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:

$$2A + B \rightarrow C$$

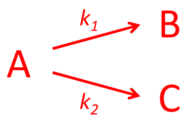
- The rate law *must* be given by:

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[C]}{dt} = -k[A]^2[B]$$

- 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:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

- 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:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

- Solutions (assuming initial A_0):

$$A(t) = A_0 e^{-k_1 t}$$

$$B(t) = \frac{k_1 A_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$C(t) = A_0\left[1 - \frac{1}{k_2 - k_1}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right)\right]$$

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:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D \xrightarrow{k_4} E$$

- If $k_2 << k_{1,}$ 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?

$$\begin{tikzcd}
A \arrow[r] & B \arrow[d] \\
D \arrow[u] & C \arrow[l]
\end{tikzcd}$$

Thermo and Kinetics 2:

Rate Constants and Equilibrium

- Reversible equilibrium:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

- 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

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

- 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

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C \overset{k_2}{\rightarrow} D$$

- 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

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C \overset{k_2}{\rightarrow} D$$

- 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!