CHAPTER 18
Reaction Rates and Equilibrium

18.1 Rates of Reaction

• The time needed to complete a chemical reaction can vary tremendously

• Rates measure changes that occur within intervals of time.

• In chemistry, rates or speeds are expressed in chemical terms

Collision Theory
Atoms, ions, and molecules must collide in order to react
Atoms, ions, and molecules can form a chemical bond when they collide, as long as the particles have enough kinetic energy and have the proper orientation.

Many atoms collide all the time, but never react because there is not enough energy or they do not collide with the proper orientation.

For a chemical reaction to occur
3 things required according to the Collision Theory
1. Atoms must collide
2. Atoms must collide with enough energy
3. Substances must collide with the correct orientation

If the 3 things occur and a chemical reaction takes place
• There is a rearrangement of Atoms
• Bonds break in reactants
• Bonds form in products
• \( \Delta H = \text{Final Energy} - \text{Initial Energy} \)

Effective Collisions
Favorable Orientations
• The Nitrogen in the NO molecule must collide with the top Oxygen in the \( O_3 \) molecule or else the molecules will bounce off each other.
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**Chemical Reactions**
- Rearrangement of Atoms
- Bonds break in reactants
- Bonds form in products
- \( \Delta H = \text{Final Energy} - \text{Initial Energy} \)

*Three things required for reaction:*
- Atoms must collide
- Atoms need enough kinetic energy
- They must collide with proper orientation

**Activation Energy**
- The minimum energy that particles must have in order to react.
- Even if molecules collide with a favorable orientation, they still need a sufficient amount of energy to react.
- It is the point that reactants must cross to form products.
- High activation energy (\( E_a \)) reactions will not occur easily & often
- Low activation energy (\( E_a \)) reactions will occur easily & often

**Activated Complex**
- Forms only if the colliding particles have sufficient energy and are oriented properly.
- Lasts momentarily, \((10^{-13} \text{ second})\)
- Unstable arrangement of atoms.

**Transition State**
- Also called the Activated Complex.
- This is the first thing that must happen in order for a chemical reaction to occur.
- In this state, the activated complex can go back to the reactants or end with the formation of products.
- Has a great deal of energy!
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**Exothermic**

\[ A + B \rightarrow C + D + \text{Energy} \]

- Energy Stored in bonds of A + B
- Reactions occur easily
- Bonds in A + B were broken when activation energy was met.
- When C + D formed, energy was released.

**Activation Energy = 300 kJ**

*Exothermic Reaction*

The \( \Delta H \) is not changed by the activation energy.

The \( \Delta H \) is the difference between the energy stored in the reactants and the energy stored in the products.

**Endothermic**

\[ A + B + \text{Energy} \rightarrow C + D \]

- No energy Stored in bonds of A + B
- Require a lot of energy to react
- Bonds in A + B were broken when activation energy was met.
- When C + D formed, the excess energy was stored in their bonds.

**Activation Energy = 750 kJ**

*Endothermic Reaction*

The \( \Delta H \) is not changed by the activation energy.

The \( \Delta H \) is the difference between the energy stored in the reactants and the energy stored in the products.

**Factors Affecting Reaction Rates**

Depends on the reactive nature of the elements

Remember, some substances are more reactive than others based on their electron arrangement.
FACTORS AFFECTING REACTION RATES

These Increase collisions and/or kinetic energy

- Temperature
- Concentration
- Particle Size
- Catalysts

Concentration
- Higher concentration increases collision rate.
- This speeds up reaction rate.
- Magnesium in 6M HCl vs. Magnesium in 1M HCl.
  > High concentration = more dissolved particles
- Flame in air vs. flame in pure oxygen.

Surface Area
- Smaller particles increase surface area, which increases reaction rate.
- Large particles have a lot of atoms inside, which are unable to react since they are not exposed to other reactants.
- How to increase surface area?
  > Grinding substance into a powder.
  > Dissolving substances.

Temperature
- Raising temperature usually speeds up the reaction and lowering the temperature usually slows it down.
- Increasing temperature causes more collisions between particles and raises their kinetic energy.

Catalysts
- Are used when increasing temperature and concentration is not an option.
- Lowers activation energy and increases the rate of a reaction without being used up itself.
- The faster rate allows reactions to occur with less energy.
- Enzymes break down protein.
- Catalysts DO NOT change ΔH.
Inhibitors
• a substance that interferes with the action of a catalyst. (Preservatives, medications)
• React with the catalyst or change the catalyst.
• The catalyst is then used up or different.

