Chemical Kinetics

Lecture notes edited by John Reif from PPT lectures by:

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• Hana El-Samad, UCSB
• John D. Bookstaver, St. Charles Community College
• Dan Reid, Champaign CHS
What are Chemical Kinetics?
Chemical Kinetics

We will now study:

• Kinetics: the study of how fast chemical reactions occur.

(in contrast to Thermodynamics: which determines if a reaction take place)

Our goal: is to understand chemical reactions at the molecular level.

Speed of a reaction: is 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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• St. Charles Community College
# Outline: Kinetics

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</tr>
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St. Charles Community College
Reaction Rates
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

• Reactions are reversible, so as products accumulate 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.

• The most useful (and general) way of measuring the rate of the reaction is in terms of change in concentration per unit time...

\[
\text{Rate} = \frac{\Delta [A]}{\Delta t} \text{ limits to } \frac{D[A]}{Dt}
\]

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

(Remember…Molarity (M) = moles/Liter)
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).

\[
\text{rate} = -\frac{D[A]}{Dt} \\
\text{rate} = \frac{D[B]}{Dt}
\]

\(D[A] = \text{change in concentration of } A \text{ over time period } Dt\)

\(D[B] = \text{change in concentration of } B \text{ over time period }Dt\)

Because \([A]\) decreases with time, \(D[A]\) is negative.
Factors Affecting Reaction Rate

Constants
Factors that Affect 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 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**
   - Bread and Butter theory: more area for reactants to be in contact

5. **Pressure of gaseous reactants or products**
   - Increased number of collisions
Factors that Affect Reaction Rate Constant

Temperature

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

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Concentration Affects Reaction Rate Constant

- Here’s another way of looking at reaction rates...

\[ 2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g) \]

- Notice that for every 1 mole of \( O_2 \) that appears, 4 x as many moles of \( NO_2 \) will also appear. In the meantime, twice as many moles of \( N_2O_5 \) will be disappearing as moles of \( O_2 \) forming.

- Changes in concentrations of the reactants and/or products is **inversely proportional** to their stoichiometric proportions.

- This means that the rate of the reaction could be written like this...

\[
\text{Rate} = -\frac{1}{2} \frac{\Delta [N_2O_5]}{\Delta t} = \frac{1}{4} \frac{\Delta [NO_2]}{\Delta t} = \frac{\Delta [O_2]}{\Delta t}
\]

* (Notice the negative sign on the rate of \([N_2O_5]\) reminds us that it is disappearing.)

- In general, for a reaction that looks like this… \( aA + bB \rightarrow cC + dD \)

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

Each reaction has its own equation that gives its rate as a function of reactant concentrations.

this is called its **Rate Law**

To determine the rate law we measure the rate at different starting concentrations.
rate = - \frac{D[A]}{Dt}

rate = \frac{D[B]}{Dt}
**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.

\[
F_2 (g) + 2\text{ClO}_2 (g) \longrightarrow 2\text{FClO}_2 (g)
\]

rate = \( k \ [F_2][\text{ClO}_2]_1 \)
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.
- Here’s what a general rate law for a reaction will look like…

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

- [A] & [B] represent the reactants.
- The exponents \( m \) and \( n \) are called “reaction orders”.
- The proportionality constant \( k \) is called the rate constant.
- The overall reaction order is the sum of the reaction orders.
- The overall “order of reaction” is therefore…

\[ m + n + \ldots \]
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)  Products (increase)
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 \( = k [A]^x[B]^y \)

- reaction is \( x \text{th order} \) in A
- reaction is \( y \text{th order} \) in B
- reaction is \( (x + y) \text{th order overall} \)
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!

