Objectives

- Be able to describe the collision and transition-state theories
- Be able to use the Arrhenius theory to determine the activation energy for a reaction and to predict rate constants
- Be able to relate the molecularity of the reaction and the reaction rate and describe the concept of the “rate-determining” step
- Be able to describe the role of a catalyst and homogeneous, heterogeneous and enzyme catalysis

Reaction Mechanisms

- Even though a balanced chemical equation may give the ultimate result of a reaction, what actually happens in the reaction may take place in several steps.
  - This “pathway” the reaction takes is referred to as the reaction mechanism.
  - The individual steps in the larger overall reaction are referred to as elementary reactions.

Often Used Terms

- Intermediate: formed in one step and used up in a subsequent step and so is never seen as a product.
- Molecularity: the number of species that must collide to produce the reaction indicated by that step.
- Elementary Step: A reaction whose rate law can be written from its molecularity.
  - uni, bi and termolecular
Elementary Reactions

- Consider the reaction of nitrogen dioxide with carbon monoxide.

$$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$$

- This reaction is believed to take place in two steps.

$$\text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g) \text{ (elementary reaction)}$$

$$\text{NO}_3(g) + \text{CO}(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g) \text{ (elementary reaction)}$$

Figure 12.9: A molecular representation of the elementary steps in the reaction of NO$_2$ and CO.

Elementary Reactions

- Each step is a singular molecular event resulting in the formation of products.

  - The overall chemical equation is obtained by adding the two steps together and canceling any species common to both sides.

$$\text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g)$$

$$\text{NO}_3(g) + \text{CO}(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g)$$

$$\text{NO}_2(g) + \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}_3(g) + \text{NO}(g) + \text{NO}_2(g) + \text{CO}_2(g)$$

Molecularity

- We can classify reactions according to their molecularity, that is, the number of molecules that must collide for the elementary reaction to occur.

  - A unimolecular reaction involves only one reactant molecule.

  - A bimolecular reaction involves the collision of two reactant molecules.

  - A termolecular reaction requires the collision of three reactant molecules.

- Higher molecularities are rare because of the small statistical probability that four or more molecules would all collide at the same instant.
Rate Equations for Elementary Reactions

- For elementary reactions, the rate is proportional to the concentrations of all reactant molecules involved.

Rate Equations for Elementary Reactions

- Since a chemical reaction may occur in several steps, there is no easily stated relationship between its overall reaction and its rate law.
- For elementary reactions, the rate is dependent only on the concentrations of all reactant molecules involved.

Rate Equations for Elementary Reactions

- For example, consider the generic equation below.

\[ \text{A} \rightarrow \text{products} \]

The rate is dependent only on the concentration of A; that is,

\[ \text{Rate} = k[A] \]

Rate Equations for Elementary Reactions

- For a termolecular reaction

\[ \text{A} + \text{B} + \text{C} \rightarrow \text{products} \]

the rate is dependent on the populations of all three participants.

\[ \text{Rate} = k[A][B][C] \]

Rate Equations for Elementary Reactions

- For a bimolecular reaction

\[ \text{A} + \text{B} \rightarrow \text{products} \]

the rate is dependent on the concentrations of both A and B.

\[ \text{Rate} = k[A][B] \]

Rate Equations for Elementary Reactions

- However, for the reaction

\[ \text{A} + \text{B} \rightarrow \text{products} \]

the rate is dependent on the concentrations of both A and B.

\[ \text{Rate} = k[A][B] \]

Rate Equations for Elementary Reactions

- Note that if two molecules of a given reactant are required, it appears twice in the rate law. For example, the reaction

\[ 2\text{A} + \text{B} \rightarrow \text{products} \]

would have the rate law:

\[ \text{Rate} = k[A][B] \text{ or } \text{Rate} = k[A]^2[B] \]
Rate Equations for Elementary Reactions

- So, in essence, for an elementary reaction, the coefficient of each reactant becomes the power to which it is raised in the rate law for that reaction.
- Note that many chemical reactions occur in multiple steps and it is, therefore, impossible to predict the rate law based solely on the overall reaction.

Rate Laws and Mechanisms

- Consider the reaction below.
  \[ 2 \text{NO}_2(g) + \text{F}_2(g) \rightarrow 2 \text{NO}_2\text{F}(g) \]
- Experiments performed with this reaction show that the rate law is
  \[ \text{Rate} = k[\text{NO}_2][\text{F}_2] \]
- This implies that the reaction above is not an elementary reaction but rather the result of multiple steps.

