Chemical Kinetics

Lecture notes edited by John Reif from PPT lectures by:

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Dan Reid, Champaign CHS

Slides revised by Xin Song for Spring 2020 Term
What are Chemical Kinetics?
Chemical Kinetics

**Kinetics** – how fast does a reaction proceed?

**Thermodynamics** – does a reaction take place?

**Reaction speed**: measured by the change in concentration with time.

**Important factors which affect rates of reactions:**
- reactant concentration
- temperature
- action of catalysts
- surface area
- pressure of gaseous reactants or products
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).

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<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 calculate 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 temperature.</td>
</tr>
<tr>
<td><strong>Mechanisms</strong></td>
<td>Link between rate and molecular scale processes.</td>
</tr>
</tbody>
</table>

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Reaction Rates
Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time $t$.

$$[A] = \text{concentration of reactant A}$$
Reaction Rate

• For the reaction $A \rightarrow B$ there are two ways of measuring rate:

  (1) the speed at which the reactants disappear
  
  (2) the speed at which the products appear

• Reversible reactions: as products accumulates, they can begin to turn back into reactants.

• Early on the rate will depend on only the amount of reactants present. We want to measure the reactants as soon as they are mixed.

• A general way of measuring the rate of the reaction is in terms of change in concentration per unit time…

  Instantaneous rate $= \Delta[A]/\Delta t$ limits to $d[A]/dt$

Most Common Units… Rate $= \text{M/s}$

Where Molarity ($\text{M}$) $= \text{moles/Liter}$
**Chemical Kinetics**

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

\[
\text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \Delta[A] = \text{change in concentration of } A \text{ over time period } \Delta t
\]

\[
\text{rate} = \frac{\Delta[B]}{\Delta t} \quad \Delta[B] = \text{change in concentration of } B \text{ over time period } \Delta t
\]

Because $[A]$ decreases with time, $\Delta[A]$ is negative.
Reaction Rates and Stoichiometry

• To generalize, for the reaction

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

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

Reactants (decrease) \hspace{2cm} Products (increase)

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Here’s another way of looking at reaction rates…

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

Notice that for every 1 mole of \text{O}_2 that appears, 4 x as many moles of \text{NO}_2 will also appear. In the meantime, twice as many moles of \text{N}_2\text{O}_5 will be disappearing as moles of \text{O}_2 forming.

However, the same reaction cannot have 3 different rates…

In stead, we write the rate of the reaction as follows:

\[
\text{Reaction Rate} = -\frac{1}{2} \frac{\Delta [\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{4} \frac{\Delta [\text{NO}_2]}{\Delta t} = \frac{\Delta [\text{O}_2]}{\Delta t}
\]

(i.e., rate of change in concentration divided by respective stoichiometric coefficient)
Br$_2$ (aq) + HCOOH (aq) $\rightarrow$ 2Br$^-$ (aq) + 2H$^+$ (aq) + CO$_2$ (g)

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[Br$_2$] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0120</td>
</tr>
<tr>
<td>50.0</td>
<td>0.0101</td>
</tr>
<tr>
<td>100.0</td>
<td>0.00846</td>
</tr>
<tr>
<td>150.0</td>
<td>0.00710</td>
</tr>
<tr>
<td>200.0</td>
<td>0.00596</td>
</tr>
<tr>
<td>250.0</td>
<td>0.00500</td>
</tr>
<tr>
<td>300.0</td>
<td>0.00420</td>
</tr>
<tr>
<td>350.0</td>
<td>0.00353</td>
</tr>
<tr>
<td>400.0</td>
<td>0.00296</td>
</tr>
</tbody>
</table>

average rate = $-\frac{\Delta [Br_2]}{\Delta t} = -\frac{[Br_2]_{\text{final}} - [Br_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$

instantaneous rate = rate for specific instance in time

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rate \propto [\text{Br}_2]

\text{rate} = k [\text{Br}_2]

k = \frac{\text{rate}}{[\text{Br}_2]} = \text{rate constant}

= 3.50 \times 10^{-3} \text{ s}^{-1}
Factors Affecting Reaction Rate

Constants
Factors that Affect the Reaction Rate Constant

1. **Temperature:** At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy
   - **Collision Theory:** When two chemicals react, their molecules have to collide with each other (in a particular orientation) with sufficient energy for the reaction to take place.
   - **Kinetic Theory:** Increasing temperature means the molecules move faster.

2. **Concentrations of reactants**
   - As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.

