Chemical Kinetics

- The speed of a chemical reaction is called its reaction rate.
- The rate of a reaction is a measure of how fast the reaction makes products or uses reactants.
- The ability to control the speed of a chemical reaction is important.

Defining Rate

- Rate is how much a quantity changes in a given period of time.
- The speed you drive your car is a rate—the distance your car travels (miles) in a given period of time (1 hour).
  - So, the rate of your car has units of mi/hr.

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

Rate = \frac{\Delta [H_2]}{\Delta t} = \frac{[H_2]_t - [H_2]_i}{t_2 - t_1}

Defining Reaction Rate

- The rate of a chemical reaction is generally measured in terms of how much the concentration of a reactant decreases (or product concentration increases) in a given period of time.
- For reactants, a negative sign is placed in front of the definition.

\[ \text{Rate} = -\frac{\Delta [I_2]}{\Delta t} \]
The Average Rate of the Reaction

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[H₂] (M)</th>
<th>Δ[H₂] (M)</th>
<th>Δt (s)</th>
<th>Rate = −Δ[H₂]/Δt (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.000</td>
<td>−0.181</td>
<td>10.000</td>
<td>0.0181</td>
</tr>
<tr>
<td>10.000</td>
<td>0.819</td>
<td>−0.149</td>
<td>10.000</td>
<td>0.0149</td>
</tr>
<tr>
<td>20.000</td>
<td>0.670</td>
<td>−0.121</td>
<td>10.000</td>
<td>0.0121</td>
</tr>
<tr>
<td>30.000</td>
<td>0.549</td>
<td>−0.100</td>
<td>10.000</td>
<td>0.0100</td>
</tr>
<tr>
<td>40.000</td>
<td>0.449</td>
<td>−0.081</td>
<td>10.000</td>
<td>0.0081</td>
</tr>
<tr>
<td>50.000</td>
<td>0.368</td>
<td>−0.067</td>
<td>10.000</td>
<td>0.0067</td>
</tr>
<tr>
<td>60.000</td>
<td>0.301</td>
<td>−0.054</td>
<td>10.000</td>
<td>0.0054</td>
</tr>
<tr>
<td>70.000</td>
<td>0.247</td>
<td>−0.045</td>
<td>10.000</td>
<td>0.0045</td>
</tr>
<tr>
<td>80.000</td>
<td>0.202</td>
<td>−0.037</td>
<td>10.000</td>
<td>0.0037</td>
</tr>
<tr>
<td>90.000</td>
<td>0.165</td>
<td>−0.030</td>
<td>10.000</td>
<td>0.0030</td>
</tr>
</tbody>
</table>

Reactant and Product Concentrations as a Function of Time

Reaction Rate Changes over Time

- As time goes on, the rate of a reaction generally slows down because the concentration of the reactants decreases.
- At some time the reaction stops, either because the reactants run out or because the system has reached equilibrium.

Reaction Rate and Stoichiometry

- In most reactions, the coefficients of the balanced equation are not all the same.
  \[ H₂(g) + I₂(g) \rightarrow 2 HI(g) \]
- For these reactions, the change in the number of molecules of one substance is a multiple of the change in the number of molecules of another.
  - For the above reaction, for every 1 mole of \( H₂ \) used, 1 mole of \( I₂ \) will also be used and 2 moles of \( HI \) made.
  - Therefore, the rate of change will be different.
- To be consistent, the change in the concentration of each substance is multiplied by \( 1/\text{coefficient} \).

Determining a Reaction Rate

There are three "types" of rates:

- Initial rate
- Average rate
- Instantaneous rate

The average rate is the change in measured concentrations in any particular time period.

- Linear approximation of a curve
- The larger the time interval, the more the average rate deviates from the instantaneous rate.

The instantaneous rate is the change in concentration at any one particular time.

- Slope at one point of a curve
- The instantaneous rate is determined by taking the slope of a line tangent to the curve at that particular point.
- First derivative of the function

\[ \text{Rate} = \frac{\text{moles}}{L \cdot \text{time}} = \text{M} \cdot \text{s}^{-1} \text{ or M} \cdot \text{min}^{-1} \]

H₂ (g) + I₂ (g) → 2 HI (g)

Using \([H₂]\), the instantaneous rate at 50 s is as follows:

\[ \text{Rate} = -\frac{0.28 \text{ M}}{40 \text{ s}} \]

Using \([HI]\), the instantaneous rate at 50 s is as follows:

\[ \text{Rate} = \frac{1 \text{ M}}{2 \text{ s}} \]

\[ \text{Rate} = \frac{0.0070 \text{ M}}{s} \]
Example 13.1 Expressing Reaction Rates

Consider the balanced chemical equation:
\[ \text{H}_2\text{O}(aq) + 3 \text{I}^-\text{(aq)} \rightarrow 2 \text{HI}^-\text{(aq)} + 2 \text{H}_2\text{(g)} \]

In the first 10.0 seconds of the reaction, the concentration of I dropped from 1.000 M to 0.868 M.

a. Calculate the average rate of this reaction in this time interval.
b. Determine the rate of change in the concentration of \[ \text{HI}^-\text{(aq)} \] during this time interval.

Solution
a. Use Equation 13.5 to calculate the average rate of the reaction:
\[
\text{Rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}} = \frac{2 \text{ moles of } \text{H}_2}{2 \text{ moles of } \text{I}^-\text{(aq)}} \times \frac{1}{10.0 \text{ s}} = 0.0100 \text{ M/s}
\]
b. Use Equation 13.5 for the relationship between the rate of the reaction and \[ \frac{\Delta \text{[I}^-\text{]}}{\Delta \text{t}} \].

\[
\text{Rate} = \frac{1}{2} \times \frac{\Delta \text{[I}^-\text{]}}{\Delta \text{t}}
\]

After solving for \[ \frac{\Delta \text{[I}^-\text{]}}{\Delta \text{t}} \], substitute the calculated rate from part (a) and calculate \[ \frac{\Delta \text{[I}^-\text{]}}{\Delta \text{t}} \].

