Chapter 14. Chemical Kinetics

14.1 Factors that Affect Reaction Rates\textsuperscript{1,2,3,4}

- Chemical kinetics is the study of how fast chemical reactions occur.
- There are several important factors which affect rates of reactions:
  - physical state of the reactants,
  - concentration of the reactants,
  - temperature of the reaction, and
  - presence or absence of a catalyst.
- The goal is to understand chemical reactions at the molecular level.

14.2 Reaction Rates\textsuperscript{5,6}

- The speed of a reaction is defined as the change that occurs per unit time.
- It is often determined by measuring the change in concentration of a reactant or product with time.
  - The speed of the chemical reaction is its reaction rate.
- For a reaction \( A \rightarrow B \)

\[
\text{Average rate with respect to } B = \frac{\text{change in concentration of } B}{\text{change in time}}
\]

- Here the change in the concentration of B is defined as:
  \((\text{concentration of } B) = (\text{concentration of } B \text{ at final time}) - (\text{concentration of } B \text{ at initial time})\)
- Illustrate this with an example:
  - Suppose \( A \) reacts to form \( B \). Let us begin with 1.00 \( M \) \( A \).
  - At \( t = 0 \) (time zero) there is 1.00 \( M \) \( A \) and no \( B \) present.
  - At \( t = 20 \) sec, there is 0.54 \( M \) \( A \) and 0.46 \( M \) \( B \).
  - At \( t = 40 \) sec, there is 0.30 \( M \) \( A \) and 0.70 \( M \) \( B \).
  - We can use this information to find the average rate with respect to \( B \):

\[
\begin{align*}
\text{AvgRate}_B &= \frac{(\text{Conc}(B)_{20s} - \text{Conc}(B)_{0s})}{20s - 0s} \\
&= \frac{0.46M - 0.00M}{20s - 0s} \\
&= \frac{0.46M}{20s} = 0.023 \text{ M/s}
\end{align*}
\]

- For the reaction \( A \rightarrow B \) there are two ways of measuring rate:
  - the rate of appearance of product \( B \) (i.e., change in moles of \( B \) per unit time) as in the preceding example, and

\textsuperscript{1}“Appearing Red” from Live Demonstrations
\textsuperscript{2}“A New Twist on the Iodine Clock Reaction: Determining the Order of a Reaction” from Live Demonstrations
\textsuperscript{3}“Hydrogen Peroxide Iodine Clock: Oxidation of Potassium Iodide by Hydrogen Peroxide” from Live Demonstrations
\textsuperscript{4}“The Starch-Iodine Clock Reaction” from Live Demonstrations
\textsuperscript{5}“Progress of Reaction” Activity from Instructor’s Resource CD/DVD
\textsuperscript{6}“The Fizz Keeper, A Case Study in Chemical Education, Equilibrium, and Kinetics” from Further Readings
• the rate of disappearance of reactant A (i.e., the change in moles of A per unit time).

\[ \text{Average Rate} = \frac{\Delta [A]}{\Delta t} \]

• Note the negative sign! This reminds us that rate is being expressed in terms of the disappearance of a reactant.
• A plot of number of moles versus time shows that as the reactants (A) disappear, the products (B) appear.

**Change of Rate with Time**

• In most chemical reactions we will determine the reaction rate by monitoring a change in concentration (of a reactant or product).
  • The most useful unit to use for rate is molarity.
  • Since volume is constant, molarity and moles are directly proportional.
• Consider the following reaction:
  \[ C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq) \]
• We can calculate the average rate in terms of the disappearance of \( C_4H_9Cl \).
• The units for average rate are \( \text{mol/L} \cdot \text{s} \) or \( \text{M/s} \).
• The average rate decreases with time.
• We can plot \( [C_4H_9Cl] \) versus time.
  • The rate at any instant in time is called the *instantaneous rate*.
  • It is the slope of the straight line tangent to the curve at that instant.
  • Instantaneous rate is different from average rate.
  • It is the rate at that particular instant in time.
  • For our discussion we will call the "instantaneous rate" the rate, unless otherwise indicated.