3. **Catalysts**
   - Speed up reactions by lowering *activation energy*

4. **Surface area of a solid reactant**
   - More area for reactants to be in contact

5. **Pressure of gaseous reactants or products**
   - Increased number of collisions
Reaction Rate Examples
Reaction Rates

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

| Time, \( t(s) \) | \([\text{C}_4\text{H}_9\text{Cl}]] \text{ M} \)
<table>
<thead>
<tr>
<th></th>
<th></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, \( t \).
Reaction Rates

\[ \text{Average Rate, M/s} \]

<table>
<thead>
<tr>
<th>Time, ( t(s) )</th>
<th>( [C_4H_9Cl] (M) )</th>
<th>( \Delta [C_4H_9Cl] )</th>
<th>( \frac{\Delta [C_4H_9Cl]}{\Delta t} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50.0</td>
<td>0.0905</td>
<td></td>
<td>1.9 \times 10^{-4}</td>
</tr>
<tr>
<td>100.0</td>
<td>0.0820</td>
<td></td>
<td>1.7 \times 10^{-4}</td>
</tr>
<tr>
<td>150.0</td>
<td>0.0741</td>
<td></td>
<td>1.6 \times 10^{-4}</td>
</tr>
<tr>
<td>200.0</td>
<td>0.0671</td>
<td></td>
<td>1.4 \times 10^{-4}</td>
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<tr>
<td>300.0</td>
<td>0.0549</td>
<td></td>
<td>1.22 \times 10^{-4}</td>
</tr>
<tr>
<td>400.0</td>
<td>0.0448</td>
<td></td>
<td>1.01 \times 10^{-4}</td>
</tr>
<tr>
<td>500.0</td>
<td>0.0368</td>
<td></td>
<td>0.80 \times 10^{-4}</td>
</tr>
<tr>
<td>800.0</td>
<td>0.0200</td>
<td></td>
<td>0.560 \times 10^{-4}</td>
</tr>
<tr>
<td>10,000</td>
<td>0</td>
<td></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:

\[
\text{average rate} = \frac{\Delta [C_4H_9]}{\Delta t} = \frac{0.1000 - 0.0905 \text{ M}}{50.0 - 0.0 \text{ s}}
\]
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>
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<td></td>
</tr>
<tr>
<td>10,000</td>
<td>0</td>
<td></td>
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</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.

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Reaction Rates

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

- 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.

\[ \frac{\Delta [A]}{\Delta t} \Rightarrow \frac{d[A]}{dt} \]

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Reaction Rates

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

- The reaction slows down with time because the concentration of the reactants decreases.

\[ \frac{\Delta [A]}{\Delta t} \Rightarrow \frac{d[A]}{dt} \]

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Reaction Rates and Stoichiometry

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

- In this reaction, the ratio of \(\text{C}_4\text{H}_9\text{Cl}\) to \(\text{C}_4\text{H}_9\text{OH}\) is 1:1.
- Thus, the rate of disappearance of \(\text{C}_4\text{H}_9\text{Cl}\) is the same as the rate of appearance of \(\text{C}_4\text{H}_9\text{OH}\).

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

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Reaction Rate Laws
Concentration and Rate

Each reaction has its own equation that expresses its rate as a function of the concentrations of the involved species (e.g., reactants, products, catalysts).

This is called its Rate Law
Rate Law

• In general, rates of reactions increase as concentrations increase since there are more collisions occurring between reactants.

• The overall concentration dependence of reaction rate is given in a rate law or rate expression.

• For reactions follow simple rate laws:

\[ v = k [A]^m [B]^n \ldots \]

- [A], [B]: reactant concentrations
- The exponents \( m \) and \( n \): reaction order (w.r.t. specific reactant)
- The constant \( k \): rate constant
- The overall reaction order is the sum of the reaction orders:

\[ m + n \]
Rate Laws

• Rate laws, rate constants, and orders are determined experimentally.

• The order of a reactant is NOT generally related to its stoichiometric coefficient in a balanced chemical equation.

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

\[ \nu = k [\text{F}_2][\text{ClO}_2]^1 \]
Simple and complex rate laws

Reactions with simple rate laws:

\[ \text{H}_2 + \text{I}_2 \rightarrow 2\text{HI} \quad \nu = k \left[ \text{H}_2 \right] \left[ \text{I}_2 \right]. \]

\[ 3\text{ClO}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^- \quad \nu = k \left[ \text{ClO}^- \right]^2 \]

Reactions with complex rate laws*:

\[ \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} \quad \nu = \frac{[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k'[\text{HBr}]/[\text{Br}_2]} \]

* imply multi-step reactions (sequence of elementary steps)

\[ \text{Br}_2 \rightarrow \text{Br} + \text{Br} \]
\[ \text{Br} + \text{H}_2 \rightarrow \text{H} + \text{HBr} \]
\[ \text{H} + \text{Br}_2 \rightarrow \text{Br} + \text{HBr} \]
\[ \text{Br} + \text{Br} \rightarrow \text{Br}_2 \]

however, the overall rate cannot involve intermediate species

Reaction Kinetics (Vallance)
Always follow simple rate laws

Unimolecular decomposition

\[ \text{A} \rightarrow \text{B} \quad \nu = k [\text{A}] \]

Bimolecular reaction

\[ \text{A} + \text{B} \rightarrow \text{P} \quad \nu = k [\text{A}][\text{B}] \]
\[ \text{A} + \text{A} \rightarrow \text{P} \quad \nu = k [\text{A}][\text{A}] = k [\text{A}]^2 \]

Reactant **order** reflects **molecularity** (# of molecules involved in reaction)

More on this later…

---

Reaction Kinetics (Vallance)
Examples of Reaction Rate Laws
Rate Law Example

• Consider the following reaction:
  \[ \text{NH}_4^+ (aq) + \text{NO}_2^- (aq) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l) \]

• Let’s say that the following observations from several experiments were made...
  – as [\text{NH}_4^+] doubles the rate doubles with [\text{NO}_2^-] constant.
  – as [\text{NO}_2^-] doubles the rate doubles with [\text{NH}_4^+] constant.

