Reaction Rates

1. Definition of Reaction Rate
a. Define reaction rate.
b. Explain instantaneous rate and average rate of a reaction.
c. Explain how the different ways of expressing reaction rates are related.
d. Calculate average reaction rate.

2. Experimental Determination of Rate
a. Describe how reaction rates may be experimentally determined.

3. Dependence of Rate on Concentration
a. Define and provide examples of a rate law, rate constant, and reaction order.
b. Determine the order of reaction from the rate law.
c. Determine the rate law from initial rates.

4. Change of Concentration with Time
a. Learn the integrated rate laws for first-order, second-order, and zero-order reactions.
b. Use an integrated rate law.
c. Define half-life of a reaction.
d. Learn the half-life equations for first-order, second-order, and zero-order reactions.
e. Relate the half-life of a reaction to the rate constant.
f. Plot kinetic data to determine the order of a reaction.

5. Temperature and Rate; Collision and Transition-State Theories
a. State the postulates of collision theory.
b. Explain activation energy ($E_a$).
c. Describe how temperature, activation energy, and molecular orientation influence reaction rates.
d. State the transition-state theory.
e. Define activated complex.
f. Describe and interpret potential-energy curves for endothermic and exothermic reactions.

6. Arrhenius Equation
a. Use the Arrhenius equation.

Reaction Mechanisms

7. Elementary Reactions
a. Define elementary reaction, reaction mechanism, and reaction intermediate. Determine the rate law from initial rates.
b. Write the overall chemical equation from a mechanism.
c. Define molecularity.
d. Give examples of unimolecular, bimolecular, and termolecular reactions.
e. Determine the molecularity of an elementary reaction.
f. Write the rate equation for an elementary reaction.
8. The Rate Law and the Mechanism
   a. Explain the rate-determining step of a mechanism.
   b. Determine the rate law from a mechanism with an initial slow step.
   c. Determine the rate law from a mechanism with an initial fast, equilibrium step.

9. Catalysis
   a. Describe how a catalyst influences the rate of a reaction.
   b. Indicate how a catalyst changes the potential-energy curve of a reaction.
   c. Define homogeneous catalysis and heterogeneous catalysis.
   d. Explain enzyme catalysis.

Chemical kinetics is the study of reaction rates, how reaction rates change under varying conditions, and what molecular events occur during the overall reaction.

- What variables affect reaction rate?
  - Concentration of reactants.
  - Concentration of a catalyst
  - Temperature at which the reaction occurs.
  - Surface area of a solid reactant or catalyst.
  - Nature of material.

Rates of Reaction

Chemical reactions require varying lengths of time for completion.

This reaction rate depends on the characteristics of the reactants and products and the conditions under which the reaction is run.

- The questions posed in this chapter will be:
  - How is the rate of a reaction measured?
  - What conditions will affect the rate of a reaction?
  - How do you express the relationship of rate to the variables affecting the rate?
  - What happens on a molecular level during a chemical reaction?

What variables affect reaction rate?

Let’s look at each in more detail.

- Concentration of reactants.
  - More often than not, the rate of a reaction increases when the concentration of a reactant is increased.
  - Increasing the population of reactants increases the likelihood of a successful collision.
  - In some reactions, however, the rate is unaffected by the concentration of a particular reactant, as long as it is present at some concentration.
Concentration of a catalyst.

- A catalyst is a substance that increases the rate of a reaction without being consumed in the overall reaction.

- The catalyst generally does not appear in the overall balanced chemical equation (although its presence may be indicated by writing its formula over the arrow).

\[
2H_2O_2(\text{aq}) \xrightarrow{\text{HBr}(\text{aq})} 2H_2O(\text{l}) + O_2(\text{g})
\]
• Temperature at which a reaction occurs.
  - Usually reactions speed up when the temperature increases.
  - A good “rule of thumb” is that reactions approximately double in rate with a 10 °C rise in temperature.

• Surface area of a solid reactant or catalyst.
  Because the reaction occurs at the surface of the solid, the rate increases with increasing surface area.
  Figure 13.3 shows the effect of surface area on reaction rate.

• The reaction rate is the increase in molar concentration of a product of a reaction per unit time.
  - It can also be expressed as the decrease in molar concentration of a reactant per unit time.
  - “The reaction rate is the change in molar concentration of a product or reactant of a reaction per unit time.”

