Determining Orders and Rate Constants

- **Method 4:** Elimination by excess
  - Add B in large molar excess compared to A
  - [B] won’t change much, so
    \[ v = k [A]^a [B]^b \rightarrow v = k' [A]^a \]
  - B will “drop out” of the rate law, measure [A] vs. t.

Rate Laws vs. Reaction Mechanism

- **Rate Law:** A differential equation describing the time-dependence of concentration

- **Reaction Mechanism:** A set of *elementary steps* that describe a reaction

- If we knew mechanism perfectly, we could *always* deduce the rate law, but frequently we only know rates
Example: Ozone Degradation
(occurs in the atmosphere)

- Overall stoichiometry:
  \[ O + O_3 \rightarrow 2O_2 \]

- Elementary steps (catalyzed by NO):
  \[ NO + O_3 \rightarrow NO_2 + O_2 \]
  \[ NO_2 + O \rightarrow NO + O_2 \]

- What will we observe if step 1 is much faster than step 2? What about vice versa?

Elementary Steps Define the Rate Law

- If I tell you this in an elementary step:
  \[ 2A + B \rightarrow C \]

- The rate law must be given by:
  \[ \frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[C]}{dt} = -k[A]^2[B] \]

- Complicated mechanisms will have more complex rate laws, because the elementary steps will combine in different ways.
Example: Parallel Reactions

- The “simplest” complex reaction:

- Differential equations:
  \[
  \frac{d[A]}{dt} = -k_1 [A] - k_2 [A] = -(k_1 + k_2) [A] \\
  \frac{d[B]}{dt} = k_1 [A] \\
  \frac{d[C]}{dt} = k_2 [A]
  \]

Example: Series Reactions

- Reaction with an intermediate:

- Differential equations:
  \[
  \frac{d[A]}{dt} = -k_1 [A] \\
  \frac{d[B]}{dt} = k_1 [A] - k_2 [B] = k_1 A_0 e^{-k_1 t} - k_2 [B] \\
  \frac{d[C]}{dt} = k_2 [B]
  \]
**Example: Series Reactions**

- Reaction with an intermediate:

  ![Chemical Reaction Diagram](https://via.placeholder.com/150)

  \[ A \xrightarrow{k_1} B \xrightarrow{k_2} C \]

- Solutions (assuming initial \( A_0 \)):
  
  \[
  A(t) = A_0 e^{-k_1 t} \\
  B(t) = \frac{k_1 A_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \\
  C(t) = A_0 \left[ 1 - \frac{1}{k_2 - k_1} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right]
  \]

**Rate Limiting Steps**

- In many reactions, one step will be significantly slower than the others

- Consequences
  - Slow rate will dominate kinetics
  - Hard to determine mechanism for fast steps
One Rate Law, Many Mechanisms

• Consider this sequence:

\[ A \xrightarrow{k_2} B \xrightarrow{k_2} C \xrightarrow{k_3} D \xrightarrow{k_4} E \]

• If \( k_2 \ll k_1, k_3, k_4 \), then overall reaction kinetics will appear first order in \([A]\) with a rate of \( k_2 \)

• You can’t distinguish the two:

\[ A \xrightarrow{k_2} E \]

Thermo and Kinetics 1:
Microscopic Reversibility

• **Question:** What’s wrong with this pathway?

\[ \begin{array}{c}
A \xrightarrow{k_2} B \\
\uparrow \quad \downarrow \\
D \leftarrow C
\end{array} \]
Thermo and Kinetics 2:
Rate Constants and Equilibrium

- Reversible equilibrium:
  \[ A \rightleftharpoons_{k_1}^{k_{-1}} B \]

- Differential equations:
  \[ \frac{d[A]}{dt} = -k_1[A] + k_{-1}[B] \]
  \[ \frac{d[B]}{dt} = k_1[A] - k_{-1}[B] \]

How to Handle Complex Mechanisms

- **Method 1:** Initial Rate Approximation
  - As reaction starts, product concentrations are approximately zero
  \[ A \rightleftharpoons_{k_1}^{k_{-1}} B \]

- Initial rate of formation of B would be:
  \[ \frac{d[B]}{dt} = k_1[A] - k_{-1}[B] \approx k_1[A] \]
How to Handle Complex Mechanisms

• **Method 2:** Fast-to-Equilibrium Approximation
  – If the kinetics of step 1 is faster than step 2

  \[ A + B \xrightleftharpoons[k_1][k_{-1}] C \rightarrow D \]

  • To a first approximation, rate of formation of C is equal to its breakdown to A and B:
  \[ k_1[A][B] = k_{-1}[C] \]

How to Handle Complex Mechanisms

• **Method 3:** Steady State Approximation
  – Concentration of intermediate is relatively constant, e.g. because \( k_2 \) is fast

  \[ A + B \xrightleftharpoons[k_1][k_{-1}] C \rightarrow D \]

  • The rate of change of C is approximately zero:
  \[ \frac{d[C]}{dt} \approx 0 = k_1[A][B] - (k_{-1} + k_2)[C] \]
Assignment:

• Read pp. 352-353 of your book, “Deducing a Mechanism from Kinetic Data.”

• Application: It is not always straightforward to identify a mechanism
  – You’ll get practice on your homework
  – Start early!