Chemical Kinetics

Study of the
TIME vs RATE
of Chemical Change
CHEMICAL KINETICS DEALS WITH

1. How **FAST**
   
   \{Speed like miles per hour\}
   
   and

2. By what **MECHANISM**
   
   does a reaction happen?
Part I

How Fast (RATE) Does a Chemical Reaction “Go”? 

What does the speed (RATE) depend upon?
REACTION RATES

• The change in the concentration of a reactant or product with time (M/s) for \( A \rightarrow B \)

\[
\text{Rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{Rate} = \frac{\Delta[B]}{\Delta t}
\]

Rate disappearance = Rate of formation
STOICHIOMETRY AFFECTS THE RATE

2A $\rightarrow$ B
A disappears at twice the rate B forms

Rate = $-\frac{1}{2} \Delta[A] = \Delta[B]$

Rate disappearance $\neq$ Rate of formation
For \( 2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2 \)

If rate of decomposition of \(\text{N}_2\text{O}_5\) = \(4.2 \times 10^{-7}\) M/s

What is the rate of APPEARANCE of

(a) \(\text{NO}_2\) ?

Twice rate of decomposition = ________ M/s

(b) \(\text{O}_2\) ?

\(\frac{1}{2}\) the rate of decomposition = ________ M/s
How is the rate of the disappearance of the reactants related to the appearance of the products for

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

\[
\text{rate} = -\frac{1}{1} \frac{\Delta[\text{CH}_4]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{1} \frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{H}_2]}{\Delta t}
\]
Consider the reaction $3A \rightarrow 2B$

The average rate of appearance of B is given by $\frac{[B]}{t}$.

How is the average rate of appearance of B related to the average rate of disappearance of A?

(a) $-\frac{2[A]}{3t}$  
(b) $\frac{2[A]}{3t}$  
(c) $-\frac{3[A]}{2t}$  
(d) $\frac{[A]}{t}$  
(e) $-\frac{[A]}{t}$

Answer on Text Book’s Web Site
THE RATES OF REACTION DEPENDS ON

1. **Nature of Reactants**  \{fixed\}
2. **Concentration of Reactants**  \{variable\}
3. **Temperature**  \{variable\}
4. **Etc.**  \{variable\}
   - **Catalysts**
   - **Particle Size**
   - **Photochemical**
The “things” that affect the rate of reaction are **Considered** one at a time
I. NATURE OF REACTING SUBSTANCES

Zn(s) + HCl(aq) → H₂ + ZnCl₂(aq)  Fast Reaction

Iron “Rusts” but not very fast

Fe(s) + O₂ → Slow Reaction

Whereas Silver does not react at all

Ag(s) + O₂ → No Reaction

THE NATURE OF REACTANTS IS FIXED
II. CONCENTRATION OF **Reactants**

Reactant → Products

\[ R \rightarrow P \]
rate \( \propto [R] \)

\[ A + B \rightarrow P + Q \]
rate \( \propto [A] [B] \)

\[ A + B + C \rightarrow P + Q + Z \]
rate \( \propto \) ___________
**Rate Constant:** $k$

A constant of proportionality between the reaction rate and the concentration of reactants.

\[ R \rightarrow P \]

rate $\propto [R]$

rate $= k \ [R]$
REACTION ORDER

\[ R \rightarrow P \]

To complete the equation
Concentrations are raised to a power of \( x \)

\[ \text{rate} = k \ [R]^x \]

[ \( x \) is determined experimentally]
Reaction order is determined experimentally.

Reaction order =

to the sum of the powers to which all reactant concentrations in the rate law are raised.
REACTION ORDER

- Zero Order Reactions
- First Order Reactions
- Second Order Reactions
- Third Order Reactions
Rate Law

• **Rate Law:** Shows the relationship of the rate of a reaction to the rate constant & the concentration of the reactants raised to some powers.

