Chapter 14: Chemical Kinetics
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(ppt modified for our requirements)
Kinetics

Studies the rate at which a chemical process occurs.

Besides information about the speed at which reactions occur, kinetics also sheds light on the reaction mechanism (exactly how the reaction occurs).

Resources and Activities
- Textbook - chapter 14 & ppt file
- Online practice quiz
- Lab activities
- POGIL activities
- Chemtour videos from Norton & Animations from Glencoe
Activities and Problem set for chapter 14  (due date_______)

Lab activities:
- Kinetics of a reaction \((\text{wet lab})\)
- Virtual lab (Iodine-Clock expt.)

POGILS (2) : Chemical Kinetics; Reaction Mechanisms

Online practice quiz ch 14 due by______

Chapter 14 reading guide and practice problems packet

In class preview and then Independent work - students to view animations & interactive activities (5 in total from Norton) and write summary notes on each. These summaries are to be included in your portfolio.

Animations to view in class and at home:

(Reaction rates, Reaction order, Arrhenius equation, Collision Theory, Reaction mechanisms)

Additional resources to explore (summaries not mandatory)
http://glencoe.mcgraw-hill.com/sites/0023654666/student_view0/chapter13/animations_center.html#
(catalysis, Kinetics simulation)
# Outline: Kinetics

<table>
<thead>
<tr>
<th>Topic</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reaction Rates</strong></td>
<td>How we measure rates.</td>
</tr>
<tr>
<td><strong>Rate Laws</strong></td>
<td>How the rate depends on amounts of reactants.</td>
</tr>
<tr>
<td><strong>Integrated Rate Laws</strong></td>
<td>How to calc amount left or time to reach a given amount.</td>
</tr>
<tr>
<td><strong>Half-life</strong></td>
<td>How long it takes to react 50% of reactants.</td>
</tr>
<tr>
<td><strong>Arrhenius Equation</strong></td>
<td>How rate constant changes with T.</td>
</tr>
<tr>
<td><strong>Mechanisms</strong></td>
<td>Link between rate and molecular scale processes.</td>
</tr>
</tbody>
</table>
Vocabulary terms

Reaction rate
(units \(M \cdot s^{-1} \equiv mol \cdot L^{-1} \cdot s^{-1}\))
- Instantaneous rate
- Initial rate (instantaneous rate at \(t = 0\))
- Average rate of reaction
- Rate constant (diff units possible depending on molecularity of reaction)

Reaction orders
- Overall reaction order
- 1\textsuperscript{st} order
- 2\textsuperscript{nd} order

Collision Model/theory
- Activation energy \((E_a)\)
- Activated complex/transition state
- Arrhenius equation

Reaction mechanisms
- Elementary reactions/processes
- Molecularity
- Unimolecular, bimolecular, termolecular

Catalysts
- Homogeneous & heterogeneous
- Adsorption vs absorption
- Enzymes, substrates, active sites, lock & key model
Important equations

\[ aA + bB \rightarrow cC + dD \quad \text{Rate} = k [A]^x[B]^y \]

For a first order reaction \( A \rightarrow \text{products} \)

\[
\text{rate} = -\frac{\Delta [A]}{\Delta t} \quad \ln [A]_t = -kt + \ln [A]_0 \\
\text{rate} = k [A] \\
\ln \frac{[A]_t}{[A]_0} = -kt
\]

Because \([A]\) at \( t_{1/2} \) is one-half of the original \([A]\), \( [A]_t = \frac{1}{2}[A]_0 = 0.5[A]_0 \)

\[
\ln \frac{0.5 [A]_0}{[A]_0} = -kt_{1/2} \\
\frac{0.693}{k} = t_{1/2}
\]
Important equations

For a second order reaction $A + B \rightarrow \text{ products}$

\[
\text{rate} = - \frac{\Delta[A]}{\Delta t} \quad \text{rate} = k [A] [B] \quad \text{rate} = k [A]^2
\]

Half life for second order reaction

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

\[
\frac{1}{k[A]_0} = t_{1/2}
\]
Important equations (to complete)

Arrhenius equation

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

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

\[ \ln(k) = -\frac{E_a}{RT} + \ln A \]
Factors That Affect Reaction Rates

• **Physical State of the Reactants**
  - In order to react, molecules must come in contact with each other.
  - The more homogeneous the mixture of reactants, the faster the molecules can react.