Measuring Reaction Rate

- To measure the reaction rate you need to be able to measure the concentration of at least one component in the mixture at many points in time.
- There are two ways of approaching this problem:
  - For reactions that are complete in less than 1 hour, it is best to use continuous monitoring of the concentration.
  - For reactions that happen over a very long time, sampling of the mixture at various times can be used.
  - When sampling is used, often the reaction in the sample is stopped by a quenching technique.

Continuous Monitoring

- Polarimetry – this measures the change in the degree of rotation of plane-polarized light caused by one of the components over time.
- Spectrophotometry – this measures the amount of light of a particular wavelength absorbed by one component over time.
  - The component absorbs its complementary color.
- Total pressure – the total pressure of a gas mixture is stoichiometrically related to partial pressures of the gases in the reaction.

Sampling the Reaction Mixture at Specific Times

- Aliquots (samples from the reaction mixture) are drawn off at specific times during the reaction, and quantitative analysis is performed.
  - Titration for one of the components
  - Gravimetric analysis

- Gas chromatography can measure the concentrations of various components in a mixture.
  - For samples that have volatile components
  - Separates mixture by adherence to a surface

Methods for Determining Concentrations in a Mixture

Problem:
Consider the reaction:
\[ 2\text{NO} (g) + \text{O}_2 (g) \rightarrow 2\text{NO}_2 (g) \]

Over a period of 50.0 to 100.0 s, the concentration of NO(g) drops from 0.0250M to 0.0100M.

a) What is the rate of rxn?
b) What is the average rate of disappearance of NO(g) during this time?
Methods for Determining Concentrations in a Mixture

Factors Affecting Reaction Rate: Nature of the Reactants

- Nature of the reactants means what kind of reactant molecules and what physical condition they are in.
  - Small molecules tend to react faster than large molecules.
  - Gases tend to react faster than liquids, which react faster than solids.
  - Powdered solids are more reactive than “blocks.”
    - More surface area for contact with other reactants
    - Certain types of chemicals are more reactive than others.
      - For example, potassium metal is more reactive than sodium
  - Ions react faster than molecules.
    - No bonds need to be broken.

Factors Affecting Reaction Rate: Temperature

- Increasing temperature increases the reaction rate.
  - Chemist’s rule—for each 10 °C rise in temperature, the speed of the reaction doubles.
    - For many reactions

- There is a mathematical relationship between the absolute temperature and the speed of a reaction discovered by Svante Arrhenius, which will be examined later.

Factors Affecting Reaction Rate: Reactant Concentration

- Generally, the larger the concentration of reactant molecules, the faster the reaction.
  - This increases the frequency of reactant molecule contact.
  - Concentration of gases depends on the partial pressure of the gas.
    - Higher pressure = higher concentration

  - Concentrations of solutions depend on the solute-to-solution ratio (molarity).

Factors Affecting Reaction Rate: Catalysts

- Catalysts are substances that affect the speed of a reaction without being consumed.
  - Most catalysts are used to speed up a reaction; these are called positive catalysts.
  - Catalysts used to slow a reaction are called negative catalysts.

  - Homogeneous = present in same phase
  - Heterogeneous = present in different phase

  - How catalysts work will be examined later.

Effect of Concentration on Reaction Rate: Concentration

\[
\text{Mg(s) + 2 HCl(aq) \rightarrow MgCl}_2(aq) + \text{H}_2(g)
\]
### The Rate Law

- The rate law of a reaction is the mathematical relationship between the rate of the reaction and the concentrations of the reactants and homogeneous catalysts as well.
- The rate law must be determined experimentally.
- The rate of a reaction is directly proportional to the concentration of each reactant raised to a power.
- For the reaction $\text{aA + bB} \rightarrow \text{products}$ the rate law would have the form given below.

$$\text{Rate} = k[A]^n [B]^y$$

$n$ is the order for each reactant $k$ is called the rate constant

### Reaction Order

- The exponent on each reactant in the rate law is called the order with respect to that reactant.
- The sum of the exponents on the reactants is called the order of the reaction.
- The rate law for the reaction $2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g)$ is $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$.

The reaction is second order with respect to $[\text{NO}]$, first order with respect to $[\text{O}_2]$, and third order overall.

### Sample Rate Laws

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{NC}$</td>
<td>$\text{Rate} = k[\text{CH}_3\text{CN}]$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$</td>
<td>$\text{Rate} = k[\text{CH}_3\text{CHO}]^{3/2}$</td>
</tr>
<tr>
<td>$2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2$</td>
<td>$\text{Rate} = k[\text{N}_2\text{O}_5]$</td>
</tr>
<tr>
<td>$\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$</td>
<td>$\text{Rate} = k[\text{H}_2][\text{I}_2]$</td>
</tr>
<tr>
<td>$\text{Ti}^{3+} + \text{Hg}_2^{2+} \rightarrow \text{Ti}^{1+} + 2 \text{Hg}^{2+}$</td>
<td>$\text{Rate} = k[\text{Ti}^{3+}][\text{Hg}_2^{2+}]$</td>
</tr>
</tbody>
</table>

The bottom reaction is autocatalytic because a product affects the rate. $\text{Hg}^{3+}$ is a negative catalyst; increasing its concentration slows the reaction.

### Reaction Orders

<table>
<thead>
<tr>
<th>Order</th>
<th>Name</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>zeroth</td>
<td>$\text{rate} = k[\text{A}]^0 = k$</td>
</tr>
<tr>
<td>1</td>
<td>first</td>
<td>$\text{rate} = k[\text{A}]$</td>
</tr>
<tr>
<td>2</td>
<td>second</td>
<td>$\text{rate} = k[\text{A}]^2$</td>
</tr>
<tr>
<td>0.5</td>
<td>one-half</td>
<td>$\text{rate} = k[\text{A}]^{1/2}$</td>
</tr>
<tr>
<td>1.5</td>
<td>three-half</td>
<td>$\text{rate} = k[\text{A}]^{3/2}$</td>
</tr>
<tr>
<td>0.667</td>
<td>two-thirds</td>
<td>$\text{rate} = k[\text{A}]^{2/3}$</td>
</tr>
</tbody>
</table>

A reaction order can be zero, or positive integer and fractional number.

