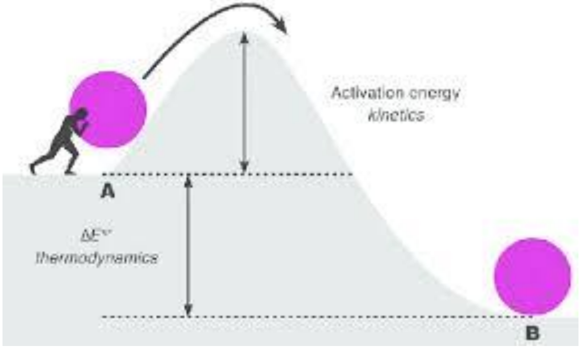
Thermodynamically Favored Reactions

- Will “go” on its own-

- may need a little push activation energy

- Speed of the reaction doesn’t matter



Rates of Reaction

- The heat given off by the corrosion reaction of an iron-magnesium alloy with salt water can produce a hot meal.
- The rate of reaction is increased by adding salt water, so heat is produced rapidly.
- You will learn some ways in which the rate of a reaction can be increased.

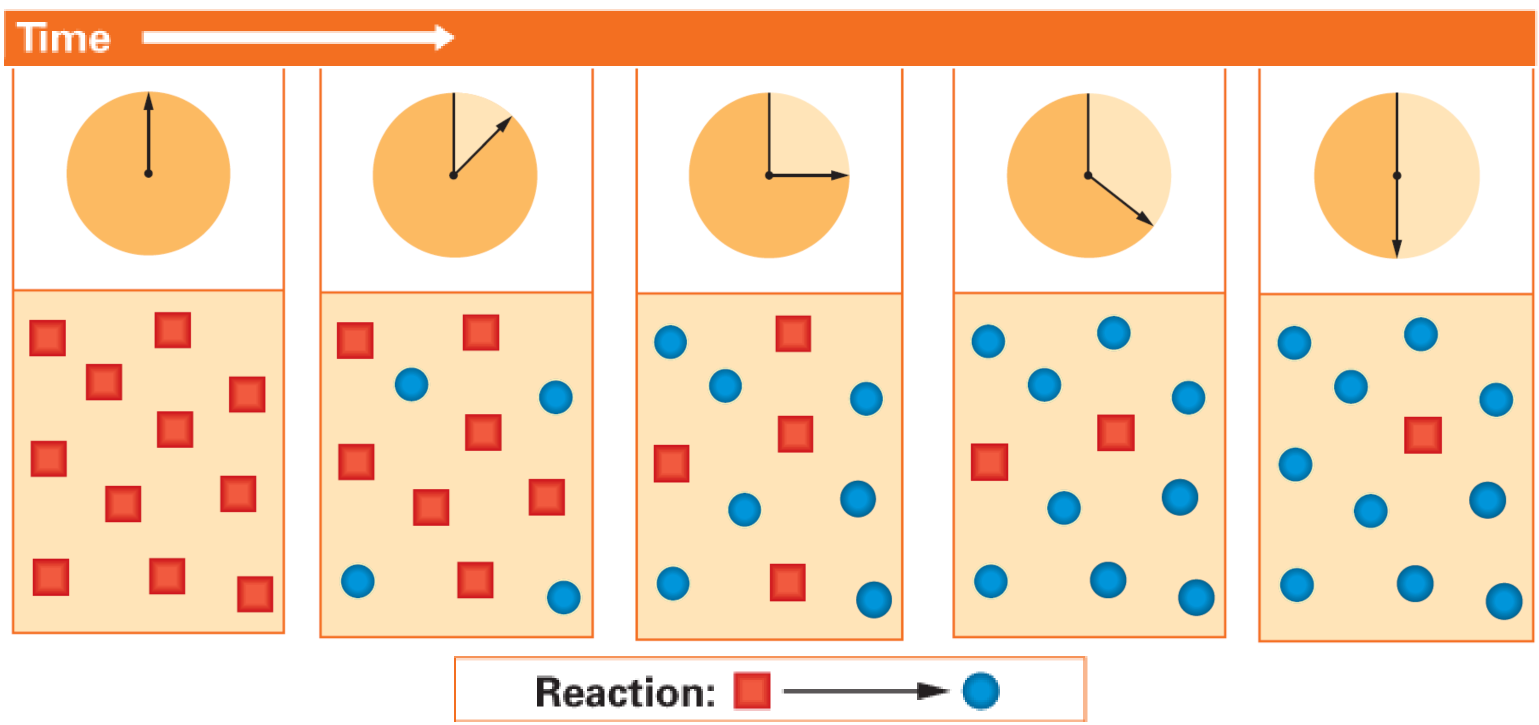
Collision Theory

- The time required for a reaction to take place can vary tremendously.
  - Strike a match ➔ fast
  - Producing crude oil ➔ slow