Dan Reid
Champaign CHS
Example Reaction Rate Law
Example Reaction: Concentration and Rate

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial $\text{NH}_4^+$ 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>

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

Compare Experiments 1 and 2:
when $[\text{NH}_4^+]$ doubles, the initial rate doubles.
Concentration and Rate

<table>
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<tr>
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<th>Initial $\text{NH}_4^+$ Concentration (M)</th>
<th>Initial $\text{NO}_2^-$ Concentration (M)</th>
<th>Observed Initial Rate (M/s)</th>
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<td>0.200</td>
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<td>0.0200</td>
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<td>0.0202</td>
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<tr>
<td>6</td>
<td>0.200</td>
<td>0.0404</td>
<td>$21.6 \times 10^{-7}$</td>
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<td>8</td>
<td>0.200</td>
<td>0.0808</td>
<td>$43.3 \times 10^{-7}$</td>
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\[
\text{NH}_4^+(aq) + \text{NO}_2^- \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)
\]

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

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Concentration and Rate

\[
\begin{align*}
\text{rate} & \propto [NH_4^+] \\
\text{rate} & \propto [NO_2^-] \\
\text{rate} & \propto [NH_4^+] [NO_2^-] \\
\text{rate} & = k [NH_4^+] [NO_2^-]
\end{align*}
\]

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

• A rate law shows the relationship between the reaction rate and the concentrations of reactants.
  – For gas-phase reactants use $P_A$ instead of $[A]$.

• The rate constant $k$ is a constant that has a specific value for each reaction.

• The value of $k$ is determined experimentally. For example

$$rate = k \left[ NH_4^+ \right] \left[ NO_2^- \right]$$

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

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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*.

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

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Integrated Reaction Rate Laws
Integrated Rate Laws

Consider a simple 1st order reaction: \[ A \rightarrow B \]

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

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

How much \( A \) is left after time \( t \)? Integrate:

\[ -d[A] = k [A] \, dt \]

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

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

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

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Integrated Rate Laws

The integrated form of first order rate law:

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

Can be rearranged to give:

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

\[ [A]_0 \] is the initial concentration of A \((t=0)\).
\[ [A]_t \] is the concentration of A at some time, \(t\), during the course of the reaction.
Integrated Rate Laws

Manipulating this equation produces...

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

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

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

...which is in the form

\[ y = mx + b \]
Example Reaction Rate Laws
\[
F_2 (g) + 2\text{ClO}_2 (g) \rightarrow 2\text{FClO}_2 (g)
\]

rate = \( k [F_2]^x[\text{ClO}_2]^y \)

Double [\( F_2 \)] with [\( \text{ClO}_2 \)] constant
Rate doubles
\( x = 1 \)

Quadruple [\( \text{ClO}_2 \)] with [\( F_2 \)] constant
Rate quadruples
\( y = 1 \)

Chung (Peter) Chieh
University of Waterloo
\[
\text{Br}_2 (aq) + \text{HCOOH} (aq) \rightarrow 2\text{Br}^- (aq) + 2\text{H}^+ (aq) + \text{CO}_2 (g)
\]

### Chemical Reaction

#### Table: Concentration of \( \text{Br}_2 \) over Time

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[\text{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>

#### Graphical Representation

- **Average Rate**: 
  \[ \text{average rate} = - \frac{D[\text{Br}_2]}{Dt} = \frac{[\text{Br}_2]_{\text{final}} - [\text{Br}_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} \]

- **Instantaneous Rate**: 
  \[ \text{instantaneous rate} = \text{rate for specific instance in time} \]

---

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rate a $[\text{Br}_2]$

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

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

= $3.50 \times 10^{-3}$ s$^{-1}$
Another Example of Reaction Kinetics
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}] \text{ 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, \( t \).
Reaction Rates

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

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

<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>
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<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>
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</table>

\[
\text{average rate} = \frac{\Delta [C_4H_9]}{\Delta t}
\]

\[
\text{average rate} = \frac{0.1000 - 0.0905}{50.0 - 0.0} \text{ M/s}
\]

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Reaction Rates

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

- 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.

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

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

- 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 Rate

- Here’s an example of a reaction...

\[ C_4H_9Cl_{(aq)} + H_2O_{(l)} \rightarrow C_4H_9OH_{(aq)} + HCl_{(aq)} \]

- We can plot \([C_4H_9Cl]\) versus time...

