

Chapter 14. Chemical Kinetics

Common Student Misconceptions

- Students often assume that reaction orders may be determined from stoichiometric coefficients *regardless* of the reaction mechanism.
- Students have difficulty comprehending zero-order processes.
- Students have difficulty understanding the relationship between various experimental results and the rate of reaction.
- Students often confuse fast reactions with those with large reaction yields.
- Students have difficulty distinguishing between kinetic and thermodynamic control of reactions.
- Students often confuse intermediates and transition states.
- Students often confuse *adsorption* and *absorption*.

Teaching Tips

- It is possible for mathematics to get in the way of some students' understanding of the chemistry of this chapter.
- Remind students that the term *change in* a quantity always refers to the *final* minus the *initial* value.
- Remind students to use the absolute temperature (in Kelvin) when manipulating the Arrhenius equation.
- Emphasize to students that the coefficients of the balanced chemical equation do not necessarily correspond to the reaction orders in the rate law. However, the rate law of an elementary step *does* follow from the coefficients of the balanced equation of the step.

Lecture Outline

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

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

14.2 Reaction Rates^{5,6}

- The speed of a reaction is defined as the change that occurs per unit time.

¹ "Appearing Red" from Live Demonstrations

² "A New Twist on the Iodine Clock Reaction: Determining the Order of a Reaction" from Live Demonstrations

³ "Hydrogen Peroxide Iodine Clock: Oxidation of Potassium Iodide by Hydrogen Peroxide" from Live Demonstrations

⁴ "The Starch-Iodine Clock Reaction" from Live Demonstrations

⁵ "Progress of Reaction" Activity from Instructor's Resource CD/DVD

⁶ "The Fizz Keeper, A Case Study in Chemical Education, Equilibrium, and Kinetics" from Further Readings

- It is often determined by measuring the change in concentration of a reactant or product with time.
- For a reaction $A \rightarrow B$

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

- Here the change in the concentration of B is defined as:
 $\Delta (\text{concentration of B}) = (\text{concentration of B at final time}) - (\text{concentration of B at initial time})$
- 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 $t = 20$ s, there is 0.54 M A and 0.46 M B.
 - At $t = 40$ s, 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:

$$\text{Avg Rate} = \frac{\Delta (\text{Conc B})}{\Delta t} = \frac{(\text{Conc of B at } t = 20\text{s}) - (\text{Conc of B at } t = 0\text{s})}{20\text{s} - 0\text{min}}$$

$$\text{Avg Rate} = \frac{0.46\text{M} - 0.00\text{M}}{20\text{s} - 0\text{s}} = 0.023 \frac{\text{M}}{\text{s}}$$

- 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
 - 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 Time⁷

- 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:

$$\text{C}_4\text{H}_9\text{Cl}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{C}_4\text{H}_9\text{OH}(aq) + \text{HCl}(aq)$$
 - We can calculate the average rate in terms of the disappearance of $\text{C}_4\text{H}_9\text{Cl}$.
 - The units for average rate are *mol/Ls* or *M/s*.
 - The average rate decreases with time.

Instantaneous Rate

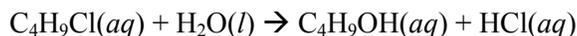
- We can plot $[\text{C}_4\text{H}_9\text{Cl}]$ versus time.
 - The rate at any instant in time is called the **instantaneous rate**.
 - It is the slope of the straight line tangent to the curve at that instant.
 - Instantaneous rate is different from average rate.

⁷ Figure 14.4 from Transparency Pack

- 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 Stoichiometry⁸

- For the reaction:



- The rate of appearance of $\text{C}_4\text{H}_9\text{OH}$ must equal the rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$.

$$\text{Rate} = -\frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = \frac{\Delta[\text{C}_4\text{H}_9\text{OH}]}{\Delta t}$$

- What if the stoichiometric relationships are not one-to-one?

- For the reaction:



- The rate may be expressed as:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$$

- We can generalize this equation a bit.

- For the reaction:

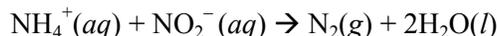


- The rate may be expressed as:

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

14.3 Concentration and Rate Laws^{9,10,11}

- 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:



- 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 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**.

⁸ Figure 14.6 from Transparency Pack

⁹ "Decomposition of N_2O_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

- 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.

Reaction Orders: The Exponents in the Rate Law¹²

- 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.
 - The overall order of reaction is $m + n + \dots$.
- 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.

