of Ag_3PO_4 ($K_{sp} = 2.6 \times 10^{-18}$)

Practice

- 4) The solubility of silver chloride (AgCl) is 1.86 x 10^{-4} g/100 g of H_2O at 298 K. Calculate K_{sp} for AgCl.

The Common Ion Effect

- The Common Ion Effect
  - How can you predict whether precipitation will occur when two salt solutions are mixed?

The Common Ion Effect

- If the product of the concentrations of two ions in the mixture is greater than the K_{sp} of the compound formed from the ions, a precipitate will form.

The Common Ion Effect

- A **common ion** is an ion that is found in both salts in a solution. The lowering of the solubility of an ionic compound as a result of the addition of a common ion is called the **common ion effect.**

Sample Problem 18.4

Finding Equilibrium Ion Concentrations in the Presence of a Common Ion

Photographic film is covered with a light-sensitive emulsion containing silver bromide. The K_{sp} of silver bromide is 5.0×10^{-13}. What is the bromide-ion concentration of a 1.00-L saturated solution of AgBr to which 0.020 mol of $AgNO_3$ is added?

for Sample Problem 18.4

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

18.3 Section Quiz.

- 1. What is the concentration of a saturated solution of silver sulfide?
- The K_{sp} of Ag_2S is 8.0×10^{-51}.
  - 2.0×10^{-17}M
  - 8.9×10^{-26}M
  - 8.9×10^{-25}M
  - 2.0×10^{17}M

18.3 Section Quiz.

- 2. Adding which of these solutions to a saturated solution of $BaSO_4$ will cause the solubility of $BaSO_4$ to decrease?
  - I. $BaCl_2(aq)$
  - II. Na_2SO_4 (aq)
- (I) only
- (II) only
- (I) and (II)
- neither solution

18.3 Section Quiz.

- 3. The K_{sp} of AgBr is 5.0×10^{-13}. When 7.1×10^{-6} mol/L solutions of NaBr(*aq*) and $AgNO_3$(*aq*) are mixed, we would expect
  - no precipitate to form.
  - a definite precipitation reaction.
  - no reaction.
  - a saturated solution but no visible precipitation.

18.3 Section Quiz.

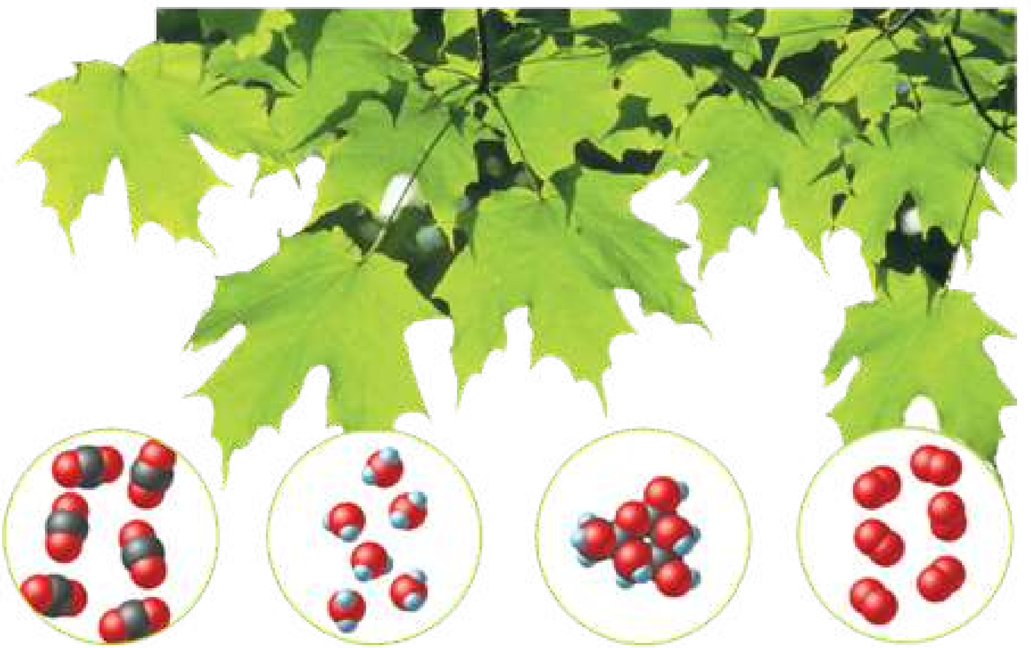
- 4. After the common ion effect causes a precipitate to form in a solution,
  - the solution will no longer be saturated.
  - the solution will again be saturated.
  - the solution will be supersaturated.
  - there will be no solute left in the solution.