**Reaction Rates and Stoichiometry**

• For the reaction:
  \[ C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq) \]
• The rate of appearance of \( C_4H_9OH \) must equal the rate of disappearance of \( C_4H_9Cl \).

\[ \text{Rate} = \frac{\Delta [C_4H_9Cl]}{\Delta t} - \frac{\Delta [C_4H_9OH]}{\Delta t} \]

• What if the stoichiometric relationships are not one-to-one?
• For the reaction:
  \[ 2HI(g) \rightarrow H_2(g) + I_2(g) \]
• The rate may be expressed as:

\[ \text{Rate} = \frac{1}{a} \frac{\Delta [A]}{\Delta t} + \frac{1}{b} \frac{\Delta [B]}{\Delta t} - \frac{1}{c} \frac{\Delta [C]}{\Delta t} - \frac{1}{d} \frac{\Delta [D]}{\Delta t} \]

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7 Figure 14.4 from Transparency Pack
8 Figure 14.5 from Transparency Pack
**Rate**

- In general, rates:
  - increase when reactant concentration is increased.
  - decrease as the concentration of reactants is reduced.

- We often examine the effect of concentration on reaction rate by measuring the way in which reaction rate at the beginning of a reaction depends on starting conditions.

- Consider the reaction:
  \[ \text{NH}_4^+(aq) + \text{NO}_2^-(aq) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l) \]

  - We measure initial reaction rates.
  - The initial rate is the instantaneous rate at time \( t = 0 \).
  - We find this at various initial concentrations of each reactant.
  - As \([\text{NH}_4^+]\) doubles with \([\text{NO}_2^-]\) constant the rate doubles.
  - We conclude that the rate is proportional to \([\text{NH}_4^+]\).
  - As \([\text{NO}_2^-]\) doubles with \([\text{NH}_4^+]\) constant the rate doubles.
  - We conclude that the rate is proportional to \([\text{NO}_2^-]\).

- The overall concentration dependence of reaction rate is given in a rate law or rate expression.

  - For our example, the rate law is:
    \[ \text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-] \]

  - The proportionality constant \( k \) is called the rate constant.

  - Once we have determined the rate law and the rate constant, we can use them to calculate initial reaction rates under any set of initial concentrations.

**Exponents in the Rate Law**

- For a general reaction with rate law:
  \[ \text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \]

  - The exponents \( m \) and \( n \) are called reaction orders.
  - The overall reaction order is the sum of the reaction orders.

  - For the reaction:
    \[ \text{NH}_4^+(aq) + \text{NO}_2^-(aq) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l) \]

    - The reaction is said to be first order in \([\text{NH}_4^+]\), first order in \([\text{NO}_2^-]\), and second order overall.

  - Note that reaction orders must be determined experimentally.
  - They do not necessarily correspond to the stoichiometric coefficients in the balanced chemical equation!

  - We commonly encounter reaction orders of 0, 1 or 2.
  - Even fractional or negative values are possible.

**Units of Rate Constants**

- Units of the rate constant depend on the overall reaction order.

  - For example, for a reaction that is second order overall:

    - Units of rate are:

    \[ \frac{M}{mol} \cdot \frac{L}{mol}^{-2} \cdot \frac{1}{s} \]

    - Thus the units of the rate constant are:

    \[ \frac{M}{mol} \cdot \frac{L}{mol}^{-2} \cdot \frac{1}{s} \]

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9 “Decomposition of N\textsubscript{2}O\textsubscript{5}” Activity from Instructor’s Resource CD/DVD
10 “Inflation Rates, Car Devaluation, and Chemical Kinetics” from Further Readings
11 “Rates of Reaction” Activity from Instructor’s Resource CD/DVD
12 “An Analogy to Help Students Understand Reaction Orders” from Further Readings
Using Initial Rates to Determine Rate Laws

- To determine the rate law, we observe the effect of changing initial concentrations.
  - If a reaction is zero order in a reactant, changing the initial concentration of that reactant will have no effect on rate (as long as some reactant is present).
  - If a reaction is first order, doubling the concentration will cause the rate to double.
  - If a reaction is second order, doubling the concentration will result in a $2^2$ increase in rate.
  - Similarly, tripling the concentration results in a $3^2$ increase in rate.
  - A reaction is $n$th order if doubling the concentration causes a $2^n$ increase in rate.
- Note that the rate, not the rate constant, depends on concentration.
- The rate constant IS affected by temperature and by the presence of a catalyst.

14.4 The Change of Concentration with Time

- Goal: Convert the rate law into a convenient equation that gives concentration as a function of time.

