Lecture 26

Kinetics

Elementary Reactions

Reaction Order

Multi-step processes, Intermediates

Steady State Approximation
• The power to which a species is raised in the rate law is the reaction order. The overall order is the sum of all of the powers of all reactants.

Examples:
1. \( v = k[\text{NO}]^2[\text{O}_2] \) First order in \( \text{O}_2 \), Second order in \( \text{NO} \), Third order overall.
2. \( v = k[\text{A}]^{1/2}[\text{B}]^2 \) Half order in \( \text{A} \), Second order in \( \text{B} \), 2 1/2 order overall.

• The order does not need to be an integer.
Reaction order and molecularity

Reaction order is an empirical quantity. Molecularity refers to an elementary reaction as a step in a reaction mechanism. The rate law of an *elementary step* can be deduced directly from the reaction. Unimolecular reactions are first order. 

\[ A \rightarrow \text{Products} \quad \frac{d[A]}{dt} = -k[A] \]

Bimolecular reactions are second order.

\[ A + B \rightarrow \text{Products} \quad \frac{d[A]}{dt} = -k[A][B] \]
An example: $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$

The formation of nitric oxide is a termolecular reaction, i.e. three molecules must collide in order for the products to be formed. In this example the reaction is also the elementary step and so the rate law is $v = k[\text{NO}]^2[\text{O}_2]$ as stated earlier. In this case the reaction is third order because of the fact that three molecules must combine simultaneously. However, the reaction stoichiometry may not always indicate the molecularity of the reaction.
Question: Reaction Order

What is the order of the reaction:

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

A. First order
B. Second order
C. Third order
D. Unknown
Question: Reaction Order

What is the order of the reaction:

$$2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$$

A. First order
B. Second order
C. Third order
D. Unknown
The detailed mechanism of many enzymes has been shown to include a rate determining step:

\[
E + S \leftrightarrow ES
\]

What is the order of the overall reaction?

A. First order
B. Second order
C. Third order
D. Unknown
The detailed mechanism of many enzymes has been shown to include a rate determining step:

\[ E + S \rightleftharpoons ES \]

What is the order of the overall reaction?
A. First order
B. Second order
C. Third order
D. Unknown
Parallel First Order Reactions

- A → B and A → C so that:
  - $\frac{d[A]}{dt} = -(k_1+k_2)[A]$
  - $\frac{d[B]}{dt} = k_1[A]$
  - $\frac{d[C]}{dt} = k_2[A]$

- Solve for $[A]$ first:
  
  $[A] = [A]_0 \exp\{- (k_1 + k_2)t \}$

then

- $\frac{d[B]}{dt} = k_1[A]_0 \exp\{- (k_1 + k_2)t \}$
- $\frac{d[C]}{dt} = k_2[A]_0 \exp\{- (k_1 + k_2)t \}$
Parallel First Order Reactions

- The solutions are:

\[
[B] = \frac{k_1[A]_0}{k_1 + k_2} \left( 1 - \exp\{-(k_1 + k_2)t \} \right)
\]

\[
[C] = \frac{k_2[A]_0}{k_1 + k_2} \left( 1 - \exp\{-(k_1 + k_2)t \} \right)
\]

- The production of B and C occurs with a constant proportion:

\[
\frac{[B]}{[C]} = \frac{k_1}{k_2}
\]
Sequential first-order reactions
Consecutive elementary reactions

- A → B → C rate equations are:
  - $\frac{d[A]}{dt} = -k_1[A]$
  - $\frac{d[B]}{dt} = k_1[A] - k_2[B]$
  - $\frac{d[C]}{dt} = k_2[B]$
  - Either $k_1$ or $k_2$ can be the rate limiting step.
Sequential first-order reactions
Consecutive elementary reactions

- First solve eqn. for A
  \[ [A] = [A]_0 e^{-k_1 t} \]
- Substitute into eqn. for B
  \[ \frac{d[B]}{dt} = k_1[A] - k_2[B] = k_1[A]_0 e^{-k_1 t} - k_2[B] \]
  \[ [B] = \frac{k_1[A]_0}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right) \]
- Similarly for C
  \[ [C] = [A]_0 \left( 1 - \frac{1}{k_2 - k_1} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right) \]
Populations as a function of time