Magnitudes and Units of Rate Constants

- In comparing reactions to evaluate which ones are relatively fast and which are relative slow, the rate constants are compared:
 - A large value of k (10^9 or greater): the reaction is fast.
 - A small value of k (10 or lower): the reaction is slow.
- Units of the rate constant depend on the overall reaction order.

Using Initial Rates to Determine Rate Laws¹³

- 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.

FORWARD REFERENCES

- The importance of pH in determining the rates of proton transfer reactions in biological systems will be mentioned in Chapter 16 (section 16.4).

14.4 The Change of Concentration with Time¹⁴

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

First-Order Reactions^{15,16,17,18}

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

¹² “An Analogy to Help Students Understand Reaction Orders” from Further Readings

¹³ “Chlorine” 3-D Model from Instructor’s Resource CD/DVD

¹⁴ “CFCs and Stratospheric Ozone” Movie from Instructor’s Resource CD/DVD

¹⁵ “First-Order Process” Animation from Instructor’s Resource CD/DVD

¹⁶ “Don’t Be Tricked by Your Integrated Rate Plot!” from Further Readings

¹⁷ “Acetonitrile” 3-D Model from Instructor’s Resource CD/DVD

¹⁸ “Methyl Isonitrile” 3-D Model from Instructor’s Resource CD/DVD

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

- Integrating, we get the *integrated rate law*:

$$\ln[\text{A}]_t - \ln[\text{A}]_0 = -kt$$

- Rearranging:

$$\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$$

- An alternate form:

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

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

Second-Order Reactions^{19,20}

- 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:

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2$$

- Integrating, we get the integrated form of the rate law:
- A plot of $1/[\text{A}]_t$ versus t is a straight line with slope k and intercept $1/[\text{A}]_0$.

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

- For a second-order reaction, a plot of $\ln[\text{A}]_t$ vs. t is not linear.
- Note that a second-order process can have a rate constant expression of the form:

$$\text{Rate} = k[\text{A}][\text{B}]$$
 - That is, the reaction is second order overall, but has first-order dependence on A and B.

Zero-Order Reactions²¹

- A **zero-order reaction** is one whose rate is independent of the reactant concentration.

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k$$

- The integrated rate law for a zero-order reaction is:

$$[\text{A}]_t = -kt + [\text{A}]_0$$

¹⁹ Figure 14.8 from Transparency Pack

²⁰ Figure 14.9 from Transparency Pack

²¹ “Mice in the Box for Zero-Order Kinetics” from Further Readings

Half-life

- **Half-life**, $t_{1/2}$, is the time required for the concentration of a reactant to decrease to half its original value.
 - That is, half life, $t_{1/2}$, is the time taken for $[A]_0$ to reach $\frac{1}{2} [A]_0$.
 - Mathematically, the half life of a first-order reaction is:

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

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

$$\ln \frac{\frac{1}{2}[A]_0}{[A]_0} = -kt_{1/2}$$

$$\ln \frac{1}{2} = -kt_{1/2}$$

$$\therefore t_{1/2} = -\frac{\ln 1/2}{k} = \frac{0.693}{k}$$

- 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:

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

- Note that, unlike for the first-order reaction, the half-life of a second-order reaction is dependent on the initial concentration of the reactant.

FORWARD REFERENCES

- Rates of radioactive decay processes, half-lives of radioactive isotopes, and radiocarbon dating will be further discussed in Chapter 21 (section 21.4).

14.5 Temperature and Rate^{22,23,24,25}

- 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?

²² “Lightsticks” from Live Demonstrations

²³ “Cool-Light Chemiluminescence” from Live Demonstrations

²⁴ “Light Sticks” from Further Readings

²⁵ Figure 14.14 from Transparency Pack

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

The Collision Model^{26,27,28}

- 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 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 Factor²⁹

- 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 Cl_2 and NO.
 - If the Cl collides with the O of NOCl, no products are formed.

Activation Energy^{30,31,32}

- Arrhenius: Molecules must possess a minimum amount of energy to react. Why?
 - In order to form products, bonds must be broken in the reactants.
 - Bond breakage requires energy.
 - Molecules moving too slowly, with too little kinetic energy, don't 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 $\text{N}\equiv\text{C}$ group to allow the $\text{N}\equiv\text{C}$ to rotate.
 - The C–C bond begins to form.