• Consider the gas-phase decomposition of dinitrogen pentoxide.
  \[2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)\]
  - If we denote molar concentrations using brackets, then the change in the molarity of \( O_2 \) would be represented as \( \Delta\left[O_2\right] \)
  - The symbol, \( \Delta \) (capital Greek delta), means “the change in.”

• Then, in a given time interval, \( \Delta t \), the molar concentration of \( O_2 \) would increase by \( \Delta\left[O_2\right] \).
  - The rate of the reaction is given by:
  \[\text{Rate of formation of oxygen} = \frac{\Delta\left[O_2\right]}{\Delta t}\]
  - This equation gives the average rate over the time interval, \( \Delta t \).
  - If \( \Delta t \) is short, you obtain an instantaneous rate, that is, the rate at a particular instant.

In the reaction
\[2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)\]
You obtain the instantaneous rate from the slope of the tangent at the point of the curve corresponding to that time.
Definition of Reaction Rate

- Previous figure shows the increase in concentration of \( \text{O}_2 \) during the decomposition of \( \text{N}_2\text{O}_5 \).

Note that the rate decreases as the reaction proceeds.

Definition of Reaction Rates

- Because the amounts of products and reactants are related by stoichiometry, any substance in the reaction can be used to express the rate.

\[ 2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g) \]

Rate of decomposition of \( \text{N}_2\text{O}_5 \) = \( \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} \)

- Note the negative sign. This results in a positive rate as reactant concentrations decrease.

1. The rate law for the chemical reaction

\[ 2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g) \]

is rate = \( k[\text{N}_2\text{O}_5(g)] \).

What units does \( k \) have?

a) mol/liter
b) mol/sec
c) 1/sec
d) liter/sec

8. For an endothermic reaction, the activation energy is

a) less than \( \Delta H \).
b) equal to \( \Delta H \).
c) greater than \( \Delta H \).
d) the negative of \( \Delta H \).
Experimental Determination of Reaction Rates

- To obtain the rate of a reaction you must determine the concentration of a reactant or product during the course of the reaction.
  - One method for slow reactions is to withdraw samples from the reaction vessel at various times and analyze them.
  - More convenient are techniques that continuously monitor the progress of a reaction based on some physical property of the system.

Gas-phase partial pressures.
- When dinitrogen pentoxide crystals are sealed in a vessel equipped with a manometer (see Figure 13.6) and heated to 45°C, the crystals vaporize and the N₂O₅(g) decomposes.
  \[2N₂O₅(g) \rightarrow 4NO₂(g) + O₂(g)\]
- Manometer readings provide the concentration of N₂O₅ during the course of the reaction based on partial pressures.

Dependence of Rate on Concentration

- Experimentally, it has been found that the rate of a reaction depends on the concentration of certain reactants as well as catalysts.
  - Let’s look at the reaction of nitrogen dioxide with fluorine to give nitryl fluoride.
    \[2NO₂(g) + F₂(g) \rightarrow 2NO₂F(g)\]
  - The rate of this reaction has been observed to be proportional to the concentration of nitrogen dioxide.

A rate law is an equation that relates the rate of a reaction to the concentration of reactants (and catalyst) raised to various powers.

\[\text{Rate} = k[\text{NO}_2][\text{F}_2]\]

- The rate constant, \(k\), is a proportionality constant in the relationship between rate and concentrations.
Dependence of Rate on Concentration

- As a more general example, consider the reaction of substances A and B to give D and E.
  
  \[ aA + bB \rightarrow ^C dD + eE \]
  
  \( C \) = catalyst

  - You could write the rate law in the form

  \[ \text{Rate} = k[A]^m[B]^n[C]^p \]

  - The exponents \( m, n, \) and \( p \) are frequently, but not always, integers. They must be determined experimentally and cannot be obtained by simply looking at the balanced equation.

Dependence of Rate on Concentration

- **Reaction Order**

  - The reaction order with respect to a given reactant species equals the exponent of the concentration of that species in the rate law, as determined experimentally.

  - The overall order of the reaction equals the sum of the orders of the reacting species in the rate law.

Do exercise 14.3 and 4 Problems 14.26, 28

Consider the reaction \( Q + R \rightarrow S + T \) and the rate law for the reaction:

\[ \text{Rate} = k[Q]^m[R]^n \]

a. You run the reaction three times, each time starting with \([R] = 2.0 \text{ M}\). For each run you change the starting concentration of \([Q]\): run 1, \([Q] = 0.0 \text{ M}\); run 2, \([Q] = 1.0 \text{ M}\); run 3, \([Q] = 2.0 \text{ M}\). Rank the rate of the three reactions using each of these concentrations.

b. The way the rate law is written in this problem is not typical for expressions containing reactants that are zero order in the rate law. Write the rate law in the more typical fashion.