- The average rate of a reaction decreases with time.

- The rate at any instant in time (instantaneous rate) is the slope of the tangent to the curve.

- Instantaneous rate is different from average rate, so when we refer to the rate of a reaction, we will be assuming it’s the instantaneous rate unless otherwise told.
Reaction Rates and Stoichiometry

\[ \text{Rate} = \frac{-D[C_4H_9Cl]}{Dt} = \frac{D[C_4H_9OH]}{Dt} \]

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Simple Example Reactions
Simple Example Reaction Kinetics

Given some initial concentrations, what is output given some prescribed input?

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Chemical reactions are collisions of molecules

$A + B \rightarrow C$

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A → \Phi

Molecule A

Reactant A

time
Average rate of change in concentration during time $Dt = \frac{\Delta[A]}{\Delta t}$
Reactant A

Change in Concentration: \( \Delta A = A_2 - A_1 \)

Instantaneous rate of change in concentration during time \( dt \) =

\[ \frac{d[A]}{dt} \]
A \rightarrow \Phi

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

Rate of change of A
Concentration of A
Degradation constant
\[ D \rightarrow A \rightarrow \Phi \]

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

- Rate of change of A
- Concentration of D
- Concentration of A
- Production constant
- Degradation constant
\[ A + B \rightarrow C \]
\[ \frac{dA}{dt} = -k [A][B] \]
\[ nA + mB \rightarrow C \]
\[
\frac{d[A]}{dt} = -k[A]^n[B]^m
\]
\[
D \rightarrow A \rightarrow \Phi \\
A + B \rightarrow C \\
C \rightarrow A + B
\]

\[
\frac{d[A]}{dt} = k_1 [D] - \gamma [A]
\]
Reaching steady-state (equilibrium)

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

Steady-state: No more change in A

\[
\frac{d[A]}{dt} = 0 \quad \Rightarrow \quad k[D] - \gamma [A] = 0
\]

Production of A balances degradation

A is constant

\[
[A] = \frac{[K][D]}{\gamma}
\]
Example of Transcription
Reaction Kinetics
mRNA Translation

Proteins

mRNA

ribosomes

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UCSB
Modeling activator binding and production of mRNA

\[ A + DNA \rightleftharpoons A : DNA \quad \text{Fast} \]

\[ A : DNA \rightarrow^k_2 mRNA + A : DNA \quad \text{slow} \]
\[ A + DNA \Leftrightarrow A:DNA \quad \text{Fast} \]

\[
\frac{d [A:DNA]}{dt} = k_1 \cdot A \cdot DNA - k_2 \cdot [A:DNA] = 0
\]

\[
k_1 \cdot A \cdot DNA = k_2 \cdot [A:DNA] \quad \Rightarrow \quad [A:DNA] = \frac{k_1 \cdot A \cdot DNA}{k_2}
\]

**but**

\[
DNA_{total} = DNA + [A:DNA] = DNA + \frac{k_1 \cdot A \cdot DNA}{k_2} = (1 + \frac{k_1 \cdot A}{k_2})DNA
\]

\[
DNA = \frac{DNA_{total}}{1 + \frac{k_1 \cdot A}{k_2}}
\]

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UCSB
\[
DNA = \frac{DNA_{\text{total}}}{\left(1 + \frac{k_1 A}{k_2}\right)}
\]

\[
[A : DNA] = \frac{k_1 A \cdot DNA}{k_2}
\]

\[
[A : DNA] = \frac{\frac{k_1}{k_2} A}{1 + \left(\frac{k_1}{k_2}\right) A}
\]

\[
\frac{k_2}{k_1} = k_d
\]