• For the general reaction: \( aA + bB \rightarrow cC + dD \)

\[
\text{rate} = k \ [A]^x \ [B]^y
\]
REACTION ORDER

Order = \( x + y \)

The sum of the powers to which all reactant concentrations appearing in the rate law are raised

\( x \) & \( y \) MAY OR MAY NOT BE THE STOICHIOMETRIC COEFFICIENTS

Reaction order is determined experimentally
A reaction $A + B \rightarrow C$ obeys the following rate law $\text{Rate} = k[A]^2[B]$

(a) If $[A]$ is doubled, how will the rate change? ______

(b) Will the rate constant change? ______

(c) What are the reaction orders for $A$ and $B$? ______

(d) Overall order? ______

(e) Units of rate constant ______
The reaction $A + B \rightarrow C$
obeys the following rate law:

$$\text{Rate} = k[A]^2[B]$$

(a) What is the order of the reaction

(i) With respect to $A$? (a) 1$^{\text{st}}$ (b) 2$^{\text{nd}}$ (c) 3$^{\text{rd}}$

(ii) With respect to $B$? (a) 1$^{\text{st}}$ (b) 2$^{\text{nd}}$ (c) 3$^{\text{rd}}$

(iii) Overall order (a) 1$^{\text{st}}$ (b) 2$^{\text{nd}}$ (c) 3$^{\text{rd}}$
Rate = $k[A]^2[B]$

(b) How does the rate change if

(i) $[A]$ is doubled?
   (a) doubles (b) triples (c) quadruples (d) no change

(ii) $[B]$ is doubled?
   (a) doubles (b) triples (c) quadruples (d) no change

(iii) $[C]$ is doubled?
   (a) doubles (b) triples (c) quadruples (d) no change
Method of Initial Rates

Uses Initial Rates to Determine Rate Law
Nitrogen monoxide reacts with hydrogen to form nitrogen gas and water

1\textsuperscript{st} Write reaction

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

2\textsuperscript{nd} balance reaction

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

Write Rate Law: \[\text{ Rate } = k [\text{NO}]^x[\text{H}_2]^y\]

Determine \(x\) and \(y\) using method of Initial rates.

What can you measure INITIALLY? ______

How many UNKNOWNS in Rate Law? ______

How many experiments are needed? ______
2 NO\((g)\) + 2 H\(_2\)(g) \rightarrow N\(_2\)(g) + 2 H\(_2\)O\((g)\)

Rate = \(k\ [\text{NO}]^x[\text{H}_2]^y\)

**METHOD OF INITIAL RATES**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>([\text{NO}]_{\text{initial}})</th>
<th>([\text{H}<em>2]</em>{\text{initial}})</th>
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<td>1.3 (\times) 10(^{-5})</td>
</tr>
<tr>
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<td>10.0 (\times) 10(^{-3})</td>
<td>2.0 (\times) 10(^{-3})</td>
<td>5.0 (\times) 10(^{-5})</td>
</tr>
<tr>
<td>3</td>
<td>10.0 (\times) 10(^{-3})</td>
<td>4.0 (\times) 10(^{-3})</td>
<td>10.0 (\times) 10(^{-5})</td>
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</table>
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}]^x \, [\text{H}_2]^y

\begin{align*}
\text{Exp 1:} & \quad 1.3 \times 10^{-5} = k \, (5.0 \times 10^{-3})^x \, (2.0 \times 10^{-5})^y \\
\text{Exp 2:} & \quad 5.0 \times 10^{-5} = k \, (10 \times 10^{-3})^x \, (2.0 \times 10^{-5})^y \\
\text{Exp 3:} & \quad 10.0 \times 10^{-5} = k \, (10 \times 10^{-3})^x \, (4.0 \times 10^{-5})^y
\end{align*}

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

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

Exp 1: \( 1.3 \times 10^{-5} = k \ (5.0 \times 10^{-3})^x \ (2.0 \times 10^{-5})^y \)

Exp 2: \( 5.0 \times 10^{-5} = k \ (10 \times 10^{-3})^x \ (2.0 \times 10^{-5})^y \)