• The rate of this reaction would be expressed as…
  \[ \text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-] \]

• The reaction is said to be “first order” with respect to [\text{NH}_4^+] and “first order” with respect to [\text{NO}_2^-].

• But the overall order of the reaction is said to be “second order.”

• Reaction rates come from experiment data, not stoichiometry!
Example Reaction: Concentration and Rate

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial NH$_4^+$ Concentration (M)</th>
<th>Initial 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>

\[
NH_4^+(aq) + NO_2^- \rightarrow N_2(g) + 2H_2O(l)
\]

Compare Experiments 1 and 2: when [NH$_4^+$] doubles, the initial rate doubles.

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**Concentration and Rate**

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<tr>
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</table>

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

Likewise, compare Experiments 5 and 6: when [NO$_2^-$] doubles, the initial rate doubles.

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Concentration and Rate

\[ \text{rate} \propto [NH_4^+] \]
\[ \text{rate} \propto [NO_2^-] \]
\[ \text{rate} \propto [NH_4^+] [NO_2^-] \]
\[ \text{rate} = k \ [NH_4^+] [NO_2^-] \]

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

\[ NH_4^+ (aq) + NO_2^- \rightarrow N_2(g) + 2H_2O(l) \]
Rate Laws

- 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*.

\[
\text{rate} = k \left[ \text{NH}_4^+ \right]^1 \left[ \text{NO}_2^- \right]^1
\]

“Constant” is relative here:
k is unique for each reaction
k changes with temperature

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# Integrated Rate Laws

**Goal:** express concentration as a function of time  
**Why:** experimental data is typically in concentration vs. time  
**How:** integrate the expression of rate law

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Order</th>
<th>Differential form</th>
<th>Integrated form</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A \rightarrow P$</td>
<td>zeroth</td>
<td>$\frac{d[A]}{dt} = -k$</td>
<td>$[A] = [A]_0 - kt$</td>
</tr>
<tr>
<td>$A \rightarrow P$</td>
<td>first</td>
<td>$\frac{d[A]}{dt} = -k [A]$</td>
<td>$\ln[A] = \ln[A]_0 - kt$</td>
</tr>
<tr>
<td>$A + A \rightarrow P$</td>
<td>second</td>
<td>$\frac{1d[A]}{2 dt} = -k [A]^2$</td>
<td>$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$</td>
</tr>
<tr>
<td>$A + B \rightarrow P$</td>
<td>second</td>
<td>$\frac{d[A]}{dt} = -k [A][B]$</td>
<td>$kt = \frac{1}{[B]_0-[A]_0} \ln\frac{[B]_0[A]}{[A]_0[B]}$</td>
</tr>
</tbody>
</table>

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**Reaction Kinetics (Vallance)**
Simple Example Reactions
Example chemical reaction that models degradation of molecule A

$$\gamma$$

$$A \rightarrow \Phi$$

$$\frac{dA}{dt} = -\gamma [A]$$

Rate of change of A

Degradation constant

Reactant A

time
Example chemical reaction that models generation (from D) and degradation of molecule A

\[
\frac{dA}{dt} = k[D] - \gamma[A]
\]

- **Rate of change of A**
- **Production constant**
- **Degradation constant**
Example chemical reaction that models generation (from $A$ and $B$) of molecule $C$

\[
A + B \rightarrow C
\]

\[
\frac{dA}{dt} = -k[A][B]
\]
Example chemical reaction that models generation (from $n$ distinct A and $m$ distinct B) of molecule C

$$nA + mB \rightarrow C$$

$$\frac{1}{n} \frac{d[A]}{dt} = -k[A]^n[B]^m$$
Order of Reactions
Order of Reactions

- A reaction is **zero order** in a reactant if the change in concentration of that reactant produces **no effect**.

- A reaction is **1st order** if **doubling** the concentration causes the rate to **double**.

- A reaction is **2nd order** if **doubling** the concentration causes a **quadruple** increase in rate.
  - **3rd order**…doubling concentration leads to $2^3$ (or 8 times) the rate.
  - extremely rare.

Dan Reid
Champaign CHS
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Order</th>
<th>Differential form</th>
<th>Integrated form</th>
</tr>
</thead>
<tbody>
<tr>
<td>A → P</td>
<td>zeroth</td>
<td>( \frac{d[A]}{dt} = -k )</td>
<td>( [A] = [A]_0 - kt )</td>
</tr>
<tr>
<td>A → P</td>
<td>first</td>
<td>( \frac{d[A]}{dt} = -k [A] )</td>
<td>( \ln[A] = \ln[A]_0 - kt )</td>
</tr>
<tr>
<td>A + A → P</td>
<td>second</td>
<td>( \frac{1}{2} \frac{d[A]}{dt} = -k [A]^2 )</td>
<td>( \frac{1}{[A]} = \frac{1}{[A]_0} + 2kt )</td>
</tr>
<tr>
<td>A + B → P</td>
<td>second</td>
<td>( \frac{d[A]}{dt} = -k [A][B] )</td>
<td>( kt = \frac{1}{[B]_0-[A]_0} \ln\frac{[B]_0[A]}{[A]_0[B]} )</td>
</tr>
</tbody>
</table>
Zero-Order Processes