• **Concentration of Reactants**
  - As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.

• **Temperature**
  - At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.
Factors That Affect Reaction Rates

• **Presence of a Catalyst**
  - Catalysts speed up reactions by changing the mechanism of the reaction.
  - Catalysts are not consumed during the course of the reaction.
Chemical Kinetics

Thermodynamics – does a reaction take place?

Kinetics – how fast does a reaction proceed?

 Reaction rate is the change in the concentration of a reactant or a product with time ($M/s$).

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

$\Delta[A] =$ change in concentration of A over time period $\Delta t$

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B] =$ change in concentration of B over time period $\Delta t$

Because $[A]$ decreases with time, $\Delta[A]$ is negative.
rate = - \frac{\Delta[A]}{\Delta t}

rate = \frac{\Delta[B]}{\Delta t}
Reaction Rates

\[ \text{C}_4\text{H}_9\text{Cl} (aq) + \text{H}_2\text{O}(l) \rightarrow \text{C}_4\text{H}_9\text{OH} (aq) + \text{HCl} (aq) \]

<table>
<thead>
<tr>
<th>Time, ( t(s) )</th>
<th>([\text{C}_4\text{H}_9\text{Cl}] (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>
<td>0.0741</td>
</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>10,000</td>
<td>0</td>
</tr>
</tbody>
</table>

In this reaction, the concentration of butyl chloride, \( \text{C}_4\text{H}_9\text{Cl} \), was measured at various times.
Reaction Rates

\[ \text{C}_4\text{H}_9\text{Cl}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{C}_4\text{H}_9\text{OH}(aq) + \text{HCl}(aq) \]

<table>
<thead>
<tr>
<th>Time, ( t(s) )</th>
<th>([\text{C}_4\text{H}_9\text{Cl}] ) ((M))</th>
<th>Average Rate ((M/s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.1000</td>
<td>1.9 \times 10^{-4}</td>
</tr>
<tr>
<td>50.0</td>
<td>0.0905</td>
<td>1.7 \times 10^{-4}</td>
</tr>
<tr>
<td>100.0</td>
<td>0.0820</td>
<td>1.6 \times 10^{-4}</td>
</tr>
<tr>
<td>150.0</td>
<td>0.0741</td>
<td>1.4 \times 10^{-4}</td>
</tr>
<tr>
<td>200.0</td>
<td>0.0671</td>
<td>1.22 \times 10^{-4}</td>
</tr>
<tr>
<td>300.0</td>
<td>0.0549</td>
<td>1.01 \times 10^{-4}</td>
</tr>
<tr>
<td>400.0</td>
<td>0.0448</td>
<td>0.80 \times 10^{-4}</td>
</tr>
<tr>
<td>500.0</td>
<td>0.0368</td>
<td>0.560 \times 10^{-4}</td>
</tr>
<tr>
<td>800.0</td>
<td>0.0200</td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

The average rate of the reaction over each interval is the change in concentration divided by the change in time:

\[
\text{Average rate} = \frac{\Delta [\text{C}_4\text{H}_9\text{Cl}]}{\Delta t}
\]
Reaction Rates

\[
\text{C}_4\text{H}_9\text{Cl}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{C}_4\text{H}_9\text{OH}(aq) + \text{HCl}(aq)
\]

<table>
<thead>
<tr>
<th>Time, ( t(s) )</th>
<th>([\text{C}_4\text{H}_9\text{Cl}] (M))</th>
<th>Average Rate (M/s)</th>
</tr>
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<tbody>
<tr>
<td>0.0</td>
<td>0.1000</td>
<td>1.9 \times 10^{-4}</td>
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<tr>
<td>50.0</td>
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<td>1.6 \times 10^{-4}</td>
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<td>150.0</td>
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<tr>
<td>200.0</td>
<td>0.0671</td>
<td>1.22 \times 10^{-4}</td>
</tr>
<tr>
<td>300.0</td>
<td>0.0549</td>
<td>1.01 \times 10^{-4}</td>
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<td>400.0</td>
<td>0.0448</td>
<td>0.80 \times 10^{-4}</td>
</tr>
<tr>
<td>500.0</td>
<td>0.0368</td>
<td>0.560 \times 10^{-4}</td>
</tr>
<tr>
<td>800.0</td>
<td>0.0200</td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