Dissociation constant
Hill Function

\[
[A : DNA] = \frac{A}{k_d} \frac{DNA_{total}}{1 + \frac{A}{k_d}}
\]
\[ A : DNA \rightarrow mRNA + A : DNA \]

\[ \frac{dmRNA}{dt} = k_3.[A : DNA] - \gamma_1 mRNA \]

\[ [A : DNA] = \frac{A}{k_d} \frac{DNA_{total}}{1 + \frac{A}{k_d}} \]

\[ \frac{dmRNA}{dt} = k_3. \frac{A}{k_d} \frac{DNA_{total}}{1 + \frac{A}{k_d}} - \gamma_1 mRNA \]
Cooperativity

\[
\frac{dmRNA}{dt} = k_3 \cdot \frac{\left(\frac{A}{k_d}\right)^3 \cdot DNA_{total} - \gamma_1 mRNA}{1 + \left(\frac{A}{k_d}\right)^3}
\]

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Cooperativity

\[
\frac{dmRNA}{dt} = k_3 \cdot \frac{\left(\frac{A}{k_d}\right)^n}{1 + \left(\frac{A}{k_d}\right)^n} \cdot DNA_{total} - \gamma_1 mRNA
\]

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UCSB
\[
\frac{dmRNA}{dt} = k_3 \cdot \frac{1}{1 + \left(\frac{X}{k_d}\right)^n} \frac{DNA_{total}}{mRNA} - \gamma_1 mRNA
\]
\[ k_3 \cdot \frac{1}{1 + \left(\frac{X}{k_d}\right)^n} \text{DNA}_{\text{total}} \]
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.

• Note-- The rate constant, $k$, does not depend on concentration!

• Once we have determined the rate law and the rate constant, we can use them to calculate initial reaction rates under any set of initial concentrations. (See Practice Problems for examples.)
Zero’th Order Reactions
Zero-Order Reactions

rate = $-\frac{D[A]}{Dt}$

rate = $k[A]^0 = k$

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

$[A]_0$ is the concentration of A at any time $t$

$[A]_0$ is the concentration of A at time $t=0$

Half life for zero order

$t_{1/2} = t$ when $[A] = [A]_0/2$

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

Chung (Peter) Chieh
University of Waterloo
Change of Concentration with Time

For Zero order reactions:

\[
\text{Rate} = k[A]^0 = k
\]

Rate does not change with concentration.

So… \( [A]_t = -kt + [A]_0 \)

where \( [A]_t \) = concentration of \( [A] \) after some time, \( t \)
\( k \) = reaction rate constant in units of \( \text{M/s} \)
\( t \) = 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 \( [A]_t \) vs. \( t \) is a straight line with slope \((-k)\) and intercept \([A]_0\).
First Order Reactions
Change of Concentration with Time

• **Goal:** to convert the rate law into a convenient equation to give concentrations as a function of time...(the book has the derivation, and it involves calculus, so we will skip to the conclusion)...

For 1\textsuperscript{st} 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 \(\ln[A]_0\).

Dan Reid
Champaign CHS
First-Order Processes

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

\[ \text{CH}_3\text{NC} \xrightarrow{} \text{CH}_3\text{CN} \]

How do we know this is a first order rxn?

John D. Bookstaver
St. Charles Community College
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 \( \text{rate}=k[\text{CH}_3\text{NC}] \) for all time intervals?

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St. Charles Community College
First-Order Processes

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

If a reaction is first-order:

a plot of \( \ln [A]_t \) vs. \( t \) will yield a straight line with a slope of \(-k\).
First-Order Processes

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

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

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

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

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

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St. Charles Community College
Half-Life

For a first-order process, set $[A]_t = 0.5 [A]_0$ in integrated rate equation:

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

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

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

$$\frac{0.693}{k} = t^{\frac{1}{2}}$$

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

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St. Charles Community College
Half-Life- 2nd order

For a second-order process, set $[A]_t=0.5 [A]_0$ in 2nd order equation.

$$\frac{1}{0.5 [A]_0} = k t^{\frac{1}{2}} + \frac{1}{[A]_0}$$

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

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

$$\frac{1}{k [A]_0} = t^{\frac{1}{2}}$$
Half-Life

- **Half-life** is the time taken for the concentration of a reactant to drop to half its original value.
- For a first order process, half life, $t_{\frac{1}{2}}$ is the time taken for $[A]_0$ to reach $\frac{1}{2}[A]_0$...(see the book for the next equation’s derivation.)