First-Order Reactions

- For a first-order reaction, the rate doubles as the concentration of a reactant doubles.
  - Therefore we can write the differential rate law:

$$\frac{d[A]}{dt} = -k[A]$$

- Integrating:

$$\ln[A]_t - \ln[A]_0 = -kt$$

- We get the integrated rate law:

$$\ln[A] = -kt + \ln[A]_0$$

- Rearranging:

$$\ln[A] = \ln[A]_0 - kt$$

- An alternate form:

$$\ln[A]_t = \ln[A]_0 - kt$$

- A plot of $\ln[A]_t$ versus $t$ is a straight line with slope $k$ and intercept $\ln[A]_0$.
- Note that in this equation we use the natural logarithm, $\ln$ (log to the base $e$).

Second-Order Reactions

- A second-order reaction is one whose rate depends on the reactant concentration to the second power or on the concentration of two reactants, each raised to the first power.
- For a second-order reaction with just one reactant we write the differential rate law:

$$\frac{d[A]}{dt} = -k[A]^2$$

- Integrating,

$$\frac{1}{[A]} = -kt + \frac{1}{[A]_0}$$

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13 “First-Order Process” Animation from Instructor’s Resource CD/DVD
14 “Don’t be Tricked by Your Integrated Rate Plot!” from Further Readings
15 Figure 14.7 from Transparency Pack
16 Figure 14.8 from Transparency Pack
• We get the integrated form of the rate law:

\[
\ln \frac{[A]_0}{[A]} = -kt
\]

• A plot of 1/[A] versus t is a straight line with slope k and intercept 1/[A]₀.
  • For a second-order reaction, a plot of ln[A] vs. t is not linear.
• Note that a second-order process can have a rate constant expression of the form:

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

• That is, the reaction is second order overall, but has first-order dependence on A and B.

Half-life

• **Half-life**, t₁/₂, is the time required for the concentration of a reactant to decrease to half its original value.
  • That is, half life, t₁/₂, is the time taken for [A]₀ to reach ½ [A]₀.
• Mathematically, the half life of a first-order reaction is:

\[
\ln \frac{[A]_0}{[A]} = -kt
\]

So, for \( t = t_{1/2} \) and \( [A]_t = \frac{1}{2} [A]_0 \)

\[
\ln \frac{1}{2} = -kt_{1/2}
\]

\[
t_{1/2} = \frac{1}{k[A]_0}
\]

• Note that the half-life of a first-order reaction is independent of the initial concentration of the reactant.
• We can show that the half-life of a second order reaction is:

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

• Note that the half-life of a second-order reaction is dependent on the initial concentration of reactant.

14.5 Temperature and Rate

• Most reactions speed up as temperature increases.
  • We can illustrate this with chemiluminescent Cyalume® light sticks.
A chemiluminescent reaction produces light.

Two light sticks are placed in water, one at room temperature and one in ice.

- The one at room temperature is brighter than the one in ice.
- Its luminescence also fades more quickly.

The chemical reaction responsible for chemiluminescence is dependent on temperature, the higher the temperature, the faster the reaction and the brighter the light.

- As temperature increases, the rate increases.
- How is the relationship between temperature and rate reflected in the rate expression?
  - The rate law has no temperature term in it, so the rate constant must depend on temperature.
  - Consider the first-order reaction \( \text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN} \).
    - As temperature increases from 190°C to 250°C the rate constant increases.
    - The temperature effect is quite dramatic.

The relationship between temperature and rate is reflected in the rate expression, which shows that the rate constant increases with temperature.

- We see an approximate doubling of the rate of the reaction with each 10°C increase in temperature.

The Collision Model

- Rates of reactions are affected by concentration and temperature.
- We need to develop a model that explains this observation.
- An explanation is provided by the collision model, based on the kinetic-molecular theory.
  - In order for molecules to react they must collide.
  - The greater the number of collisions the faster the rate.
  - The more molecules present, the greater the probability of collision and the faster the rate.
  - Thus, reaction rate should increase with an increase in the concentration of reactant molecules.
  - The higher the temperature, the more energy available to the molecules and the more frequently the molecules collide.
    - Thus, reaction rate should increase with an increase in temperature.
  - However, not all collisions lead to products.
  - In fact, only a small fraction of collisions lead to products.
  - In order for a reaction to occur the reactant molecules must collide in the correct orientation and with enough energy to form products.