### Reaction Constant

To find the units of the rate constant, divide the rate units by the Molarity raised to the power of the overall reaction order. $\text{Rate (Ms}^{-1}) = k[\text{A}]^x[\text{B}]^y$

- $\text{Ms}^{-1} = k \times M^x M^y$
- $\text{Ms}^{-1} = k \times M^{(x+y)}$

$$k = \frac{\text{Ms}^{-1}}{M^{(x+y)}} = M^{(1-(x+y))} \text{S}^{-1}$$

- if $(x+y) = 1$ \( k \) has units of $\text{s}^{-1}$
- if $(x+y) = 2$ \( k \) has units of $\text{M}^{1}\text{s}^{-1}$
EXAMPLE: The reaction,

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

is experimentally found to be first order in \( \text{H}_2 \) and third order in NO.

\[ \text{a) Write the rate law.} \]

\[ \text{Rate(Ms}^{-1}) = k[\text{H}_2][\text{NO}]^3 \]

\[ \text{b) What is the overall order of the reaction?} \]

\[ \text{Overall order } r = 1 + 3 = 4 \quad \text{"4th order"} \]

\[ \text{c) What are the units of the rate constant?} \]

\[ \text{Rate} = \frac{M}{s} = k \cdot M \cdot M^3 = k \cdot M^4 \quad k = \frac{M}{s} = M^4 \cdot s^{-1} \]

---

Finding the Rate Law: the Initial Rate Method

- The rate law must be determined experimentally.
- The rate law shows how the rate of a reaction depends on the concentration of the reactants.
- Changing the initial concentration of a reactant will therefore affect the initial rate of the reaction.

---

Rate = \( k[A]^n \)

- If a reaction is zero order, the rate of the reaction is always the same.
  - Doubling \([A]\) will have no effect on the reaction rate.

- If a reaction is first order, the rate is directly proportional to the reactant concentration.
  - Doubling \([A]\) will double the rate of the reaction.

- If a reaction is second order, the rate is directly proportional to the square of the reactant concentration.
  - Doubling \([A]\) will quadruple the rate of the reaction.

---

Determining the Rate Law When There Are Multiple Reactants

- Changing each reactant will affect the overall rate of the reaction.

- By changing the initial concentration of one reactant at a time, the effect of each reactant's concentration on the rate can be determined.

- In examining results, we compare differences in rate for reactions that only differ in the concentration of one reactant.

---

Example 13.2 Determine the Order and Rate Constant of a Reaction

Consider the reaction between nitrogen dioxide and carbon monoxide:

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

The initial rate of the reaction is measured at several different concentrations of the reactants with the accompanying results:

<table>
<thead>
<tr>
<th>[NO] (M)</th>
<th>[CO] (M)</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>0.0021</td>
</tr>
<tr>
<td>0.20</td>
<td>0.20</td>
<td>0.0082</td>
</tr>
<tr>
<td>0.40</td>
<td>0.40</td>
<td>0.033</td>
</tr>
</tbody>
</table>

**Solution**

1. Begin by examining how the rate changes for each change in concentration. Between the first two experiments, the concentrations of \( \text{NO}_2 \) double, the concentration of \( \text{CO} \) stays constant, and the rate quadruples, suggesting that the reaction is second order in \( \text{NO}_2 \).
2. Between the second and third experiments, the concentration of \( \text{NO}_2 \) stays constant, the concentration of \( \text{CO} \) doubles, and the rate remains constant (the small change in the least significant figure is simply experimental error), suggesting that the reaction is zero order in \( \text{CO} \).
3. Between the third and fourth experiments, the concentration of \( \text{NO}_2 \) again doubles and the concentration of \( \text{CO} \) halves, yet the rate quadruples again, confirming that the reaction is second order in \( \text{NO}_2 \) and zero order in \( \text{CO} \).

Write the overall rate expression:

\[ \text{Rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2 \]
Example 13.2 Determining the Order and Rate Constant of a Reaction

Continued

To determine the rate constant for the reaction, solve the rate law for \( k \) and substitute the concentration and the initial rate from any one of the four measurements. In this case, we use the first measurement.

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

For Practice 13.2

Consider the equation:

\[
\text{CH}_4(g) + C(s) \rightarrow \text{CO}_2(g) + 2 \text{H}_2(g)
\]

The initial rate of reaction is measured at several different concentrations of the reactants with the following results:

<table>
<thead>
<tr>
<th>Trial</th>
<th>([\text{NO}]_0) (M)</th>
<th>([\text{H}_2]) (M)</th>
<th>Initial Rate (M/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0100</td>
<td>0.0100</td>
<td>0.00600</td>
</tr>
<tr>
<td>2</td>
<td>0.0200</td>
<td>0.0300</td>
<td>0.144</td>
</tr>
<tr>
<td>3</td>
<td>0.0100</td>
<td>0.0200</td>
<td>0.0120</td>
</tr>
</tbody>
</table>

From the data, determine:

- Is the rate law for the reaction \( k [\text{NO}]^2 \)?
- Is the rate law for the reaction \( k [\text{NO}]^2 [\text{H}_2]^3 \)?
- Is the rate law for the reaction \( k [\text{NO}]^2 [\text{H}_2]^2 \)?

To determine the rate constant for the reaction, solve the rate law for \( k \). For Practice 13.2, \( k \) is the rate constant (1) for the reaction.