- Note that the average rate decreases as the reaction proceeds.
- This is because as the reaction goes forward, there are fewer collisions between reactant molecules.
Reaction Rates

\[ \text{C}_4\text{H}_9\text{Cl}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{C}_4\text{H}_9\text{OH}(aq) + \text{HCl}(aq) \]

- A plot of concentration vs. time for this reaction yields a curve like this.
- The slope of a line tangent to the curve at any point is the instantaneous rate at that time.
Reaction Rates

\[ C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq) \]

- All reactions slow down over time.
- Therefore, the best indicator of the rate of a reaction is the instantaneous rate near the beginning.
### Reaction Rates and Stoichiometry

\[ C_4H_9Cl(\text{aq}) + H_2O(l) \rightarrow C_4H_9OH(\text{aq}) + HCl(\text{aq}) \]

- In this reaction, the ratio of \( C_4H_9Cl \) to \( C_4H_9OH \) is 1:1.
- Thus, the rate of disappearance of \( C_4H_9Cl \) is the same as the rate of appearance of \( C_4H_9OH \).

\[
\text{Rate} = \frac{-\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}
\]
Reaction Rates and Stoichiometry

• What if the ratio is not 1:1?

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

• Therefore,

\[
\text{Rate} = -\frac{1}{2} \frac{\Delta [\text{HI}]}{\Delta t} = \frac{\Delta [\text{I}_2]}{\Delta t}
\]
Reaction Rates and Stoichiometry

• To generalize, then, for the reaction

\[ aA + bB \rightarrow cC + dD \]

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

One can gain information about the rate of a reaction by seeing how the rate changes with changes in concentration.

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial $\text{NH}_4^+\text{ concentration (M)}$</th>
<th>Initial $\text{NO}_2^-$ concentration (M)</th>
<th>Observed Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0100</td>
<td>0.200</td>
<td>$5.4 \times 10^{-7}$</td>
</tr>
<tr>
<td>2</td>
<td>0.0200</td>
<td>0.200</td>
<td>$10.8 \times 10^{-7}$</td>
</tr>
<tr>
<td>3</td>
<td>0.0400</td>
<td>0.200</td>
<td>$21.5 \times 10^{-7}$</td>
</tr>
<tr>
<td>4</td>
<td>0.0600</td>
<td>0.200</td>
<td>$32.3 \times 10^{-7}$</td>
</tr>
<tr>
<td>5</td>
<td>0.200</td>
<td>0.0202</td>
<td>$10.8 \times 10^{-7}$</td>
</tr>
<tr>
<td>6</td>
<td>0.200</td>
<td>0.0404</td>
<td>$21.6 \times 10^{-7}$</td>
</tr>
<tr>
<td>7</td>
<td>0.200</td>
<td>0.0606</td>
<td>$32.4 \times 10^{-7}$</td>
</tr>
<tr>
<td>8</td>
<td>0.200</td>
<td>0.0808</td>
<td>$43.3 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

$\text{NH}_4^+(aq) + \text{NO}_2^-(aq) \rightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(l)$

Comparing Experiments 1 and 2, when [NH$_4^+$] doubles, the initial rate doubles.
NH$_4^+$ (aq) + NO$_2^-$ (aq) $\rightarrow$ N$_2$(g) + 2 H$_2$O(l)

Likewise, comparing Experiments 5 and 6, when [NO$_2^-$] doubles, the initial rate doubles.
Concentration and Rate

• This means

\[\text{Rate} \propto [\text{NH}_4^+]\]
\[\text{Rate} \propto [\text{NO}_2^-]\]
\[\text{Rate} \propto [\text{NH}^+] [\text{NO}_2^-]\]

or

\[\text{Rate} = k [\text{NH}_4^+] [\text{NO}_2^-]\]

• This equation is called the rate law, and \(k\) is the rate constant.
Rate Laws

- A rate law shows the relationship between the reaction rate and the concentrations of reactants.
- The exponents tell the order of the reaction with respect to each reactant.
- This reaction is
  
  First-order in \([\text{NH}_4^+]\)
  
  First-order in \([\text{NO}_2^-]\)

- The overall reaction order can be found by adding the exponents on the reactants in the rate law.
- This reaction is second-order overall.
The Rate Law