The Orientation Factor

- The orientation of a molecule during collision can have a profound effect on whether or not a reaction occurs.
  - Consider the reaction between Cl and NOCl:
    
    \[ \text{Cl} + \text{NOCl} \rightarrow \text{NO} + \text{Cl}_2 \]

  - If the Cl collides with the Cl of NOCl, the products are Cl₂ and NO.
  - If the Cl collides with the O of NOCl, no products are formed.

Activation Energy

- Arrhenius: Molecules must posses a minimum amount of energy to react. Why?
- In order to form products, bonds must be broken in the reactants.

22 “Audience-Appropriate Analogies: Collision Theory” from Further Readings
23 “Arrhenius Model” Activity from Instructor’s Resource CD/DVD
24 “The Collision Theory and an American Tradition” from Further Readings
25 Figure 14.13 from Transparency Pack
26 Figure 14.15 from Transparency Pack
27 Figure 14.16 from Transparency Pack
28 “Just What Is a Transition State?” from Further Readings
• Bond breakage requires energy.
• Molecules moving too slowly, with too little kinetic energy, do not react when they collide.
• **Activation energy,** $E_a$, is the minimum energy required to initiate a chemical reaction.
  • $E_a$ will vary with the reaction.
• Consider the rearrangement of methyl isonitrile to form acetonitrile:
  • Energy is required to stretch the bond between the CH$_3$ group and the N≡C group to allow the N≡C to rotate.
  • The C–C bond begins to form.
    • The energy associated with the molecule drops.
    • The energy barrier between the starting molecule and the highest energy state found along the reaction pathway is the activation energy.
      • The species at the top of the barrier is called the **activated complex**, or **transition state**.
      • The change in energy for the reaction is the difference in energy between CH$_3$NC and CH$_3$CN.
      • $E_{rxn}$ has no effect on reaction rate.
      • The activation energy is the difference in energy between reactants, (CH$_3$NC) and the transition state.
        • The rate depends on the magnitude of the $E_a$.
          • In general, the lower the $E_a$, the faster the rate.
• Notice that if a forward reaction is exothermic (CH$_3$NC $\rightarrow$ CH$_3$CN), then the reverse reaction is endothermic (CH$_3$CN $\rightarrow$ CH$_3$NC).
• How does this relate to temperature?
  • At any particular temperature, the molecules present have an average kinetic energy associated with the population.
    • In the same distribution, some molecules have less energy than the average while others have more than the average value.
    • The fraction of molecules with an energy equal to or greater than $E_a$ is given by:
      $$k \frac{[E_a]}{Ae^{R/T}}$$
      • R is the gas constant (8.314 J/molK) and T is the absolute temperature.
      • Molecules that have an energy equal to or greater than $E_a$ have sufficient energy to react.
      • As we increase the temperature, the fraction of the population that has an energy equal to or greater than $E_a$ increases.
        • Thus, more molecules can react.

**The Arrhenius Equation**

• Arrhenius discovered that most reaction-rate data obeyed an equation based on three factors:
  • the number of collisions per unit time,
  • the fraction of collisions that occur with the correct orientation, and
  • the fraction of the colliding molecules that have an energy equal to or greater than $E_a$.
• From these observations Arrhenius developed the **Arrhenius equation**.
  $$k = \frac{k_0}{Ae^{R/T}}$$
  • Where $k$ is the rate constant, $E_a$ is the activation energy, $R$ is the gas constant (8.314 J/Kmol), and $T$ is the temperature in K.
  • $A$ is called the **frequency factor**.
    • It is related to the frequency of collisions and the probability that a collision will have a favorable orientation.
    • Both $A$ and $E_a$ are **specific to a given reaction**.

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29 “The Arrhenius Law and Storage of Food” from Further Readings
**Determining the Activation Energy**\(^{30}\)

- \(E_a\) may be determined experimentally.
- We need to take the natural log of both sides of the Arrhenius equation:

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

- A graph of \(\ln k\) vs \(1/T\) will have a slope of \(-E_a/R\) and a y-intercept of \(\ln A\).
- Alternatively we can use:

\[
f \equiv e^{E_a/RT}
\]

**14.6 Reaction Mechanisms**\(^{31,32}\)

- The balanced chemical equation provides information about substances present at the beginning and end of the reaction.
- The **reaction mechanism** is the process by which the reaction occurs.
- Mechanisms provide a picture of which bonds are broken and formed during the course of a reaction.