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.**

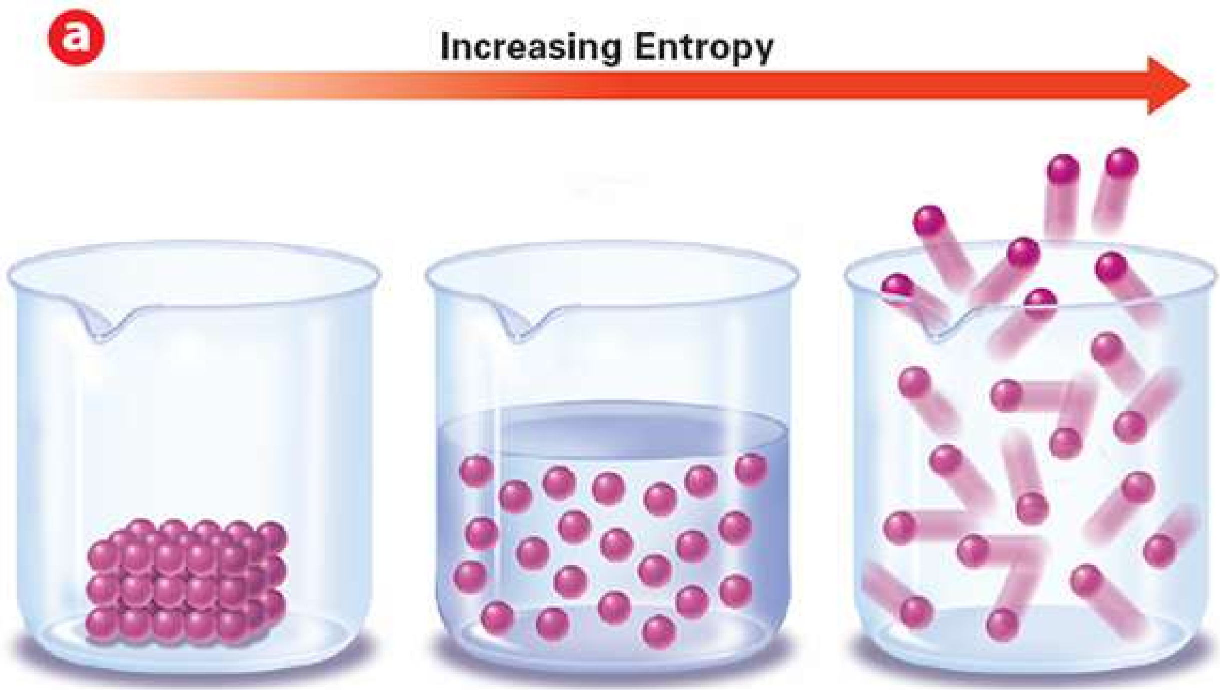
Entropy

- **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.