Exp 3: \( 10.0 \times 10^{-5} = k \ (10 \times 10^{-3})^x \ (4.0 \times 10^{-5})^y \)

Take RATIO of Exp 2 to Exp 1

\[
\frac{\text{exp 2}}{\text{exp 1}} = \frac{5.0 \times 10^{-5}}{1.3 \times 10^{-5}} = \frac{k \ (10 \times 10^{-3})^x}{k \ (5.0 \times 10^{-3})^x} \left(\frac{2.0 \times 10^{-5})^y}{(2.0 \times 10^{-5})^y}\right)
\]
\[
2 \text{NO(g)} + 2 \text{H}_2\text{(g)} \rightarrow \text{N}_2\text{(g)} + 2 \text{H}_2\text{O(g)}
\]

\[
\text{Exp 1: } 1.3 \times 10^{-5} = k \ (5.0 \times 10^{-3})^x \ (2.0 \times 10^{-5})^y
\]

\[
\text{Exp 2: } 5.0 \times 10^{-5} = k \ (10 \times 10^{-3})^x \ (2.0 \times 10^{-5})^y
\]

\[
\frac{\text{Exp 2}}{\text{Exp 1}} : \frac{5.0 \times 10^{-5}}{1.3 \times 10^{-5}} = \frac{k \ (10 \times 10^{-3})^x}{k \ (5.0 \times 10^{-3})^x} \frac{(2.0 \times 10^{-5})^y}{(2.0 \times 10^{-5})^y}
\]

\[
3.9 = \frac{5.0 \times 10^{-5}}{1.3 \times 10^{-5}} = \frac{(10 \times 10^{-3})^x}{(5.0 \times 10^{-3})^x} = (2)^x
\]

What is x? (a) 0 (b) 1 (c) 2 (d) 3
\[ 2 \text{NO}(g) + 2 \text{H}_2(g) \rightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(g) \]

Exp 1: \[ 1.3 \times 10^{-5} = k \ (5.0 \times 10^{-3})^x \ (2.0 \times 10^{-5})^y \]
Exp 2: \[ 5.0 \times 10^{-5} = k \ (10 \times 10^{-3})^x \ (2.0 \times 10^{-5})^y \]
Exp 3: \[ 10.0 \times 10^{-5} = k \ (10 \times 10^{-3})^x \ (4.0 \times 10^{-5})^y \]

Take RATIO of Exp 3 to Exp 2 to find \( y \)

\[ \frac{\text{exp 3}}{\text{exp 2}} : \frac{10 \times 10^{-5}}{5 \times 10^{-5}} = \frac{k \ (10 \times 10^{-3})^x \ (4.0 \times 10^{-5})^y}{k \ (10 \times 10^{-3})^x \ (2.0 \times 10^{-5})^y} \]
\[2 \text{NO}(g) + 2 \text{H}_2(g) \rightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(g)\]

Exp 2: \[5.0 \times 10^{-5} = k \left(10 \times 10^{-3}\right)^x \left(2.0 \times 10^{-5}\right)^y\]

Exp 3: \[10.0 \times 10^{-5} = k \left(10 \times 10^{-3}\right)^x \left(4.0 \times 10^{-5}\right)^y\]

\[
\frac{\text{exp 3}}{\text{exp 2}} = \frac{10 \times 10^{-5}}{5 \times 10^{-5}} = \frac{k \left(10 \times 10^{-3}\right)^x \left(4.0 \times 10^{-5}\right)^y}{k \left(10 \times 10^{-3}\right)^x \left(2.0 \times 10^{-5}\right)^y}
\]

\[2 = \frac{10 \times 10^{-5}}{5 \times 10^{-5}} = \frac{(4.0 \times 10^{-3})^y}{(2.0 \times 10^{-3})^y} = (2)^y\]