  0.0 M slowest (No Reaction), the other two are equal

  \[ \text{Rate} = k[R]^2 \]

Molecular view of the reaction

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

Dependence of Rate on Concentration

- **Reaction Order**

  - Consider the reaction of nitric oxide with hydrogen according to the following equation.

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

  - The experimentally determined rate law is

  \[ \text{Rate} = k[\text{NO}]^2[\text{H}_2] \]

  - Thus, the reaction is second order in NO, first order in \( \text{H}_2 \), and third order overall.

Do exercise 14.3 and 4 Problems 14.26, 28

- **Zero and negative orders are also possible.**

  - The concentration of a reactant with a zero-order dependence has no effect on the rate of the reaction.

- Although reaction orders frequently have whole number values (particularly 1 and 2), they can be fractional.
Dependence of Rate on Concentration

• Determining the Rate Law.
  - One method for determining the order of a reaction with respect to each reactant is the method of initial rates.
  - It involves running the experiment multiple times, each time varying the concentration of only one reactant and measuring its initial rate.
  - The resulting change in rate indicates the order with respect to that reactant.

A Problem to Consider

• Iodide ion is oxidized in acidic solution to triiodide ion, $I_3^-$, by hydrogen peroxide.

$$H_2O_2(aq) + 3I^- (aq) + 2H^+ (aq) \rightarrow I_3^- (aq) + 2H_2O(l)$$
  - A series of four experiments was run at different concentrations, and the initial rates of $I_3^-$ formation were determined.
  - From the following data, obtain the reaction orders with respect to $H_2O_2$, I, and $H^+$.
  - Calculate the numerical value of the rate constant.

<table>
<thead>
<tr>
<th>Initial Concentrations (mol/L)</th>
<th>$H_2O_2$</th>
<th>I</th>
<th>$H^+$</th>
<th>Initial Rate [mol/(L·s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. 1</td>
<td>0.010</td>
<td>0.010</td>
<td>0.00050</td>
<td>$1.15 \times 10^{-6}$</td>
</tr>
<tr>
<td>Exp. 2</td>
<td>0.020</td>
<td>0.010</td>
<td>0.00050</td>
<td>$2.30 \times 10^{-6}$</td>
</tr>
<tr>
<td>Exp. 3</td>
<td>0.010</td>
<td>0.020</td>
<td>0.00050</td>
<td>$2.30 \times 10^{-6}$</td>
</tr>
<tr>
<td>Exp. 4</td>
<td>0.010</td>
<td>0.010</td>
<td>0.00100</td>
<td>$1.15 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

- Comparing Experiment 1 and Experiment 2, you see that when the $H_2O_2$ concentration doubles (with other concentrations constant), the rate doubles.
- This implies a first-order dependence with respect to $H_2O_2$.

<table>
<thead>
<tr>
<th>Initial Concentrations (mol/L)</th>
<th>$H_2O_2$</th>
<th>I</th>
<th>$H^+$</th>
<th>Initial Rate [mol/(L·s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. 1</td>
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<td>0.010</td>
<td>0.00050</td>
<td>$1.15 \times 10^{-6}$</td>
</tr>
<tr>
<td>Exp. 2</td>
<td>0.020</td>
<td>0.010</td>
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<td>Exp. 4</td>
<td>0.010</td>
<td>0.010</td>
<td>0.00100</td>
<td>$1.15 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

- Comparing Experiment 1 and Experiment 3, you see that when the I concentration doubles (with other concentrations constant), the rate doubles.
- This implies a first-order dependence with respect to I.

<table>
<thead>
<tr>
<th>Initial Concentrations (mol/L)</th>
<th>$H_2O_2$</th>
<th>I</th>
<th>$H^+$</th>
<th>Initial Rate [mol/(L·s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. 1</td>
<td>0.010</td>
<td>0.010</td>
<td>0.00050</td>
<td>$1.15 \times 10^{-6}$</td>
</tr>
<tr>
<td>Exp. 2</td>
<td>0.020</td>
<td>0.010</td>
<td>0.00050</td>
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<tr>
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</tr>
<tr>
<td>Exp. 4</td>
<td>0.010</td>
<td>0.010</td>
<td>0.00100</td>
<td>$1.15 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