Entropy

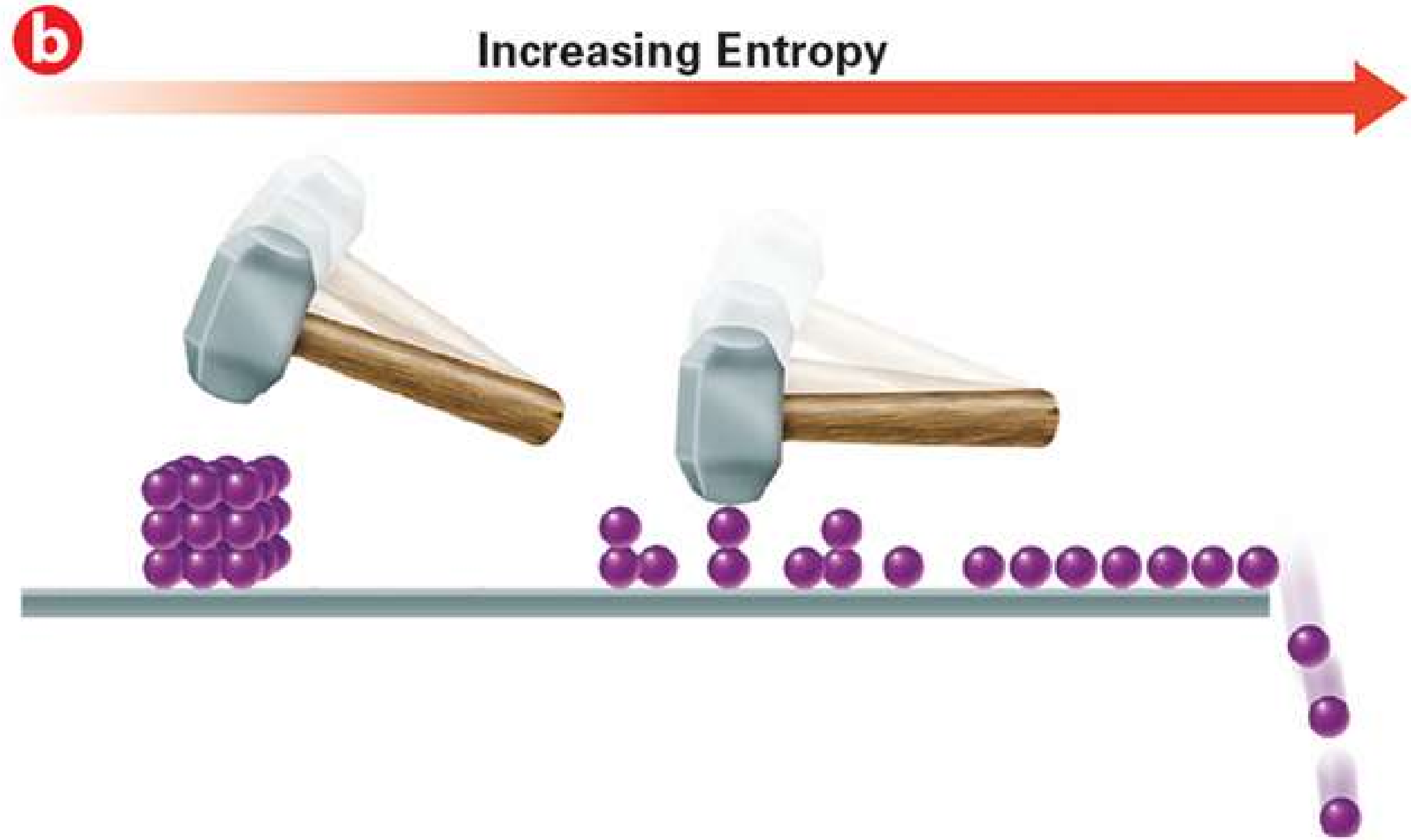
- An increase in entropy favors the spontaneous chemical reaction; a decrease favors the nonspontaneous reaction.

- 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.