Similarly for \( x \):

\[
\text{Rate(2)} = \frac{k [\text{NO}]^2 [\text{H}_2]^2}{k [\text{NO}]^2 [\text{H}_2]^2} = \frac{0.144}{0.00600} = \frac{0.0200}{0.0100} = 24 = (2)^1 \times (3)
\]

\( x \log(2) = \log(8) \)

\( x = 3 \)

Determining Reaction Order: The Method of Initial Rates

The reaction of nitric oxide with hydrogen at 1280 °C is as follows:

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

This means that any changes to the rate must be due to the changes in \( \text{H}_2 \) which is related to the concentration of \( \text{H}_2 \) & its order!

<table>
<thead>
<tr>
<th>Trial</th>
<th>([\text{NO}]_0) (M)</th>
<th>([\text{H}_2]) (M)</th>
<th>Initial Rate (M/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0100</td>
<td>0.0100</td>
<td>0.00600</td>
</tr>
<tr>
<td>2</td>
<td>0.0200</td>
<td>0.0300</td>
<td>0.144</td>
</tr>
<tr>
<td>3</td>
<td>0.0100</td>
<td>0.0200</td>
<td>0.0120</td>
</tr>
</tbody>
</table>

\[
0.0120 \text{ M/min} = k [\text{NO}]^2 [\text{H}_2]^2
\]

\[
0.00600 \text{ M/min} = k [\text{NO}]^2 [\text{H}_2]^2
\]

\[
k = \frac{0.00600}{0.0120} = \frac{0.0300}{0.0100} = 2.00
\]

\[
\text{log}(2.00) = \text{log}(2.00)
\]

\[
y = \frac{\text{log}(2.00)}{\text{log}(2.00)} = 1
\]

\[
\text{Rate (M/min)} = k [\text{NO}]^2 [\text{H}_2]^2
\]

Determining Reaction Order: The Method of Initial Rates

2NO(g) + 2H_2(g) → N_2(g) + 2H_2O(g)

The rate law for the reaction is given by:

\[
\text{Rate(M/min)} = k [\text{NO}]^2 [\text{H}_2]^y
\]

Taking the ratio of the rates of Trials 3 and 1 one finds:

\[
\frac{\text{Rate (Trial 3)}}{\text{Rate (Trial 1)}} = k [\text{NO}]^2 [\text{H}_2]^2
\]

Plugging in the values from the data:

\[
\frac{0.0120 \text{ M/min}}{0.00600 \text{ M/min}} = k \frac{[0.0200]^2}{[0.0100]^2}
\]

\[
y \log(2.00) = \log(2.00)
\]

\[
y = 1
\]

\[
\text{Rate (M/min)} = k [\text{NO}]^2 [\text{H}_2]^2
\]

Determining Reaction Order: The Method of Initial Rates

2NO(g) + 2H_2(g) → N_2(g) + 2H_2O(g)

The Rate Law expression is:

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

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

The order for NO is 3

The order for \( \text{H}_2 \) is 2

The over all order is 3 + 1 = 4
**Determining Reaction Order: The Method of Initial Rates**

**The Rate constant**

\[ \text{Rate (M/min)} = k \left[ \text{NO} \right] \left[ \text{H}_2 \right] \]

To find the rate constant, choose one set of data and solve:

\[ 0.0120 \ \text{M min}^{-1} = k (0.0100 \ \text{M})^3 (0.0200 \ \text{M}) \]

\[ k = \frac{0.0120 \ \text{M min}^{-1}}{(0.0100 \ \text{M})^3 (0.0200 \ \text{M})} = 0.0120 \ \text{M min}^{-1} \]

\[ k = 6.00 \times 10^5 \ \text{M}^{-3} \ \text{min}^{-1} \]

---

**Finding the Rate Law: Graphical Methods**

- The rate law must be determined experimentally.
- A graph of concentration of reactant versus time can be used to determine the effect of concentration on the rate of a reaction.
- This involves using calculus to determine the area under a curve, which is beyond the scope of this course.
- Later we will examine the results of this analysis so we can use graphs to determine rate laws for several simple cases.

---

**Integrated Rate Laws**

- For the reaction A \( \rightarrow \) products, the rate law depends on the concentration of A.
- Applying calculus to integrate the rate law gives another equation showing the relationship between the concentration of A and the time of the reaction; this is called the integrated rate law.

---

**Half-Life**

- The half-life, \( t_{1/2} \), of a reaction is the length of time it takes for the concentration of the reactant to fall to \( \frac{1}{2} \) its initial value.
- The half-life of the reaction depends on the order of the reaction.

---

**Zero Order Reactions**

- Rate = \( k[A]^0 = k \)
  - Constant rate reactions
- \([A] = -kt + [A]_{\text{initial}}\)
- Graph of \([A] \) versus time – straight line with slope = \(-k\) and y-intercept = \([A]_{\text{initial}}\)
- \( t_{1/2} = [A]_{\text{initial}}/2k \)
- When Rate = M/sec, \( k = M/\text{sec} \)

\[ \frac{[A]_{\text{initial}}}{[A]} \]

Slope = \(-k\)

---
First Order Reactions

- Rate = $k[A]^1 = k[A]$
- $\ln[A] = -kt + \ln[A]_{initial}$
- Graph $\ln[A]$ versus time – straight line with slope = $-k$ and y-intercept = $\ln[A]_{initial}$
  - Used to determine the rate constant
- $t_{1/2} = 0.693/k$
- The half-life of a first order reaction is constant.
- When Rate $= M/sec$, $k = s^{-1}$

The Half-Life of a First-Order Reaction Is Constant

Rate Data for $C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>$[C_4H_9Cl]$, M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.1000</td>
</tr>
<tr>
<td>50.0</td>
<td>0.0905</td>
</tr>
<tr>
<td>100.0</td>
<td>0.0820</td>
</tr>
<tr>
<td>150.0</td>
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</tr>
<tr>
<td>200.0</td>
<td>0.0671</td>
</tr>
<tr>
<td>300.0</td>
<td>0.0549</td>
</tr>
<tr>
<td>400.0</td>
<td>0.0448</td>
</tr>
<tr>
<td>500.0</td>
<td>0.0368</td>
</tr>
<tr>
<td>800.0</td>
<td>0.0200</td>
</tr>
<tr>
<td>10000.0</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Second Order Reactions

