CHEM 3332 Chapter 23
the kinetics of complex reactions

Chain reactions: the reaction mechanism and the rate law

Characteristics of Catalysis
Enzyme catalysis: the mechanism and the rate law

An example of radical chain reaction

An overall reaction

\[ \text{H}_2(g) + \text{Br}_2(g) \rightarrow 2\text{HBr}(g) \]

Initiation step

\[ \text{Br-Br} \rightarrow \text{Br} + \text{Br} \]

Formation of reactive intermediate-chain carriers

Propagation reactions

\[ \text{Br} + \text{H} \rightarrow \text{H-Br} + \text{H} \]

an intermediate react but form another

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

Reaction cycle continues

\[ \cdots \]

Termination reactions

\[ \text{Br} + \text{Br} \rightarrow \text{Br-Br} \]

chain carriers combine

\[ \text{Br} + \text{H} \rightarrow \text{H-Br} \]

\[ \text{H} + \text{H} \rightarrow \text{H-H} \]

Reaction mechanism ~ rate laws

Consider the following reaction

\[ \text{CH}_4(g) + \text{Cl}_2(g) \rightarrow \text{CH}_3\text{Cl}(g) + \text{HCl}(g) \]

•Propose a reaction mechanism
•Derive a rate law based on the proposed mechanism
•Check if the rate law is consistent with the experimentally determined rate law

Experimental studies have shown that the rate law for this reaction is one-half order with respect to \( \text{Cl}_2 \).
The mechanism of a chain reaction

\[ \text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g}) \]

One possible mechanism is proposed as following:

**Initiation:**  \( \text{Cl}_2(\text{g}) \rightarrow 2\text{Cl} \cdot \quad k_1 \)

**Propagation:**  
- \( \text{Cl} \cdot + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \cdot \quad k_2 
- \text{CH}_3 \cdot + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl} \cdot \quad k_3 
- \text{Cl} \cdot + \text{Cl} \cdot \rightarrow \text{Cl}_2 \quad k_4 
- \text{CH}_3 \cdot + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl} \cdot \quad k_3 

**Termination:**  \( \text{Cl} + \text{Cl} \rightarrow \text{Cl}_2 \quad k_4 \)

What could be the rate law if the mechanism is right?

The strategy

\[ \text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g}) \]

Is rate of reaction \( v = k[\text{CH}_4][\text{Cl}_2] \) correct?

The rate law is based on the reaction mechanism, NOT the equation of reaction!

First, choose a substance, such as the product HCl. Then, Look for HCl in the mechanism.

**Steady-state approximation**

\[ \begin{align*}
\text{Initiation} & : \quad \text{Cl}_2(\text{g}) \rightarrow 2\text{Cl} \cdot \quad k_1 \\
\text{Propagation} & : \quad \text{Cl} \cdot + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \cdot \quad k_2 \\
& \quad \text{CH}_3 \cdot + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl} \cdot \quad k_3 \\
& \quad \text{Cl} \cdot + \text{Cl} \cdot \rightarrow \text{Cl}_2 \quad k_4 \\
\text{Termination} & : \quad \text{Cl} + \text{Cl} \rightarrow \text{Cl}_2 
\end{align*} \]

\[ v = \frac{d[\text{HCl}]}{dt} = k_2[\text{Cl} \cdot ][\text{CH}_4] \]

Steady-state approximation to calculate \([\text{Cl} \cdot]\)

\[ \frac{d[\text{CH}_3\text{Cl}]}{dt} = 0 \]

Intermediate cannot be included!!!

Calculating intermediate \([\text{Cl} \cdot]\)

\[ \begin{align*}
\text{Steady state} & : \quad 2k_1[\text{Cl} \cdot ] - k_1[\text{Cl} \cdot ][\text{CH}_4] + k_2[\text{CH}_3 \cdot ][\text{Cl} \cdot ] - 2k_4[\text{Cl} \cdot ]^2 = 0 \quad (1) \\
& \quad k_2[\text{Cl} \cdot ][\text{CH}_4] - k_3[\text{CH}_3 \cdot ][\text{Cl} \cdot ] = 0 \quad (2) \\
(1) + (2) \quad [\text{Cl} \cdot ] = \sqrt{\frac{k_1}{k_4}} [\text{Cl} \cdot ] \\
\text{Substituting into (2)} \quad [\text{CH}_3\text{Cl}] = \frac{k_2[\text{Cl} \cdot ][\text{CH}_4]}{k_3[\text{CH}_3 \cdot ][\text{Cl} \cdot ]} = \frac{k_2}{k_3} \left( \frac{k_1}{k_4} \right)^{1/2} \left[ \text{CH}_4 \right] \left[ \text{Cl}_2 \right]^{1/2}
\end{align*} \]
The rate laws

