Lecture 10 – Chapter 15, Section 5
Mechanism in detail

- Requirements of mechanism
- First step fast – review
- Later step fast – complicated
- Steady-state approximation
- Example – ozone
Mechanisms

• Recall mechanisms explain reactions in detail
• True mechanism must have the following behaviors:
  – Mechanism is composed of one or more elementary reactions that are uni-, bi-, or termolecular
  – Sum of individual steps must yield overall reaction stoichiometry
  – Mechanism must be consistent with experimental rate law

• Multiple mechanisms may yield the same rate law
  – Agreement with experiment does NOT prove a mechanism is correct
  – Disagreement with experiment DOES prove a mechanism incorrect
Rate-determining step

- Already discussed importance of rate-determining step
- Have done several examples with rate-determining step
  - The only step of a one-step mechanism
  - The first step of a multi-step mechanism
- In these cases we get an overall rate law that matches the rate-determining elementary reaction
- We’ll do one more example like this…
\[
\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}
\]

One step mechanism
1. CO collides with NO\(_2\)
2. CO steals an O
3. Result is CO\(_2\) and NO

So elementary reaction is same as overall reaction
- \[
\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}
\]
What is the rate law corresponding to this 1-step mechanism?
\[ \text{CO } + \text{ NO}_2 \rightarrow \text{CO}_2 + \text{NO} \]

0%  1. Rate = k[CO]
0%  2. Rate = k[NO\textsubscript{2}]
0%  3. Rate = k[CO][NO\textsubscript{2}]
0%  4. Rate = k[CO\textsubscript{2}][NO]
0%  5. Rate = k[CO][NO\textsubscript{2}][CO\textsubscript{2}][NO]
CO + NO₂ → CO₂ + NO

Two step mechanism
1. Collision between two NO₂ gives NO + NO₃
2. NO₃ collides with CO and gives up an O
3. Result is CO₂ and NO₂

So two elementary reactions
- NO₂ + NO₂ → NO₃ + NO (fast/slow?)
- NO₃ + CO → NO₂ + CO₂ (fast/slow?)
Slow = rate determining

- NO₃ is unstable so it reacts quickly
- \( \text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO} \) (slow – rate determining)
- \( \text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2 \) (fast)

- Since slow step is first, the overall rate law matches the rate law from the rate-determining elementary reaction

- Notice that sum of two steps gives overall stoichiometry

\[
\begin{align*}
\text{NO}_2 + \text{NO}_2 & \rightarrow \text{NO}_3 + \text{NO} \\
\text{NO}_3 + \text{CO} & \rightarrow \text{NO}_2 + \text{CO}_2 \\
\text{NO}_2 + \text{CO} & \rightarrow \text{NO} + \text{CO}_2
\end{align*}
\]
What is the rate law corresponding to this 2-step mechanism?

1. \( \text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO} \) (slow)
2. \( \text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2 \) (fast)

20% 1. Rate = \( k[\text{NO}_2] \)
20% 2. Rate = \( k[\text{NO}_2]^2 \)
20% 3. Rate = \( k[\text{NO}_3][\text{CO}] \)
20% 4. Rate = \( k[\text{NO}_2][\text{NO}_3][\text{CO}] \)
20% 5. Rate = \( k[\text{NO}_2]^2[\text{NO}_3][\text{CO}] \)
Experiment

• Experiments reveal that reaction rate is second-order in \(\text{NO}_2\)
• So, the 1-step mechanism is wrong
• The 2-step mechanism could be correct
What if rate-determining step is not first?

- For example \( \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} \)
- Careful experiments (see Example 15-7 p.635) show that \( \text{Rate} = k[\text{H}_2][\text{Br}_2]^{1/2} \)

- One possibility is 4-step mechanism

1. \( \text{Br}_2 \rightarrow 2\text{Br} \)

2. \( 2\text{Br} \rightarrow \text{Br}_2 \)

3. \( \text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H} \)

4. \( \text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br} \)
Is this mechanism possible?

• Does it yield overall stoichiometry?
  \[ \text{Br}_2 \rightarrow 2\text{Br} \]
  \[ 2\text{Br} \rightarrow \text{Br}_2 \]
  \[ \text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H} \]
  \[ \text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br} \]
  \[ \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} \]

• Yes – check

• Next, need to figure out rate law
  – Start by just looking at rate-determining step
What is the rate law corresponding to this elementary reaction?

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

1. Rate = \( k[\text{Br}] \)
2. Rate = \( k[\text{H}_2] \)
3. Rate = \( k[\text{H}]^2 \)
4. Rate = \( k[\text{Br}][\text{H}_2] \)
5. Rate = \( k[\text{HBr}][\text{H}] \)
Steady-state Approximation

- What is concentration of Br?
  - Intermediates hard to measure experimentally
  - Need to relate back to reactants
- Steady state approximation says that an intermediate is in equilibrium
  
  rate of production = rate of decomposition

- In this case this means
  
  rate of \( \text{Br}_2 \rightarrow 2\text{Br} \) = rate of \( 2\text{Br} \rightarrow \text{Br}_2 \)

  \[ k_1[\text{Br}_2] = k_{-1}[\text{Br}]^2 \]

  (use \( k_1 \) and \( k_{-1} \) to denote forward and reverse reactions)
Just a little math

- Let’s see our mechanism again, but now let’s define each rate constant

\[ Br_2 \xrightarrow{k_1} 2Br \]

\[ 2Br \xrightarrow{k_{-1}} Br_2 \]

\[ Br + H_2 \xrightarrow{k_2} HBr + H \]

\[ H + Br_2 \xrightarrow{k_3} HBr + Br \]

- Our rate-determining step gives \( \text{Rate} = k_2[Br][H_2] \)
- And we just figured out \( k_1[Br_2] = k_{-1}[Br]^2 \)
- How do we get rid of \([Br]\)?
Fractional order

\[ k_1[Br_2] = k_{-1}[Br]^2 \]

\[ [Br]^2 = \frac{k_1}{k_{-1}}[Br_2] \]

\[ [Br] = \left( \frac{k_1}{k_{-1}}[Br_2] \right)^{1/2} \]

\[ Rate = k_2[Br][H_2] \]

\[ Rate = k_2 \left( \frac{k_1}{k_{-1}}[Br_2] \right)^{1/2}[H_2] \]

\[ Rate = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2}[Br_2]^{1/2}[H_2] \]

\[ Rate = k[Br_2]^{1/2}[H_2] \]

where \[ k = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} \]
Atmospheric Ozone Chemistry

Net: $3O_2 + h\nu \rightarrow 2O_3$
$\lambda < 240 \text{ nm}$

Net: $2O_3 + h\nu \rightarrow 3O_2$
$\lambda = 240-340 \text{ nm}$
Today

- Finish CAPA #6

Friday

- Start on CAPA #7 (last one before exam)
- Begin serious review of previous chapters…