A → P  

Zeroth order  

\[ \frac{d[A]}{dt} = -k \]

reaction rate = \[ - \frac{\Delta[A]_t}{\Delta t} = k \text{ (constant)} \]

So… \[ [A]_t = -kt + [A]_0 \]

• This equation has the general form for a straight line, \( y = mx + b \), so a plot of \([A]_t\) vs. \( t \) is a straight line with slope \((-k)\) and intercept \([A]_0\).
First-Order Processes

For 1st order reactions: \( \ln[A]_t = -kt + \ln[A]_0 \)

where \([A]_t\) = concentration of \([A]\) after some time, \(t\)
\(k\) = reaction rate constant in units of \(s^{-1}\)
\(t\) = time in seconds
\([A]_0\) = initial concentration of \(A\)

• This equation has the general form for a straight line, \(y=mx+b\), so a plot of \(\ln[A]_t\) vs. \(t\) is a straight line with slope \((-k)\) and intercept \(\ln[A]_0\).
Example: First-Order Processes

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

\[
\text{CH}_3\text{NC} \quad \rightarrow \quad \text{CH}_3\text{CN}
\]

How do we know this is a first order reaction?
First-Order Processes

\[
\text{CH}_3\text{NC} \quad \rightarrow \quad \text{CH}_3\text{CN}
\]

This data was collected for this reaction at 198.9° C. Does rate = \( k[\text{CH}_3\text{NC}] \) for all time intervals?

John D. Bookstaver
St. Charles Community College
First-Order Processes

If a reaction is first-order:

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

If a reaction is first-order: a plot of \( \ln [A]_t \) versus \( t \) will yield a straight line with a slope of \(-k\).
First-Order Processes

When \( \ln[A] \) is plotted as a function of time, a straight line results.

- The process is first-order.
- \( k \) is the negative slope: \( 5.1 \times 10^{-5} \) s\(^{-1}\).

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

\[
\ln [A]_t = -kt + \ln [A]_0
\]
Second-Order Processes

For 2\textsuperscript{nd} order reactions: \[ \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \]

where \([A]_t\) = concentration of \([A]\) after some time, \(t\)
\(k\) = reaction rate constant in units of \(M^{-1}s^{-1}\)
\(t\) = time in seconds
\([A]_0\) = initial concentration of \(A\)

• This equation has the general form for a straight line, \(y=mx+b\), so a plot of \(\frac{1}{[A]_t}\) vs. \(t\) is a straight line with slope \((k)\) and intercept of \(\frac{1}{[A]_0}\).
Determining Reaction order

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 these data:

<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>

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St. Charles Community College
Determining Reaction order

Graphing $\ln [\text{NO}_2]$ versus $t$ 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>$[\text{NO}_2], M$</th>
<th>$\ln [\text{NO}_2]$</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>

$\ln [A]_t = -kt + \ln [A]_0$
Second-Order Processes

A graph of $1/[\text{NO}_2]$ vs. $t$ gives this plot.

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

- This is a straight line. Therefore, the process is second-order in $[\text{NO}_2]$. 

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>$[\text{NO}_2]$, M</th>
<th>$1/[\text{NO}_2]$</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>

John D. Bookstaver
St. Charles Community College
Half Life
Half-Life

- Half-life is the time taken for the concentration of a reactant to drop to half its original value.
- Substitute into integrated rate laws: $t_{1/2}$ is the time taken for $[A]$ to reach $\frac{1}{2}[A]_0$

Zeroth order reaction: $t_{1/2} = \frac{[A]_0}{2k}$

First order reaction: $t_{1/2} = \frac{\ln2}{k}$

Second order reaction: $t_{1/2} = \frac{1}{k[A]_0}$

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

Dan Reid
Champaign CHS

Reaction Kinetics (Vallance)
For a first-order process, set $[A]_t = 0.5 [A]_0$ in the integrated rate equation:

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

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

$$\ln(0.5) = -kt^{\frac{1}{2}}$$

$$\ln(2) = 0.693 = +kt^{\frac{1}{2}}$$

$$\frac{0.693}{k} = t^{\frac{1}{2}}$$
What is the half-life of \( \text{N}_2\text{O}_5 \) if it decomposes with a rate constant of \( 5.7 \times 10^{-4} \text{ s}^{-1} \)?