- Rate = $k[A]^2$
- $1/[A] = kt + 1/[A]_{initial}$
- Graph $1/[A]$ versus time – straight line with slope = $k$ and y-intercept = $1/[A]_{initial}$
  - Used to determine the rate constant
- $t_{1/2} = 1/(k[A_0])$
- When Rate $= M/sec$, $k = M^{-1} \cdot s^{-1}$
Graphical Determination of the Rate Law for A → Product

- Plots of [A] versus time, ln[A] versus time, and 1/[A] versus time allow determination of whether a reaction is zero, first, or second order.
- Whichever plot gives a straight line determines the order with respect to [A].
  - If linear is [A] versus time, Rate = $k[A]^0$.
  - If linear is ln[A] versus time, Rate = $k[A]^1$.
  - If linear is 1/[A] versus time, Rate = $k[A]^2$.

Relationship between Order and Half-Life

- For a zero order reaction, the lower the initial concentration of the reactants, the shorter the half-life.
  - $t_{1/2} = [A]_0 / 2k$
- For a first order reaction, the half-life is independent of the concentration.
  - $t_{1/2} = \ln(2) / k$
- For a second order reaction, the half-life is inversely proportional to the initial concentration, increasing the initial concentration shortens the half-life.
  - $t_{1/2} = 1/(k[A]_0)$
Example 13.3 The First-Order Integrated Rate Law: Using Graphical Analysis of Reaction Data

Consider the equation for the decomposition of \( \text{SO}_2\text{Cl}_2(g) \):
\[
\text{SO}_2\text{Cl}_2(g) \rightarrow \text{SO}_2(g) + \text{Cl}_2(g)
\]

The concentration of \( \text{SO}_2\text{Cl}_2 \) was monitored at a fixed temperature as a function of time during the decomposition reaction, and the following data were tabulated:

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>([\text{SO}_2\text{Cl}_2]) (M)</th>
<th>([\text{SO}_2]) (M)</th>
<th>([\text{Cl}_2]) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.100</td>
<td>0.100</td>
<td>0.0793</td>
</tr>
<tr>
<td>100</td>
<td>0.0191</td>
<td>0.0094</td>
<td>0.0770</td>
</tr>
<tr>
<td>200</td>
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<td>0.0774</td>
</tr>
<tr>
<td>300</td>
<td>0.0016</td>
<td>0.0003</td>
<td>0.0777</td>
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<td>0.0003</td>
<td>0.0001</td>
<td>0.0780</td>
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<tr>
<td>500</td>
<td>0.0001</td>
<td>0.0000</td>
<td>0.0798</td>
</tr>
<tr>
<td>600</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0806</td>
</tr>
<tr>
<td>700</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0846</td>
</tr>
</tbody>
</table>

Show that the reaction is first order, and determine the rate constant for the reaction.

Solution
In order to show that the reaction is first order, prepare a graph of \( \ln([\text{SO}_2\text{Cl}_2]) \) versus time as shown.

Example 13.4 The First-Order Integrated Rate Law: Determining the Concentration of a Reactant at a Given Time

In Example 13.3, you determined that the decomposition of \( \text{SO}_2\text{Cl}_2 \) (under the given reaction conditions) is first order and has a rate constant of \( +2.90 \times 10^{-4} \text{ s}^{-1} \). If the reaction is carried out at the same temperature, and the initial concentration of \( \text{SO}_2\text{Cl}_2 \) is \( 0.0225 \text{ M} \), what will the \( \text{SO}_2\text{Cl}_2 \) concentration be after 865 s?

**Solution**

Given:
- Initial concentration of \( \text{SO}_2\text{Cl}_2 \): \( 0.0225 \text{ M} \)
- Rate constant: \( +2.90 \times 10^{-4} \text{ s}^{-1} \)
- Time: \( 865 \text{ s} \)

Find:
- Concentration of \( \text{SO}_2\text{Cl}_2 \) after \( 865 \text{ s} \)

The concentration is smaller than the original concentration as expected. If the concentration were larger than the initial concentration, this would indicate a mistake in the signs of one of the quantities on the right hand side of the equation.

Check
The concentration is smaller than the initial concentration as expected. If the concentration were larger than the initial concentration, this would indicate a mistake in the signs of one of the quantities on the right hand side of the equation.

For Practice 13.4
Cyclopropene rearranges to form propene in the gas phase.

The reaction is first order in cyclopropene and has a measured rate constant of \( 3.36 \times 10^{-4} \text{ s}^{-1} \) at 720 K. If the initial cyclopropene concentration is \( 0.0445 \text{ M} \), what will the cyclopropane concentration be after 235 s?

**Check it out!**

You don’t need the volume of the container!

**Problem:**

The decomposition of \( \text{N}_2\text{O}_5(g) \) following 1st order kinetics. If 2.56 mg of \( \text{N}_2\text{O}_5 \) is initially present in a container and 2.50 mg remains after 4.26 min, what is the rate constant in s\(^{-1}\)?

Begin with the integrated rate law for a 1st order process:

\[
[A]_t = [A]_o e^{-kt}
\]

\[
\frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_o} = e^{kt}
\]

**Check it out!**

You don’t need the volume of the container!

\[
\frac{2.50 \text{ mg}}{10^8 \text{ mg}} \times \frac{1 \text{ mol}}{108 \text{ g}} = 2.56 \text{ mg}
\]

**Problem:**

The decomposition of \( \text{N}_2\text{O}_5(g) \) following 1st order kinetics. If 2.56 mg of \( \text{N}_2\text{O}_5 \) is initially present in a container and 2.50 mg remains after 4.26 min, what is the rate constant in s\(^{-1}\)?

\[
\frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_o} = e^{kt}
\]
Problem:
The decomposition of $N_2O_5(g)$ following 1st order kinetics. If 2.56 mg of $N_2O_5$ is initially present in a container and 2.50 mg remains after 4.26 min, what is the rate constant in s$^{-1}$?

\[
\frac{[N_2O_5]_t}{[N_2O_5]_0} = e^{-kt} = \frac{2.50 \text{ mg}}{2.56 \text{ mg}}
\]

taking the natural log and substituting time in seconds:

\[
\ln\left(\frac{2.50 \text{ mg}}{2.56 \text{ mg}}\right) = -k \times (256 \text{ s})
\]

\[
k = 9.3 \times 10^{-5} \text{ s}^{-1}
\]

Problem:
A certain reaction proceeds through first order kinetics. The half-life of the reaction is 180 s. What percent of the initial concentration remains after 900 s?