What is \(y = ?\)  
(a) 0  (b) 1  (c) 2  (d) 3
**METHOD OF INITIAL RATES**

2 NO\( (g) \) + 2 H\( _2 \)(g) → N\(_2\)\( (g) \) + 2 H\(_2\)O\( (g) \)

Rate = \( k \) [NO]\(^x\) [H\(_2\)]\(^y\)

The order with respect to NO is 2nd order

The order with respect to H\(_2\) is 1\(^{st}\) order

Rate = \( k \) [NO]\(^2\) [H\(_2\)]\(^1\)

The overall order of the reaction is \( 2 + 1 = 3 \)
2 NO(g) + 2 H₂(g) → N₂(g) + 2 H₂O(g)

Rate = k [NO]² [H₂]¹

What is the rate constant?

Exp 1: 1.3 x 10⁻⁵ = k (5.0x10⁻³)² (2.0x10⁻⁵)¹
Exp 2: 5.0 x 10⁻⁵ = k (10x10⁻³)² (2.0x10⁻⁵)¹
Exp 3: 10.0 x 10⁻⁵ = k (10x10⁻³)² (4.0x10⁻⁵)¹

Solve for k from any of the equations

k = 2.5 x 10⁴ Units???
EXAMPLE 2

\[ S_{2}O_{8}^{2-}(aq) + 3 I^{-}(aq) \rightarrow 2SO_{4}^{2-}(aq) + I_{3}^{-}(aq) \]

\[ \text{Rate} = k \ [S_{2}O_{8}^{2-}]^X \ [I^{-}]^Y \]

Determine
– the rate law
– the order
– and rate constant
\[ \text{Rate}_1 = \frac{2.2 \times 10^{-4}}{0.080 \times 0.034} \]

\[ \text{Rate}_2 = \frac{1.1 \times 10^{-4}}{0.080 \times 0.017} \]

\[ \text{Rate}_3 = \frac{2.2 \times 10^{-4}}{0.16 \times 0.017} \]
Divide Rate 1 by Rate 2 to find Y

\[
\frac{R_1}{R_2} = \frac{k}{k} \left[ \frac{0.08}{0.08} \right]^x \left[ \frac{0.034}{0.017} \right]^y = \left[ \frac{0.034}{0.017} \right]^y = [2]^y
\]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>([S_2O_8^{2-}])</th>
<th>([I^-])</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.080</td>
<td>0.034</td>
<td>2.2 \times 10^{-4}</td>
</tr>
<tr>
<td>2</td>
<td>0.080</td>
<td>0.017</td>
<td>1.1 \times 10^{-4}</td>
</tr>
<tr>
<td>3</td>
<td>0.16</td>
<td>0.017</td>
<td>2.2 \times 10^{-4}</td>
</tr>
</tbody>
</table>
\[
\frac{R_2}{R_1} = \frac{k \left[ 0.08 \right]^X \left[ 0.034 \right]^Y}{k \left[ 0.08 \right]^X \left[ 0.017 \right]^Y} = \left[ \frac{0.034}{0.017} \right]^Y = [2]^Y
\]

Now put in values for Rates:

\[
\frac{R_2}{R_1} = \frac{2.2 \times 10^{-4}}{1.1 \times 10^{-4}} = 2 = [2]^Y
\]

and guess what \( Y \) is

(a) \( Y = 0 \)  (b) \( Y = 1 \)  (c) \( Y = 2 \)  (d) \( Y = 3 \)
<table>
<thead>
<tr>
<th>Experiment</th>
<th>$[\text{S}_2\text{O}_8^{2-}]$</th>
<th>$[\text{I}^-]$</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.080</td>
<td>0.034</td>
<td>$2.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>0.080</td>
<td>0.017</td>
<td>$1.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>0.16</td>
<td>0.017</td>
<td>$2.2 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Divide Rate 3 by Rate 2 to find $X$

\[
\frac{R_3}{R_2} = \frac{k \left[0.16\right]^X \left[0.017\right]^Y}{k \left[0.08\right]^X \left[0.017\right]^Y} = \left[\frac{0.16}{0.08}\right]^X = [2]^X
\]
\[
\frac{R_3}{R_2} = k \frac{[.16]^X}{[.08]^X} \frac{[.017]^Y}{[.017]^Y} = \left[ \frac{.16}{.08} \right]^X = [2]^X
\]