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

How do you know decomposition is first order?

hint: units of \( k \ (\text{s}^{-1}) \)
A product

First-order reaction

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

# of half-lives

<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>

NOTE: For a first-order process, the half-life does not depend on \([A]_0\).
Half-Life - 2nd order

For a second-order process, set \( [A]_t = 0.5 \, [A]_0 \) in 2nd order equation:

\[
\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt
\]

\[
\frac{1}{0.5 \, [A]_0} = kt^{\frac{1}{2}} + \frac{1}{[A]_0}
\]

\[
\frac{2}{[A]_0} = kt^{\frac{1}{2}} + \frac{1}{[A]_0}
\]

\[
\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt^{\frac{1}{2}}
\]

\[
\frac{1}{k \, [A]_0} = t^{\frac{1}{2}}
\]

---

John D. Bookstaver  
St. Charles Community College
Equations of Reactions of Various Orders
# Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

<table>
<thead>
<tr>
<th>Order</th>
<th>Rate Law</th>
<th>Concentration-Time Equation</th>
<th>Half-Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>rate = $k$</td>
<td>$[A] - [A]_0 = -kt$</td>
<td>$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$</td>
</tr>
<tr>
<td>1</td>
<td>rate = $k [A]$</td>
<td>$\ln[A] - \ln[A]_0 = -kt$</td>
<td>$t_{\frac{1}{2}} = \frac{\ln 2}{k}$</td>
</tr>
<tr>
<td>2</td>
<td>rate = $k [A]^2$</td>
<td>$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$</td>
<td>$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$</td>
</tr>
</tbody>
</table>

Chung (Peter) Chieh
University of Waterloo
## Summary of Kinetics

<table>
<thead>
<tr>
<th></th>
<th>First order</th>
<th>Second order (1 reactant)</th>
<th>General Second order</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rate Laws</strong></td>
<td>$rate = -k[A]$</td>
<td>$rate = -k[A]^2$</td>
<td>$rate = -k[A][B]$</td>
</tr>
<tr>
<td><strong>Integrated Rate Laws</strong></td>
<td>$ln\left[\frac{[A]_t}{[A]_0}\right] = -kt$</td>
<td>$\frac{1}{[A]_0} = kt + \frac{1}{[A]_0}$</td>
<td>complicated</td>
</tr>
<tr>
<td><strong>Half-life</strong></td>
<td>$\frac{0.693}{k} = t_{\frac{1}{2}}$</td>
<td>$\frac{1}{k[A]<em>0} = t</em>{\frac{1}{2}}$</td>
<td>complicated</td>
</tr>
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John D. Bookstaver
St. Charles Community College
# Summary of Kinetics

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<td>Integrated Rate Laws</td>
<td>$ln \frac{[A]_t}{[A]_0} = -kt$</td>
<td>$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$</td>
<td>complicated</td>
</tr>
</tbody>
</table>

| Half-life | $\frac{0.693}{k} = t \frac{1}{2}$ | $\frac{1}{k [A]_0} = t \frac{1}{2}$ | complicated |

| $k(T)$ | $k = Ae^{-\frac{E_a}{RT}}$ | $ln(k) = -\frac{E_a}{RT} + lnA$ |

---

John D. Bookstaver  
St. Charles Community College
Reaction Mechanisms
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.
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.

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

\[
\text{N}_2\text{O}_2 \text{ is detected during the reaction!}
\]

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: \[
2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2
\]
Writing plausible reaction mechanisms:

- The **sum** of the elementary steps must give the overall **balanced** equation for the reaction.
- The rate-determining step should predict the **same** rate law that is determined experimentally.

The *rate-determining step* is the **slowest** step in the sequence of steps leading to product formation.
Reaction Mechanisms

- Up until now, we have only been concerned with the reactants and products. Now we will examine what path the reactants took in order to become the products.
- The reaction mechanism gives the path of the reaction.
- Mechanisms provide a very detailed picture of which bonds are broken and formed during the course of a reaction.

Elementary Steps & Molecularity

- **Elementary step**: any process that occurs in a single step.
- **Molecularity**: number of molecules present in an elementary step.
  - **Unimolecular**: one molecule in the elementary step,
  - **Bimolecular**: two molecules in the elementary step, and
  - **Termolecular**: three molecules in the elementary step.

(It is uncommon to see termolecular processes...statistically improbable for an effective collision to occur.)
Rate Laws of Elementary Steps

• Since this process occurs in one single step, the stoichiometry can be used to determine the rate law!

• **Law of Mass Action:** The rate of a simple (one step) reaction is directly proportional to the concentration of the reacting substances.

<table>
<thead>
<tr>
<th>Molecularity</th>
<th>Elementary Step</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unimolecular</td>
<td>A → products</td>
<td>Rate = k[A]</td>
</tr>
<tr>
<td>Bimolecular</td>
<td>A + A → products</td>
<td>Rate = k[A]^2</td>
</tr>
<tr>
<td>Bimolecular</td>
<td>A + B → products</td>
<td>Rate = k[A][B]</td>
</tr>
<tr>
<td>Termolecular</td>
<td>A + A + A → products</td>
<td>Rate = k[A]^3</td>
</tr>
<tr>
<td>Termolecular</td>
<td>A + A + B → products</td>
<td>Rate = k[A]^2[B]</td>
</tr>
<tr>
<td>Termolecular</td>
<td>A + B + C → products</td>
<td>Rate = k[A][B][C]</td>
</tr>
</tbody>
</table>

• Notice that the coefficients become the exponents.
Reaction Mechanisms

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

- The **molecularity** of a process tells how many molecules are involved in the process.