- Comparing Experiment 1 and Experiment 4, you see that when the $H^+$ concentration doubles (with other concentrations constant), the rate is unchanged.
- This implies a zero-order dependence with respect to $H^+$. 
Because $[H^+]^0 = 1$, the rate law is:

$$\text{Rate} = k[H_2O_2][I^-][H^+]$$

You can calculate the rate constant by substituting values from any of the experiments. Using Experiment 1 you obtain:

$$1.15 \times 10^{-6} \text{ mol} \text{L}^{-1} \text{s}^{-1} = k \times 0.010 \times 0.010 \text{ mol L}^{-1}$$

You can now calculate the rate constant by substituting values from any of the experiments. Using Experiment 1 you obtain:

$$k = \frac{1.15 \times 10^{-6} \text{ L}(\text{mol s})^{-1}}{0.010 \times 0.010 \text{ mol L}^{-1}} = 1.2 \times 10^{-2} \text{ L}(\text{mol s})^{-1}$$

Change of Concentration with Time

- A rate law simply tells you how the rate of reaction changes as reactant concentrations change.
- A more useful mathematical relationship would show how a reactant concentration changes over a period of time.
- Using calculus we can transform a rate law into a mathematical relationship between concentration and time.
- This provides a graphical method for determining rate laws.

Concentration-Time Equations

- First-Order Integrated Rate Law
  - You could write the rate law in the form
    $$\frac{\Delta [A]}{\Delta t} = k[A]$$
  - Using calculus, you get the following equation.
    $$\ln \left[ \frac{[A]_t}{[A]_0} \right] = -kt$$
  - Here $[A]_t$ is the concentration of reactant A at time t, and $[A]_0$ is the initial concentration.
  - The ratio $[A]_t/[A]_0$ is the fraction of A remaining at time t.

A Problem to Consider

- The decomposition of $N_2O_5$ to NO$_2$ and O$_2$ is first order with a rate constant of $4.8 \times 10^{-4} \text{ s}^{-1}$. If the initial concentration of $N_2O_5$ is $1.65 \times 10^{-2} \text{ mol/L}$,
  - what is the concentration of $N_2O_5$ after 825 seconds?
  - How long would it take for the concentration of $N_2O_5$ to decrease to $1.00 \times 10^{-2} \text{ mol/L}$?
  - The first-order time-concentration equation for this reaction would be:
    $$\ln \left[ \frac{[N_2O_5]_t}{[N_2O_5]_0} \right] = -kt$$
Substituting the given information we obtain:
\[
\ln \frac{[N_2O_5]}{1.65 \times 10^{-2} \text{ mol/L}} = -(4.80 \times 10^{-4} \text{ s}^{-1}) \times (825 \text{ s})
\]
Substituting the given information we obtain:
\[
\ln \frac{[N_2O_5]}{1.65 \times 10^{-2} \text{ mol/L}} = -0.396
\]
Taking the inverse natural log of both sides we obtain:
\[
\frac{[N_2O_5]}{1.65 \times 10^{-2} \text{ mol/L}} = e^{-0.396} = 0.673
\]
Solving for \([N_2O_5]\) at 825 s we obtain:
\[
[N_2O_5] = (1.65 \times 10^{-2} \text{ mol/L}) \times (0.673) = 0.0111 \text{ mol/L}
\]

**Concentration-Time Equations**

- **First-Order Integrated Rate Law**
  - Using calculus, you get the following equation.
  \[
  \ln \frac{[A]_t}{[A]_0} = -kt
  \]
  - Here \([A]_t\) is the concentration of reactant A at time t, and \([A]_0\) is the initial concentration.
  - The ratio \([A]_t/[A]_0\) is the fraction of A remaining at time t.

- **Second-Order Integrated Rate Law**
  \[
  \frac{1}{[A]_t} = kt + \frac{1}{[A]_0}
  \]
  - Here \([A]_t\) is the concentration of reactant A at time t, and \([A]_0\) is the initial concentration.