\[ t_{\frac{1}{2}} = -\ln\left(\frac{1}{2}\right) = 0.693 \quad \text{where } k = \text{the rate constant} \]

- For a 2nd order reaction, half-life depends on the reactant concentrations… $t_{\frac{1}{2}} = 1/ k[A]_0$

- For Zero order reactions… $t_{\frac{1}{2}} = [A]_0 / 2k$

Dan Reid
Champaign CHS
First-Order Reactions

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

\[
t_{\frac{1}{2}} = t \text{ when } [A] = \frac{[A]_0}{2}
\]

\[
t_{\frac{1}{2}} = \frac{\ln \frac{[A]_0}{[A]_{0/2}}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}
\]

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?

units of \( k \) (s\(^{-1}\))
First-order reaction

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

$\# \text{ of half-lives}$ | $[A] = [A]_0/n$
--- | ---
1 | 2
2 | 4
3 | 8
4 | 16

Chung (Peter) Chieh
University of Waterloo
Second Order Reactions
Second-Order Processes

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

So if a process is second-order in A, a plot of \( \frac{1}{[A]} \) vs. \( t \) will yield a straight line with a slope of \( k \).

First order:

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

If a reaction is first-order, a plot of \( \ln [A]_t \) vs. \( t \) will yield a straight line with a slope of \( -k \).

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St. Charles Community College
Determining rxn 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 rxn order

Graphing ln [NO₂] 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>[NO₂], M</th>
<th>ln [NO₂]</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>

Does not fit:

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

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St. Charles Community College
Change of Concentration with Time

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

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 \(1/[A]_t\) vs. \(t\) is a straight line with slope \((k)\) and intercept of \(1/[A]_0\).
Second-Order Reactions

\[ \text{rate} = -\frac{D[A]}{Dt} \quad \text{rate} = k[A]^2 \]

[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

\[ t_{\frac{1}{2}} = t \quad \text{when} \quad [A] = \frac{[A]_0}{2} \]

\[ t_{\frac{1}{2}} = \frac{1}{k[A]_0} \]
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_{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_{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_{1/2} = \frac{1}{k[A]_0})</td>
</tr>
</tbody>
</table>
### Outline: Kinetics

<table>
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<tr>
<th>Rate Laws</th>
<th>First order</th>
<th>Second order</th>
<th>Second order</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>rate</strong></td>
<td>$-k[A]$</td>
<td>$-k[A]^2$</td>
<td>$-k[A][B]$</td>
</tr>
<tr>
<td><strong>Integrate Rate Laws</strong></td>
<td>$ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$</td>
<td>$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$</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>
</tbody>
</table>

John D. Bookstaver  
St. Charles Community College
## Outline: Kinetics

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<td><strong>Rate Laws</strong></td>
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<td>complicated</td>
</tr>
<tr>
<td>$k(T)$</td>
<td>$ln(k) = -\frac{E_a}{RT} + lnA$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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St. Charles Community College
Discrete Models for Chemical Kinetics
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.

Furthermore, molecules must collide with the correct orientation and with enough energy to
Collision Model

- Most reactions speed up as temperature increases.
  - Example: food spoils when not refrigerated.

- Since the rate law equation has no temperature term in it, the rate constant, \( k \), must depend on temperature.

- The collision model assumes that in order for molecules to react they must collide.
  - The greater the number of collisions the faster the rate.
  - The more molecules present, the greater the probability of collisions and the faster the rate.
  - The higher the temperature, the more energy available to the molecules and the faster the rate.
  - Complication: not all collisions lead to products. In fact, only a small fraction of collisions lead to product.
The Orientation Factor

• In order for reaction to occur the reactant molecules must collide in the correct orientation and with enough energy to form products.