Using the integrated rate law, substituting in the value of $k$ and 900 s we find:

\[
t_{1/2} = \frac{\ln 2}{k} \quad \text{and} \quad k = \frac{\ln 2}{180 \text{ s}} = 0.00385 \text{ s}^{-1}
\]

\[
\frac{[A]_t}{[A]_0} = e^{-kt} = e^{-0.00385 \text{ s}^{-1} \times 900 \text{ s}} = 0.0312
\]

Since the ratio of $[A]_t$ to $[A]_0$ represents the fraction of $[A]$ that remains, the % is given by:

\[
100 \times 0.0312 = 3.12\%
\]

The Effect of Temperature on Rate

- Changing the temperature changes the rate constant of the rate law.

- Svante Arrhenius investigated this relationship and showed the following:

\[
k = A \left(\frac{-E_a}{e^{RT}}\right)
\]

where $T$ is the temperature in kelvins.

$R$ is the gas constant in energy units, 8.314 J/(mol · K).

$A$ is called the frequency factor, the rate the reactant energy approaches the activation energy.

$E_a$ is the activation energy, the extra energy needed to start the molecules reacting.

Activation Energy and the Activated Complex

- There is an energy barrier to almost all reactions.

- The activation energy is the amount of energy needed to convert reactants into the activated complex.
  - Also known as, transition state

- The activated complex is a chemical species with partially broken and partially formed bonds.
  - Always very high in energy because of its partial bonds

Isomerization of Methyl Isonitrile

Methyl isonitrile rearranges to acetonitrile.

For the reaction to occur, the $H_3C$–N bond must break, and a new $H_3C$–C bond must form.
As the reaction begins, the C─N bond weakens enough for the C≡N group to start to rotate.

The activated complex is a chemical species with partial bonds.

The activation energy is the difference in energy between the reactants and the activated complex.

The frequency is the number of molecules that begin to form the activated complex in a given period of time.

The exponential factor in the Arrhenius equation is a number between 0 and 1.

It represents the fraction of reactant molecules with sufficient energy so they can make it over the energy barrier.

The higher the energy barrier (larger activation energy), the fewer molecules that have sufficient energy to overcome it.

That extra energy comes from converting the kinetic energy of motion to potential energy in the molecule when the molecules collide.

- temperature = the average kinetic energy of the molecules
- Increases the number of molecules with sufficient energy to overcome the energy barrier
- temperature will the reaction rate

The Arrhenius equation can be algebraically solved to give the following form:

\[
\ln(k) = \frac{-E_a}{R} \left( \frac{1}{T} \right) + \ln(A)
\]

This equation is in the form \(y = mx + b\), where \(y = \ln(k)\) and \(x = (1/T)\).

A graph of \(\ln(k)\) versus \((1/T)\) is a straight line.

\((-8.314 \text{ J/mol} \cdot \text{K})(\text{slope of the line}) = E_a\) (in Joules)

\(E\)-intercept = \(A\) (unit is the same as \(k\))

\[
\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]
Example 13.8
Using the Two-Point Form of the Arrhenius Equation

You are given the rate constant of a reaction at two different temperatures and asked to find the activation energy.

**Given:**

- Rate constant at 701 K: 2.57 M⁻¹·s⁻¹
- Rate constant at 895 K: 567 M⁻¹·s⁻¹

**Find:**

- Activation energy ($E_a$)

**Strategize**

Use the two-point form of the Arrhenius equation, which relates the activation energy to the given information and a constant ($R$).

**Equation**

Solve the equation for $E_a$, the activation energy, and convert to kJ/mol.

**Check**

The magnitude of the answer is reasonable. Activation energies for most reactions range from tens to hundreds of kilojoules per mole.

---

Collision Theory of Kinetics

- For most reactions, for a reaction to take place, the reacting molecules must collide with each other.
- Once molecules collide, they may react together or they may not, depending on two factors:
  - Whether the collision has enough energy to "break the bonds holding reactant molecules together"
  - Whether the reacting molecules collide in the proper orientation for new bonds to form

Effective Collisions: Orientation Effect

- When two molecules have an effective collision, the faster the reaction rate, the higher the frequency of effective collisions.
- Effective collisions in which these two conditions are met (and therefore lead to reaction) are called effective collisions.

Effective Collisions: Kinetic Energy Factor

- For a collision to lead to overcoming the energy barrier, the reacting molecules must have sufficient kinetic energy so that the activated complex can form.
- When two molecules have an effective collision, a temporary, high energy (unstable) chemical species is formed—the activated complex.
Collision Frequency

- The collision frequency is the number of collisions that happen per second.
- The more collisions there are per second, the more collisions can be effective and lead to product formation.

\[ k = A \left( \frac{-E_a}{RT} \right) \]

Orientation Factor

- The orientation factor, \( p \), is a statistical term relating the frequency factor to the collision frequency.
- For most reactions, \( p < 1 \).
- Generally, the more complex the reactant molecules, the smaller the value of \( p \).
- For reactions involving atoms colliding, \( p \approx 1 \) because of the spherical nature of the atoms.
- Some reactions actually can have \( p > 1 \).
  - Generally involve electron transfer.