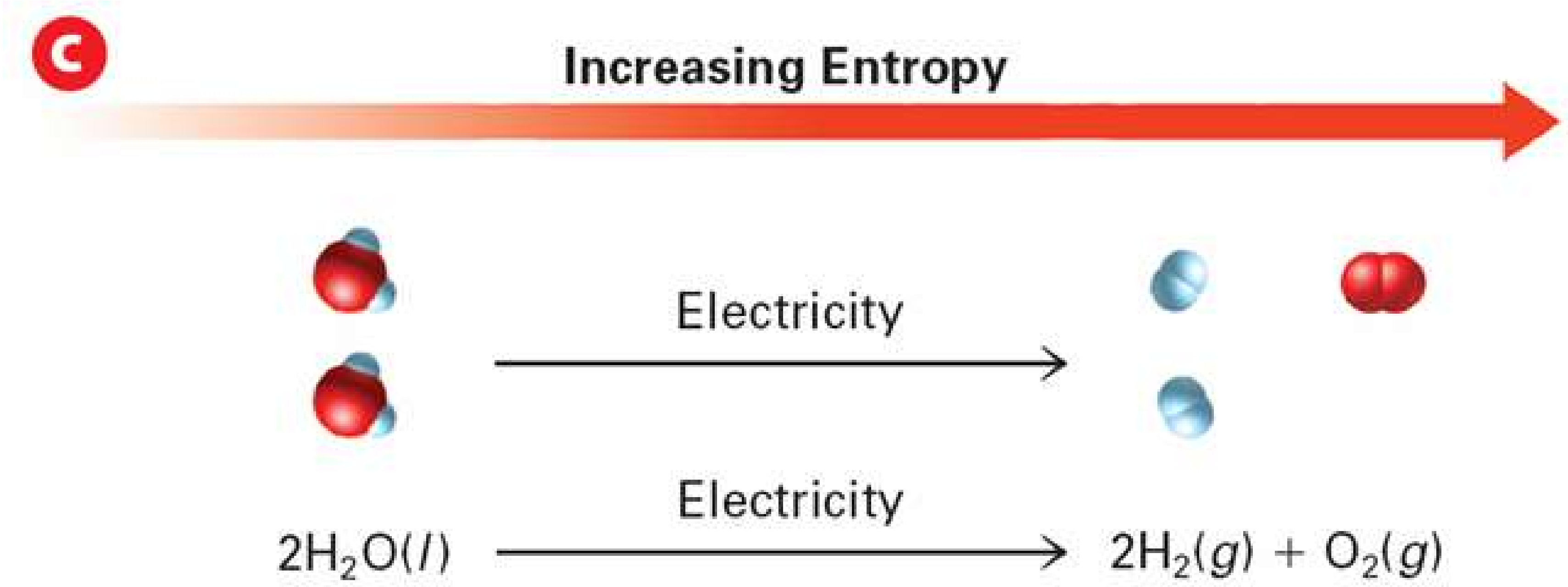


Entropy

- Entropy increases when a substance is divided into parts.