Now put in values for Rates:

\[
\frac{R_3}{R_2} = \frac{2.2 \times 10^{-4}}{1.1 \times 10^{-4}} = 2 = [2]^X
\]

and guess what X is

(a) X = 0  (b) X = 1  (c) X = 2  (d) X = 3
For the Reaction
\[ \text{S}_2\text{O}_8^{2-}(aq) + 3 \text{I}^-(aq) \rightarrow \text{2SO}_4^{2-}(aq) + \text{I}_3^-(aq) \]

the rate law: \[ \text{Rate} = k \ [\text{S}_2\text{O}_8^{2-}] \ [\text{I}^-] \]

the order: \[ X + Y = 1 + 1 = 2 \]

and rate constant:
\[ R_1 = 2.2 \times 10^{-4} = k \ (0.08)(0.034) \]
\[ k = 8.0882353 \times 10^{-2} \]

Really?
Problem 14.26 page 566

\[ \text{S}_2\text{O}_8^{2-} (aq) + 3\text{I}^- (aq) \rightarrow 2\text{SO}_4^{2-} (aq) + \text{I}_3^- (aq) \]

<table>
<thead>
<tr>
<th>Exp</th>
<th>[S(_2)O(_8)]</th>
<th>[I(^-)]</th>
<th>Rate(M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.018</td>
<td>0.036</td>
<td>2.6 x 10(^{-6})</td>
</tr>
<tr>
<td>2</td>
<td>0.027</td>
<td>0.036</td>
<td>3.9 x 10(^{-6})</td>
</tr>
<tr>
<td>3</td>
<td>0.036</td>
<td>0.054</td>
<td>7.8 x 10(^{-6})</td>
</tr>
<tr>
<td>4</td>
<td>0.050</td>
<td>0.072</td>
<td>1.4 x 10(^{-5})</td>
</tr>
</tbody>
</table>

How is this problem different from the previous example?
Additional Topics:

I. Integrated form of rate equation
II. Half-life
III. Temperature
IV. Catalyst
For 1st Order Reactions: \( A \rightarrow B \)

Instead of \( \text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A] \)

use \( \text{Rate} = -\frac{d[A]}{dt} = k[A] \)

or \( -\frac{d[A]}{[A]} = k \, dt \)
Integrated form of rate equation

\[- \int_{\text{initial}}^{\text{final}} \frac{d[A]}{[A]} = \int_0^t k \, dt\]

\[[A]_0 = \text{initial concentration at time } t = 0\]
\[[A] = \text{concentration at time } t\]

\[\ln \frac{[A]_0}{[A]} = k \, t\]
II. Reaction Rates & Half-Life

The half-life \((t_{1/2})\) of a reaction is the TIME required for the concentration of a reactant to decrease to one half its initial value.
Half-life is defined as the time required for one-half of a reactant to react.

- Because $[A]$ at $t_{1/2}$ is one-half of the original $[A]$, $[A]_t = 0.5 [A]_0$. 
The concentration of A at $t_{1/2}$ is one half the original concentration $[A]_t = 0.5 \ [A]_0$
[A] is one-half of the original [A]$_o$ at $t_{1/2} = 13,500$ sec

The Concentration [A] is one-half of that at two half lives $t_{1/2} = 28,000$ sec
Consider the Reaction

\[ 2 \text{H}_2\text{O}_2 (\text{aq}) \rightarrow \text{H}_2\text{O} (\text{liq}) + \text{O}_2 (\text{g}) \]

What will the concentration of Hydrogen Peroxide be after 3 half-lives? The half-life \((t_{1/2})\) of the decomposition of Hydrogen Peroxide is 654 mins
If the initial concentration of $\text{H}_2\text{O}_2$ is 0.020 M

How long will it take for the concentration of Hydrogen Peroxide to drop to 0.010?

