# Reaction Rates and Equilibrium

### Rates of Reaction

**Essential Question:** 

How is the rate of a chemical change expressed, and what four factors influence the rate of a chemical reaction?

#### Reaction Rates

- The speed of chemical reactions can vary from instantaneous to extremely slow.
- A rate is a measure of the speed of any change per interval time.
- Reaction rate = amount of reactant changing per unit time.

### Collision Theory

- Particles react when they collide with one another.
- The collision must have sufficient kinetic energy to break existing bonds.
- This minimum energy is called activation energy.

### **Energy Diagrams**

### **Energy Changes in a Reaction** Activated complex Activation energy Energy of reactants Energy Reactants Energy released by reaction Energy of products

### **Energy Diagrams**

- Activation Energy minimum energy that colliding particles must have in order to react.
- Activated Complex unstable arrangement of atoms that forms momentarily
- Transition State synonym for the activated complex

### Factors Affecting Reaction Rates

Temperature

Concentration

Particle Size

Presence of a catalyst (or inhibitor)

### Effect of a Catalyst

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### 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** 

# Reversible Reactions and Equilibrium

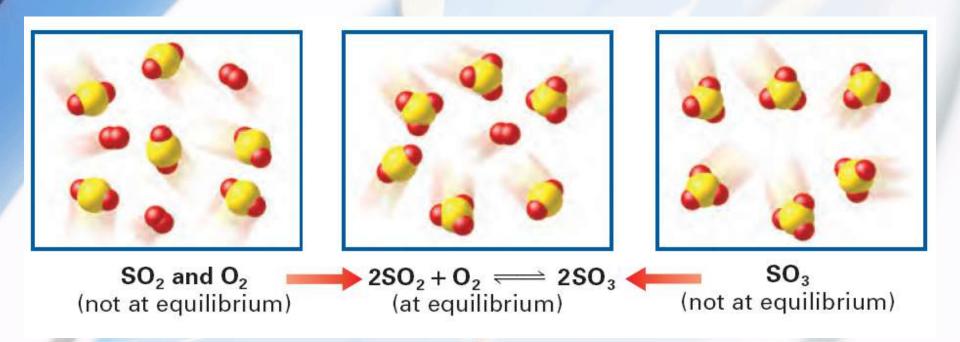
### **Essential Question**

 How do the amounts of reactants and products change at equilibrium, and what three stresses can cause a change in the equilibrium position?

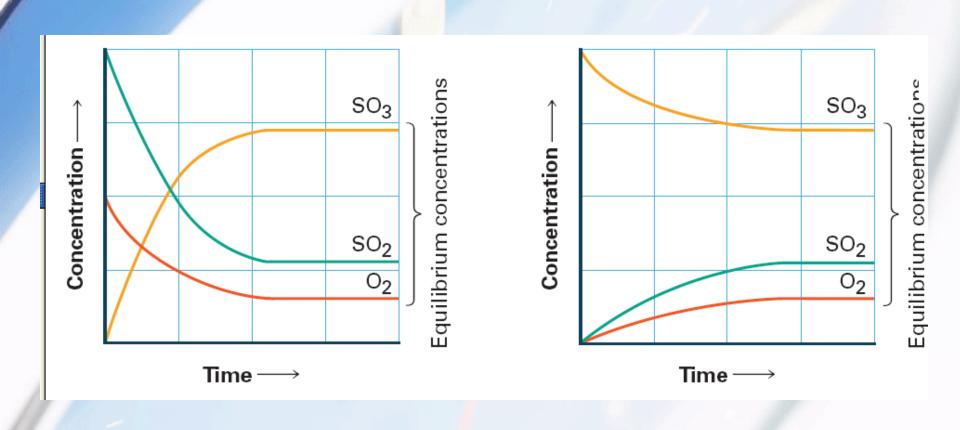
### At Chemical Equilibrium

- Products are being formed...
- ...reactants are being formed...
- ...but no net change occurs in the actual amounts of either the reactants or products.

### Reversible Reactions



### **Changes in Concentrations**



### Equilibrium Position

 Expresses the relative concentrations of reactants and products at equilibrium.

Certain factors can affect this position

### 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."

### **Equilibrium Constants**

 The ratio of product concentrations to reactant concentrations at equilibrium

 Each concentration is raised to a power equal to their coefficient in a balance chemical equation.

### **Equilibrium Constants**

$$aA + bB \rightleftharpoons cC + dD$$

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

### What Keq Tells Us

- K<sub>eq</sub> greater than 1 means that products are favored
- K<sub>eq</sub> less than 1 means that reactants are favored
- K<sub>eq</sub> equal to 1 means that products and reactants are equally favored

### Factors Affecting Equilibrium

Changes in concentration of reactants or products

Changes in temperature

Changes in pressure (of gases)

### Changes in Concentration

$$\begin{array}{c} \operatorname{Add}\operatorname{CO_2}\\ \operatorname{H_2CO_3}(aq) \xrightarrow{\leftarrow \operatorname{Direction} \text{ of shift}} \operatorname{CO_2}(aq) + \operatorname{H_2O}(l) \\ \\ \operatorname{Remove}\operatorname{CO_2}\\ <1\% & \operatorname{Direction} \text{ of shift} \rightarrow \end{array} >99\% \end{array}$$