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

Collision Theory

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

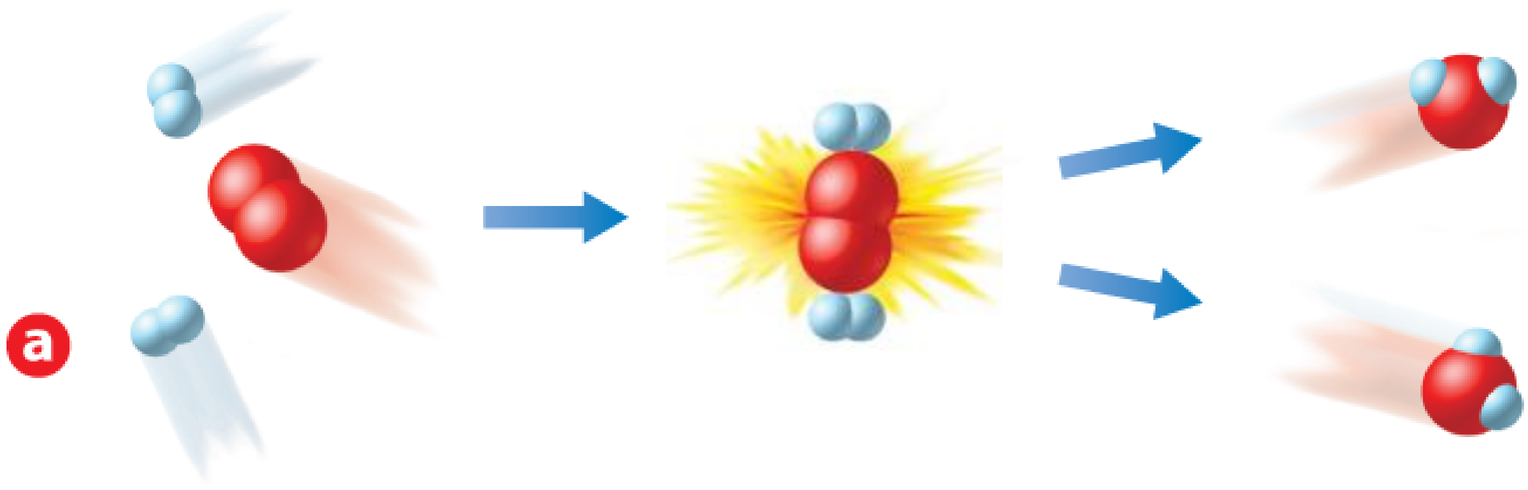


Collision Theory

- 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.**

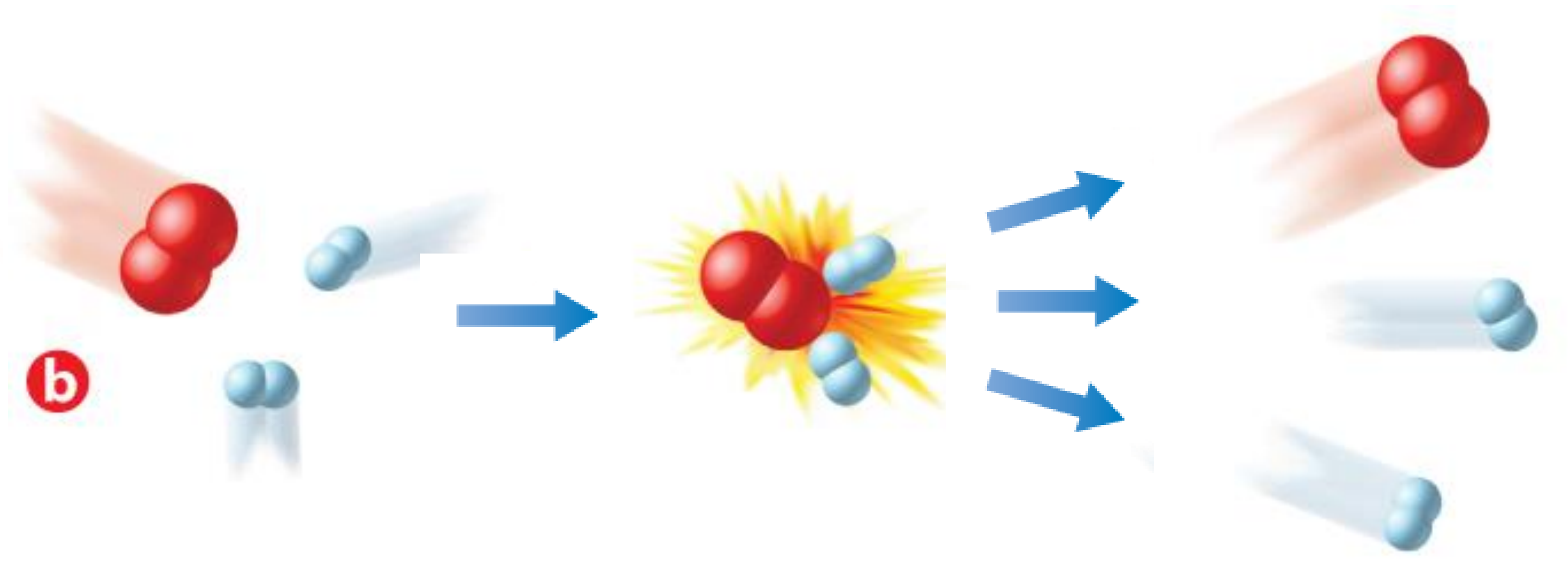
Collision Theory

- **Effective Collision: Product is formed.**

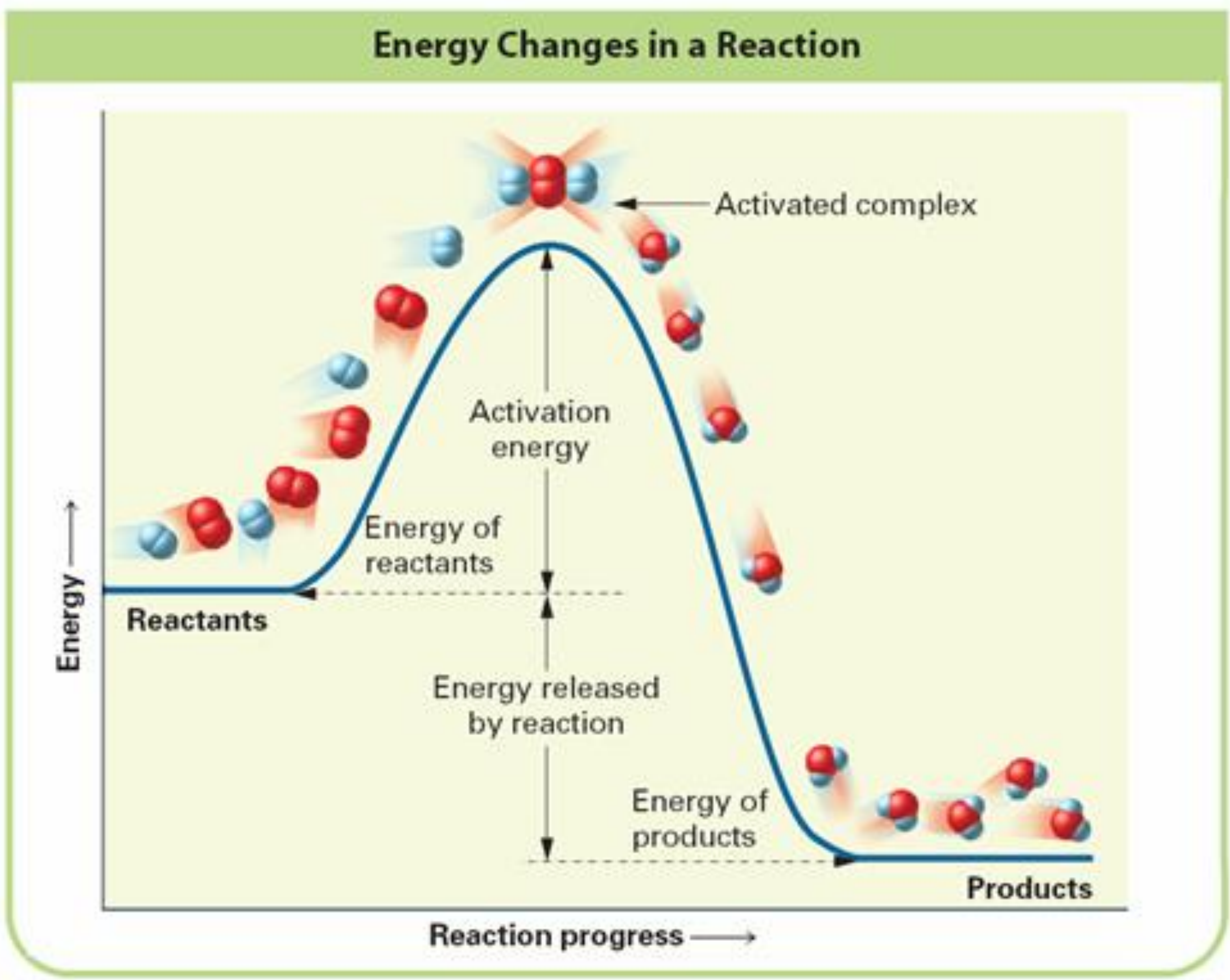


Collision Theory

- **Ineffective Collision: No product formed.**



- 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
- use of a catalyst, pressure and mixing / presence of an inhibitor

Temperature

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

Temperature

- Increasing the temperature tends to speed up a reaction, while decreasing the temperature tends to slow down a reaction.

Temperature

- Increasing the temperature increases the motion of the reactant particles.
  - The particles are moving faster and more chaotic.

- Increasing the temperature increases the number of particles that collide and have enough kinetic energy to react when they collide.

Concentration

- The number of reacting particles in a given volume affects the rate of reaction.

- The more particles you have, the more collisions you will have.

- The more collision you have, the faster the rate of reaction.

Concentration