**Elementary Reactions**\(^{33}\)

- **Elementary reactions** are any processes that occur in a single step.
- The number of molecules present in an elementary step is the **molecularity** of that elementary step.
  - **Unimolecular** reactions involve one molecule.
  - **Bimolecular** elementary reactions involve the collision of two molecules.
  - **Termolecular** elementary reactions involve the simultaneous collision of three molecules.
- It is not common to see termolecular processes (statistically improbable).

**Multistep Mechanisms**

- A multistep mechanism consists of a sequence of elementary steps.
- The elementary steps must add to give the balanced chemical equation.
- Some multistep mechanisms will include **intermediates**.
- These are species that appear in an elementary step but are neither a reactant nor product.
- Intermediates are formed in one elementary step and consumed in another.
- They are not found in the balanced equation for the overall reaction.

**Rate Laws of Elementary Reactions**

- The rate laws of the elementary steps determine the overall rate law of the reaction.
- The rate law of an elementary step is determined by its molecularity.
  - Unimolecular processes are first order.
  - Bimolecular processes are second order.
- Termolecular processes are third order.

**The Rate Determining Step for a Multistep Mechanism**\(^{34,35}\)

- Most reactions occur by mechanisms with more than one elementary step.
  - Often one step is much slower than the others.

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\(^{30}\) “Rates of Reaction” Activity from Instructor’s Resource CD/DVD

\(^{31}\) “Pictorial Analogies XIII: Kinetics and Mechanisms” from Further Readings

\(^{32}\) “Doing the Dishes: An Analogy for Use in Teaching Reaction Kinetics” from Further Readings

\(^{33}\) “Bimolecular Reaction” Animation from Instructor’s Resource CD/DVD

\(^{34}\) “Auto Analogies” from Further Readings

\(^{35}\) “Another Auto Analogy: Rate Determining Steps” from Further Readings
• The slow step limits the overall reaction rate.
  • This is called the **rate-determining step** (rate-limiting step) of the reaction.
  • This step governs the overall rate law for the overall reaction.

**Mechanisms with a Slow Initial Step**

- Consider the reaction:
  
  \[
  \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)
  \]

  • The experimentally derived rate law is: \( \text{Rate} = k[\text{NO}_2]^2 \)
  • We propose a mechanism for the reaction:
    
    - **Step 1:** \( \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g) \) slow step
    
    - **Step 2:** \( \text{NO}_3(g) + \text{CO}(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g) \) fast step

    • Note that \( \text{NO}_3 \) is an intermediate.
    • If \( k_2 \gg k_1 \), then the overall reaction rate will depend on the first step (the rate-determining step).
    • \( \text{Rate} = k_1[\text{NO}_2]^2 \)
    • This theoretical rate law is in agreement with the experimental rate law.
    • This supports (but does not prove) our mechanism.

**Mechanisms with a Fast Initial Step**

- Consider the reaction:
  
  \[
  2\text{NO}(g) + \text{Br}_2(g) \rightarrow 2\text{NOBr}(g)
  \]

  • The experimentally determined rate law is:
    
    \( \text{Rate} = k[\text{NO}]^2[\text{Br}_2] \)

  • Consider the following proposed mechanism:
    
    - **Step 1:** \( \text{NO}(g) + \text{Br}_2(g) \rightarrow \text{NOBr}_2(g) \) fast step
    
    - **Step 2:** \( \text{NOBr}_2(g) \rightarrow \text{NO}(g) + 2\text{NOBr}(g) \) slow step

    • The theoretical rate law for this mechanism is based on the rate-determining step, step 2:
      
      \( \text{Rate} = k_2[\text{NOBr}_2][\text{NO}] \)

    • Problem: This rate law depends on the concentration of an intermediate species.
    • Intermediates are usually unstable and have low/unknown concentrations.
    • We need to find a way to remove this term from our rate law.
    • We can express the concentration of [NOBr₂] in terms of NOBr and Br₂ by assuming that there is an equilibrium in step 1.
      