²⁶ “Audience-Appropriate Analogies: Collision Theory” from Further Readings

²⁷ “Arrhenius Model” Activity from Instructor’s Resource CD/DVD

²⁸ “The Collision Theory and an American Tradition” from Further Readings

²⁹ Figure 14.15 from Transparency Pack

³⁰ Figure 14.17 from Transparency Pack

³¹ Figure 14.18 from Transparency Pack

³² “Just What Is a Transition State?” from Further Readings

- 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_3NC and CH_3CN .
 - ΔE_{rxn} has no effect on reaction rate.
- The activation energy is the difference in energy between reactants, (CH_3NC) 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 ($\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$), then the reverse reaction is endothermic ($\text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{NC}$).
- 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:

$$f = e^{-\frac{E_a}{RT}}$$

- R is the gas constant (8.314 J/mol·K) 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^{33,34}

- 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.
 - 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**.

$$k = Ae^{-\frac{E_a}{RT}}$$

- Where k is the rate constant, E_a is the activation energy, R is the gas constant (8.314 J/K·mol), 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*.

Determining the Activation Energy

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

$$\ln k = -\frac{E_a}{RT} + \ln A$$

³³ “The Arrhenius Law and Storage of Food” from Further Readings

³⁴ “Visualizing the Transition State: A Hands-On Approach to Arrhenius Equation” from Further Readings

- 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:

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

FORWARD REFERENCES

- The role of temperature in affecting the position of equilibrium will be discussed in Chapter 15 (section 15.7).

14.6 Reaction Mechanisms^{35,36}

- 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 Reactions³⁷

- **Elementary reactions** or elementary processes 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 Mechanisms³⁸

- 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.
 - Intermediates are NOT the same as transition states.

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^{39,40}

- Most reactions occur by mechanisms with more than one elementary step.
 - Often one step is much slower than the others.
 - The slow step limits the overall reaction rate.
 - This is called the **rate-determining step** (*rate-limiting step*) of the reaction.

³⁵ “Pictorial Analogies XIII: Kinetics and Mechanisms” from Further Readings

³⁶ “Doing the Dishes: An Analogy for Use in Teaching Reaction Kinetics” from Further Readings

³⁷ “Bimolecular Reaction” Animation from Instructor’s Resource CD/DVD

³⁸ “Fluorine” 3-D Model from Instructor’s Resource CD/DVD

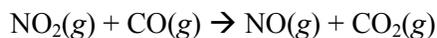
³⁹ “Auto Analogies” from Further Readings

⁴⁰ “Another Auto Analogy: Rate Determining Steps” from Further Readings

- This step governs the overall rate law for the overall reaction.

Mechanisms with a Slow Initial Step

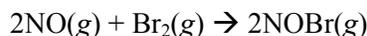
- Consider the reaction:



- The experimentally derived rate law is: $\text{Rate} = k[\text{NO}_2]^2$
- We propose a mechanism for the reaction:
 - Step 1: $\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \xrightarrow{k_1} \text{NO}_3(\text{g}) + \text{NO}(\text{g})$ slow step
 - Step 2: $\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \xrightarrow{k_2} \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$ fast step
 - Note that 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:



- The experimentally determined rate law is:

$$\text{Rate} = k[\text{NO}]^2[\text{Br}_2]$$
- Consider the following proposed mechanism:
 - Step 1: $\text{NO}(\text{g}) + \text{Br}_2(\text{g}) \xrightleftharpoons[k_{-1}]{k_1} \text{NOBr}_2(\text{g})$ fast step
 - Step 2: $\text{NOBr}_2(\text{g}) + \text{NO}(\text{g}) \xrightarrow{k_2} 2\text{NOBr}(\text{g})$ 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 $[\text{NOBr}_2]$ in terms of NOBr and Br_2 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:

$$k_1[\text{NO}][\text{Br}_2] = k_{-1}[\text{NOBr}_2]$$
- Solving for NOBr_2 we get:

$$[\text{NOBr}_2] = \frac{k_1}{k_{-1}}[\text{NO}][\text{Br}_2]$$

- Therefore, the overall rate law becomes:

$$\text{Rate} = k_2 \frac{k_1}{k_{-1}}[\text{NO}][\text{Br}_2][\text{NO}] = k[\text{NO}]^2[\text{Br}_2]$$

- Note that the final rate law is consistent with the experimentally observed rate law.

FORWARD REFERENCES

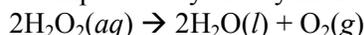
- The relationship between k_1 and k_{-1} will be exploited in Chapter 15 (section 15.1).
- Mechanism of organic addition reactions will be discussed in Chapter 24 (section 24.4).

14.7 Catalysis^{41,42}

- 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 and
 - heterogeneous.
- Catalysts are common in the body, in the environment, and in the chemistry lab!