- The population as a function of time is given by the solutions to the sequential first order reactions.
- The case shown is intermediate with $k_1 = 1.5k_2$.
- The population of B grows and reaches a maximum and then decays.
**Rate determining step**

- If $k_2 \gg k_1$ then the first ($A \rightarrow B$) step becomes the rate-limiting step.
- If the $A \rightarrow B$ step is rate limiting then little or no $B$ will be observed even though it is formed on the reaction path.
- If $k_1 \gg k_2$ then the second ($B \rightarrow C$) step becomes the rate limiting step.
- If the $B \rightarrow C$ step is rate limiting then there will be a significant build-up of the intermediate state $B$.
Steady-state approximation

• Equations representing kinetic networks of more than three states are not soluble analytically.

• One means of pushing the techniques as far as possible using analytical solutions is to set the derivatives of intermediates equal to zero:

\[ \frac{d[\text{Intermediate}]}{dt} = 0 \]

• The build-up of intermediate B shown in the figure (two slides back) implies that the steady state approximation does not work for the system shown there.
Application of the steady-state approximation

- The steady state approximation can be applied to the consecutive reaction scheme

\[ \begin{align*}
  k_1 & \quad k_2 \\
  A & \rightarrow B \rightarrow C.
\end{align*} \]

if the concentration of B is fairly constant.

- The result of setting \( \frac{d[B]}{dt} = 0 \) is:

\[ k_1[A] - k_2[B] = 0 \quad \text{and} \quad \frac{d[C]}{dt} = k_1[A]. \]

Since \( \frac{d[A]}{dt} = - k_1[A] \) we see that \( \frac{d[C]}{dt} = - \frac{d[A]}{dt} \) and \([C] = (1 - \exp\{-k_1 t\})\)
Question: Rate schemes

Which rate equation describes the rate of disappearance of A?

\[ \begin{align*}
\text{B} & \xrightleftharpoons[k_1]{k_2} \text{A} \xrightarrow[k_3]{k_{-1}} \text{C} \\
\text{D} & \quad \text{A} \\
\end{align*} \]

A. \( \frac{d[A]}{dt} = -(k_1 + k_2 + k_3)[A] + k_{-1}[B] \)
B. \( \frac{d[A]}{dt} = (k_1 + k_2 + k_3)[A] - k_{-1}[B] \)
C. \( \frac{d[A]}{dt} = - k_1[B] - k_2[C] - k_3[D] + k_{-1}[A] \)
D. \( \frac{d[A]}{dt} = k_1[B] + k_2[C] + k_3[D] - k_{-1}[A] \)
Question: Rate schemes

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A. \( \frac{d[A]}{dt} = -(k_1 + k_2 + k_3)[A] + k_{-1}[B] \)

B. \( \frac{d[A]}{dt} = (k_1 + k_2 + k_3)[A] - k_{-1}[B] \)

C. \( \frac{d[A]}{dt} = -k_1[B] - k_2[C] - k_3[D] + k_{-1}[A] \)

D. \( \frac{d[A]}{dt} = k_1[B] + k_2[C] + k_3[D] - k_{-1}[A] \)
Example using the steady state approximation

For the following folding scheme involving a single intermediate determine the rate of appearance of the folded form F.

\[ \begin{align*}
  &k_1 & k_2 \\
  &U \leftrightarrow I \rightarrow F \\
  &k_{-1} \\
  \frac{d[F]}{dt} &= k_2[I] \\
  \frac{d[I]}{dt} &= k_1[U] - (k_2 + k_{-1})[I] \\
  \frac{d[U]}{dt} &= -k_1[U] + k_{-1}[I]
\end{align*} \]
Example using the steady state approximation

Assuming that you have information that allows you to use the steady state approximation determine the form of $d[F]/dt$ in terms of $[U]$.

$$
\begin{align*}
&k_1 & k_2 \\
&U \leftrightarrow I \rightarrow F \\
k_{-1}
\end{align*}
$$

A. $d[F]/dt = [U] k_1 k_2 / (k_2 + k_{-1})$
B. $d[F]/dt = [U] k_1 k_2$
C. $d[F]/dt = [U] (k_2 + k_{-1})/k_1 k_2$
D. $d[F]/dt = [U] (k_2 + k_{-1})$
**Example using the steady state approximation**