18.2 Reversible Reactions
A reaction that can occur in both the forward and reverse direction. These are really two reactions.
The double arrow indicates a reaction is reversible.
• \( \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \) \text{Forward Reaction}
• \( \text{N}_2(g) + 3\text{H}_2(g) \leftrightharpoons 2\text{NH}_3(g) \) \text{Reverse Reaction}
• \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \)

Reversible Reactions
The forward and reverse reactions can occur simultaneously
The rate of the forward and reverse reactions depends on the concentration of the substances.
At first, there cannot be a reverse reaction
• \( \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \) \text{Forward Reaction}
• \( \text{N}_2(g) + 3\text{H}_2(g) \leftrightharpoons 2\text{NH}_3(g) \) \text{Reverse Reaction}
• \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \)

Chemical Equilibrium
The state in which the forward and reverse reactions balance each other because they take place at equal rates
\[
\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}
\]
This does not mean that the concentrations of the products equals the concentrations of the reactants
Typically gases and aqueous solutions!!!
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**Two houses at equilibrium**

| 5 People | 25 People |

**Le Chateliers’s principle**

If a stress is applied to a system in a dynamic equilibrium, the system changes to relieve the stress.

**FACTORS AFFECTING EQUILIBRIUM**

Factors that cause SHIFTS:
- Changes in concentration *(Amount)*
- Changes in Temperature
- Changes in Pressure *(gases only)*

**Changes in Concentration**

- Add reactant at equilibrium & it will shift the reaction toward the products.
- Removing reactant will shift the reaction toward the reactants.

**Changes in Temperature**

- Increase Temperature at equilibrium & the reaction will shift in the direction that absorbs heat. *(Endothermic)*
- Removing heat will shift it toward the side that releases heat. *(Exothermic)*

**2A(g) + B(g) ⇌ 3C(g) + 4D(g) + Heat**

- Add B
- Remove A
- Add C
- Remove D
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2A(g) + B(g) $\rightleftharpoons$ 3C(g) + 4D(g) + Heat

- Increase temperature
- Lower the temperature

Changes in Pressure/Volume

NO gases = NO SHIFT

- Affects only gases at Equilibria.
- Add pressure and the rxn shifts toward the side with the fewest gas molecules.
- Reduce pressure and it shifts to the side with more gas molecules.

2A(g) + B(g) $\rightleftharpoons$ 3C(g) + 4D(g) + Heat

- Raise the pressure
- Decrease Pressure

Equilibrium Constant

- The numerical value of the ratio of product concentration compared to the reactant concentration.
- Occurs only had a specified temperature.
- If the $K_{eq} > 1$, then more products exist at equilibrium.
- If the $K_{eq} < 1$, then more reactants exist at equilibrium.
- A $K_{eq}$ of 5 versus a $K_{eq}$ of 1/5. What does this mean?

EQUILIBRIUM CONSTANTS

- Relate the amounts of reactants to products at equilibrium
- Equilibrium formula

\[ aA + bB \rightleftharpoons cC + dD \]

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

Remember, the coefficients give you the ratio of the reactants and products.
Example Problem #1

\[
\begin{align*}
\text{H}_2(g) + \text{I}_2(g) & \rightleftharpoons 2\text{HI}(g) \\
3 \text{ mol/L of HI are at equilibrium with 1.5 mol/L of H}_2 \text{ and I}_2 \text{, what is the equilibrium constant?}
\end{align*}
\]

\(K_{eq} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}\)

Example Problem #2

\[
\begin{align*}
\text{N}_2(g) + 3\text{H}_2(g) & \rightleftharpoons 2\text{NH}_3(g) \\
[\text{N}_2] = 0.5 \text{ mol/L, } [\text{H}_2] = 0.2 \text{ mol/L, } [\text{NH}_3] = 0.02 \text{ mol/L}
\end{align*}
\]

\(K_{eq} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}\)

EQUILIBRIUM CONSTANTS

Only includes gases and aqueous solutions!

Do not use liquids or solids when using the equilibrium constant.

Calculating Equilibrium Concentrations

- Knowing the equilibrium constant can help to determine the concentrations of a reactant or product at equilibrium.

\[
\begin{align*}
\text{CO(g) + 3H}_2 & \rightleftharpoons \text{CH}_4(g) + \text{H}_2\text{O(g)} \\
\text{At } 1200 \text{ K, the } K_{eq} \text{ for the reaction is 3.933.}
\end{align*}
\]

Example Problem

- At 1200 K, the \(K_{eq}\) for the reaction is 3.933.
- The known concentrations are:
  \(\text{CO} = 0.850-\text{M}, \text{H}_2 = 1.333-\text{M}, \text{H}_2\text{O} = 0.286-\text{M}\)

\[
\begin{align*}
\text{CO(g) + 3H}_2 & \rightleftharpoons \text{CH}_4(g) + \text{H}_2\text{O(g)} \\
K_{eq} & = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} \\
& = \frac{0.850[1.333]}{[0.286]^3} \\
& = 27.7-\text{M}
\end{align*}
\]
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Forward is Exothermic:
- Increase Temp, K decreases
- Decrease Temp, K increases

Forward is Endothermic:
- Increase Temp, K increases
- Decrease Temp, K decreases

When does Equilibrium Constant (K) change?
- Not if concentration changes.
- Not if pressure changes.
- Only if temperature changes.