a. In air, a lighted splint glows and soon goes out.
b. When placed in pure oxygen (higher oxygen concentration), the splint bursts into flame.

Concentration

– Most reactions increase in rate when the concentration of the reactants increases.

$$NO_2 + CO \rightarrow NO + CO_2$$

- Doubling the concentration of NO_2 will double the number of NO_2 molecules, and the number of collisions with CO will double.

Concentration

- Reaction rates decrease with time because the rate depends on the concentration of the reactants.
- As the reaction proceeds, the reactant is consumed and its concentration declines.
- This change in concentration decreases the rate.

Particle size

- Remember: The smaller the particle size, the greater the surface area.

- Increasing surface area increases the amount of reactant exposed for reaction.

- More reactant exposed causes an increase in collisions and therefore an increase in rate.

Particle Size

- The minute size of the reactant particles (grain dust), and the mixture of the grain dust with oxygen in the air cause this reaction to be explosive, destroying the grain elevator.

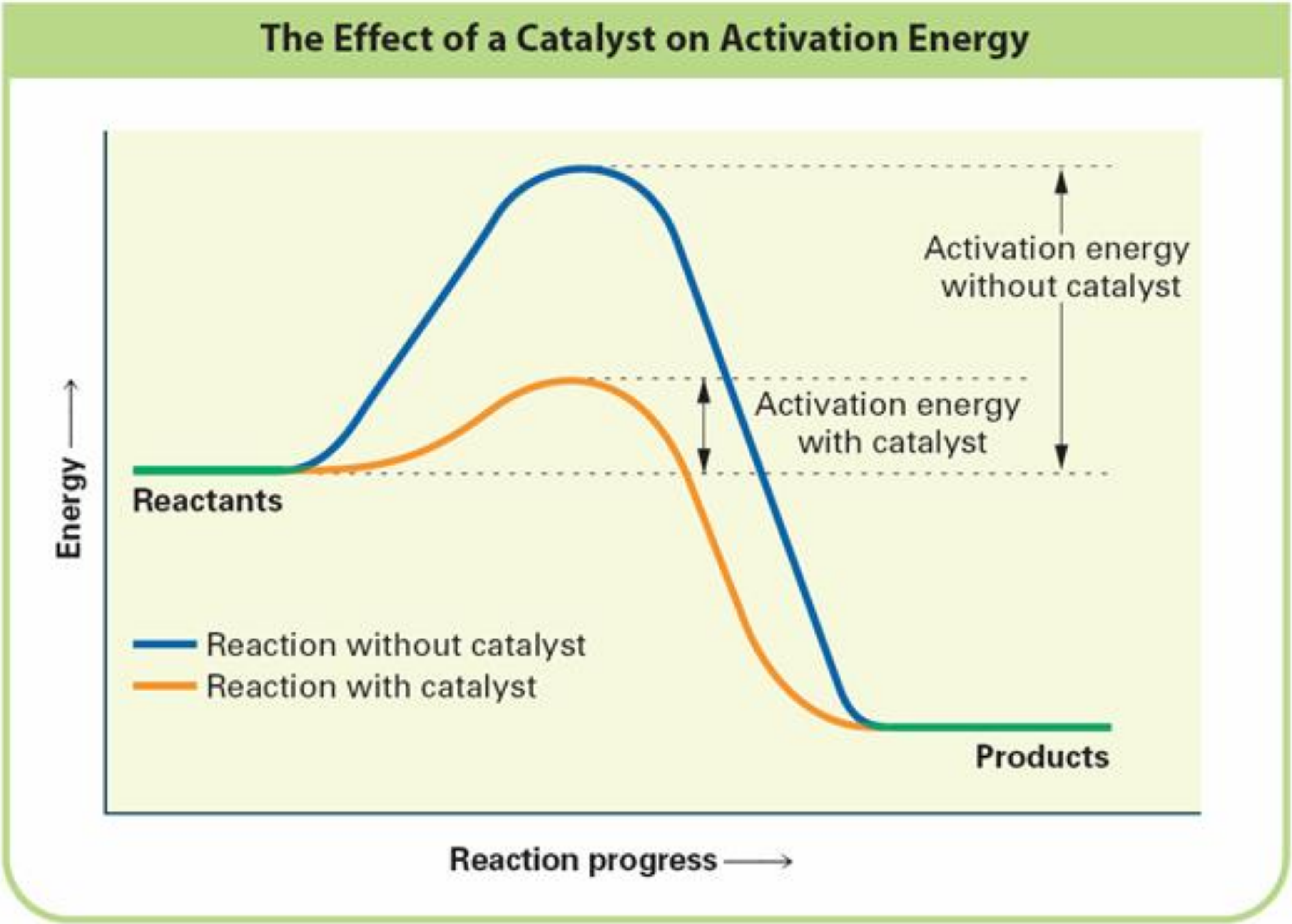
Catalyst

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

- A catalyst increases the rate of a reaction by lowering the activation-energy barrier.