Rate-Determining Step

- In a multistep reaction, it is the slowest step. It therefore determines the rate of reaction.
- In multiple-step reactions, one of the elementary reactions in the sequence is often slower than the rest.
- The overall reaction cannot proceed any faster than this slowest rate-determining step.

Rate Laws and Mechanisms

- Consider the reaction below.
  \[ 2 \text{NO}_2(g) + \text{F}_2(g) \rightarrow 2 \text{NO}_2\text{F}(g) \]
- Experiments performed with this reaction show that the rate law is
  \[ \text{Rate} = k[\text{NO}_2][\text{F}_2] \]
- The reaction is first order with respect to each reactant, even though the coefficient for NO₂ in the overall reaction is.

Rate-Determining Step

- In multiple-step reactions, one of the elementary reactions in the sequence is often slower than the rest.
- Our previous example occurs in two elementary steps where the first step is much slower.
  \[ \text{NO}_2(g) + \text{F}_2(g) \xrightarrow{k_{\text{slow}}} \text{NO}_2\text{F}(g) + \text{F}(g) \]
  \[ \text{NO}_2(g) + \text{F}(g) \xrightarrow{k_{\text{fast}}} \text{NO}_2\text{F}(g) \]
  \[ 2 \text{NO}_2(g) + \text{F}_2(g) \rightarrow 2 \text{NO}_2\text{F}(g) \]
Rate-Determining Step

• In multiple-step reactions, one of the elementary reactions in the sequence is often slower than the rest.
  • Since the overall rate of this reaction is determined by the slow step, it seems logical that the observed rate law is \( \text{Rate} = k_1[\text{NO}_2][\text{F}_2] \).

\[
\text{NO}_2(g) + F_2(g) \xrightarrow{k_1} \text{NO}_2F(g) + F(g) \quad \text{(slow)}
\]

Rate-Determining Step

• In a mechanism where the first elementary step is the rate-determining step, the overall rate law is simply expressed as the elementary rate law for that slow step.
  • A more complicated scenario occurs when the rate-determining step contains a reaction intermediate, as you’ll see in the next section.

Rate-Determining Step

• Consider the reduction of nitric oxide with H\(_2\).

\[
2\text{NO}(g) + 2\text{H}_2(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g)
\]

• A proposed mechanism is:

\[
\begin{align*}
2\text{NO} & \xrightarrow{k_1} \text{N}_2\text{O}_2 & \text{(fast, equilibrium)} \\
\text{N}_2\text{O}_2 + \text{H}_2 & \xrightarrow{k_2} \text{N}_2\text{O} + \text{H}_2\text{O} & \text{(slow)} \\
\text{N}_2\text{O} + \text{H}_2 & \xrightarrow{k_3} \text{N}_2 + \text{H}_2\text{O} & \text{(fast)}
\end{align*}
\]

• It has been experimentally determined that the rate law is \( \text{Rate} = k[\text{NO}][\text{H}_2] \).

Rate-Determining Step

• The rate-determining step (step 2 in this case) generally outlines the rate law for the overall reaction.

\[
\text{Rate} = k_2[N_2O_2][H_2] \\
\text{(Rate law for the rate-determining step)}
\]

• As mentioned earlier, the overall rate law can be expressed only in terms of substances represented in the overall reaction and cannot contain reaction intermediates.
Rate-Determining Step

• The rate-determining step (step 2 in this case) generally outlines the rate law for the overall reaction.
  \[ \text{Rate} = k_2 [N_2O_2][H_2] \]
  (Rate law for the rate-determining step)

• It is necessary to re-express this proposed rate law after eliminating \([N_2O_2]\).

Rate-Determining Step

• The rate-determining step (step 2 in this case) generally outlines the rate law for the overall reaction.
  \[ \text{Rate} = k_2 [N_2O_2][H_2] \]
  (Rate law for the rate-determining step)

• Therefore,
  \[ [N_2O_2] = \frac{k_1}{k_{-1}} [NO]^2 \]

• If we substitute this into our proposed rate law we obtain:

Rate-Determining Step

• The rate-determining step (step 2 in this case) generally outlines the rate law for the overall reaction.
  \[ \text{Rate} = k_2 [N_2O_2][H_2] \]
  (Rate law for the rate-determining step)

• We can do this by looking at the first step, which is fast and establishes equilibrium.

Rate-Determining Step

• The rate-determining step (step 2 in this case) generally outlines the rate law for the overall reaction.
  \[ \text{Rate} = k_2 [N_2O_2][H_2] \]
  (Rate law for the rate-determining step)

• At equilibrium, the forward rate and the reverse rate are equal.
  \[ k_2 [NO]^2 = k_{-1} [N_2O_2] \]

Collision Theory

• Collision theory assumes that for a reaction to occur, reactant molecules must collide with sufficient energy and the proper orientation.