- For Example:

\[
\text{Cl} + \text{NOCl} \rightleftharpoons \text{NO} + \text{Cl}_2
\]

• There are two possible ways that Cl atoms and NOCl molecules can collide; one is effective and one is not.
Activation Energy
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.
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
(b) Activation energy (Ea) for the reverse reaction
(c) Delta H

50 kJ/mol 300 kJ/mol
150 kJ/mol 100 kJ/mol
-100 kJ/mol +200 kJ/mol

Chung (Peter) Chieh
University of Waterloo
Activation Energy

• Arrhenius: 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 $E_a$. 

Dan Reid
Champaign CHS
Activation Energy

- Consider the rearrangement of methyl isonitrile:

\[
\begin{align*}
\text{H}_3\text{C}\!&\!-\text{N}≡\text{C}: & \rightarrow & \left[ \begin{array}{c} \text{H}_3\text{C} \vdash \text{N} \\ \vdash \text{C} \end{array} \right] & \rightarrow & \text{H}_3\text{C}\!&\!-\text{C}≡\text{N}: \\
\end{align*}
\]

- In \( \text{H}_3\text{C}-\text{N}≡\text{C} \), the \( \text{C}-\text{N} \equiv \text{C} \) bond bends until the \( \text{C}≡\text{N} \) bond breaks and the \( \text{N}≡\text{C} \) portion is perpendicular to the \( \text{H}_3\text{C} \) 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 \( \text{C}-\text{N} \) bond is broken, the \( \text{N}≡\text{C} \) portion can continue to rotate forming a \( \text{C}-\text{C}≡\text{N} \) bond.

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

• The change in energy, $\Delta E$, for the reaction is the difference in energy between CH$_3$NC and CH$_3$CN.

• The activation energy, $E_a$, is the difference in energy between reactants, CH$_3$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… (CH$_3$NC $\rightarrow$ CH$_3$CN), then the reverse reaction is endothermic… (CH$_3$CN $\rightarrow$ CH$_3$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.
Reaction Mechanisms
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

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*.

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

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

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

Overall reaction: \(2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2\)

Chung (Peter) Chieh
University of Waterloo
Rate Laws and Rate Determining Steps

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.
Rate Laws and Elementary Steps

Unimolecular reaction

\[ \text{A} \rightarrow \text{products} \quad \text{rate} = k [\text{A}] \]

Bimolecular reaction

\[ \text{A} + \text{B} \rightarrow \text{products} \quad \text{rate} = k [\text{A}][\text{B}] \]

Bimolecular reaction

\[ \text{A} + \text{A} \rightarrow \text{products} \quad \text{rate} = k [\text{A}]^2 \]
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 (\rightarrow) products</td>
<td>Rate = (k[A])</td>
</tr>
<tr>
<td>Bimolecular</td>
<td>A + A (\rightarrow) products</td>
<td>Rate = (k[A]^2)</td>
</tr>
<tr>
<td>Bimolecular</td>
<td>A + B (\rightarrow) products</td>
<td>Rate = (k[A][B])</td>
</tr>
<tr>
<td>Termolecular</td>
<td>A + A + A (\rightarrow) products</td>
<td>Rate = (k[A]^3)</td>
</tr>
<tr>
<td>Termolecular</td>
<td>A + A + B (\rightarrow) products</td>
<td>Rate = (k[A]^2[B])</td>
</tr>
<tr>
<td>Termolecular</td>
<td>A + B + C (\rightarrow) products</td>
<td>Rate = (k[A][B][C])</td>
</tr>
</tbody>
</table>

- Notice that the coefficients become the exponents.
Reaction Mechanisms

<table>
<thead>
<tr>
<th>Molecularity</th>
<th>Elementary Reaction</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unimolecular</td>
<td>A \rightarrow \text{products}</td>
<td>Rate = k[A]</td>
</tr>
<tr>
<td>Bimolecular</td>
<td>A + A \rightarrow \text{products}</td>
<td>Rate = k[A]^2</td>
</tr>
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<td>A + B \rightarrow \text{products}</td>
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</tr>
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<td>Termolecular</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.
- The rate law for an elementary step is written directly from that step.