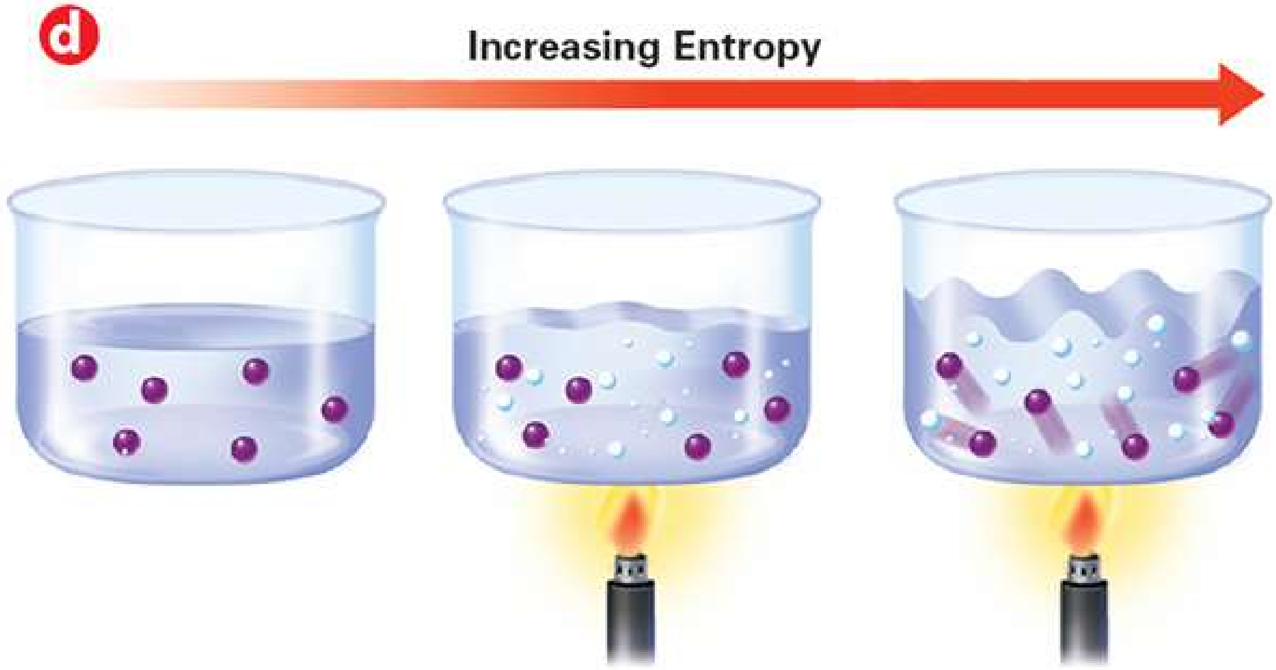


- Entropy tends to increase in chemical reactions in which the total number of product molecules is greater than the total number of reactant molecules.



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

Enthalpy, Entropy, and Free Energy

- The size and direction of enthalpy changes and entropy changes together determine whether a reaction is spontaneous; that is, whether it favors products and releases free energy.

Enthalpy, Entropy, and Free Energy

Table 18.3

How Changes in Enthalpy and Entropy Affect Reaction Spontaneity		
Enthalpy change	**Entropy**	**Spontaneous reaction?**
Decreases (exothermic)	Increases (more disorder in products than in reactants)	Yes
Increases (endothermic)	Increases	Only if unfavorable enthalpy change is offset by favorable entropy change
Decreases (exothermic)	Decreases (less disorder in products than in reactants)	Only if unfavorable entropy change is offset by favorable enthalpy change
Increases (endothermic)	Decreases	No

Gibbs Free-Energy

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

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

- The numerical value of ΔG is negative in spontaneous processes because the system loses free energy.

Example

- For a process, ΔH = 145 kJ and ΔS = 322 J/K. Is the process spontaneous at 382 K?

Practice

- Determine whether the reaction is spontaneous
  - A) $\Delta H = -75.9$ kJ; $\Delta S = 138$ J/K; $T = 273$ K
  - B) $\Delta H = -27.6$ kJ; $\Delta S = -55.2$ J/K; $T = 535$ K
  - C) $\Delta H = 365$ kJ; $\Delta S = -55.2$ J/K; $T = 388$ K

Practice

- Given ΔH = -144 kJ and ΔS = -36.8 J/K for a reaction, determine the lowest temperature in kelvins at which the reaction would be spontaneous.

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. Free energy is always available from reactions that are
  - endothermic.
  - nonspontaneous.
  - at equilibrium.
  - spontaneous.

18.4 Section Quiz.

- 3. Choose the correct words for the spaces: Spontaneous reactions produce __________ and substantial amounts of ___________ at equilibrium.
  - free energy, products
  - no free energy, reactants
  - free energy, reactants
  - no free energy, products

18.4 Section Quiz.

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

18.4 Section Quiz.

- 5. A reaction is spontaneous if
  - enthalpy decreases and entropy increases.
  - enthalpy increases and entropy increases.
  - enthalpy decreases and entropy decreases.
  - enthalpy increases and entropy decreases.

18.4 Section Quiz.

- 6. Choose the correct words for the spaces: Gibbs free-energy change is the ___________ amount of energy that can be _____________ another process to do useful work.
  - maximum, coupled to
  - maximum, duplicated by
  - spontaneous, coupled to
  - minimum, duplicated by