- **Zero-Order Integrated Rate Law**
  \[
  [A]_t = -kt + [A]_0
  \]

**How long would it take for the concentration of \(N_2O_5\) to decrease to \(1.00 \times 10^{-2}\) mol/L?**
\[
\ln \frac{[A]_t}{[A]_0} = -kt
\]
\[
\ln \frac{[N_2O_5]_t}{[N_2O_5]_0} = -kt
\]
\[
\ln \frac{1.00 \times 10^{-2} \text{ mol/L}}{1.65 \times 10^{-2} \text{ mol/L}} = -4.80 \times 10^{-4} \text{ s}^{-1} \times t
\]
\[
0.501 = 4.80 \times 10^{-4} \text{ s}^{-1} \times t
\]
\[
t = \frac{0.501}{4.80 \times 10^{-4} \text{ s}^{-1}} = 1.04 \times 103 \text{ s} (17.4 \text{ min})
\]

**Concentration-Time Equations**

- **Second-Order Integrated Rate Law**
  - You could write the rate law in the form
  \[
  \text{Rate} = -\frac{\Delta [A]}{\Delta t} = k[A]^2
  \]

- **Zero-Order Integrated Rate Law**
  \[
  [A]_t = -kt + [A]_0
  \]

Do exercises 14.6, 7, 8, 9

Problems 14.46-77
Half-life

- The half-life of a reaction is the time required for the reactant concentration to decrease to one-half of its initial value.
  - For a first-order reaction, the half-life is independent of the initial concentration of reactant.
  - In one half-life the amount of reactant decreases by one-half. Substituting into the first-order concentration-time equation, we get:

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

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

- Substitute the value of k into the relationship between k and \( t_{1/2} \).

\[
t_{1/2} = \frac{0.693}{k}
\]

- Sulfuryl chloride, \( \text{SO}_2\text{Cl}_2 \), decomposes in a first-order reaction to \( \text{SO}_2 \) and \( \text{Cl}_2 \).

\[
\text{SO}_2\text{Cl}_2(g) \rightarrow \text{SO}_2(g) + \text{Cl}_2(g)
\]

- At 320 °C, the rate constant is \( 2.2 \times 10^{-5} \text{ s}^{-1} \). What is the half-life of \( \text{SO}_2\text{Cl}_2 \) vapor at this temperature?
- Substitute the value of k into the relationship between k and \( t_{1/2} \).

\[
t_{1/2} = \frac{0.693}{k}
\]

- Problems 14.78 – 14.87

Half-life

- For a second-order reaction, half-life depends on the initial concentration and becomes larger as time goes on.
- Again, assuming that \([A]_t = \frac{1}{2}[A]_0\), after one half-life, it can be shown that:

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

- Each succeeding half-life is twice the length of its predecessor.

Half-life

- For Zero-Order reactions, the half-life is dependent upon the initial concentration of the reactant and becomes shorter as the reaction proceeds.

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

• In addition to the method of initial rates, rate laws can be deduced by graphical methods.

  If we rewrite the first-order concentration-time equation in a slightly different form, it can be identified as the equation of a straight line.

  \[ \ln \frac{[A]_t}{[A]_0} = -kt \]
  \[ \ln[A]_i = -kt + \ln[A]_0 \]
  \[ y = mx + b \]

• If we rewrite the second-order concentration-time equation in a slightly different form, it can be identified as the equation of a straight line.

  \[ \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \]
  \[ y = mx + b \]

• This means if you plot \(1/[A]\) versus time, you will get a straight line for a second-order reaction.

• Figure 13.10 illustrates the graphical method of deducing the order of a reaction.

\[ \text{Figure 13.10: Plotting the data for the decomposition of nitrogen dioxide at 330°C} \]

\[ \text{Table 14.4 page 638} \]
Let's look again at the integrated rate laws:

<table>
<thead>
<tr>
<th>Order</th>
<th>Rate Law</th>
<th>Integrated Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Rate = ( k )</td>
<td>([A] = -kt + [A]_0)</td>
</tr>
<tr>
<td>1</td>
<td>Rate = ( k[A] )</td>
<td>(\ln[A] = -kt)</td>
</tr>
<tr>
<td>2</td>
<td>Rate = ( k[A]^2 )</td>
<td>(\frac{1}{[A]} = \frac{kt}{[A]_0} + \frac{1}{[A]_0})</td>
</tr>
</tbody>
</table>

In each case, the rate law is in the form of \( y = mx + b \), allowing us to use the slope and intercept to find the values.

### Zero Order: \([A]_f = -kt + [A]_0\)
For a zero-order reaction, a plot of \([A]\) versus \( t \) is linear. The \( y \)-intercept is \([A]_0\).

### First Order: \(\ln[A]_f = -kt + \ln[A]_0\)
For a first-order reaction, a plot of \(\ln[A]\) versus \( t \) is linear. The graph crosses the origin (\( b = 0 \)).