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St. Charles Community College
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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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 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.

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Fast Initial Step

• A proposed mechanism is

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

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

Step 1 is an equilibrium:

it includes the forward and reverse reactions.
Fast Initial Step

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

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

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

\[
rate_2 = k_2 [NOBr_2][NO]
\]

- But how can we find \([NOBr_2]\)?
Fast Initial Step

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

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

- NOBr_2 can react two ways:
  - With NO to form NOBr
  - By decomposition to reform NO and Br_2
- The reactants and products of the first step are in equilibrium with each other.
- Therefore,

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

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

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

- Because \( Rate_f = Rate_r \),
  \[
  k_1 [NO] [Br_2] = k_{-1} [NOBr_2]
  \]

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

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

\[
= \frac{k_2k_1}{k_{-1}} [NO]^2 [Br_2]
\]
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…
  \[
  \begin{align*}
  \text{NO}_2(g) + \text{NO}_2(g) & \rightarrow \text{NO}_3(g) + \text{NO}(g) \quad \text{(slow step)} \\
  \text{NO}_3(g) + \text{CO}(g) & \rightarrow \text{NO}_2(g) + \text{CO}_2(g) \quad \text{(fast step)}
  \end{align*}
  \]

- 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: \(\text{NO}_3(g)\)
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.
Rate Laws for Multistep Mechanisms

• Let’s look at another example…

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

• The \textit{experimentally} determined rate law is…

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

• Consider the following mechanism…

\begin{align*}
\text{Step 1:} & \quad \text{NO}_\text{(g)} + \text{Br}_2\text{(g)} & \underset{k_1}{\rightleftharpoons} & \text{NOBr}_2\text{(g)} & \quad \text{(fast)} \\
\text{Step 2:} & \quad \text{NOBr}_2\text{(g)} + \text{NO}_\text{(g)} & \overset{k_2}{\rightarrow} & 2\text{NOBr}_\text{(g)} & \quad \text{(slow)}
\end{align*}

• The rate law is based on Step 2:

\[ \text{Rate} = k_2[\text{NOBr}_2][\text{NO}] \]
Rate Laws for Multistep Mechanisms

- 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.
- So we have to express \([\text{NOBr}_2]\) in terms of \(\text{NOBr}\) and \(\text{Br}_2\) by assuming there is an equilibrium in step 1.
- In a dynamic equilibrium, the forward rate equals the reverse rate. Therefore, by definition of equilibrium we get:

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

Rearranging…

\[
[\text{NOBr}_2] = \left( \frac{k_1}{k_{-1}} \right)[\text{NO}][\text{Br}_2]
\]
Rate Laws for Multistep Mechanisms

• Now we substitute \([\text{NOBr}_2] = \frac{k_1}{k_{-1}}[\text{NO}][\text{Br}_2]\) into our previous rate law…

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

  And we get…

  \[
  \text{Rate} = (k_2k_1/k_{-1})[\text{NO}][\text{Br}_2][\text{NO}]
  \]

  Combining terms…

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

• This matches the experimentally determined rate law equation, so this supports, (but does not prove) our reaction mechanism.
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.

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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)

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

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

• This is how the rate constant of a chemical reaction varies with respect to temperature and other variables.

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

where...

- \( k \) = rate constant
- \( E_a \) = Activation Energy (in kJ/mole)
- \( R \) = Gas Constant
- \( T \) = Kelvin temperature
- \( A \) = “Frequency Factor” -- a constant indicating how many collisions have the correct orientation to lead to products.
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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Plot of Arrhenius Equation

\[
\ln A \quad \ln k \quad 1/T
\]

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.

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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.
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, $E$).
- 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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Catalysts
A **catalyst** is a substance that increases the rate of a chemical reaction without itself being consumed.