Assuming that you have information that allows you to use the steady state approximation determine the form of \( \frac{d[F]}{dt} \) in terms of \([U]\).

\[
\begin{align*}
U & \leftrightarrow I \rightarrow F \\
& \quad \quad \quad \quad k_1 \\
\end{align*}
\]

- A. \( \frac{d[F]}{dt} = [U] \frac{k_1 k_2}{(k_2 + k_{-1})} \)
- B. \( \frac{d[F]}{dt} = [U] k_1 k_2 \)
- C. \( \frac{d[F]}{dt} = [U] \frac{(k_2 + k_{-1})/k_1 k_2}{(k_2 + k_{-1})} \)
- D. \( \frac{d[F]}{dt} = [U] (k_2 + k_{-1}) \)
Example using the steady state approximation

The equations below show the reasoning behind the solution:

\[
\begin{align*}
    &k_1 & k_2 \\
    \text{U} & \leftrightarrow & \text{I} & \rightarrow & \text{F} \\
    &k_{-1}
\end{align*}
\]

\[
\begin{align*}
    \frac{d[I]}{dt} &= k_1[U] - (k_2 + k_{-1})[I] = 0 \\
    k_1[U] &= (k_2 + k_{-1})[I] \\
    [I] &= [U] \frac{k_1}{k_2 + k_{-1}} \\
    \frac{d[F]}{dt} &= k_2[I] = [U] \frac{k_1 k_2}{k_2 + k_{-1}}
\end{align*}
\]
Biexponential kinetics result when the steady-state approximation fails

- We cannot apply the steady state approximation if the concentration of B changes significantly during the process

\[ k_1 \quad k_2 \]
\[
A \rightarrow B \rightarrow C.
\]

- In this case we must solve the rate equations
- In general, for N processes the result will be kinetics with N exponential time constants.

Here: \([B](t) = \Phi_1 e^{-k_1 t} + \Phi_2 e^{-k_2 t}\)
The intensity, $I$ is measured in power per unit area of photons per second per unit area. The intensity is given in photons/s/m$^2$ or einsteins/s/m$^2$.

1 einstein = 1 mole of photons.

To convert the intensity in W/m$^2$ to intensity in number of photons we use the relation:

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$
Photochemistry

- Beer-Lambert law is:
  \[ I = I_0 10^{-A} \], \[ A = \varepsilon/c \], \[ c = [E] \]
- The concentration is \( c \) or \([E]\)
- The intensity of absorbed light is \( I_0 - I \).
- The extinction coefficient \( \varepsilon \) has units of \( M^{-1} \text{cm}^{-1} \). The extinction coefficient depends on the frequency \( \varepsilon(\omega) \). Often \( \varepsilon \) is tabulated at the peak of absorption spectrum.
Therefore, the rate of excitation of the excited state of molecule E is:

$$- \frac{d[E]}{dt} = \phi (I_o - I) \frac{1000}{l} = \phi I_o (1 - 10^{-A}) \frac{1000}{l}$$

The quantum yield is $\phi$.

1000 converts from cm$^3$ to L.
• We use the approximation:

\[ 10^{-A} \approx 1 - 2.303A \]

• Thus,

\[ - \frac{d[E]}{dt} = \frac{2303\phi I_o \varepsilon [E]}{N_A} \]

• Photoexcitation is a pseudo-first order process where the excitation rate constant is:

\[ k = \frac{2303\phi I_o \varepsilon}{N_A} \]
Competing or parallel processes

- Decay of the singlet $S_1$ state can occur either radiatively by fluorescence ($k_f$) or by internal conversion ($k_{IC}$).
- $\frac{d[S_1]}{dt} = -(k_f + k_{IC})[S_1]$
- The overall decay rate constant is the sum of the rate constants.

The fluorescence quantum yield is

$$\Phi = \frac{k_f}{k_f + k_{IC}}$$
The observed fluorescence quantum yield of Rhodamine is $\Phi_f = 0.7$. The observed lifetime is 13.0 ns. What is the intrinsic fluorescence lifetime?
A. 18.6 ns
B. 13.0 ns
C. 9.1 ns
D. 0.7 ns
Question: Quantum yield

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A. 18.6 ns  
B. 13.0 ns  
C. 9.1 ns  
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