- Enzyme: A protein catalyst that speeds up biological reactions.

Catalysts



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

Inhibitor

- 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.

Pressure

- Pressure has little effect on reactions taking place in the liquid or solid states.
- In the gas phase, increasing the pressure will increase the concentration, therefore increasing the rate of reaction.

Mixing

- Mixing can increase the rate of reaction by increasing collisions.

- Mixing can increase the exposure between reactants.

Rate Laws

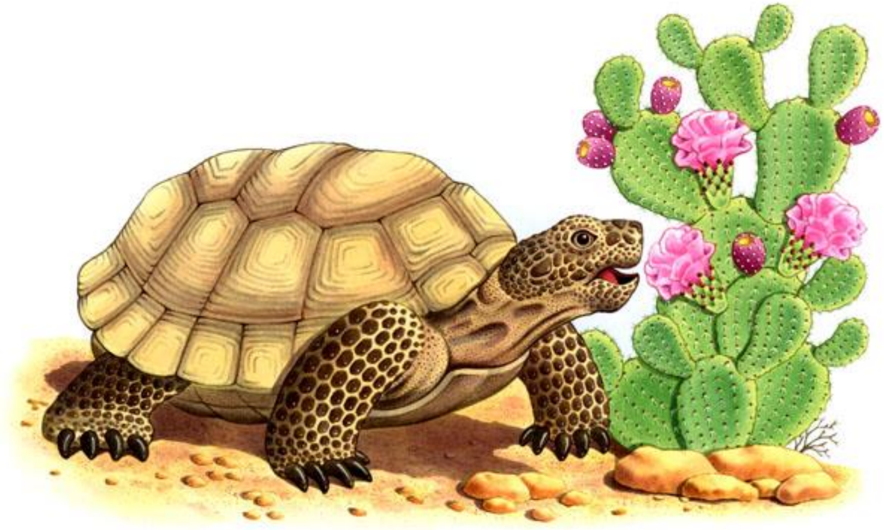
- The **rate law** is an expression for the rate of a reaction in terms of the concentration of reactants.
- In the rate law, a and b represent the **reaction order** with respect to that compound and are independent of the mole ratio in the balanced chemical equation.
- The **specific rate constant** (*k*) for a reaction is a proportionality constant relating the concentrations of reactants to the rate of the reaction.

$$\text{Rate} = k[\text{A}]^a[\text{B}]^b$$

Rate Laws

- The value of the specific rate constant, *k*, is large if the products form quickly;

- the value is small if the products form slowly.



Reversible Reactions and Equilibrium

- In the early 1900s, the German chemist Fritz Haber

  (BAD BAD MAN)
- refined the process of making ammonia from elemental nitrogen and hydrogen.

- This process allows the manufacture of nitrogen fertilizers. (and explosives)

- You will learn how reaction conditions can influence the yield of a chemical reaction.

Reversible Reactions

- At **chemical equilibrium**, or no net change occurs in the actual amounts of the components of the system.
  - Also known as **dynamic equilibrium**, because reactions are still continuing from products to reactants and reactants to products, just at equal rates.
- A **reversible reaction** is one in which the conversion of reactants to products and the conversion of products to reactants occur simultaneously.

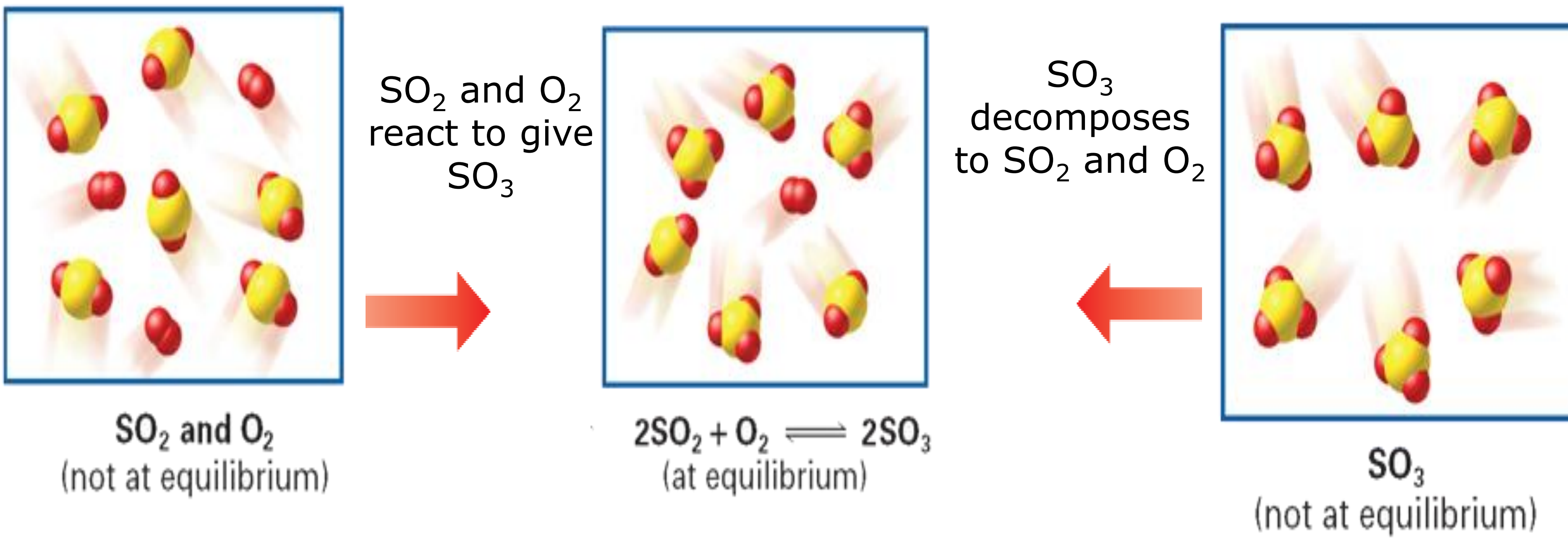
Reversible Reactions

- If the rate of the shoppers going up the escalator is equal to the rate of the shoppers going down, then the number of shoppers on each floor remains constant, and there is an equilibrium.