The rate law expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

\[ aA + bB \rightarrow cC + dD \]

Rate = \( k \left[ A \right]^x \left[ B \right]^y \)

reaction is \( x \text{th order} \) in A
reaction is \( y \text{th order} \) in B
reaction is \( (x + y)\text{th order} \) overall
\[ \text{F}_2 (g) + 2\text{ClO}_2 (g) \rightarrow 2\text{FClO}_2 (g) \]

rate = \( k [\text{F}_2]^x[\text{ClO}_2]^y \)

**Table 13.2  Rate Data for the Reaction between F\textsubscript{2} and Cl\textsubscript{2}O\textsubscript{2}**

<table>
<thead>
<tr>
<th><a href="M">F\textsubscript{2}</a></th>
<th><a href="M">ClO\textsubscript{2}</a></th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 0.10</td>
<td>0.010</td>
<td>1.2 \times 10^{-3}</td>
</tr>
<tr>
<td>2. 0.10</td>
<td>0.040</td>
<td>4.8 \times 10^{-3}</td>
</tr>
<tr>
<td>3. 0.20</td>
<td>0.010</td>
<td>2.4 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Double [F\textsubscript{2}] with [ClO\textsubscript{2}] constant
Rate doubles
\( x = 1 \)

Quadruple [ClO\textsubscript{2}] with [F\textsubscript{2}] constant
Rate quadruples
\( y = 1 \)

rate = \( k [\text{F}_2][\text{ClO}_2] \)
<table>
<thead>
<tr>
<th>Run #</th>
<th>Initial [A] ([A]₀)</th>
<th>Initial [B] ([B]₀)</th>
<th>Initial Rate (v₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00 M</td>
<td>1.00 M</td>
<td>1.25 x 10⁻² M/s</td>
</tr>
<tr>
<td>2</td>
<td>1.00 M</td>
<td>2.00 M</td>
<td>2.5 x 10⁻² M/s</td>
</tr>
<tr>
<td>3</td>
<td>2.00 M</td>
<td>2.00 M</td>
<td>2.5 x 10⁻² M/s</td>
</tr>
</tbody>
</table>

What is the order with respect to A? 0

What is the order with respect to B? 1

What is the overall order of the reaction? 1
<table>
<thead>
<tr>
<th>([\text{NO}_{(g)}]) (mol dm(^{-3}))</th>
<th>([\text{Cl}_2(g)]) (mol dm(^{-3}))</th>
<th>Initial Rate (mol dm(^{-3}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.250</td>
<td>0.250</td>
<td>1.43 x 10(^{-6})</td>
</tr>
<tr>
<td>0.250</td>
<td>0.500</td>
<td>2.86 x 10(^{-6})</td>
</tr>
<tr>
<td>0.500</td>
<td>0.500</td>
<td>1.14 x 10(^{-5})</td>
</tr>
</tbody>
</table>

What is the order with respect to Cl\(_2\)? 1

What is the order with respect to NO? 2

What is the overall order of the reaction? 3
Rate Laws

- Rate laws are **always** determined experimentally.

- Reaction order is **always** defined in terms of reactant (not product) concentrations.

- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.

\[ \text{F}_2 (g) + 2\text{ClO}_2 (g) \rightarrow 2\text{FClO}_2 (g) \]

\[
\text{rate} = k [\text{F}_2][\text{ClO}_2]^{1}
\]
Determine the rate law and calculate the rate constant for the following reaction from the following data:

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

<table>
<thead>
<tr>
<th>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>0.08</td>
<td>0.034</td>
<td>$2.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>0.08</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>

rate = $k [\text{S}_2\text{O}_8^{2-}]^x[\text{I}^-]^y$

$y = 1$

$x = 1$

rate = $k [\text{S}_2\text{O}_8^{2-}][\text{I}^-]$

Double $[\text{I}^-]$, rate doubles (experiment 1 & 2)

Double $[\text{S}_2\text{O}_8^{2-}]$, rate doubles (experiment 2 & 3)

$$k = \frac{\text{rate}}{[\text{S}_2\text{O}_8^{2-}][\text{I}^-]} = \frac{2.2 \times 10^{-4} \text{ M/s}}{(0.08 \text{ M})(0.034 \text{ M})} = 0.08/\text{M} \cdot \text{s}$$
Integrated Rate Laws

Using calculus to integrate the rate law for a first-order process gives us

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

Where

$[A]_0$ is the initial concentration of A.

