Lecture 10 – Chapter 15, Section 1
Introduction to kinetics

• Reaction Mechanisms
• Elementary Reactions

Since 1995, three Nobel Prizes in chemistry have been awarded for kinetics studies.
Mechanisms

- Chemistry seeks to explain how reactions occur
- Mechanism is a detailed description of a reaction
  - Exactly which bonds are made and broken when & where
- For instance: \[2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4\]

\[\text{NO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4\]
Not every collision $\rightarrow \text{N}_2\text{O}_4$

It must be the Ns that collide to form an N-N bond.

Other collisions give no reaction.
Review: What is the reaction quotient (Q) for 
\[2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4\]

<table>
<thead>
<tr>
<th></th>
<th>25% 1.</th>
<th>( \frac{P_{\text{N}_2\text{O}<em>4}}{P</em>{\text{NO}_2}} )</th>
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<tr>
<td></td>
<td>25% 2.</td>
<td>( \frac{P_{\text{NO}<em>2}^2}{P</em>{\text{N}_2\text{O}_4}} )</td>
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<td>25% 3.</td>
<td>( \frac{P_{\text{NO}<em>2}}{P</em>{\text{N}_2\text{O}_4}^2} )</td>
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<td>25% 4.</td>
<td>( \frac{P_{\text{N}_2\text{O}<em>4}}{P</em>{\text{NO}_2}^2} )</td>
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Reaction Molecularity

• The $2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$ reaction is bimolecular
  – Two NO$_2$ molecules collide to form N$_2$O$_4$

• If the reaction is written in reverse it is unimolecular
  – One N$_2$O$_4$ spontaneously falls apart
How many molecules collide?

- \( A \rightarrow \text{Products} \)  
  - Unimolecular

- \( A + B \rightarrow \text{Products, } 2A \rightarrow \text{Products} \)  
  - Bimolecular

- \( A + B + C \rightarrow \text{Products, } 2A + B \rightarrow \text{Products} \)  
  - Termolecular
Elementary Reactions

• Each individual step in the mechanism is called an elementary reaction

• For the simple things we have looked at so far, the overall reaction is just a single step
  – So, the overall reaction is also an elementary reaction
  – This is not usually the case

• The overall reaction mechanism is usually a sum of several elementary reactions
  – We’ll do a couple examples…
  – The key is that different mechanisms suggest different behavior. We can do experiments to test behaviors.
More with NO₂

• Let’s look at \[ 2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2 \]
• Multiple possibilities for mechanisms
• Mechanism I: unimolecular followed by bimolecular

\[
\begin{array}{c|c|c|c|c|c|c}
\text{Step I-1} & \text{NO}_2 & \rightarrow & \text{NO} + \text{O} \\
\text{Step I-2} & \text{O} + \text{NO}_2 & \rightarrow & \text{O}_2 + \text{NO} \\
\text{Overall} & 2\text{NO}_2 & \rightarrow & 2\text{NO} + \text{O}_2 \\
\end{array}
\]

O is called an **intermediate**. It is present in the reaction mechanism but does not appear in overall reaction.
Mechanism II

- Bimolecular followed by unimolecular reaction
- Also consistent with overall reaction

\[ 2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2 \]

- Two mechanisms give different behaviors
  - Dependence of rate on pressure of \( \text{NO}_2 \)
  - Can test for presence of intermediates (O vs. \( \text{NO}_3 \))
In Mechanism II, NO₃ is called...

1. Reactant
2. Product
3. Intermediate
4. Catalyst
The first step in the following reaction is?

Step 1: \( \text{NO}_2 (g) + \text{NO}_2 (g) \rightarrow \text{NO} (g) + \text{NO}_3 (g) \)  
Elementary Reaction

Step 2: \( \text{NO}_3 (g) + \text{CO} (g) \rightarrow \text{NO}_2 (g) + \text{CO}_2 (g) \)  
Elementary Reaction

\( \text{NO}_2(g) + \text{CO} (g) \rightarrow \text{NO} (g) + \text{CO}_2 (g) \)  
Overall Reaction

25%  1.  Unimolecular
25%  2.  Bimolecular
25%  3.  Termolecular
25%  4.  Tetramolecular
Reaction Rate

- Reaction rates are key reporters of mechanisms
- Measured as amount of product formed per unit time (sec.)

- In multistep reactions, the slowest step is the most important in controlling the overall rate
  - Called the rate determining step
Grocery shopping

1. Walk from car to store (30 seconds)
2. Get cart (5 seconds)
3. Select ice cream (1-3 minutes)
4. Get in line (1 minute)
5. Checkout (15 minutes)
6. Take food to car (1 minute)

If you are at Meier at 5:30 then you know step 5 will take forever. Doesn’t matter how fast you do other steps it is always going to take something like 20 minutes.

To say it another way… sprinting to the ice cream aisle won’t significantly speed up your trip. But, you just use the self check line, then you will greatly speed up your trip.
Today
• Finish CAPA #6

Friday
• Seminar
• Read Chapter 15!
• Are you working extra homework problems?