### Second Order: \(\frac{1}{[A]} = \frac{kt}{[A]_0} + \frac{1}{[A]_0}\)
For a second-order reaction, a plot of \(1/[A]\) versus \( t \) is linear. The \( y \)-intercept is \(1/[A]_0\).

---

**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 be explained by **collision theory**.

---

**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**, \( E_a \).

---

The reaction is second order.

The rate constant is given by the product of three factors.

\[
K = Z \cdot f \cdot p
\]

- The initial concentration decreases in each time interval. The only equation that results in a larger value for \( t_{1/2} \) is the second-order equation.
- The rate constant is given by the product of three factors.

\[
K = Z \cdot f \cdot p
\]

- \( Z = \text{Collision frequency} \)
- \( f = \text{fraction of collisions with energy to react} \)
- \( f = e^{-E_a/RT} \)
- \( p = \text{fraction of collisions with molecules properly oriented} \)
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.

Molecular view of the transition-state theory

- Suppose two balls are coated with a slightly stick adhesive.
- We’ll take a third ball covered with an extremely sticky adhesive and collide it with our joined pair.
- At the instant of impact, when all three spheres are joined, we have an unstable transition-state 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.”

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.
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.

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 is illustrated using the kinetic theory of gases, which shows the relationship between the velocity of gas molecules and their absolute temperature.

\[
velocity = \frac{3RT_{\text{abs}}}{M_m} \quad \text{or} \quad velocity \propto \sqrt{\frac{T_{\text{abs}}}{M_m}}
\]
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.

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.

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

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

The Arrhenius Equation

- 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.

The Arrhenius Equation

- It is useful to recast the Arrhenius equation in logarithmic form.
  - Taking the natural logarithm of both sides of the equation, we get:

\[ \ln k = \ln A -\frac{E_a}{RT} \]
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.
    $$ \ln k = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right) $$
    $$ y = b + m x $$
  - 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]

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

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
    $$ \ln k_1 = \ln A - \frac{E_a}{R} \left( \frac{1}{T_1} \right) $$
    $$ \ln k_2 = \ln A - \frac{E_a}{R} \left( \frac{1}{T_2} \right) $$
  - We can eliminate $\ln A$ by subtracting the two equations to obtain
    $$ \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) $$
  - 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, $T_2$.

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 $2.7 \times 10^{-4}$ L/(mol·s) at 600 K and $3.5 \times 10^{-3}$ L/(mol·s) at 650 K. Find the activation energy, $E_a$.
  - Substitute the given data into the Arrhenius equation.
    $$ \ln \frac{3.5 \times 10^{-3}}{2.7 \times 10^{-2}} = \frac{E_a}{8.31 \text{ J/(mol·K)}} \left( \frac{1}{600 \text{ K}} - \frac{1}{650 \text{ K}} \right) $$
• The rate constant for the formation of hydrogen iodide from its elements

\[ \text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g) \]

- Simplifying, we get:

\[ \ln(1.30 \times 10^4) = 1.11 = \frac{E_a}{8.31 \text{J/(mol) } \times (1.28 \times 10^{-4})} \]

- Solving for \(E_a\):

\[ E_a = \frac{1.11 \times 8.31 \text{J/mol}}{1.28 \times 10^{-4}} = 1.66 \times 10^5 \text{J} \]

• In a series of experiments on the decomposition of dinitrogen pentoxide, \(\text{N}_2\text{O}_5\), rate constants were determined at two different temperatures:
  - At 35°C, the rate constant was \(1.4 \times 10^{-4}\)/s.
  - At 45°C, the rate constant was \(5.0 \times 10^{-4}\)/s.
  - What is the activation energy?
  - What is the value of the rate constant at 55°C?

\[ T_1 = 35^\circ\text{C} = 308 \text{K} \quad T_2 = 45^\circ\text{C} = 318 \text{K} \]

\[ k_1 = 1.4 \times 10^{-4}/s \quad k_2 = 5.0 \times 10^{-4}/s \]

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

\[ \ln\left(\frac{5.0 \times 10^{-4}/s}{1.4 \times 10^{-7}/s}\right) = \frac{E_a}{8.314} \left(\frac{1}{308 \text{K}} - \frac{1}{318 \text{K}}\right) \]

\[ 1.273 = E_a \left(\frac{10 \text{K}}{8.3145 \text{J/mol} \cdot \text{K} (318 \text{K})(308 \text{K})}\right) \]

\[ E_a = \frac{1.273 \times 8.3145 \text{J/mol} \cdot \text{K}}{10 \text{K}} = 1.04 \times 10^5 \text{J/mol} \]

• This is actually two problems.
  