### Changes in Temperature

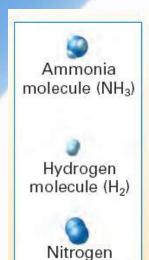
$$2SO_2(g) + O_2(g) \xrightarrow{\leftarrow \text{Direction of shift}} 2SO_3(g) + \text{heat}$$

$$\stackrel{\text{Remove heat (cool)}}{\longrightarrow} \text{Direction of shift} \rightarrow$$

### Changes in Pressure

$$N_2(g) + 3H_2(g) \xrightarrow{\begin{array}{c} \text{Direction of shift} \rightarrow \\ \text{Reduce pressure} \end{array}} 2NH_3(g) \\ \leftarrow \text{Direction of shift} \end{array}$$

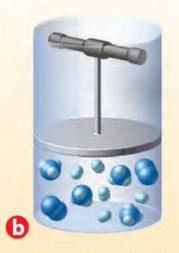
### Effect of Pressure on Equilibrium



molecule (N<sub>2</sub>)



Initial equilibrium condition (11 gas molecules)



Pressure increased, equilibrium disturbed



New equilibrium condition at increased pressure (9 gas molecules)

### Solubility Equilibrium

### **Essential Question**

 What does the solubility product constant tell you about the solubility of a compound, and how can you predict whether a precipitate will form when salt solutions are mixed?

### Solubility Product Constant

Takes the same form as equilibrium constants

• AgCl(s) 
$$\rightarrow$$
 Ag<sup>+</sup>(aq) + Cl<sup>-</sup>(aq)

$$K_{eq} = \frac{[Ag^+] \times [Cl^-]}{[AgCl]}$$

#### Common Ion Effect

 Lowering the solubility of an ionic compound as a result of the addition of a common ion

 If the product of the concentrations of two ions in the mixture is greater than K<sub>sp</sub> of the compound formed from the ions, a precipitate will form.

## Entropy and Free Energy

### **Essential Question**

 What two factors determine the spontaneity of a reaction, and what are the characteristics of spontaneous reactions?

### **Spontaneous** Reactions

Occur naturally and favor the formation of products

 Produce substantial amounts of products at equilibrium

### Nonspontaneous Reactions

Does not favor the formation of products

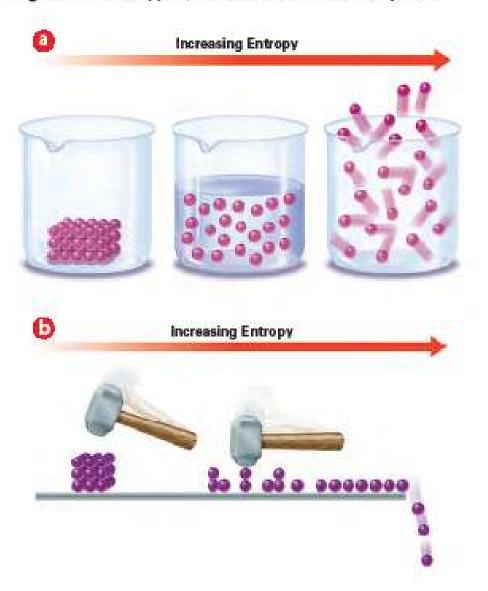
 Do not produce substantial amounts of products at equilibrium

Note: Speed is NOT a factor

### **Entropy Changes**

- A measure of the disorder of a system
- Law of Disorder: the natural tendency is for systems to move in the direction of maximum disorder or randomness
- An increase in entropy favors spontaneous chemical reactions

Figure 18.24 Entropy is a measure of the disorder of a system.

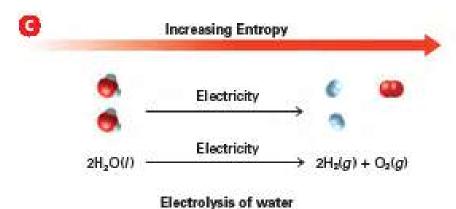


For a given substance, the entropy of the gas is greater than the entropy of the liquid or the solid. Similarly, the entropy of the liquid is greater than that of the solid. Thus entropy increases in reactions in which solid reactants form liquid or gaseous products. Entropy also increases when liquid reactants form gaseous products.

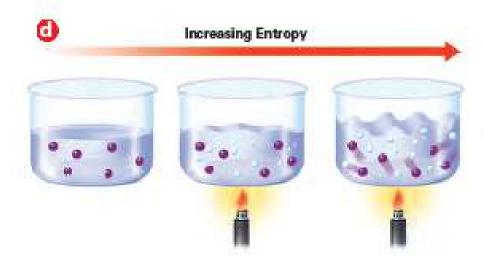
Entropy increases when a substance is divided into parts. For instance, entropy increases when a crystalline ionic compound, such as sodium chloride, dissolves in water. This is because the solute particles sodium ions and chloride ions—are more separated in solution than they are in the crystal form.



water. This is because the solute particles sodium ions and chloride ions—are more separated in solution than they are in the crystal form.



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

### **Enthalpy Changes**

- The decrease in enthalpy (exothermic reactions) indicates a spontaneous reaction.
- An increase in enthalpy (endothermic reactions) indicates a non-spontaneous reaction.

### The Progress of Reactions

### **Essential Question**

 What does the specific rate constant, k, communicate and how does one interpret a reaction progress curve?

### Specific Rate Constant

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

The value is small if the products form slowly.