The overall reaction

\[
\text{CH}_4(g) + \text{Cl}_2(g) \rightarrow \text{CH}_3\text{Cl}(g) + \text{HCl}(g)
\]

The concentration of intermediates

\[
\left[\text{Cl}^{-}\right] = \frac{k_1}{k_4} [\text{Cl}_2]; \quad \left[\text{CH}_3\text{Cl}\right] = \frac{k_2}{k_4} \sqrt{\left[\text{Cl}_2\right]}
\]

The rate of reaction in terms of product HCl

\[
v = \frac{d[\text{HCl}]}{dt} = k_2 \left[\text{Cl}^{-}\right][\text{CH}_4] = k_1 \frac{[\text{Cl}^{-}][\text{Cl}_2]}{\sqrt{k_4}}
\]

This is consistent with the experimentally observed one-half order dependence on [Cl_2]

What is the rate of reaction in terms of CH_4 or CH_3Cl?

Explosions

Overall reaction

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

Initiation

\[
2\text{H}_2 + \text{O}_2 \rightarrow 2\text{OH}
\]

propagation

\[
2\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}
\]

Branching reactions

\[
\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \quad \text{Single radical}
\]

\[
\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} \quad \text{produce two radicals}
\]

termination

\[
\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}^*
\]

The steady-state approximation cannot be used here!

Here, the number of radicals increases twofold in branching steps.

The concentration of radicals grow rapidly in time, leading to chain-branching explosion

Retardation step

Sometimes a chain carrier may attack a product and thus the net rate of formation of product is reduced. This step is called retardation step.

\[
\text{Br}_2 + \text{H}_2 \rightarrow 2\text{HBr}
\]

Initiation step

\[
\text{Br} + \text{Br} \rightarrow \text{Br} + \text{Br}
\]

propagation reactions

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

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

retardation step

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

termination reactions

\[
\text{Br} + \text{Br} \rightarrow \text{BrBr}
\]

By steady-state approximations, the corresponding rate law can be derived:

\[
\frac{d[\text{HBr}]}{dt} = \frac{2k_1 (k_4 / k_2)^{1/2} [\text{H}_2] [\text{Br}_2]^{1/2}}{[\text{Br}_2] + (k_1 / k_2) [\text{HBr}]}
\]

Please derive this equation and check example 26.1

Catalysis

Definition:

A catalyst is a substance that increase the rate of a reaction without being consumed in the reaction.

Characteristics:

A catalyst participates in chemical reactions to provide an alternative path to the product with a lower activation energy, and after the reaction is complete, the catalyst is regenerated.

A homogeneous catalyst: the catalyst in the same phase as the reaction mixture.

A heterogeneous catalyst: the catalyst in a different phase from the reaction mixture.

Does catalysts change equilibrium constant $K_{eq}$?

If a reaction has a small $K_{eq}$, can you choose a catalyst to increase $K_{eq}$?
**A example of homogeneous catalysis**

**Bromide-catalyzed decomposition of hydrogen peroxide**

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

**Reaction mechanism**

**Pre-equilibrium**

\[ \text{H}_3\text{O}^+ + \text{H}_2\text{O}_2 \rightleftharpoons \text{H}_2\text{O}_2^+ + \text{H}_2\text{O} \text{ K} = \frac{[\text{H}_2\text{O}_2^+]}{[\text{H}_3\text{O}^+][\text{H}_2\text{O}_2]} \]

**Rate-determining**

\[ \text{H}_2\text{O}_2^+ + \text{Br}^- \rightarrow \text{HOBr} + \text{H}_2\text{O} \quad \text{v} = k[H_2O_2^+][Br^-] \]

\[ \text{HOBr} + \text{H}_2\text{O}_2 \rightarrow \text{Br}^- + \text{H}_3\text{O}^+ + \text{O}_2 \quad \text{(fast)} \]

Br\(^-\) participates in the reaction, changes the reaction path (make faster), and it is regenerated in the end.