  First, we will use the Arrhenius equation to find \(E_a\).

Then, we will use the Arrhenius equation with \(E_a\) to find the rate constant at a new temperature.

\[ T_1 = 35^\circ\text{C} = 308 \text{K} \quad T_2 = 55^\circ\text{C} = 328 \text{K} \]

\[ k_1 = 1.4 \times 10^{-4}/s \quad k_2 = ? \]

\[ E_a = 1.04 \times 10^5 \text{J/mol} \]

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

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.

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

Elementary Reactions

• Each step is a singular molecular event resulting in the formation of products.
  – Note that NO$_2$ does not appear in the overall equation, but is formed as a temporary reaction intermediate.
  – The overall chemical equation is obtained by adding the two steps together and canceling any species common to both sides.

See Sections 14.9 and 14.10 and problems 33-41

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.

• Reaction Mechanism

• A balanced chemical equation is a description of the overall result of a chemical reaction. However, what actually happens on a molecular level may be more involved than what is represented by this single equation. For example, the reaction may take place in several steps. That set of steps is called the reaction mechanism.

• Each step in the reaction mechanism is called an elementary reaction and is a single molecular event.

• The set of elementary reactions, which when added give the balanced chemical equation, is called the reaction mechanism.
• Because an elementary reaction is an actual molecular event, the rate of an elementary reaction is proportional to the concentration of each reactant molecule. This means we can write the rate law directly from an elementary reaction.

Rate Equations for Elementary Reactions

• However, for the reaction

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

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

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

Rate Equations for Elementary Reactions

• 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 proportional to the concentrations of all reactant molecules involved.

Rate Equations for Elementary Reactions

• For example, consider the generic equation below.

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

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

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

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

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

Rate Equations for Elementary Reactions

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

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

would have the rate law:

\[ \text{Rate} = k[A][A][B] \text{ or } \text{Rate} = k[A]^2[B] \]
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 
  \[ \text{Rate} = k[\text{NO}_2][\text{F}_2] \]
  - The reaction is first order with respect to each reactant, even though the coefficient for NO\(_2\) in the overall reaction is 2.

Rate-Determining Step

• 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.
  - Our previous example occurs in two elementary steps where the first step is much slower.

\[
\begin{align*}
\text{NO}_2(g) + \text{F}_2(g) &\xrightleftharpoons[k_2]{k_1} \text{NO}_2\text{F}(g) + \text{F}(g) \quad \text{(slow)} \\
\text{NO}_2(g) + \text{F}(g) &\xrightleftharpoons[k_3]{k_4} \text{NO}_2\text{F}(g) \quad \text{(fast)} \\
\end{align*}
\]

\[ 2 \text{NO}_2(g) + \text{F}_2(g) \rightarrow 2 \text{NO}_2\text{F}(g) \]

- Since the overall rate of this reaction is determined by the slow step, it seems logical that the observed rate law is 
  \[ \text{Rate} = k[\text{NO}_2][\text{F}_2]. \]

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

1. The following reaction is zero order with respect to N\(_2\)O. What is the rate law for the reaction?
   a. Rate = k [N\(_2\)O]
   b. Rate = k'
   c. Rate = 0
   d. Rate = k [N\(_2\)O]
   e. None of these

\[ 2\text{N}_2\text{O}(g) \xrightarrow{\text{Pt}} 2\text{N}_2(g) + \text{O}_2(g) \]
2. Reaction orders can be which of the following?
   a. Zero order
   b. Orders that are whole numbers.
   c. Orders that are negative.
   d. Fractional orders
   e. All of the above

Rate-Determining Step

• Mechanisms with an Initial Fast Step
  – There are cases where the rate-determining step of a mechanism contains a reaction intermediate that does not appear in the overall reaction.
  – The experimental rate law, however, can be expressed only in terms of substances that appear in the overall reaction.