Test Question
Which will cause the Equilibrium constant to decrease in the following reaction?

\[ 2A(g) + B(g) \rightleftharpoons 3C(g) + 4D(g) + \text{Heat} \]

A. Removing substance B
B. Decreasing Temperature
C. Increasing Pressure
D. Increasing Temperature.

18.4 Enthalpy vs. Entropy

- The heat change (enthalpy) is not the only factor in determining whether a reaction will be spontaneous.
- Entropy is the measure of the disorder or randomness that the particles of a system possess.
- The Law of Disorder states that particles tend to be arranged randomly and that spontaneous processes increase the entropy in the universe.

ENTROPY

- The disorder of a system is measured as its entropy.
- The law of disorder states that things move in the direction of maximum disorder or randomness.
  
  Low = Packed  
  High = spread out
**Predicting Entropy Change ΔS**

1. Solids → Liquids → Gases
2. Dissolving gases in a solvent decreases entropy
3. When products have more gas particles than the reactants
4. A solid or liquid is dissolved in a solution increases entropy
5. Increasing temperature increases entropy

Reactants with High Entropy are less likely to react because they collide less due to their randomness.

Reactants with Low Entropy are more likely to react because they collide more due to their fixed positions.

Entropy increases when:
- Solid reactants give gas or liquid products
- Liquid reactants give gas products

Entropy of phases:
- Gases > Liquids > Solids

**Changing the number of parts**

Entropy increases when a substance is divided into parts

Dissolved substances

Ionic compounds are dissolved in water and become more separated.

**Enthalpy = ΔH**

- Exothermic: energy stored in reactant
  > \( A + B \rightarrow C + \text{Heat} \)
  > Spontaneous

- Endothermic: reactants have no energy
  > \( A + \text{Heat} \rightarrow B + C \)
  > Nonspontaneous
ΔS\_universe = ΔS\_system + ΔS\_surrounding

The ΔS\_universe is positive, then it is a spontaneous process.
- The entropy of the surroundings increases during an exothermic reaction because heat is released, making the ΔS\_surrounding positive.
- The entropy of a system increases, causing the ΔS\_system to be positive.

Entropy Increase
- Fewer particles to more particles
- Solid → Gas
- Liquid → Gas
- More disorder and randomness on products side

Entropy Decrease
- More particles to fewer particles
- Gas → Solid
- Gas → Liquid
- More disorder and randomness on reactants side

Number of Molecules
- Entropy increases when the total number of product molecules is greater than the number of reactant molecules.
- 2H\_2 + O\_2 ⇌ 2H\_2O + heat
- 3 molecules ⇌ 2 molecules
- Entropy decreased

Ideal Spontaneous Reaction
1. Exothermic: releasing energy
   - Enthalpy Decrease, -ΔH
2. Entropy Increase: high disorder & randomness = many collisions
   - N\_2 → 2N + heat

C\_6H\_12O\_6(s) + 6O\_2(g) → 6CO\_2(g) + 6H\_2O(l) + HEAT

1) Exothermic → ΔH
   Enthalpy Decrease

2) Entropy Increase
   Solid + gas → liquid + Gas
**Ideal NonSpontaneous Reaction**

1. **Endothermic**: absorb energy
   - Enthalpy Increase, $\Delta H^+$
2. **Entropy Decrease**: low disorder & randomness = no collisions
   - $2N + \text{heat} \rightarrow N_2$

$\text{Hg}_2^0 + \text{Br}_2^0 + \text{Free Energy} \rightarrow \text{HgBr}_2^0$

1.) Endothermic
   - Enthalpy Increase
2.) Entropy Decrease
   - liquids $\rightarrow$ solid

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**Reaction Scenarios**

- The following diagrams are “hypothetical” scenarios that will occur if a reaction takes place.
- Look at the scenarios and determine whether or not the reaction will be spontaneous or nonspontaneous.