- The rate law for an elementary step is written directly from that step.
Intermediates are species that appear in a reaction mechanism but not in the overall balanced equation.

An intermediate is always formed in an early elementary step and consumed in a later elementary step.

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*.

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Example of Slow & Fast Reaction Mechanisms
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.

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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 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 (experimentally) to be

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

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

• A proposed mechanism is

\[
\text{Step 1: } NO + Br_2 \rightleftharpoons NOBr_2 \ (\text{fast})
\]

\[
\text{Step 2: } NOBr_2 + NO \rightarrow 2NOBr \ (\text{slow})
\]

Step 1 is an \textit{equilibrium}: it includes the forward \textit{and} reverse reactions.
Fast Initial Step

\[ \text{Step 1: } NO + Br_2 \rightleftharpoons NOBr_2 \text{ (fast)} \]
\[ \text{Step 2: } NOBr_2 + NO \rightarrow 2NOBr \text{ (slow)} \]

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

\[ \text{rate}_2 = k_2 \left[ NOBr_2 \right] \left[ NO \right] \]

But we have a problem... This rate law depends on the concentration of an intermediate species.

Intermediates are usually unstable and have low/unknown concentrations. We need to find a way to remove this term from our rate law.

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St. Charles Community College
Fast Initial Step

\[ \text{Step 1: } NO + Br_2 \rightleftharpoons NOBr_2 \ (\text{fast}) \]
\[ \text{Step 2: } NOBr_2 + NO \rightarrow 2NOBr \ (\text{slow}) \]

- NOBr\(_2\) can react two ways:
  - With NO to form NOBr (however, \text{slow})
  - By decomposition to reform NO and Br\(_2\)

- The reactants and products of the \textbf{first step} are in equilibrium with each other.

- Therefore,

\[ \text{Rate}_f = \text{Rate}_r \]

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St. Charles Community College
Fast Initial Step

Step 1: \( NO + Br_2 \xrightleftharpoons[k_2]{k_1} NOBr_2 \) (fast)
Step 2: \( NOBr_2 + NO \xrightarrow{k_3} 2NOBr \) (slow)

Assume \( k_2 \gg k_3 \)

Because \( \text{Rate}_f = \text{Rate}_r \),

\[
 k_1 [NO] [Br_2] = k_{-1} [NOBr_2]
\]

Solving for \( [NOBr_2] \) gives us

\[
 \frac{k_1}{k_{-1}} [NO] [Br_2] = [NOBr_2]
\]
Fast Initial Step

Step 1: \( NO + Br_2 \rightleftharpoons NOBr_2 \) (fast)

Step 2: \( NOBr_2 + NO \rightarrow 2NOBr \) (slow)

Substituting this expression for \([NOBr_2]\) in the rate law for the rate-determining step gives

\[
rate = \frac{k_2k_1}{k_{-1}} [NO] [Br_2] [NO]
\]

\[
= \frac{k_2k_1}{k_{-1}} [NO]^2 [Br_2]
\]
11. Pre-equilibria

A situation that is only slightly more complicated than the sequential reaction scheme described above is

\[ A + B \xrightleftharpoons[{-k_1}]{k_1} C \xrightarrow{k_2} D \]

The rate equations for this reaction are:

\[
\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k_1 [A][B] + k_1 [C]
\]

\[
\frac{d[C]}{dt} = k_1 [A][B] - k_2 [C]
\]

\[
\frac{d[D]}{dt} = k_2 [C]
\]

These cannot be solved analytically, and in general would have to be integrated numerically to obtain an accurate solution. However, the situation simplifies considerably if \( k_1 \gg k_2 \). In this case, an equilibrium is reached between the reactants A and B and the intermediate C, and the equilibrium is only perturbed very slightly by C ‘leaking away’ very slowly to form the product D.

If we assume that we can neglect this perturbation of the equilibrium, then once equilibrium is reached, the rates of the forward and reverse reactions must be equal. i.e.

\[ k_1 [A][B] = k_1 [C] \]

Rearranging this equation, we find

\[ \frac{k_1}{k_1} = \frac{[C]}{[A][B]} = K \]
Rate Laws for Multistep Reactions
Rate Laws for Multistep Mechanisms

• Most reactions proceed through more than one step:
  \[ \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \]

• A proposed mechanism is as follows…
  \[
  \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g) \quad \text{(slow step)} \\
  \text{NO}_3(g) + \text{CO}(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g) \quad \text{(fast step)}
  \]

• Notice that if we add the above steps, we get the overall reaction:
  \[ \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \]

• If a reaction proceeds via several elementary steps, then the elementary steps must add to give the balanced chemical equation.

• **Intermediate**: a species which appears in an elementary step which is not a reactant or product. They are formed in one elementary step and consumed in another…Our Example: NO\textsubscript{3}(g)
Rate Laws for Multistep Mechanisms

• Often one step is much slower than the others. The slow step limits the overall reaction rate.

• This is called the rate-determining step of the reaction.