      • In a dynamic equilibrium, the forward rate equals the reverse rate.
      • Therefore, by definition of equilibrium we get:
        
        \( k_1[\text{NO}][\text{Br}_2] = k_{-1}[\text{NOBr}_2] \)

      • Rearranging we get:
        
        \[
        \text{Rate} = \frac{k_2}{k_1} [\text{NO}][\text{Br}_2][\text{NO}][\text{NO}][\text{Br}_2]
        \]

      • Therefore, the overall rate law becomes
        
        \[
        \text{Rate} = \frac{k_2}{k_1} \text{t} \frac{[\text{NO}][\text{Br}_2][\text{NO}]^2[\text{Br}_2]}{t}
        \]

    • Note that the final rate law is consistent with the experimentally observed rate law.
14.7 Catalysis

- A catalyst is a substance that changes the rate of a chemical reaction without itself undergoing a permanent chemical change in the process.
- There are two types of catalysts:
  - homogeneous
  - heterogeneous.
- Catalysts are common in the body, in the environment, and in the chemistry lab!

Homogeneous Catalysis

- A homogeneous catalyst is one that is present in the same phase as the reacting molecules.
- For example, hydrogen peroxide decomposes very slowly in the absence of a catalyst:
  \[ 2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) \]
- In the presence of bromide ion, the decomposition occurs rapidly in acidic solution:
  \[
  2\text{Br}^-(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Br}_2(\text{aq}) + 2\text{H}_2\text{O}(l) \\
  \text{Br}_2(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) + 2\text{Br}^-(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{O}_2(g)
  \]
- \(\text{Br}^-\) is a catalyst because it is regenerated at the end of the reaction.
- The net reaction is still:
  \[ 2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) \]
- How do catalysts increase reaction rates?
  - In general, catalysts operate by lowering the overall activation energy for a reaction.
  - However, catalysts can operate by increasing the number of effective collisions.
    - That is, from the Arrhenius equation catalysts increase \( k \) by increasing \( A \) or decreasing \( E_a \).
  - A catalyst usually provides a completely different mechanism for the reaction.
    - In the preceding peroxide decomposition example, in the absence of a catalyst, \( \text{H}_2\text{O}_2 \) decomposes directly to water and oxygen.
    - In the presence of \( \text{Br}^- \), \( \text{Br}_2(\text{aq}) \) is generated as an intermediate.
    - When a catalyst adds an intermediate, the activation energies for both steps must be lower than the activation energy for the uncatalyzed reaction.

Heterogeneous Catalysis

- A heterogeneous catalyst exists in a different phase than the reactants.
- Often we encounter a situation involving a solid catalyst in contact with gaseous reactants and gaseous products (example: catalytic converters in cars) or with reactants in a liquid.
  - Many industrial catalysts are heterogeneous.
- How do they do their job?
  - The first step is adsorption (the binding of reactant molecules to the catalyst surface).
  - Adsorption occurs due to the high reactivity of atoms or ions on the surface of the solid.

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36 “Catalysts” from Further Readings
37 “Catalysis” Movie from Instructor’s Resource CD/DVD
38 “Catalytic Decomposition of Hydrogen Peroxide: Foam Production” from Live Demonstrations
39 Figure 14.19 from Transparency Pack
40 “Catalysis: New Reaction Pathways, Not Just a Lowering of the Activation Energy” from Further Readings
41 Figure 14.20 from Transparency Pack
42 “Catalysts on Surfaces” from Further Readings
43 Figure 14.21 from Transparency Pack
44 “Surface Reaction-Hydrogenation” Animation from Instructor’s Resource CD/DVD
45 “Solid Acid Catalysts” from Further Readings
46 “Getting Auto Exhaussts to Pristine” from Further Readings
47 “Driving Down Emissions” from Further Readings
• **Absorption** refers to the uptake of molecules into the interior of another substance.

• Molecules are adsorbed onto **active sites** on the catalyst surface.
  • The number of active sites on a given amount of catalyst depends on several factors such as:
    • the nature of the catalyst,
    • how the catalyst was prepared, and
    • how the catalyst was treated prior to use.