Reversible Reactions

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

(at equilibrium)



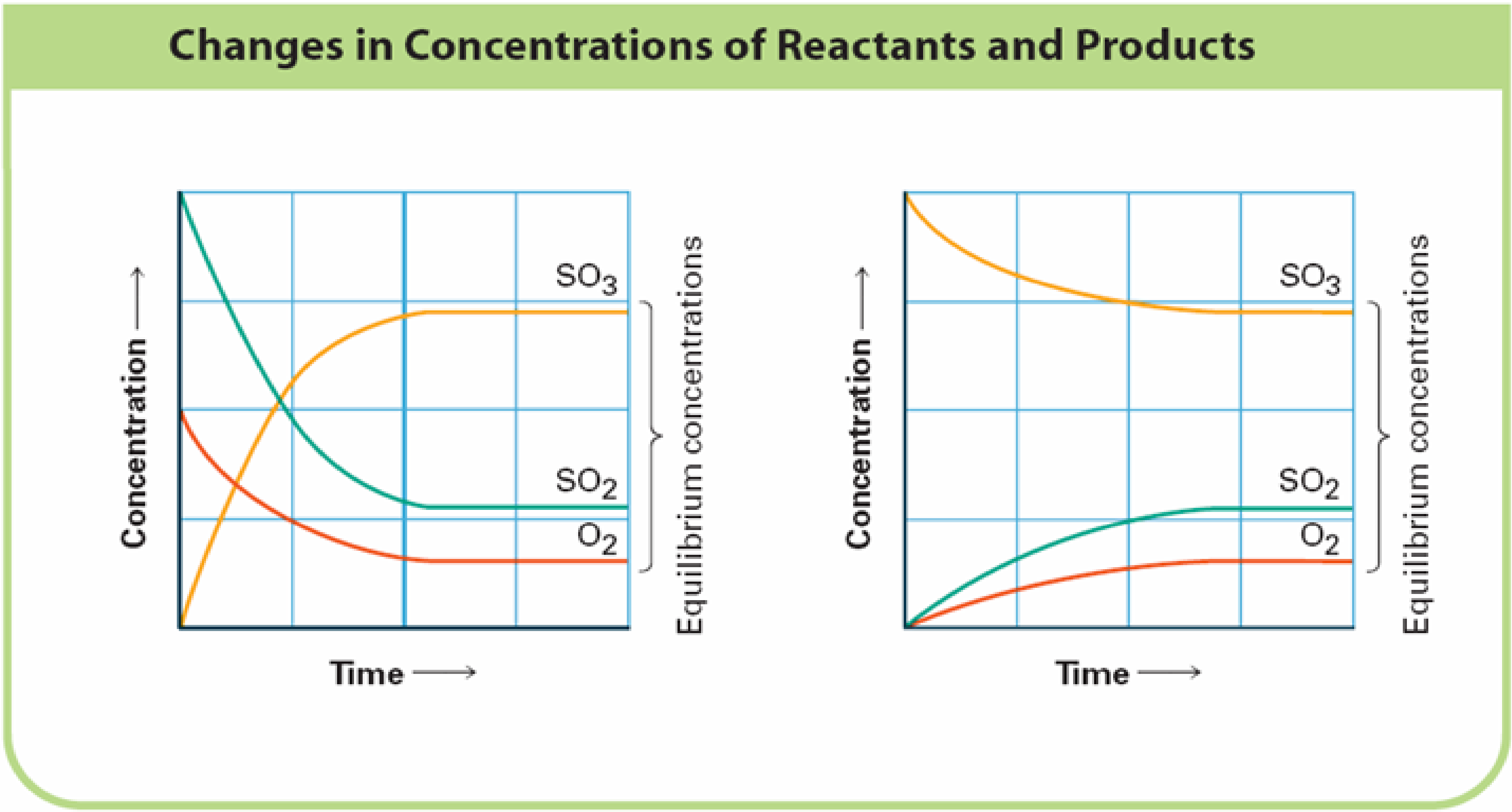
At equilibrium, all three types of molecules are present.

Reversible Reactions

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

- The relative concentrations of the reactants and products at equilibrium constitute the **equilibrium position** of a reaction.

Reversible Reactions



Factors Affecting Equilibrium: Le Châtelier’s Principle

- Stresses that upset the equilibrium of a chemical system include
  - changes in the concentration of reactants or products
  - changes in temperature
  - changes in pressure

Factors Affecting Equilibrium: Le Châtelier’s Principle

- The French chemist Le Châtelier proposed **Le Châtelier’s principle**:

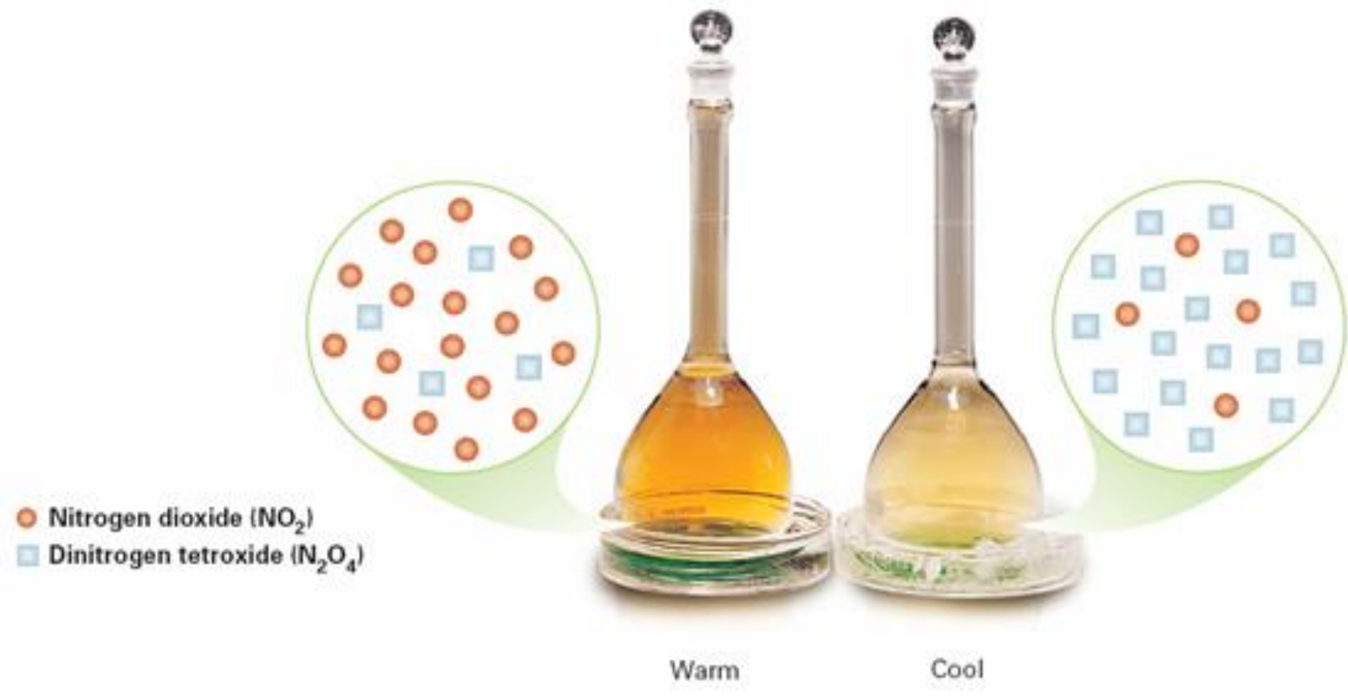
- If a stress is applied to a system in dynamic equilibrium, the system changes in a way that relieves the stress.

Factors Affecting Equilibrium: Concentration

- Rapid breathing during and after vigorous exercise helps reestablish the body's correct CO_2:H_2CO_3 equilibrium, keeping the acid concentration in the blood within a safe range.

Factors Affecting Equilibrium: Temperature

- Dinitrogen tetroxide is a colorless gas; nitrogen dioxide is a brown gas. The flask on the left is in a dish of hot water; the flask on the right is in ice.



Factors Affecting Equilibrium: Pressure

- Pressure affects a mixture of nitrogen, hydrogen, and ammonia at equilibrium

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

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.

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.

Knowns

- $[N_2O_4] = 0.0045$ mol/L
- $[NO_2] = 0.030$ mol/L
- $K_{eq} = \dfrac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$

Unknowns

- K_{eq} (algebraic expression) = ?
- K_{eq} (numerical value) = ?

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.030\ \text{mol/L})^2}{0.0045\ \text{mol/L}}$$

$$= \frac{(0.030\ \text{mol/L} \times 0.030\ \text{mol/L})}{0.0045\ \text{mol/L}} = 0.20$$

Section Quiz.

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

- the amount of NO to increase.
- the amount of NO_2 to increase.
- nothing to happen.
- the amount of O_2 to increase.

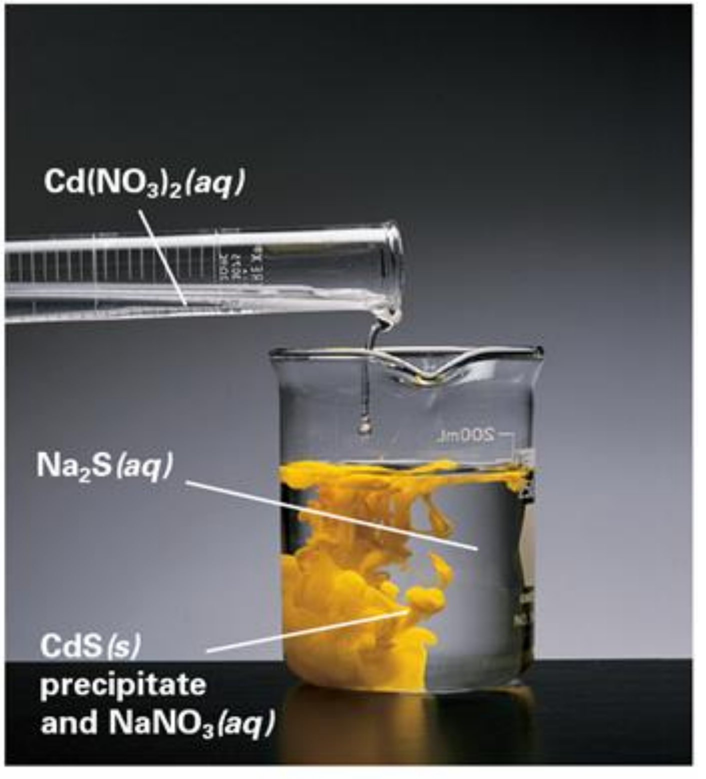
Entropy and Free Energy

- Inside a pile of oily rags or a stack of hay that has not been thoroughly dried, decomposition causes heat to build up.

- When heat cannot escape, the temperature can become high enough to cause a fire.
- You will learn about the conditions that will produce a spontaneous chemical reaction.

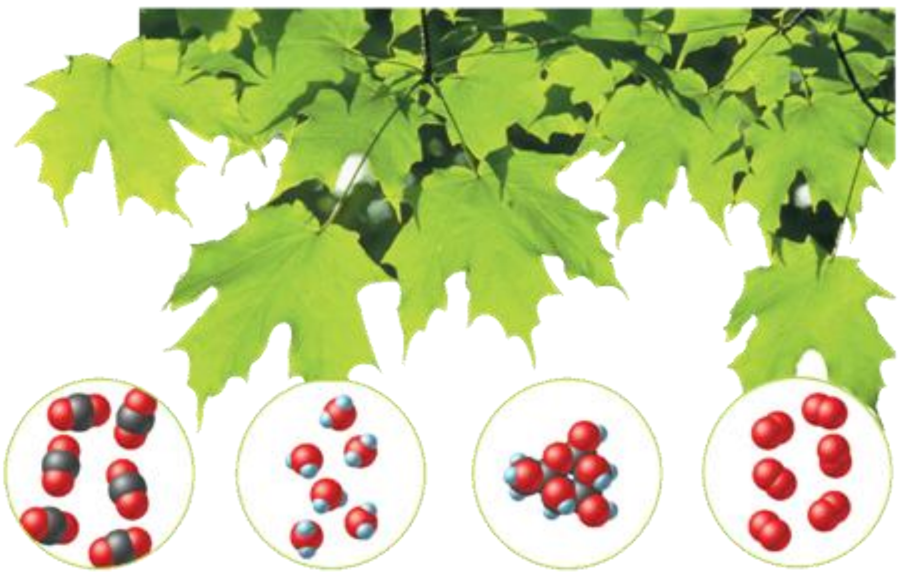
Free Energy & Thermodynamically Favored Reactions