$[A]_t$ is the concentration of A at some time, $t$, during the course of the reaction.
Manipulating this equation produces…

\[
\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt
\]

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

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

…which is in the form

\[
y = mx + b
\]
First-Order Processes

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

Therefore, if a reaction is first-order, a plot of \( \ln [A] \) vs. \( t \) will yield a straight line, and the slope of the line will be \(-k\).
First-Order Reactions (other forms of equations)

\[
\text{rate} = - \frac{\Delta [A]}{\Delta t}
\]

\[
\text{rate} = k [A]
\]

\[
[A] = [A]_0 e^{-kt}
\]

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

[A] is the concentration of A at any time \( t \)

[A]_0 is the concentration of A at time \( t=0 \)
First-Order Processes

Consider the process in which methyl isonitrile is converted to acetonitrile.

\[ \text{Methyl isonitrile} \rightarrow \text{Acetonitrile} \]

\[ \text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN} \]
First-Order Processes

$\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$

This data was collected for this reaction at 198.9°C.
When $\ln P$ is plotted as a function of time, a straight line results.

Therefore,

- The process is first-order.
- $k$ is the negative slope: $5.1 \times 10^{-5} \text{ s}^{-1}$.
The reaction $2A \rightarrow B$ is first order in $A$ with a rate constant of $2.8 \times 10^{-2} \text{ s}^{-1}$ at $80^0\text{C}$. How long will it take for $A$ to decrease from $0.88 \text{ M}$ to $0.14 \text{ M}$?

$$[A] = [A]_0 e^{-kt}$$

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

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

$$t = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \frac{[A]_0}{[A]}}{k} = \frac{\ln \frac{0.88 \text{ M}}{0.14 \text{ M}}}{2.8 \times 10^{-2} \text{ s}^{-1}} = 66 \text{ s}$$
First-Order Reactions

The **half-life**, \( t_{1/2} \), is the time required for the concentration of a reactant to decrease to half of its initial concentration.

\[
\begin{align*}
t_{1/2} &= t \quad \text{when} \quad [A] = [A]_0/2 \\
&= \frac{\ln \frac{[A]_0}{[A]_0/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}
\end{align*}
\]

What is the half-life of \( \text{N}_2\text{O}_5 \) if it decomposes with a rate constant of \( 5.7 \times 10^{-4} \text{ s}^{-1} \)?

\[
t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{5.7 \times 10^{-4} \text{ s}^{-1}} = 1200 \text{ s} = 20 \text{ minutes}
\]

How do you know decomposition is first order? 

units of \( k \) (s\(^{-1}\))
A first-order reaction is represented by the equation:

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

The concentration of \([A]\) over the number of half-lives elapsed is given by:

\[ [A] = \frac{[A]_0}{n} \]

<table>
<thead>
<tr>
<th># of half-lives</th>
<th>([A] = \frac{[A]_0}{n})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
</tr>
</tbody>
</table>
Second-Order Reactions

rate = - \frac{\Delta [A]}{\Delta t} \quad \text{rate} = k [A]^2

[A] is the concentration of A at any time \( t \)

\([A]_0\) is the concentration of A at time \( t=0 \)

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

Half life for second order

\( t_{\frac{1}{2}} = t \) when \([A] = [A]_0/2\)

\[
t_{\frac{1}{2}} = \frac{1}{k[A]_0}
\]
Second-Order Processes

Similarly, integrating the rate law for a process that is second-order in reactant A, we get

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

also in the form

\[ y = mx + b \]
Second-Order Processes

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

So if a process is second-order in A, a plot of \(1/[A]\) vs. \(t\) will yield a straight line, and the slope of that line is \(k\).
Second-Order Processes

The decomposition of NO$_2$ at 300° C is described by the equation

\[
\text{NO}_2 (g) \rightarrow \text{NO} (g) + \frac{1}{2} \text{O}_2 (g)
\]

and yields data comparable to this:

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[NO$_2$], M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.01000</td>
</tr>
<tr>
<td>50.0</td>
<td>0.00787</td>
</tr>
<tr>
<td>100.0</td>
<td>0.00649</td>
</tr>
<tr>
<td>200.0</td>
<td>0.00481</td>
</tr>
<tr>
<td>300.0</td>
<td>0.00380</td>
</tr>
</tbody>
</table>
Second-Order Processes

- Graphing $\ln [\text{NO}_2]$ vs. $t$ yields:
- The plot is not a straight line, so the process is not first-order in $[A]$.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[NO$_2$], M</th>
<th>$\ln$ [NO$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.01000</td>
<td>-4.610</td>
</tr>
<tr>
<td>50.0</td>
<td>0.00787</td>
<td>-4.845</td>
</tr>
<tr>
<td>100.0</td>
<td>0.00649</td>
<td>-5.038</td>
</tr>
<tr>
<td>200.0</td>
<td>0.00481</td>
<td>-5.337</td>
</tr>
<tr>
<td>300.0</td>
<td>0.00380</td>
<td>-5.573</td>
</tr>
</tbody>
</table>
Second-Order Processes

- Graphing $\ln \frac{1}{[NO_2]}$ vs. $t$, however, gives this plot.
- Because this is a straight line, the process is second-order in [A].

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[NO₂], M</th>
<th>1/[NO₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.01000</td>
<td>100</td>
</tr>
<tr>
<td>50.0</td>
<td>0.00787</td>
<td>127</td>
</tr>
<tr>
<td>100.0</td>
<td>0.00649</td>
<td>154</td>
</tr>
<tr>
<td>200.0</td>
<td>0.00481</td>
<td>208</td>
</tr>
<tr>
<td>300.0</td>
<td>0.00380</td>
<td>263</td>
</tr>
</tbody>
</table>
Half-Life

- 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 $[A]$, 
  $$[A]_t = 0.5 \ [A]_0.$$
Half-Life

For a first-order process, this becomes

$$\ln \left( \frac{0.5 [A]_0}{[A]_0} \right) = -kt_{1/2}$$

$$\ln 0.5 = -kt_{1/2}$$

$$-0.693 = -kt_{1/2}$$

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

NOTE: For a first-order process, the half-life does not depend on $[A]_0$. 
Half-Life

For a second-order process,

\[ \frac{1}{0.5 [A]_0} = k t_{1/2} + \frac{1}{[A]_0} \]

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

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

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

• Generally, as temperature increases, so does the reaction rate.
• This is because $k$ is temperature dependent.
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.
Activation Energy

• In other words, there is a minimum amount of energy required for reaction: the activation energy, $E_a$.
• Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.
Reaction Coordinate Diagrams

It is helpful to visualize energy changes throughout a process on a reaction coordinate diagram like this one for the rearrangement of methyl isonitrile.
Reaction Coordinate Diagrams

- It shows the energy of the reactants and products (and, therefore, $\Delta E$).
- The high point on the diagram is the **transition state**.
- The species present at the transition state is called the **activated complex**.
- The energy gap between the reactants and the activated complex is the activation energy barrier.
Maxwell–Boltzmann Distributions

- Temperature is defined as a measure of the average kinetic energy of the molecules in a sample.

- At any temperature there is a wide distribution of kinetic energies.
Maxwell–Boltzmann Distributions

- As the temperature increases, the curve flattens and broadens.
- Thus at higher temperatures, a larger population of molecules has higher energy.
Maxwell–Boltzmann Distributions

• If the dotted line represents the activation energy, as the temperature increases, so does the fraction of molecules that can overcome the activation energy barrier.

• As a result, the reaction rate increases.
Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression

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

where \( R \) is the gas constant and \( T \) is the Kelvin temperature.
Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between $k$ and $E_a$:

$$k = A \ e^{-E_a/RT}$$

where $A$ is the *frequency factor*, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.
Chemical Kinetics

Arrhenius Equation

Taking the natural logarithm of both sides, the equation becomes

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

Therefore, if \( k \) is determined experimentally at several temperatures, \( E_a \) can be calculated from the slope of a plot of \( \ln k \) vs. \( 1/T \).
Reaction Mechanisms

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

- Reactions may occur all at once or through several discrete steps.
- Each of these processes is known as an elementary reaction or elementary process.
Reaction Mechanisms