Rate-Determining Step

• Consider the reduction of nitric oxide with H₂:

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

  – A proposed mechanism is:
    \[2\text{NO} \xrightarrow{k_1} \text{N}_2\text{O}_2\quad \text{(fast, equilibrium)}\]
    \[\text{N}_2\text{O}_2 + \text{H}_2 \xrightarrow{k_2} \text{N}_2\text{O} + \text{H}_2\text{O}\quad \text{(slow)}\]
    \[\text{N}_2\text{O} + \text{H}_2 \xrightarrow{k_3} \text{N}_2 + \text{H}_2\text{O}\quad \text{(fast)}\]

  – It has been experimentally determined that the rate law is \(\text{Rate} = k [\text{NO}]^2[\text{H}_2]\)

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

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

  \[\text{Rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]\]

  (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.
  – It is necessary to re-express this proposed rate law after eliminating \([\text{N}_2\text{O}_2]\).
\[ \text{Rate} = k_2[N_2O_2][H_2] \]
Rate law for the rate-determining step

- We can do this by looking at the first step, which is fast and establishes equilibrium.
- At equilibrium, the forward rate and the reverse rate are equal.
\[ k_1[\text{NO}]^2 = k_{-1}[N_2O_2] \]
- Therefore,
\[ [N_2O_2] = (k_1 / k_{-1})[\text{NO}]^2 \]
- If we substitute this into our proposed rate law we obtain:
\[ \text{Rate} = k_2[\text{NO}]^2[H_2] \]

Catalysts

- **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.
  
  \[
  2\text{SO}_2(g) + \text{O}_2(g) \xrightarrow{\text{NO}_2(g)} 2\text{SO}_3(g)
  \]

- **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.

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.
- To avoid being consumed, the catalyst must participate in at least one step of the reaction and then be regenerated in a later step.
- Its presence increases the rate of reaction by either increasing the frequency factor, \( A \) (from the Arrhenius equation) or lowering the activation energy, \( E_a \).

What would a reaction energy diagram look like with a catalyst added to the reaction?
Enzyme Catalysis

- **Enzymes have enormous catalytic activity.**
  - The substance whose reaction the enzyme catalyzes is called the substrate. (see Figure 13.20)
  - Figure 13.21 illustrates the reduction in activation energy resulting from the formation of an enzyme-substrate complex.

Figure 13.20: Enzyme Action (Lock-and-Key Model)

Figure 13.21: Potential-Energy Curves for the Reaction of Substrate S, to Products, P

Operational Skills

- Relating the different ways of expressing reaction rates
- Calculating the average reaction rate
- Determining the order of reaction from the rate law
- Determining the rate law from initial rates
- Using the concentration-time equation for first-order reactions
- Relating the half-life of a reaction to the rate constant
Operational Skills

- Using the Arrhenius equation
- Writing the overall chemical equation from a mechanism
- Determining the molecularity of an elementary reaction
- Writing the rate equation for an elementary reaction
- Determining the rate law from a mechanism

Quiz over Kinetics

1. What do we mean by the term ‘activation energy’?
2. What are the three factors involved in determining the activation energy?
3. Draw a potential energy curve and then, on the same curve indicate what happens when a catalyst is added.
4. What is the Arrhenius equation?

Short Clicker Quiz

2. Which equation correctly describes the rates at which SO₂ and O₂ are being consumed in the following reaction?
   \[ 2\text{SO}_2(g) + \text{O}_2(g) \rightarrow \text{SO}_3(g) \]
   a) \(-\frac{1}{2}\frac{d[\text{SO}_2(g)]}{dt} = -\frac{d[\text{O}_2(g)]}{dt}\)
   b) \(-\frac{d[\text{SO}_2(g)]}{dt} = -\frac{1}{2}\frac{d[\text{O}_2(g)]}{dt}\)
   c) \(-2\frac{d[\text{SO}_2(g)]}{dt} = -\frac{d[\text{O}_2(g)]}{dt}\)
   d) \(-\frac{1}{2}\frac{d[\text{SO}_2(g)]}{dt} = \frac{d[\text{O}_2(g)]}{dt}\)

4. The reaction \( A \rightarrow B + C \) is suspected of being first order: rate = \( k[A] \). How should the data \([A]\) versus time, \( t \), be plotted to confirm this suspicion?
   a) \([A]\) vs \( t \)
   b) \([A]\) vs \( 1/t \)
   c) \(\ln[A]\) vs \( t \)
   d) \(\ln[A]\) vs \( 1/t \)

6. A bone sample contains 23.4% of the \(^{14}\text{C}\) expected in living tissue. How old is the bone if the half-life of \(^{14}\text{C}\) is 5730 years?
   a) 1,340 years
   b) 12,000 years
   c) 5,730 years
   d) 8,430 years
12. A zero-order reaction is one where

- a) the initial rate of the reaction is independent of the concentrations of reactants and products.
- b) the forward and reverse rates are equal.
- c) the rate of the reaction is independent of the concentration of the solvent.
- d) the mechanism of the reaction is not known.