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



Free Energy & Thermodynamically Favored Reactions

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



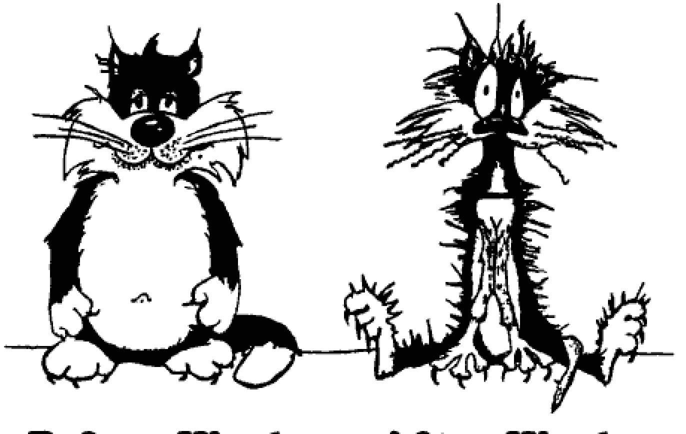
$$6CO_2 + 6H_2O \xrightarrow{\text{light energy}} C_6H_{12}O_6 + 6O_2$$

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

Free Energy and Thermodynamically favored

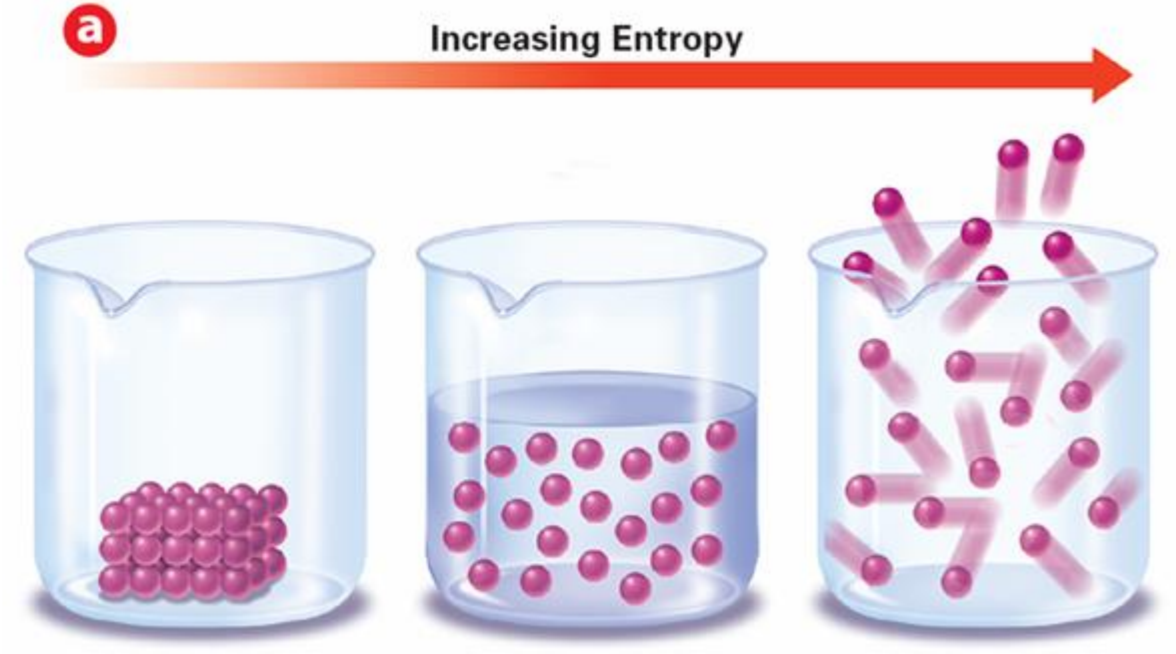
- Spontaneous reactions produce substantial amounts of products at equilibrium and release free energy.

- **Free energy** is energy that is available to do work.



Entropy

- Entropy is a measure of the disorder or randomness of a system.