Orientation Factor

- The proper orientation results when the atoms are aligned in such a way that the old bonds can break and the new bonds can form.
- The more complex the reactant molecules, the less frequently they will collide with the proper orientation.
  - Reactions where symmetry results in multiple orientations leading to a reaction have \( p \) slightly less than 1.
- For most reactions, the orientation factor is less than 1.

Molecular Interpretation of Factors Affecting Rate – Reactant Nature

- Some materials undergo similar reactions at different rates either because they have a 1) higher initial potential energy and are therefore closer in energy to the activated complex, or 2) because their reaction has a lower activation energy.
  - \( \text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl} \) is about 12 times faster than \( \text{CD}_4 + \text{Cl}_2 \rightarrow \text{CD}_3\text{Cl} + \text{DCl} \) because the C–H bond is weaker and less stable than the C–D bond.
  - \( \text{CH}_4 + X_2 \rightarrow \text{CH}_3X +HX \) occurs about 100 times faster with \( F_2 \) than with \( Cl_2 \) because the activation energy for \( F_2 \) is 5 kJ/mol, but for \( Cl_2 \) is 17 kJ/mol.

Molecular Interpretation of Factors Affecting Rate – Temperature

- Increasing the temperature raises the average kinetic energy of the reactant molecules.
- There is a minimum amount of kinetic energy needed for the collision to be converted into enough potential energy to form the activated complex.
- Increasing the temperature increases the number of molecules with sufficient kinetic energy to overcome the activation energy.
Molecular Interpretation of Factors Affecting Rate – Concentration

- Reaction rate generally increases as the concentration or partial pressure of reactant molecules increases.
  - Except for zero order reactions
- More molecules leads to more molecules with sufficient kinetic energy for effective collision.
  - Distribution the same, just bigger curve

Reaction Mechanisms

- We generally describe chemical reactions with an equation listing all the reactant molecules and product molecules.
- But the probability of more than three molecules colliding at the same instant with the proper orientation and sufficient energy to overcome the energy barrier is negligible.
- Most reactions occur in a series of small reactions involving one, two, or (at most) three molecules.
- Describing the series of reactions that occurs to produce the overall observed reaction is called a reaction mechanism.
- Knowing the rate law of the reaction helps us understand the sequence of reactions in the mechanism.

An Example of a Reaction Mechanism

- Overall reaction: \( \text{H}_2(g) + 2 \text{ICl}(g) \rightarrow 2 \text{HCl}(g) + \text{I}_2(g) \)
- Mechanism:
  1. \( \text{H}_2(g) + \text{ICl}(g) \rightarrow \text{HCl}(g) + \text{HI}(g) \)
  2. \( \text{HI}(g) + \text{ICl}(g) \rightarrow \text{HCl}(g) + \text{I}_2(g) \)
- The reactions in this mechanism are elementary steps, meaning that they cannot be broken down into simpler steps and that the molecules actually interact directly in this manner without any other steps.

Elements of a Mechanism Intermediates

- Notice that the HI is a product in step 1, but then a reactant in step 2.
- Because HI is made but then consumed, HI does not show up in the overall reaction.
- Materials that are products in an early mechanism step, but then reactants in a later step, are called intermediates.

Molecularity

- The number of reactant particles in an elementary step is called its molecularity.
- A unimolecular step involves one particle.
- A bimolecular step involves two particles.
  - However, they may be the same kind of particle.
- A termolecular step involves three particles.
  - However, these are exceedingly rare in elementary steps.

Rate Laws for Elementary Steps

- Each step in the mechanism is like its own little reaction with its own activation energy and own rate law.
- The rate law for an overall reaction must be determined experimentally.
- But the rate law of an elementary step can be deduced from the equation of the step.
  \[
  \text{H}_2(g) + 2 \text{ICl}(g) \rightarrow 2 \text{HCl}(g) + \text{I}_2(g)
  \]
  1) \( \text{H}_2(g) + \text{ICl}(g) \rightarrow \text{HCl}(g) + \text{HI}(g) \)  Rate = \( k_1[\text{H}_2][\text{ICl}] \)
  2) \( \text{HI}(g) + \text{ICl}(g) \rightarrow \text{HCl}(g) + \text{I}_2(g) \)  Rate = \( k_2[\text{HI}][\text{ICl}] \)
Rate Laws of Elementary Steps

<table>
<thead>
<tr>
<th>Elementary Step</th>
<th>Molecularity</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>A → products</td>
<td>1</td>
<td>Rate = kA</td>
</tr>
<tr>
<td>A + B → products</td>
<td>2</td>
<td>Rate = kAB</td>
</tr>
<tr>
<td>A + B + A → products</td>
<td>3 (rare)</td>
<td>Rate = kA^2B</td>
</tr>
<tr>
<td>A + B + C → products</td>
<td>3 (rare)</td>
<td>Rate = kAB[C]</td>
</tr>
</tbody>
</table>

Rate Determining Step

- In most mechanisms, one step occurs slower than the other steps.
- The result is that product production cannot occur any faster than the slowest step; the step determines the rate of the overall reaction.
- We call the slowest step in the mechanism the rate determining step.
  - The slowest step has the largest activation energy.
- The rate law of the rate determining step determines the rate law of the overall reaction.

The overall stoichiometry of a chemical reaction is most often the sum of several steps:

1. \(2AB \rightarrow A_B^2\)
2. \(A_B^2 + C_2 \rightarrow A_B + C_2B\)
3. \(A_2B + C_2 \rightarrow A_2 + C_2B\)

Net: \(2AB + A_2B_2 + A_2B + 2C_2 \rightarrow A_B^2 + A_2B + A_2 + 2C_2B\)

The sequence of steps (1-3) describes a possible "reaction mechanism".

Another Reaction Mechanism

\(NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)\)

1. \(NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)\)
2. \(NO_2(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)\)

The rate law of the first step is the same as the rate law of the overall reaction.

Validating a Mechanism

- To validate (not prove) a mechanism, two conditions must be met:
  1. The elementary steps must sum to the overall reaction.
  2. The rate law predicted by the mechanism must be consistent with the experimentally observed rate law.