654 mins = one half-life

What will the concentration of Hydrogen Peroxide be after 3 half-lives? __________
All radioactive decay is 1\textsuperscript{st} order

\[
\ln \frac{[A]_0}{[A]} = k t
\]

At \(t_{1/2}\) concentration is \(1/2\) initial

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

\[
\ln 2 = k t_{1/2}
\]
III. Temperature and Rate

Rates of reactions are affected by
1. concentration
2. and temperature.

Since the rate law has no temperature term in it, *the rate constant must depend on temperature.*
As temperature increases, the rate increases.

Temperature and Rate

![Graph showing the relationship between temperature and rate]
Rule of Thumb for Reaction Rates & Temperature

Ten degree increase in temperature Doubles Rate of Reaction
Energy of Activation

• 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.
Activation Energy

A ball cannot get over a hill if it does not roll up the hill with enough energy.
Activation Energy

- In other words, there is a minimum amount of energy required for reaction: the activation energy, $E_a$.
- A reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.
Energy of Activation $E_a$

the minimum energy required to initiate a chemical reaction.
Figure 14.15.
Potential energy

Reactants

Products

Reaction pathway

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Reaction pathway

[Diagram showing energy levels with labels A + B leading to C]
Energy Profiles - determine

1. Energy of Activation
2. Heat of Reaction
Consider the reaction \( A \rightarrow D \)

(a) What is the value of \( E_a \)?

(b) Is the reaction exothermic, or endothermic?

![Potential energy diagram](image)
Is this an Endo or Exo Thermic Process?
Reaction Rates and Catalysis

Increases Rate
Takes Part in Reaction
Is not consumed
A catalyst is a substance that increases the rate of a reaction without being consumed in the reaction.

Catalysts change the mechanism by which the process occurs.

Enzymes are catalysts in biological systems.
**Homogeneous catalyst:** Exists in the **SAME** phase as the reactants.  

**Heterogeneous catalyst:** Exists in **DIFFERENT** phase to the reactants.
Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.
CATALYSTS

Potential energy

Reaction pathway

Uncatalyzed reaction

Catalyzed reaction

$2 \text{H}_2\text{O}_2 + 2 \text{Br}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + 2 \text{H}_2\text{O} + \text{Br}_2$

$2 \text{H}_2\text{O} + \text{O}_2 + 2 \text{Br}^- + 2 \text{H}^+$
PART II
Mechanism

How does the reaction go from Reactants to Products
Reaction Mechanisms

The sequence of events that describes the actual process by which reactants become products is called the reaction mechanism.
Reaction Mechanisms

• Reactions may occur all at once or through several discrete steps.
• Each of these processes is known as an elementary reaction or elementary process.
The Collision Model

• In a chemical reaction, bonds are broken and new bonds are formed.
• Molecules can only react if they collide with each other.
The Collision Model

Furthermore, molecules must collide with the correct **orientation** and with enough **energy** to cause bond breakage and formation.
Collision Theory

1. molecules MUST collide
2. collide with sufficient energy. *
3. correctly oriented molecules

*Activation Energy ($E_a$): The energy barrier that must be surmounted before reactants can be converted to products.
Activation Energy

[A diagram showing the energy profile of a chemical reaction, with reactants labeled as A + BC, transition state labeled as A ---- B ---- C, and products labeled as AB + C. The energy barrier represented by $E_a$ and the energy difference $\Delta E$.]
The Collision Theory

• Not all collisions lead to products.
• In order for reaction to occur the reactant molecules must collide in the correct orientation and with enough energy to form products.
• The higher the temperature, the more energy available to the molecules and the faster the rate.
Collision Theory

\[ A + B - C \rightarrow A - B - C \rightarrow A - B + C \]
The fraction of collisions having correct orientation is called the **steric factor**, $p$.