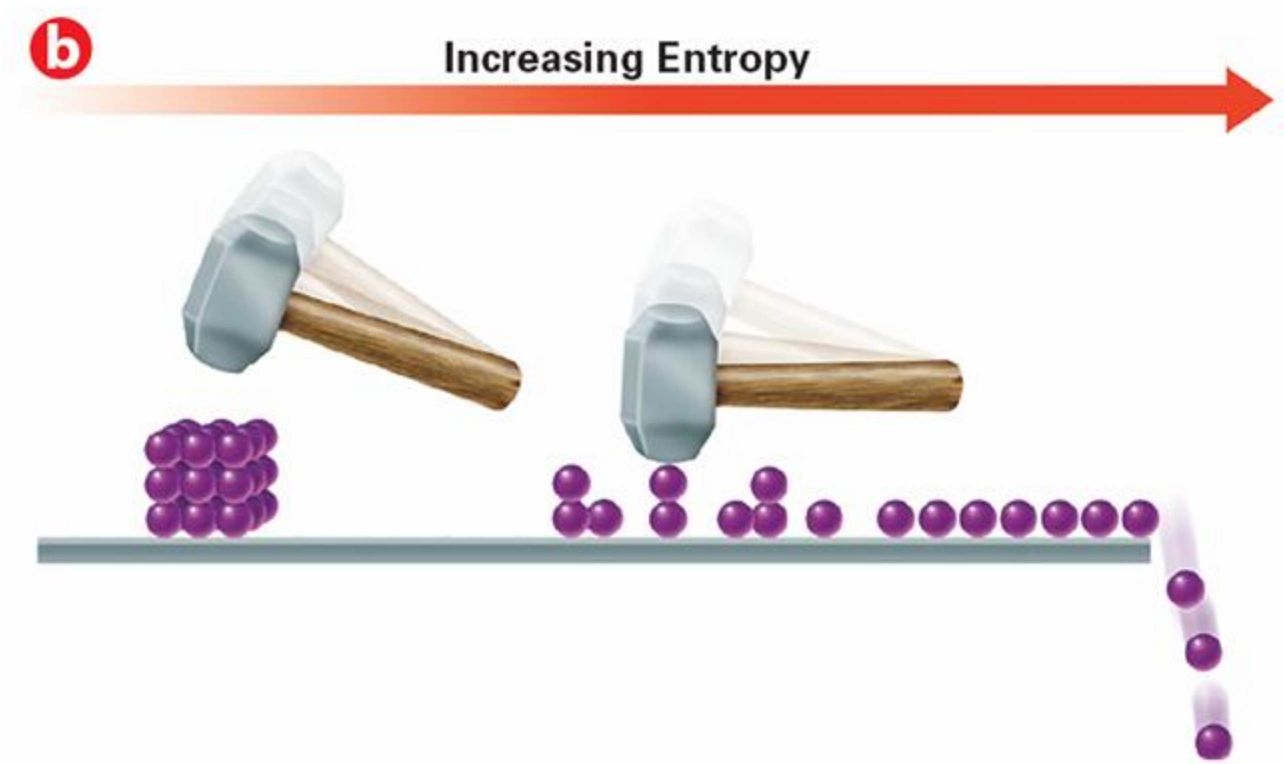
Entropy

- An increase in entropy favors the spontaneous chemical reaction

- A decrease in entropy favors the nonspontaneous reaction.

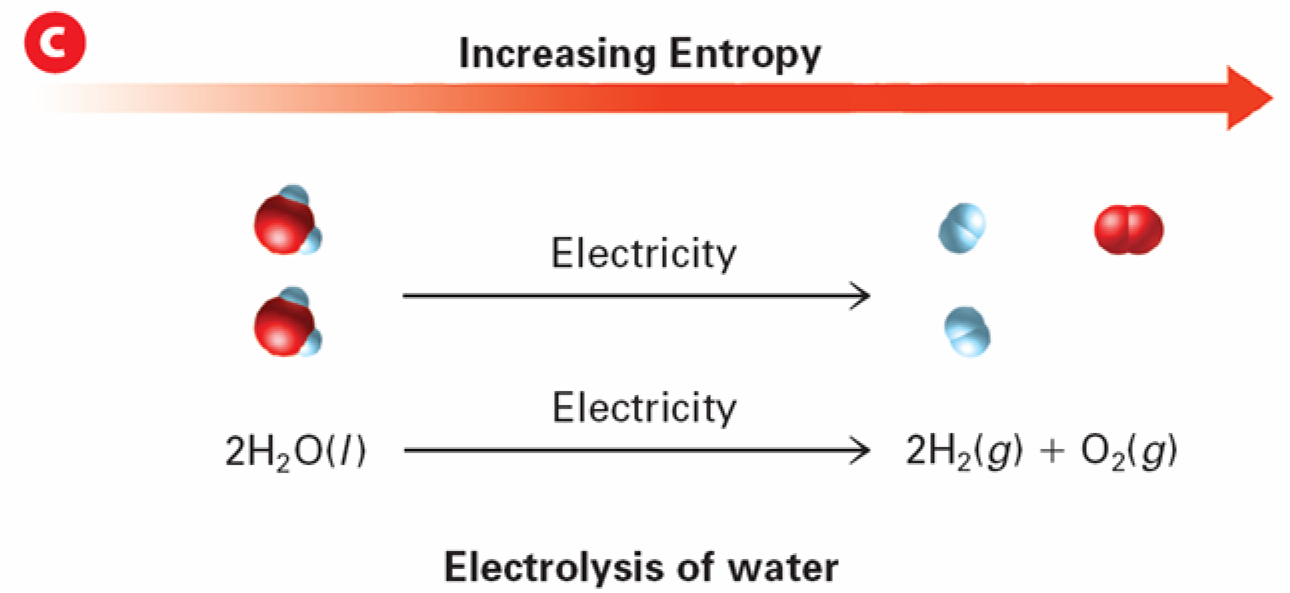
Entropy

- Entropy increases when a substance is divided into parts.



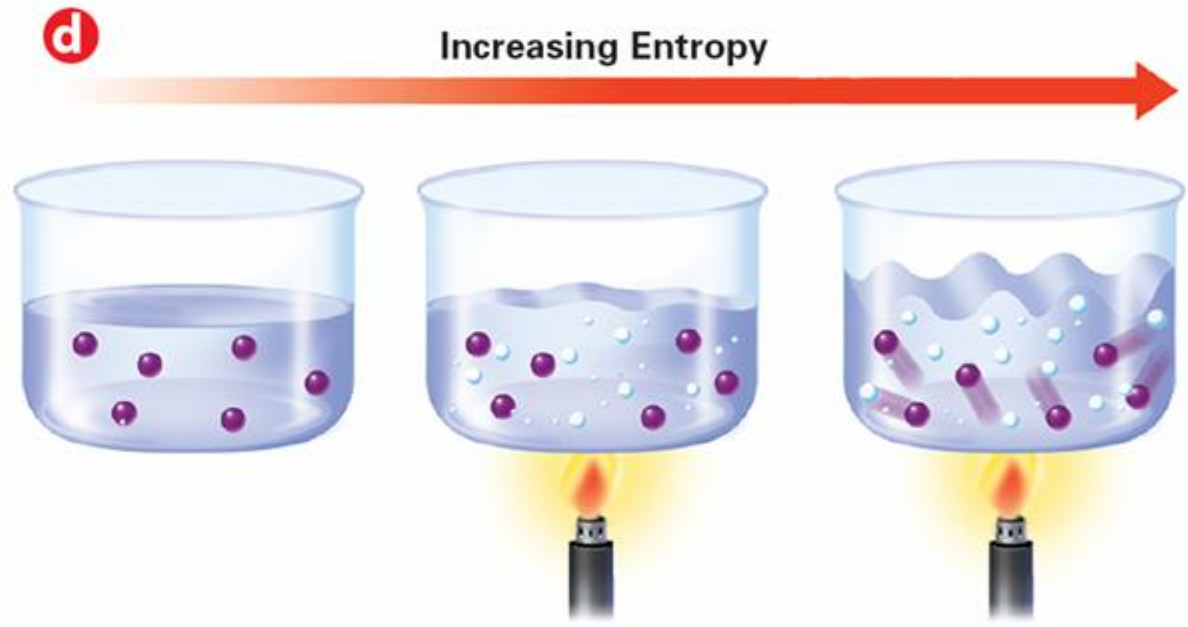
Entropy

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



Entropy

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



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

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.