**The rate law of the overall reaction**

\[ \frac{d[\text{O}_2]}{dt} = k[H_2O_2^+][Br^-] = k_{\text{eff}}[\text{H}_2\text{O}_2][\text{H}_3\text{O}^+][\text{Br}^-] \]

The rate law involves catalyst (Br\(^-\) and pH of the solution).

---

**Enzyme catalysis**

**Enzymes** are protein molecules that serve as biological catalysts. They contain active sites that bind the substrates (reactants) to form products. The structure of the active site is specific to the reaction that is catalyzed.

**Deriving rate law**

Overall reaction:

\[ S \rightarrow P \text{ Reactant (substrate) forms product} \]

**E (catalyst) and ES (enzyme-substrate complex) do not appear in the overall reaction.**

**Deriving rate law in terms of product P**: Only last step involves product P

The rate of product formation:

\[ v = \frac{k_2[ES]}{k_1} \text{Intermediate concentration} \]

**How to replace the intermediate [ES] with reactants [S] and/or catalyst [E]?**
Rate law

\[ E + S \xrightarrow[k_1^{-1}]{} ES \xrightarrow[k_2]{} E + P \]

\[ v = k_2[ES] \]

Steady-state approximation:

\[ \frac{d[ES]}{dt} = k_1[E][S] - k_2[ES] - k_1^{-1}[ES] = 0 \]

\[ \frac{d[ES]}{dt} = \frac{k_1}{k_1 + k_2} [E][S] - \frac{1}{K_M} [E][S] \]

Michaelis constant

\[ v = \frac{k_2}{K_M} \frac{[E][S]}{1 + [S]} \]

Free enzyme concentrations

Free substrate concentrations

What is the initial reaction rate when reaction just starts?

How to express the rate law in terms of initial concentration \([E]_0\) and \([S]_0\)?

Michaelis-Menten equation

At the beginning of the reaction:

1. Usually the substrate is in large excess \(\Rightarrow [S]_0 \approx [S]_0\)
2. Total enzyme concentration is constant
   \[ [E]_0 = [E] + [ES] \]
3. Steady state approximation
   \[ [ES] = \frac{[E][S]}{1 + [S]} \]

Plug (2) into (1):

\[ v = \frac{k_2}{K_M} \frac{[E][S]}{1 + [S]} \]

thus

\[ v_0 = \frac{k_2}{K_M} \frac{[E]_0 [S]_0}{1 + [S]_0 K_M} \]

The limiting rate value by \([S]_0\)

\[ v = \frac{[S]_0}{[S]_0 + K_M} k_2[E]_0 \]

Michaelis-Menten equation

- when \([S]_0\) increases, \(v\) increases
- At very low \([S]_0\), \(v\) is first order with respect to S
- At extremely high \([S]_0\), denominator\([S]_0\)

\[ v_0 = \frac{k_2}{K_M} \frac{[E]_0 [S]_0}{1 + [S]_0 K_M} \]

constant if \([E]_0\) is constant

An hypothetical rate when \([S]_0\) is infinitely high

\[ v_{max} = k_2[E]_0 \]

With fixed amount of \([E]_0\)

\[ V_0 = \frac{[S]_0}{[S]_0 + K_M} v_{max} \]

in general

Lineweaver-Burk plot

How to measure \(K_M\), \(k_2\)?

\[ v_0 = \frac{[S]_0}{[S]_0 + K_M} \frac{k_2[E]_0}{1 + \frac{[S]_0}{K_M}} \]

Michaelis-Menten equation

Compare with

\[ y = b + kx \]

A plot of the inverse of the initial reaction rate versus \([S]_0\)^{-1} should yield a straight line. The y intercept and slope provide a measure of the maximum reaction rate and the Michaelis constant.
Example

Enzyme catalyzed carbonic anhydrase reaction: \( CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \)

CO\(_2\) is converted to bicarbonate ion. The initial enzyme concentration is 2.3 nM and temperature is 0.5°C. The initial reaction rates for the hydration reaction were obtained for different initial CO\(_2\) concentrations. Determine \( K_M \) and \( k_2 \).