<table>
<thead>
<tr>
<th>Molecularity</th>
<th>Elementary Reaction</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Unimolecular</em></td>
<td>$A \rightarrow \text{products}$</td>
<td>Rate = $k[A]$</td>
</tr>
<tr>
<td><em>Bimolecular</em></td>
<td>$A + A \rightarrow \text{products}$</td>
<td>Rate = $k[A]^2$</td>
</tr>
<tr>
<td><em>Bimolecular</em></td>
<td>$A + B \rightarrow \text{products}$</td>
<td>Rate = $k[A][B]$</td>
</tr>
<tr>
<td><em>Termolecular</em></td>
<td>$A + A + A \rightarrow \text{products}$</td>
<td>Rate = $k[A]^3$</td>
</tr>
<tr>
<td><em>Termolecular</em></td>
<td>$A + A + B \rightarrow \text{products}$</td>
<td>Rate = $k[A]^2[B]$</td>
</tr>
<tr>
<td><em>Termolecular</em></td>
<td>$A + B + C \rightarrow \text{products}$</td>
<td>Rate = $k[A][B][C]$</td>
</tr>
</tbody>
</table>

The molecularity of a process tells how many molecules are involved in the process.
Reaction Mechanisms

The overall progress of a chemical reaction can be represented at the molecular level by a series of simple *elementary steps* or *elementary reactions*.

The sequence of *elementary steps* that leads to product formation is the *reaction mechanism*.

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

\(\text{N}_2\text{O}_2\) is detected during the reaction!

Elementary step: \(\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}_2\)

+ Elementary step: \(\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2\)

Overall reaction: \(2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2\)
Multistep Mechanisms

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, rate-determining step.
Slow Initial Step

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

• The rate law for this reaction is found experimentally to be

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

• CO is necessary for this reaction to occur, but the rate of the reaction does not depend on its concentration.

• This suggests the reaction occurs in two steps.
Slow Initial Step

- A proposed mechanism for this reaction is:
  
  **Step 1:** \( \text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO} \) (slow)
  
  **Step 2:** \( \text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2 \) (fast)
  
- The \( \text{NO}_3 \) intermediate is consumed in the second step.
  
- As \( \text{CO} \) is not involved in the slow, rate-determining step, it does not appear in the rate law.
Fast Initial Step

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

• The rate law for this reaction is found to be

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

• Because termolecular processes are rare, this rate law suggests a two-step mechanism.
Fast Initial Step

• A proposed mechanism is

Step 1: \( \text{NO} + \text{Br}_2 \longrightarrow \text{NOBr}_2 \) (fast)
Step 2: \( \text{NOBr}_2 + \text{NO} \longrightarrow 2 \text{NOBr} \) (slow)

Step 1 includes the forward and reverse reactions.
Fast Initial Step

- The rate of the overall reaction depends upon the rate of the slow step.
- The rate law for that step would be

\[ \text{Rate} = k_2 [\text{NOBr}_2] [\text{NO}] \]

- But how can we find [NOBr\(_2\)]?
Fast Initial Step

• NOBr₂ can react two ways:
  ➢ With NO to form NOBr
  ➢ By decomposition to reform NO and Br₂

• The reactants and products of the first step are in equilibrium with each other.

• Therefore,

  \[ \text{Rate}_f = \text{Rate}_r \]
Fast Initial Step

- Because Rate$_f$ = Rate$_r$,

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

- Solving for [NOBr$_2$] gives us

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

Substituting this expression for \([\text{NOBr}_2]\) in the rate law for the rate-determining step gives

\[
\text{Rate} = \frac{k_2k_1}{k_{-1}} \text{[NO]} \text{[Br}_2\text{]} \text{[NO]}
\]

\[
= k \text{[NO]}^2 \text{[Br}_2\text{]}
\]
Catalysts

- Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.
- Catalysts change the mechanism by which the process occurs.
Catalysts

One way a catalyst can speed up a reaction is by holding the reactants together and helping bonds to break.
Catalytic Converters

CO + Unburned Hydrocarbons + O\textsubscript{2} \rightarrow CO\textsubscript{2} + H\textsubscript{2}O

2NO + 2NO\textsubscript{2} \rightarrow 2N\textsubscript{2} + 3O\textsubscript{2}
Enzyme Catalysis

Substrate + Enzyme $\rightarrow$ Enzyme-substrate complex $\rightarrow$ Products + Enzyme