The first step is slower than the second step because its activation energy is larger.

The first step in this mechanism is the rate determining step.

Rate law of the first step:

\(Rate = k[NO_2]^2\)

Slow

Rate law of the second step:

\(Rate = k_2[NO_3][CO]\)

Fast

The species that cancel out (not part of the overall reaction) are called "reaction intermediates".

Reaction Mechanisms

The overall stoichiometry of a chemical reaction is most often the sum of several steps:

1. \(2AB \rightarrow A_B^2\)
2. \(A_B^2 + C_2 \rightarrow A_B + C_2B\)
3. \(A_2B + C_2 \rightarrow A_2 + C_2B\)

Net: \(2AB + A_2B_2 + A_2B + 2C_2 \rightarrow A_B^2 + A_2B + A_2 + 2C_2B\)

The sequence of steps (1-3) describes a possible "reaction mechanism".

NO\(_2\)(g) + CO(g) → NO(g) + CO\(_2\)(g)

Rate\(_{obs}\) = \(k[NO_2]^2\)

Slow

Rate = \(k_1[NO_2]^2\)

Fast

Rate = \(k_2[NO_3][CO]\) Fast

Because \(k_1\) is larger than \(k_2\), the first step has the smaller activation energy and is rate limiting.
Mechanisms with a Fast Initial Step

• When a mechanism contains a fast initial step, the rate limiting step may contain intermediates.
• When a previous step is rapid and reaches equilibrium, the forward and reverse reaction rates are equal, so the concentrations of reactants and products of the step are related and the product is an intermediate.
• Substituting into the rate law of the RDS will produce a rate law in terms of just reactants.

An Example

1. \(2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)\) Fast
2. \(\text{H}_2(g) + \text{N}_2\text{O}_4(g) \rightarrow \text{H}_2\text{O}(g) + \text{N}_2(g)\) Slow Rate = \(k_2[\text{H}_2][\text{N}_2\text{O}_2]\)
3. \(2 \text{H}_2(g) + 2 \text{NO}(g) \rightarrow 2 \text{H}_2\text{O}(g) + \text{N}_2(g)\) Rate_{obs} = \(k[\text{H}_2][\text{NO}]^2\)

for Step 1 \(\text{Rate}_{forward} = \text{Rate}_{reverse}\)
\(k_1[\text{NO}]^2 = k_4[\text{N}_2\text{O}_2]\)
\([\text{N}_2\text{O}_2] = \frac{k_1}{k_4}[\text{NO}]^2\)

Example 13.9

Ozone naturally decomposes to oxygen by this reaction:
\(2 \text{O}_3(g) \rightarrow 3 \text{O}_2(g)\)
The experimentally observed rate law for this reaction is:
\(\text{Rate} = k[\text{O}_3]^2[\text{O}_2]^{-1}\)
Show that this proposed mechanism is consistent with the experimentally observed rate law.

\(\text{O}_3(g) \xrightarrow{k_1} \text{O}_2(g) + \text{O}(g)\) Fast
\(\text{O}_3(g) + \text{O}(g) \xrightarrow{k_2} 2 \text{O}_2(g)\) Slow

Rate (forward) = Rate (backward)
\(k_1[\text{O}_3] = k_{-1}[\text{O}_2][\text{O}]\)
\([\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}\)
Rate = \(k_2[\text{O}_3][\text{O}]\)
\(= k_2[\text{O}_3] \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}\)
\(= k_2 \frac{k_1}{k_{-1}} [\text{O}_3]^2[\text{O}_2]\)
\(= k[\text{O}_3]^2[\text{O}_2]^{-1}\)

Catalysts

• Catalysts are substances that affect the rate of a reaction without being consumed.
• Catalysts work by providing an alternative mechanism for the reaction with a lower activation energy.
• Catalysts are consumed in an early mechanism step, and then made in a later step.
**Molecular Interpretation of Factors Affecting Rate – Catalysts**

- Catalysts generally speed a reaction.
- They give the reactant molecules a different path to follow with a lower activation energy.
  - Heterogeneous catalysts hold one reactant molecule in proper orientation for reaction to occur when the collision takes place.
  - Sometimes they also help to start breaking bonds.
  - Homogeneous catalysts react with one of the reactant molecules to form a more stable activated complex with a lower activation energy.

**Energy Profile of a Catalyzed Reaction**

Polar stratospheric clouds contain ice crystals that catalyze reactions that release Cl from atmospheric chemicals.

**Ozone Depletion over the Antarctic**

Figure 13.19 pg 630

**Catalysts**

- **Homogeneous catalysts** are in the same phase as the reactant particles.
  - Cl\(_{2}\) in the destruction of O\(_3\)
- **Heterogeneous catalysts** are in a different phase than the reactant particles.
  - Solid catalytic converter in a car’s exhaust system

**Types of Catalysts**

**Catalytic Hydrogenation**

\[ \text{H}_2\text{C} = \text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3 \]
**Enzymes**

- Because many of the molecules are large and complex, most biological reactions require a catalyst to proceed at a reasonable rate.
- Protein molecules that catalyze biological reactions are called **enzymes**.
- Enzymes work by adsorbing the substrate reactant onto an active site that orients the substrate for reaction.

1) Enzyme $+$ Substrate $\rightleftharpoons$ Enzyme–Substrate Fast
2) Enzyme–Substrate $\rightarrow$ Enzyme + Product Slow

**Enzymatic Hydrolysis of Sucrose**

\[ E + S \rightleftharpoons ES \quad \text{Fast} \]
\[ ES \rightarrow E + P \quad \text{Slow, rate limiting} \]

- Enzyme–Substrate Binding: The Lock and Key Mechanism

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enzyme</td>
<td>Enzyme–substrate complex</td>
</tr>
</tbody>
</table>

\[ C_{12}H_{22}O_{11} \quad \text{Sucrose} \rightarrow C_6H_{12}O_6 \quad \text{Glucose} + C_6H_{12}O_6 \quad \text{Fructose} \]