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

• In our previous example, the theoretical rate law is therefore…

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

• The experimentally determined rate law is…

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

• This supports, (but does not prove), our mechanism.
Activation Energy
Activation Energy

• There is a minimum amount of energy required for a 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.
Activation Energy

• Molecules must possess a minimum amount of energy to react. Why?
  – In order to form products, bonds must be broken in the reactants. **Bond breakage** requires energy.
  – Molecules moving too slowly, with too little kinetic energy, don’t react when they collide.

• **Activation energy,** $E_a$, is the minimum energy required to initiate a chemical reaction.
  – $E_a$ will vary with the reaction.

Next we will look at an example of $E_a$. 
Activation Energy

• Consider the rearrangement of methyl isonitrile:

\[
\text{H}_3\text{C}\text{–N≡C:} \rightarrow \begin{array}{c}
\text{H}_3\text{C}\text{–N} \\
\text{H}_3\text{C}\text{–C} \\
\end{array} \rightarrow \text{H}_3\text{C}\text{–C≡N:}
\]

– In H\(_3\)C-N≡C, the C-N≡C bond bends until the C≡N bond breaks and the N≡C portion is perpendicular to the H\(_3\)C portion. This structure is called the **activated complex** or **transition state**.

– The energy required for the above twist and break is the **activation energy**, \(E_a\).

– Once the C-N bond is broken, the N≡C portion can continue to rotate forming a C-C≡N bond.

* Here”s what the reaction looks like in terms of a graph of the energies that are involved in the process…
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Activation Energy

- The **change in energy** $\Delta E$ for the reaction is the difference in energy between $\text{CH}_3\text{NC}$ (reactant) and $\text{CH}_3\text{CN}$ (product).
- The **activation energy** $E_a$ is the difference in energy between reactants, $\text{CH}_3\text{NC}$, and the transition state.
- The rate depends on $E_a$. If the “hill” is taller, the reaction rate is slower. If the “hill” is shorter the rate is faster.
- Notice that if a forward reaction is exothermic… ($\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$), then the reverse reaction is endothermic… ($\text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{NC}$).
- The methyl isonitrile molecule needs to gain enough energy to overcome the activation energy barrier.
- From kinetic molecular theory, we know that as temperature increases, the total kinetic energy increases and the number of molecules with energy greater than $E_a$ increases.
- So as long as the temperature is high enough, the reaction can make it “over the hill” and proceed.
The activation energy ($E_a$) is the minimum amount of energy required to initiate a chemical reaction.
Energy Diagrams

(a) Activation energy (Ea) for the forward reaction
50 kJ/mol
(b) Activation energy (Ea) for the reverse reaction
150 kJ/mol
(c) Delta H
-100 kJ/mol

Exothermic

Endothermic

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Reaction Coordinate Diagrams
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.

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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.

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Arrhenius Equation
Arrhenius Equation

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

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

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

Taking the natural logarithm of both sides, the equation becomes

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

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

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Temperature Dependence of the Rate Constant

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

(Arrhenius equation)

- \( k \) is the rate constant
- \( E_a \) is the activation energy (J/mol)
- \( R \) is the gas constant (8.314 J/K\( \cdot \)mol)
- \( T \) is the Kelvin temperature
- \( A \) is the frequency factor

\[ \ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A \]
Plot of Arrhenius Equation

\[ \text{slope} = -\frac{E_a}{R} \]
Maxwell–Boltzmann Distributions
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.

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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.

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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 temperature in Kelvin.

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Catalysts
A **catalyst** is a substance that increases the rate of a chemical reaction without itself being consumed.

\[ E_a \downarrow \quad k \uparrow \]

\[ \text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}} \]
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.

\[ \text{Catalyzed reaction: } 2 \text{H}_2\text{O}_2 + 2 \text{Br}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + 2 \text{H}_2\text{O} + \text{Br}_2 \]

\[ \text{Uncatalyzed reaction: } 2 \text{H}_2\text{O} + \text{O}_2 + 2 \text{Br}^- + 2 \text{H}^+ \rightarrow 2 \text{H}_2\text{O} + \text{O}_2 + 2 \text{Br}^- + 2 \text{H}^+ \]
Catalysts

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

There are two types of catalyst: **Heterogeneous** – one that is present in a different **phase** as the reacting molecules. **Homogeneous** – one that is present in the same phase as the reacting molecules.

Example: Hydrogen peroxide decomposes very slowly in the absence of a catalyst:

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

In the presence of bromide ions, the decomposition occurs rapidly in an acidic environment:

\[
\text{Br}^-\text{(aq)} + \text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Br}_2(\text{aq}) + 2\text{H}_2\text{O}(l)
\]

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

Br\(^-\) is a homogeneous catalyst because it is regenerated at the end of the reaction.

The net reaction is still...

\[
2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)
\]
Catalysts and Reaction Rates

How do catalysts increase reaction rates?

• In general, catalysts operate by lowering the overall activation energy, $E_a$, for a reaction. (It lowers the “hill”.)
• However, catalysts can operate by increasing the number of effective collisions.
• A catalyst usually provides a completely different mechanism for the reaction.
• In the preceding peroxide decomposition example, in the absence of a catalyst, $\text{H}_2\text{O}_2$ decomposes directly to water and oxygen.
• In the presence of $\text{Br}^-$, $\text{Br}_2(aq)$ is generated as an intermediate.
• When a catalyst adds an intermediate, the activation energies for both steps must be lower than the activation energy for the uncatalyzed reaction.