- The fraction of collisions leading to product is further reduced by an orientation requirement.

$$A + C-B \rightarrow A\cdots C\cdots B \rightarrow A-B + C$$
The Orientation Factor

(a) Effective collision

(b) Ineffective collision
REACTION MECHANISMS

Most Chemical Reactions DO NOT Occur In A Single Step

Chemical Equations Normally Represent the OVERALL Reaction Not the Series of INDIVIDUAL Steps By Which The Reaction Actually Occurs
HOW DOES

OZONE “turn into” OXYGEN?

\[ 2 \text{ O}_3 \quad \rightarrow \quad 3 \text{ O}_2 \]

What is “BETWEEN” Reactants and Products
HOW DOES

The reaction of Hydrogen with Iodine monochloride form Hydrogen Chloride and Iodine?

\[ \text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{I}_2(\text{g}) \]

What Happens BETWEEN Reactants & Products?
REACTION MECHANISM

The SEQUENCE Of Reaction STEPS That Defines The PATHWAY From Reactants To Products
ELEMENTARY STEPS

• Single steps in a mechanism are called elementary steps (reactions).
• An elementary step describes the behavior of individual molecules.
• An overall reaction describes the reaction stoichiometry.
Terms You Need To Know

Molecularity: is the number of molecules (or atoms) on the reactant side of the chemical equation.

Unimolecular Reactions: Single reactant molecule.

Bimolecular Reactions: Two reactant molecules.

Termolecular: Three reactant molecules.
Rate Laws and Reaction Mechanisms

• Rate law for an **overall reaction** MUST be determined experimentally.

• Rate law for **elementary steps** follows from its molecularity.

• Elementary steps: Processes in a chemical reaction that occur in a single event or step
Rate Laws and Reaction Mechanisms

• The rate law of each elementary step follows its molecularity.

• The overall reaction is a sequence of elementary steps called the reaction mechanism.
Rate Laws and Reaction Mechanisms

Therefore, the experimentally observed rate law for an overall reaction must depend on the reaction mechanism.
Determine the rate law by experiment

Devise a mechanism

Try again

If the predicted and experimental rate laws do not agree

Predict the rate law for the mechanism

If the predicted and experimental rate laws agree

Look for additional supporting evidence
“How” does ozone “turn into” oxygen?

$$2 \text{O}_3 \rightarrow ??? \rightarrow 3 \text{O}_2$$
It has been proposed that the mechanism of ozone into O$_2$ proceeds by a two-step:

\[
\begin{align*}
0_3(g) & \rightarrow 0_2(g) + 0(g) \\
0_3(g) + 0(g) & \rightarrow 2 0_2(g)
\end{align*}
\]

(a) Describe the molecularity of each elementary reaction in this mechanism.
(b) Write the equation for the overall reaction
(c) Identify the intermediate(s).
SAMPLE EXERCISE 14.14 Determining the Rate Law

For the decomposition of nitrous oxide, N₂O

\[ \ce{N_2O(g) \rightarrow N_2(g) + O(g)} \quad \text{(slow)} \]
\[ \ce{N_2O(g) + O(g) \rightarrow N_2(g) + O_2(g)} \quad \text{(fast)} \]

(a) Write the equation for the overall reaction.
(b) Write the rate law for the overall reaction.
Ozone reacts with nitrogen dioxide to produce dinitrogen pentoxide and oxygen:

The reaction is believed to occur in two steps

\[
\text{O}_3(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{O}_2(g)
\]

\[
\text{NO}_3(g) + \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_5(g)
\]

1. Write the overall reaction
2. Is the proposed mechanism possible?
3. Identify the intermediate(s)?
NO catalyzes the decomposition of N$_2$O by the following mechanism

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

(a) Write the balanced equation for the reaction
(b) Why is NO considered a catalyst and not an intermediate?
(c) Identify intermediates in mechanism