<table>
<thead>
<tr>
<th>Rate (Ms(^{-1}))</th>
<th>([CO_2]) (mM)</th>
<th>(1/[E]_0) (M(^{-1})s(^{-1}))</th>
<th>(1/[S]_0) (mM(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.78 × 10^{-1}</td>
<td>1.25</td>
<td>3.6 × 10^{-4}</td>
<td>0.8</td>
</tr>
<tr>
<td>5.00 × 10^{-1}</td>
<td>2.5</td>
<td>2 × 10^{-4}</td>
<td>0.4</td>
</tr>
<tr>
<td>8.33 × 10^{-1}</td>
<td>5.0</td>
<td>1.2 × 10^{-4}</td>
<td>0.2</td>
</tr>
<tr>
<td>1.67 × 10^{-1}</td>
<td>20.0</td>
<td>6.10^{-1}</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Solution: calculate \(1/v_0\) and \(1/[CO_2]\)

plot \(1/v_0\) vs. \(1/[CO_2]\) (left)

The y intercept is 4000 M\(^{-1}\)s, which is equal to \(1/v_{max}\), thus \(v_{max}=2.5 \times 10^{-4}\)Ms\(^{-1}\).

\(v_{max}=\frac{[E]_0}{K_M+S}\)

The slope is 40s, which is \(K_M/v_{max}\)

Thus \(K_M=(40s)(2.5 \times 10^{-4}\)Ms\(^{-1}\)) = 10 mM

The turnover number \(k_2\)

**Heterogeneous catalysis**

Ammonia synthesis (80% for fertilizer) world annual production 140 million tones

\(N_2(g) + 3H_2(g) \xrightarrow{Fe} 2NH_3 (g)\) Haber process

Manufacture of sulphuric acid world annual production greater than 140 million tones per year

\(2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)\)

Isomerisation (to improve gasoline octane rating)

pentane \(\xrightarrow{Pt}\) 2-methylbutane

Octane no. 62 93

The reactants and products are gaseous or liquid, and the catalysts are solids. The chemical reactions must occur at the surface of the solid

\(C_2H_4(g) + H_2(g) \xrightarrow{Ni} C_2H_6 (g)\)

**Heterogeneous catalysis**

Turnover number, \(k_0\), the number of molecules of a substrate reacted by a single enzyme molecule per unit of time, with the enzyme working at a maximum rate.

\(k_2 [E]_0 \xrightarrow{k_1} ES \xrightarrow{k_2} E+P\)

\(v_{max} = \frac{k_2 [E]_0}{K_M + [S]}\) The substrate concentration change of per unit of time

\(\frac{[E]_0}{k_2}\) the concentration enzyme

\(\frac{K_M}{k_2}\) The number of substrate converted to products per enzyme molecular per unit of time

How does a heterogeneous catalyst work?

\(C_2H_4(g) + H_2(g) \xrightarrow{Ni} C_2H_6 (g)\)
An outline of heterogeneous catalysis process

Reactant molecule $\rightarrow$ physical adsorbed molecule
(adsorption without changing internal bonding)

surface $\rightarrow$ dissociated atoms $\rightarrow$ chemisorbed atoms
(adsorption accompanied by dissociation)

surface $\rightarrow$ products

Why does an increase in surface area of the catalyst automatically lead to an increase in catalytic activity?

Enzymes catalysis

The primary function of the enzyme in animals is to interconvert carbon dioxide and bicarbonate to maintain acid-base balance in blood and other tissues, and to help transport carbon dioxide out of tissues.

The reaction catalyzed by carbonic anhydrase is:

$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+$

The reaction rate of carbonic anhydrase is one of the fastest of all enzymes, and its rate is typically limited by the diffusion rate of its substrates. Typical catalytic rates of the different forms of this enzyme range between $10^4$ and $10^6$ reactions per second.

The reverse reaction is also relatively slow (kinetics in the 15-second range), which is why carbonated drink does not instantly degas when opening the container, but will rapidly degas in one's mouth when carbonic anhydrase is added with saliva. An anhydrase is defined as an enzyme that catalyzes the removal of a water molecule from a compound, and so it is this "reverse" reaction that gives carbonic anhydrase its name, because it removes a water molecule from carbonic acid.

$\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

(in lungs and nephrons of the kidney - low CO$_2$ concentration, in plant cells)

Langmuir isotherm

$R \ (g) + M \ (surface) \overset{k_{ads}}{\rightarrow} RM \ (surface)$

Adsorption rate $v_{ads} = k_{ads}PN(1-\theta)$

At equilibrium, $v_{ads} = v_{des}$

Langmuir isotherm

$0 = \frac{KP}{KP + 1}$

where $K = \frac{k_{ads}}{k_d}$