• The minimum energy of collision required for two molecules to react is called the activation energy, \(E_a\).
Collision Model

- **Key Idea:** Molecules must collide to react.
- However, only a small fraction of collisions produces a reaction. Why?
- **Arrhenius:** An activation energy must be overcome.

Collision Theory

- Rate constants vary with temperature. Consequently, the actual rate of a reaction is very temperature dependent.
- Why the rate depends on temperature can by explained by collision theory.
Collision Theory and the Arrhenius Equation

- Collision theory maintains that the rate constant for a reaction is the product of three factors.
  1. \( Z \), the collision frequency
  2. \( f \), the fraction of collisions with sufficient energy to react
  3. \( p \), the fraction of collisions with the proper orientation to react

\[
k = Zpf
\]

Collision Theory and the Arrhenius Equation

- \( Z \) is only slightly temperature dependent.
  - This alone does not account for the observed increases in rates with only small increases in temperature.
  - From kinetic theory, it can be shown that a 10 °C rise in temperature will produce only a 2% rise in collision frequency.

\[
f = e^{-\frac{E_a}{RT}}
\]

- Here \( e = 2.718 \ldots \) and \( R \) is the ideal gas constant, 8.31 J/(mol·K).

Collision Theory and the Arrhenius Equation

- On the other hand, \( f \), the fraction of molecules with sufficient activation energy, turns out to be very temperature dependent.
  - It can be shown that \( f \) is related to \( E_a \) by the following expression.

\[
f = e^{-\frac{E_a}{RT}}
\]

- Also, a decrease in the activation energy, \( E_a \), increases the value of \( f \).

Collision Theory and the Arrhenius Equation

- On the other hand, \( f \), the fraction of molecules with sufficient activation energy turns out to be very temperature dependent.
  - From this relationship, as temperature increases, \( f \) increases.

\[
f = e^{-\frac{E_a}{RT}}
\]

- Also, a decrease in the activation energy, \( E_a \), increases the value of \( f \).
Collision Theory and the Arrhenius Equation

- On the other hand, $f$, the fraction of molecules with sufficient activation energy turns out to be very temperature dependent.
  - This is the primary factor relating temperature increases to observed rate increases.
  $$ f = e^{-\frac{E_a}{RT}} $$

The reaction rate also depends on $p$, the fraction of collisions with the proper orientation.

- This factor is independent of temperature changes.
- So, with changes in temperature, $Z$ and $p$ remain fairly constant.
- We can use that fact to derive a mathematical relationship between the rate constant, $k$, and the absolute temperature.

The Arrhenius Equation

- If we were to combine the relatively constant terms, $Z$ and $p$, into one constant, let’s call it $A$. We obtain the Arrhenius equation:
  $$ k = A e^{-\frac{E_a}{RT}} $$
- The Arrhenius equation expresses the dependence of the rate constant on absolute temperature and activation energy.

Arrhenius Equation (continued)

$$ k = A e^{-\frac{E_a}{RT}} $$

- $k =$ rate constant
- $A =$ frequency factor
- $E_a =$ activation energy
- $T =$ temperature
- $R =$ gas constant

Figure 12.10: A plot showing the exponential dependence of the rate constant on absolute temperature.

Figure 14.15: Plot of $\ln k$ versus $1/T$.  

The Arrhenius Equation

- It is useful to recast the Arrhenius equation in logarithmic form.
  - We can relate this equation to the (somewhat rearranged) general formula for a straight line.
    \[
    \ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T}\right)
    \]
    \[y = b + mx\]
  - A plot of ln \(k\) versus \(1/T\) should yield a straight line with a slope of \(-E_a/R\) and an intercept of \(\ln A\).
    (See Figure 14.15)

The Arrhenius Equation

- A more useful form of the equation emerges if we look at two points on the line this equation describes that is, \((k_1, (1/T_1))\) and \((k_2, (1/T_2))\).
  - The two equations describing the relationship at each coordinate would be
    \[
    \ln k_1 = \ln A - \frac{E_a}{R} \left(\frac{1}{T_1}\right)
    \]
    \[\text{and} \]
    \[
    \ln k_2 = \ln A - \frac{E_a}{R} \left(\frac{1}{T_2}\right)
    \]
  - We can eliminate \(\ln A\) by subtracting the two equations to obtain
    \[
    \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
    \]
The Arrhenius Equation