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**Spontaneous or Nonspontaneous**

1. **Enthalpy**: $(-\Delta H)$ Large Release, **Entropy**: Large Increase
2. **Enthalpy**: $(+\Delta H)$ Large Gain, **Entropy**: Large Decrease
3. **Enthalpy**: $(+\Delta H)$ Small Gain, **Entropy**: Large Increase
4. **Enthalpy**: $(-\Delta H)$ Small Loss, **Entropy**: Large Decrease
5. **Enthalpy**: $(-\Delta H)$ Large Loss, **Entropy**: Small Decrease
6. **Enthalpy**: $(+\Delta H)$ Large Gain, **Entropy**: Small Increase

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**Ideal Spontaneous**

- **Exothermic**
  - $\Delta H^-$
  - Enthalpy Decrease
  - Stored energy in Reactants
  - Low Entropy Reactants
  - Solids form Gases
  - Entropy Increase

**Ideal NonSpontaneous**

- **Endothermic**
  - $\Delta H^+$
  - Enthalpy Increase
  - No energy stored in Reactants
  - High Entropy Reactants
  - Gaseous Reactants
  - Gases form Solids
  - Entropy Decrease
Spontaneous RXN

Reactants | Products

Enthalpy

Entropy $\Delta S$

Non-Spontaneous RXN

Reactants | Products

Enthalpy

Entropy 

Non-Spontaneous RXN

Reactants | Products

Enthalpy

Entropy
In reversible reactions, one of the reactions is always spontaneous and the other is always nonspontaneous.

\[ A + B \rightarrow C + D + \text{Heat} \]

If \( A + B \) release enough energy, \( C + D \) will react and make this reaction reversible...

- Most spontaneous reactions are exothermic and release energy.
  
  \[ \text{STORED} + \text{FREE} \rightarrow \text{RELEASED} \]

- Most nonspontaneous reactions are endothermic and absorb energy.
  
  \[ \text{NO STORED} + \text{FREE} \rightarrow \text{STORED} \]

**Free Energy**

- Useful energy that is liberated in chemical reactions that can be harnessed to do work.
- Just because it is available, it will not necessarily be used.
- Exergonic = release of free energy
- This energy is called Gibbs Free Energy

\[ \Delta G_{\text{system}} = \Delta H - (T \Delta S) \]

**Gibbs Free-Energy Summary**

- \( \Delta G = \) Free Energy Change
  - Negative if spontaneous
  - Positive if nonspontaneous
- \( \Delta H = \) Enthalpy change
- \( T = \) Temperature in Kelvin
- \( \Delta S = \) Entropy change

**Calculating Free Energy Change**

- \( \Delta H = -91.8 \text{ kJ} \)
- \( T = 298 \text{ Kelvin (Standard Conditions)} \)
- \( \Delta S = -197 \text{ J/K} \)

\[ \Delta G = -91,800 \text{ J} - (298 \text{ K} \times -197 \text{ J/K}) = 91,800 \text{ J} + 58,700 \text{ J} = 33,100 \text{ J of Free Energy (Spontaneous Reaction)} \]

**Calculating Free Energy Change**

- \( \Delta H = +2000 \text{ kJ} \)
- \( T = 100 \text{ Kelvin} \)
- \( \Delta S = -10 \text{ kJ} \)

\[ \Delta G = +2000 \text{ kJ} - (100 \times -10 \text{ kJ}) = +2000 \text{ kJ} - (-1000 \text{ kJ}) = +3000 \text{ kJ (No free energy) (Nonspontaneous)} \]
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Calculating Free Energy Change

- $\Delta H = +2000 \text{ kJ}$
- $T = 100 \text{ Kelvin}$
- $\Delta S = +10 \text{ kJ}$
- $\Delta G = 2000 \text{ kJ} - (100 \times 10 \text{ kJ}) = 2000 \text{ kJ} - 1000 \text{ kJ} = +1000 \text{ kJ}$ (No free energy)
  Nonspontaneous

What happens if?

$2\text{SO}_2 + \text{O}_2 \leftrightarrow 2\text{SO}_3 + \text{Heat}$

- The reaction is reversed?
- You increase temperature?
- You decrease the temperature
- Add a catalyst?
- Decrease particle size of reactant?
- Increase the concentration of Q?

What happens at equilibrium if?

$2\text{H}_2 + \text{O}_2 \leftrightarrow 2\text{H}_2\text{O} + \text{Heat}$

- You add hydrogen?
- You lower the pressure?
- You raise the pressure?
- You increase temperature?
- You lower the temperature?
- You remove oxygen?

$2\text{A(g)} + \text{B(g)} \leftrightarrow 3\text{C(g)} + 4\text{D(g)} + \text{Heat}$

- Add B
- Remove A
- Raise the pressure
- Decrease temperature
- Decrease Pressure
- Lower the temperature
- Add C
- Remove D
- Name 5 ways to increase D
- Name 5 ways to decrease C

$2\text{A(g)} + \text{B(g)} \leftrightarrow 3\text{C(g)} + 4\text{D(g)} + \text{Heat}$

- Which way is Exothermic?
- Which way is Endothermic?
- Which way is spontaneous?
- Does Entropy increase?
- What is the Enthalpy change?
- Why can this reaction reverse?
- Are these Ideal or Not Ideal?
- What is the expression for Eq. constant?
- Can all substances be used to determine K?
- Which direction is favored?