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

![Diagram showing potential energy changes with and without a catalyst](image)

\[ \text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}} \]
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.
One way a catalyst can speed up a reaction is by holding the reactants together and helping bonds to break.
Catalysts

• A **catalyst** is a substance that changes the rate of a chemical reaction without itself undergoing a permanent chemical change in the process.

• 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:

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

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

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

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

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

The net reaction is still…

\[ 2\text{H}_2\text{O}_2(aq) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) \]
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, $H_2O_2$ decomposes directly to water and oxygen.

• In the presence of $Br^-$, $Br_2(aq)$ 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.
Catalysts and Reaction Rates

\[ 2\text{H}_2\text{O}_2 + 2\text{Br}^- + 2\text{H}^+ \]

\[ \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} + \text{Br}_2 \]

\[ 2\text{H}_2\text{O} + \text{O}_2 + 2\text{Br}^- + 2\text{H}^+ \]
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: \[ \text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g) \]

- 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 \( \text{C}_2\text{H}_4 \) molecule on the surface.
- Third, when an H atom collides with a \( \text{C}_2\text{H}_4 \) molecule on the surface, the C–C \( \pi \)-bond breaks and a C–H \( \sigma \)-bond forms.
- Lastly, When \( \text{C}_2\text{H}_6 \) 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

Dan Reid
Champaign CHS
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. (Ex: 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.

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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.
Enzyme Catalysis

Substrate + Enzyme → Enzyme-substrate complex → Products + Enzyme

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University of Waterloo
Another example...Nitrogen gas cannot be used in the soil for plants or animals. Nitrogen compounds, NH₃, NO₂⁻, and NO₃⁻ are used in the soil. The conversion between N₂ and NH₃ 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, catalyses the reduction of nitrogen to ammonia. It lowers the Eₐ, and the reaction proceeds.
Other Examples of Catalysts
The experimental rate law for the reaction between NO$_2$ and CO to produce NO and CO$_2$ is \( \text{rate} = k[\text{NO}_2]^2 \). 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?

\[
\text{NO}_3 \quad \quad \text{NO}_2
\]

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
Proposed Mechanism:

1. \( HBr(g) + O_2(g) \xrightarrow{k_1} \text{HOOBr}(g) \)  
   (Slow)
2. \( \text{HOOBr}(g) + HBr(g) \xrightarrow{k_2} 2 \text{HOBr}(g) \)  
   (Fast)
3. \( \text{HOBr}(g) + HBr(g) \xrightarrow{k_3} \text{H}_2\text{O}(g) + \text{Br}_2(g) \)  
   (Fast)
4. \( \text{HOBr}(g) + HBr(g) \xrightarrow{k_4} \text{H}_2\text{O}(g) + \text{Br}_2(g) \)  
   (Fast)

\[
4 \text{HBr}(g) + O_2(g) \xrightarrow{k_{exp}} 2 \text{H}_2\text{O} + 2 \text{Br}_2(g) \quad \text{overall}
\]

Write the rate law for this reaction.  
Rate = \( k [\text{HBr}] [O_2] \)

List all intermediates in this reaction.  
HOOBr, HOBr

List all catalysts in this reaction.  
None
Ostwald Process

\[
4\ce{NH3} (g) + 5\ce{O2} (g) \xrightarrow{\text{Pt catalyst}} 4\ce{NO} (g) + 6\ce{H2O} (g)
\]

\[
2\ce{NO} (g) + \ce{O2} (g) \rightarrow 2\ce{NO2} (g)
\]

\[
2\ce{NO2} (g) + \ce{H2O} (l) \rightarrow \ce{HNO2} (aq) + \ce{HNO3} (aq)
\]

Pt-Rh catalysts used in Ostwald process

Hot Pt wire over \ce{NH3} solution
Catalytic Converters

\[ CO + \text{Unburned Hydrocarbons} + O_2 \xrightarrow{\text{catalytic converter}} CO_2 + H_2O \]

\[ 2NO + 2NO_2 \xrightarrow{\text{catalytic converter}} 2N_2 + 3O_2 \]