- A more useful form of the equation emerges if we look at two points on the line this equation describes that is, \((k_1, (1/T_1))\) and \((k_2, (1/T_2))\).
- With this form of the equation, given the activation energy and the rate constant \(k_1\) at a given temperature \(T_1\), we can find the rate constant \(k_2\) at any other temperature, \(T_2\).

\[
\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

A Problem to Consider

- The rate constant for the formation of hydrogen iodide from its elements

\[
H_2(g) + I_2(g) \rightarrow 2HI(g)
\]

is \(2.7 \times 10^{-4} \text{ L/(mol·s)}\) at 600 K and \(3.5 \times 10^{-3} \text{ L/(mol·s)}\) at 650 K. Find the activation energy, \(E_a\).

- Solving for \(E_a\):

\[
E_a = \frac{1.11 \times 8.31 \text{ J/mol·K}}{1.28 \times 10^{-4}} = 1.66 \times 10^4 \text{ J}
\]

Transition-State Theory

- Transition-state theory explains the reaction resulting from the collision of two molecules in terms of an activated complex.
  - An activated complex (transition state) is an unstable grouping of atoms that can break up to form products.
  - A simple analogy would be the collision of three billiard balls on a billiard table.
Transition-State Theory

- Transition-state theory explains the reaction resulting from the collision of two molecules in terms of an **activated complex**.
  - The “incoming” billiard ball would likely stick to one of the joined spheres and provide sufficient energy to dislodge the other, resulting in a new “pairing.”
  - At the instant of impact, when all three spheres are joined, we have an unstable transition-state complex.

Potential-Energy Diagrams for Reactions

- The potential-energy diagram for an exothermic reaction shows that the products are more stable than the reactants.
  - Figure 14.14 illustrates the potential-energy diagram for an exothermic reaction.
  - We see again that the forward activation energy is required to form the transition-state complex.
  - In both of these graphs, the reverse reaction must still supply enough activation energy to form the activated complex.

Potential-Energy Diagrams for Reactions

- To illustrate graphically the formation of a transition state, we can plot the potential energy of a reaction versus time.
  - Figure 14.13 illustrates the endothermic reaction of nitric oxide and chlorine gas.
  - Note that the forward activation energy is the energy necessary to form the activated complex.
  - The $\Delta H$ of the reaction is the net change in energy between reactants and products.
Catalysis

- Catalyst: A substance that speeds up a reaction without being consumed
- Enzyme: A large molecule (usually a protein) that catalyzes biological reactions.
- Homogeneous catalyst: Present in the same phase as the reacting molecules.
- Heterogeneous catalyst: Present in a different phase than the reacting molecules.

Catalysts

- **A catalyst** is a substance that provides a good “environment” for a reaction to occur, thereby increasing the reaction rate without being consumed by the reaction.
  - Its presence increases the rate of reaction by either increasing the frequency factor, \( A \) (from the Arrhenius equation) or lowering the activation energy, \( E_a \).

Homogeneous catalysis is the use of a catalyst in the same phase as the reacting species.
- The oxidation of sulfur dioxide using nitric oxide as a catalyst is an example where all species are in the gas phase.
  
  \[
  2\text{SO}_2(g) + \text{O}_2(g) \xrightarrow{\text{NO}} \text{2SO}_3(g)
  \]

Figure 12.15: Energy plots for a catalyzed and an uncatalyzed pathway for a given reaction.

Figure 12.16: Effect of a catalyst on the number of reaction-producing collisions.
Catalysts

- **Heterogeneous catalysis** is the use of a catalyst that exists in a different phase from the reacting species, usually a solid catalyst in contact with a liquid or gaseous solution of reactants.
  - Such surface catalysis is thought to occur by chemical adsorption of the reactants onto the surface of the catalyst.
  - Adsorption is the attraction of molecules to a surface. [see Figure 14.18]

Enzyme Catalysis

- **Enzymes have enormous catalytic activity.**
  - The substance whose reaction the enzyme catalyzes is called the substrate. [see Figure 14.21]
  - Figure 14.22 illustrates the reduction in activation energy resulting from the formation of an enzyme-substrate complex.

Heterogeneous Catalysis

**Steps:**

1. Adsorption and activation of the reactants.
2. Migration of the adsorbed reactants on the surface.
3. Reaction of the adsorbed substances.
4. Escape, or desorption, of the products.
Figure 12.18: The exhaust gases from an automobile engine are passed through a catalytic converter to minimize environmental damage.

Figure 14.19: Proposed mechanism of a catalytic converter.

Figure 12.17: Heterogeneous catalysis of the hydrogenation of ethylene.