Homogeneous Catalysis^{43,44,45,46,47,48}

- 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:



- In the presence of bromide ion, the decomposition occurs rapidly in acidic solution:



- Br^- is a catalyst because it is regenerated at the end of the reaction.
- The net reaction is still:

$$2\text{H}_2\text{O}_2(aq) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$$
- How do catalysts increase reaction rates?
 - In general, catalysts operate by *lowering the overall activation energy for a chemical 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, H_2O_2 decomposes directly to water and oxygen.
 - In the presence of Br^- , $\text{Br}_2(aq)$ 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.

⁴¹ “Catalysis” from Further Readings

⁴² “Catalysis” Movie from Instructor’s Resource CD/DVD

⁴³ “Catalytic Decomposition of Hydrogen Peroxide: Foam Production” from Live Demonstrations

⁴⁴ Figure 14.22 from Transparency Pack

⁴⁵ “Catalysis: New Reaction Pathways, Not Just a Lowering of the Activation Energy” from Further Readings

⁴⁶ “Hydrogen Peroxide” 3-D Model from Instructor’s Resource CD/DVD

⁴⁷ “Oxygen” 3-D Model from Instructor’s Resource CD/DVD

⁴⁸ “Bromine” 3-D Model from Instructor’s Resource CD/DVD

Heterogeneous Catalysis^{49,50,51,52,53,54,55}

- 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.
 - *Absorption* refers to the uptake of molecules into the interior of another substance.
 - Molecules are adsorbed onto 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.
 - how the catalyst was treated prior to use.
 - For example, consider the hydrogenation of ethylene to form ethane:

$$\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) \quad \Delta H^\circ = -137 \text{ kJ/mol}$$
 - 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 π bond breaks and a C–H σ bond forms.
 - An *ethyl group*, C_2H_5 , is weakly bonded to the metal surface with a metal-carbon σ bond.
 - When C_2H_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.

⁴⁹ “Catalysis on Surfaces” from Further Readings

⁵⁰ “Surface Reaction-Hydrogenation” Animation from Instructor’s Resource CD/DVD

⁵¹ “Solid Acid Catalysts” from Further Readings

⁵² “Getting Auto Exhausts to Pristine” from Further Readings

⁵³ “Driving Down Emissions” from Further Readings

⁵⁴ “Ethylene” 3-D Model from Instructor’s Resource CD/DVD

⁵⁵ “Ethane” 3-D Model from Instructor’s Resource CD/DVD

Enzymes^{56,57,58,59,60,61,62,63,64,65}

- **Enzymes** are biological catalysts.
- Most enzymes are large protein molecules.
 - Molar masses are in the range of 10^4 to 10^6 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.
 - However, there may be a significant amount of flexibility at the active site.
 - It may change shape as it binds substrate.
 - A reaction occurs very quickly once 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^{66,67}

- 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.

⁵⁶ “Enzyme Catalysis: Cleaner, Safer, Energy Efficient” from Further Readings

⁵⁷ “Environmental Catalysts” from Further Readings

⁵⁸ “Practical Enzyme Kinetics” from Further Readings

⁵⁹ Figure 14.27 from Transparency Pack

⁶⁰ “Breaking Bonds versus Chopping Heads: The Enzyme as Butcher” from Further Readings

⁶¹ “Biocatalysis Makes Headway in Chemicals” From Further Readings

⁶² “The Catalytic Function of Enzymes” from Further Readings

⁶³ “Frank Westheimer’s Early Demonstration of Enzymatic Specificity” from Further Readings

⁶⁴ “Enzyme Activity: A Simple Analogy” from Further Readings

⁶⁵ “Enzyme Kinetics: Effects of Temperature and an Inhibitor on Catalase Extracted from Potato” from Live Demonstrations

⁶⁶ “FeMo-cofactor of Nitrogenase” 3-D Model from Instructor’s Resource CD/DVD

⁶⁷ “Nitrogen Dioxide” 3-D Model from Instructor’s Resource CD/DVD

- The conversion between N_2 and NH_3 is a process with a high activation energy (the N_2 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.

FORWARD REFERENCES

- The effect of catalysts on equilibrium and catalytic converters will be discussed in Chapter 15 (section 15.7).
- Metal ions will be mentioned as integral parts of many enzymes in Chapter 23 (section 23.4).
- Chiral enzymes will be mentioned in Chapter 23 (section 23.4).
- The degree of subdivision of a catalyst will be mentioned in Chapter 24 (section 24.4).
- The role of proteins as enzymes will be discussed in Chapter 24 (section 24.10).

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