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Heterogeneous Catalysts

- Often we encounter a situation involving a solid catalyst in contact with gaseous reactants and gaseous products...
- Example: catalytic converters in cars.
  - Many industrial catalysts are heterogeneous.

**How do they do their job?**

- The first step is adsorption (the binding of reactant molecules to the catalyst surface).
- Adsorption occurs due to the high reactivity of atoms or ions on the surface of the solid.
- Molecules are adsorbed onto active sites on the catalyst surface.
- The number of active sites on a given amount of catalyst depends on several factors such as:
  - The nature of the catalyst.
  - How the catalyst was prepared.
  - How the catalyst was treated prior to use.
Heterogeneous Catalysts

Example: \[ \text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) \]

- In the presence of a metal catalyst (Ni, Pt or Pd) the reaction occurs quickly at room temperature.

Here are the steps…

- First, the ethylene and hydrogen molecules are adsorbed onto active sites on the metal surface.
- Second, the H–H bond breaks and the H atoms migrate about the metal surface and runs into a C\(_2\)H\(_4\) molecule on the surface.
- Third, when an H atom collides with a C\(_2\)H\(_4\) molecule on the surface, the C–C \(\pi\)-bond breaks and a C–H \(\sigma\)-bond forms.
- Lastly, When C\(_2\)H\(_6\) forms it desorbs from the surface.

- When ethylene and hydrogen are adsorbed onto a surface, less energy is required to break the bonds.
- The \(E_a\) for the reaction is lowered, thus the reaction rate increases.
Heterogeneous Catalysts

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Examples of Catalysts:
Enzymes
Enzymes

- Enzymes are catalysts in biological systems.

- The **substrate** fits into the **active site** of the enzyme much like a key fits into a lock.
Enzyme Catalysts

- **Enzymes** are biological catalysts. There may be as many as 30,000 enzymes in the human body. (e.g., Lactase)
- Most enzymes are **protein molecules** with large molecular masses (10,000 to $10^6$ amu).
- Enzymes have very **specific shapes**.
- Most enzymes catalyze very **specific reactions**.
- The substances that undergo reaction at the active site on enzymes are called **substrates**.
- A substrate locks into an enzyme and a fast reaction occurs. The products then move away from the enzyme.
Enzyme Catalysts

• Only substrates that fit into the enzyme lock can be involved in the reaction.

• If a molecule binds tightly to an enzyme so that another substrate cannot displace it, then the active site is blocked and the catalyst is inhibited (enzyme inhibitors).

• Many poisons act by binding to the active site blocking the binding of substrates. The binding can also lead to changes in the enzyme.

• Enzymes are extremely efficient catalysts.

• The number of individual catalytic events occurring at an active site per unit time is called the turnover number.

• Large turnover numbers correspond to very low $E_a$ values. For enzymes, turnover numbers are very large $\approx 10^3$ to $10^7$/sec
Other Examples of Catalysts
The experimental rate law for the reaction between NO$_2$ and CO to produce NO and CO$_2$ is rate = $k[\text{NO}_2]^2$. The reaction is believed to occur via two steps:

**Step 1:**  \( \text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_3 \)

**Step 2:**  \( \text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2 \)

What is the equation for the overall reaction?

\[
\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2
\]

What is the intermediate? Catalyst?

\( \text{NO}_3 \quad \text{NO}_2 \)

What can you say about the relative rates of steps 1 and 2?

rate = $k[\text{NO}_2]^2$ is the rate law for step 1 so step 1 must be slower than step 2
Write the rate law for this reaction. 

\[ \text{Rate} = k \ [\text{HBr}] \ [\text{O}_2] \]

List all intermediates in this reaction. 

HOOBr, HOBr

List all catalysts in this reaction. 

None
Another example:

Nitrogen gas cannot be used in the soil for plants or animals. Nitrogen compounds, NH$_3$, NO$_2^-$, and NO$_3^-$ are used in the soil. The conversion between N$_2$ and NH$_3$ is a process with a high activation energy (the N≡N triple bond needs to be broken). Nitrogenase, an enzyme in bacteria that lives in root nodules of legumes such as clover and alfalfa, catalyzes the reduction of nitrogen to ammonia. It lowers the E$_a$, and the reaction proceeds.
Ostwald Process

Ammonia

\[ 4\text{NH}_3 (g) + 5\text{O}_2 (g) \xrightarrow{\text{Pt catalyst}} 4\text{NO} (g) + 6\text{H}_2\text{O} (g) \]

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

\[ 2\text{NO}_2 (g) + \text{H}_2\text{O} (l) \rightarrow \text{HNO}_2 (aq) + \text{HNO}_3 (aq) \]

Pt-Rh catalysts used in Ostwald process

Nitric acid

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Catalytic Converters

CO + Unburned Hydrocarbons + O₂ → \text{catalytic converter} → CO₂ + H₂O

2NO + 2NO₂ → \text{catalytic converter} → 2N₂ + 3O₂