• For example, consider the hydrogenation of ethylene to form ethane:
  \[
  \text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) \quad H = 137 \text{ kJ/mol}
  \]
  • The reaction is slow in the absence of a catalyst.
  • In the presence of a finely divided metal catalyst (Ni, Pt or Pd) the reaction occurs quickly at room temperature.
  • First, the ethylene and hydrogen molecules are adsorbed onto active sites on the metal surface.
  • The H–H bond breaks and the H atoms migrate about the metal surface.
  • When an H atom collides with an ethylene molecule on the surface, the C–C bond breaks and a C–H bond forms.
    • An **ethyl group**, C\textsubscript{2}H\textsubscript{5}, is weakly bonded to the metal surface with a metal-carbon bond.
    • When C\textsubscript{2}H\textsubscript{6} forms it desorbs from the surface.
    • When ethylene and hydrogen are adsorbed onto a surface, less energy is required to break the bonds.
  • The activation energy for the reaction is lowered.
  • Thus the reaction rate is increased.

**Enzymes**

• **Enzymes** are biological catalysts.

• Most enzymes are large protein molecules.
  • Molar masses are in the range of 10\textsuperscript{4} to 10\textsuperscript{6} amu.

• Enzymes are capable of catalyzing very specific reactions.

• For example, **catalase** is an enzyme found in blood and liver cells.
  • It catalyzes the decomposition of hydrogen peroxide:
    \[
    2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})
    \]
  • This reaction is important in removing peroxide, a potentially harmful oxidizing agent.

• The enzyme catalyzes the reaction at its active site.

• The substances that undergo reaction at the active site on enzymes are called **substrates**.

• A simple view of enzyme specificity is the **lock-and-key model**.
  • Here, a substrate is pictured as fitting into the active site of an enzyme in a manner similar to a specific key fitting into a lock. This forms an **enzyme-substrate (ES) complex**.
  • Only substrates that fit into the enzyme lock can be involved in the reaction.
  • The enzyme’s active site and the substrate thus have complementary shapes.

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48 “Enzyme Catalysis: Cleaner, Safer, Energy Efficient” from Further Readings
49 “Environmental Catalysts” from Further Readings
50 “Practical Enzyme Kinetics” from Further Readings
51 Figure 14.24 from Transparency Pack
52 “Breaking Bonds versus Chopping Heads: The Enzyme as Butcher” from Further Readings
53 “Biocatalysis Makes Headway in Chemicals” From Further Readings
54 Figure 14.26 from Transparency Pack
55 “The Catalytic Function of Enzymes” from Further Readings
56 “Enzyme Activity: A Simple Analogy” from Further Readings
57 “Enzyme Kinetics: Effects of Temperature and an Inhibitor on Catalase Extracted from Potato” from Live Demonstrations
• However, there may be a significant amount of flexibility at the active site.
  • It may change shape as it binds to the substrate.
  • A reaction occurs very quickly once the substrate is bound.
  • Products depart the active site at the end of the reaction.
  • This allows new substrate molecules to bind to the enzyme.
• If a molecule binds so tightly to an enzyme that substrate molecules cannot displace it, then the active site is blocked and the catalyst is inhibited.
  • Such molecules are called *enzyme inhibitors*.
  • Many poisons act by binding to the active site, blocking the binding of substrates.
  • Some poisons bind to *other* locations on the enzyme.
    • Binding ultimately causes a change in the enzyme that interferes with enzyme activity.
• Enzymes are extremely efficient catalysts.
  • The number of individual catalytic events occurring at an active site per unit time is called the *turnover number*.
    • Large turnover numbers correspond to very low $E_a$ values.
    • For enzymes, turnover numbers are very large (typically $10^3–10^7$ per second).

**Nitrogen Fixation and Nitrogenase**
• Nitrogen gas cannot be used in the soil for plants or animals.
• Nitrogen compounds, NH$_3$, NO$_2^-$, and NO$_3^-$ are used in the soil.
• The conversion between N$_2$ and NH$_3$ is a process with a high activation energy (the NN triple bond needs to be broken).
• Nitrogenase, an enzyme in bacteria that lives in root nodules of legumes such as clover and alfalfa, catalyses the reduction of nitrogen to ammonia.
  • The fixed nitrogen (NH$_3$, NO$_2^-$, and NO$_3^-$) is consumed by plants and then eaten by animals.
  • Animal waste and dead plants are attacked by bacteria that break down the fixed nitrogen and produce N$_2$ gas for the atmosphere.
Further Readings:
4. Elizabeth Wilson, “Light Sticks,” *Chemical and Engineering News*, **January 18, 1999**, 65. This is a brief article on chemiluminescent light sticks.


**Live Demonstrations:**


