Lecture 11 – Chapter 15, Sections 2-3
Rate Laws

- Reactions controlled by collisions
- Rate constants
- Rate laws
- Reaction orders
- Orders & mechanisms
Collisions

- Talked last time about collisions being critical
  - Molecules often collide to react
  - Must collide with right orientation & enough energy
- If there are more collisions between reactants, there are more opportunities to react, so more product should be formed.
- If there are more reactants there should be more collisions

- More reactant particles $\rightarrow$ more collisions $\rightarrow$ more product
- Higher concentration $\rightarrow$ more collisions $\rightarrow$ faster rate
For the reaction between O₃ and NO, if the rate in picture (a) is 10 reactions/s, what is the rate in picture (b)?

25%  1.  5 rxns/s

25%  2.  10 rxns/s

25%  3.  20 rxns/s

25%  4.  100 rxns/s
Rates during reactions

- As reaction progresses, # of reactants left decreases
  - Fewer reactants $\rightarrow$ less collisions $\rightarrow$ slower rate

$$2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$$
Rates during reactions

- Usually measured and displayed as concentrations of each component as a function of time.

- For instance, for the $2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$ reaction from last time...

![Graph showing the concentration of NO and O as a function of time](image)

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>0</th>
<th>5.0</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>80</th>
<th>120</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{NO}_2]$ (10^{-2} M)</td>
<td>4.1</td>
<td>3.1</td>
<td>2.5</td>
<td>2.1</td>
<td>1.8</td>
<td>1.4</td>
<td>1.0</td>
<td>0.70</td>
<td>0.50</td>
<td>0.30</td>
</tr>
<tr>
<td>$[\text{NO}]$ (10^{-2} M)</td>
<td>0.50</td>
<td>0.80</td>
<td>1.0</td>
<td>1.1</td>
<td>1.3</td>
<td>1.6</td>
<td>1.7</td>
<td>1.8</td>
<td>1.9</td>
<td></td>
</tr>
</tbody>
</table>
Reaction Rate

- Reaction rate is defined as change in concentration per unit time.
- For $\text{2NO}_2 \rightarrow \text{2NO} + \text{O}_2$

Rate of production of $\text{O}_2 = \frac{\Delta [\text{O}_2]}{\Delta t} = \frac{0.0080 \text{M} - 0.0050 \text{M}}{10 \text{s} - 5.0 \text{s}} = 6.0 \times 10^{-4} \text{M/s}$

Rate of consumption of $\text{NO}_2 = -\frac{\Delta [\text{NO}_2]}{\Delta t} = -\frac{0.025 \text{M} - 0.031 \text{M}}{10 \text{s} - 5.0 \text{s}} = 12 \times 10^{-4} \text{M/s}$
Reaction Rate

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

Reaction rate: \[
\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = 6 \times 10^{-4} \text{ M/s}
\]

In general, for the reaction:
\[a\text{A} + b\text{B} \rightarrow d\text{D} + e\text{E}\]

Reaction rate: \[
-\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t} = \frac{1}{e} \frac{\Delta[E]}{\Delta t}
\]

Relationships between rates follow from overall reaction stoichiometry. Almost nothing else does!
Rate Constants

- Reaction rate changes continuously during reaction
  - Complicated – yuck
- This is true because # collisions is decreasing
- But, the fraction of collisions that yield products stays constant.
- This ‘effectiveness of collisions’ is called the **Rate Constant**

- Each reaction has a different inherent ‘effectiveness’
  - Rate constants ($k$) must be measured for each reaction
  - But, for any one reaction, the rate constant is always the same regardless of concentration.
    - Rate constant does depend on things like temperature
Rate Laws

• Rate depends on # of effective collisions
• Rate constant \((k)\) gives something like the fraction of total collisions that are effective
• Total collisions related to concentration

• Put these all together to give Rate Law

\[
\text{Rate} = k[A]^y [B]^z
\]

• \(k\) is the rate constant
• \(y\) and \(z\) are reaction orders
• Overall reaction order is \(y + z\)
Reaction Orders

- $y$ and $z$ must be determined experimentally
- **CANNOT** be deduced from overall reaction
- Depend on which collisions are relevant to reaction
- $y$ and $z$ **CAN** be deduced from elementary reactions – **mechanism**

From this elementary reaction we can predict:

\[ \text{Rate} = k[O_3][\text{NO}] \]
Overall Reaction does NOT predict rate law

\[ 2\text{NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2 \]

experimental rate law: \( \text{Rate} = k[\text{NO}_2][\text{O}_3] \)

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]

experimental rate law: \( \text{Rate} = k[\text{NO}][\text{O}_3] \)
Given this 3-step reaction mechanism, select the most likely rate law:

\[
\begin{align*}
N_2O_5 & \rightarrow NO_2 + NO_3 \quad \text{slow} \\
NO_2 + NO_3 & \rightarrow NO_2 + O_2 + NO \quad \text{fast} \\
NO + NO_3 & \rightarrow 2NO_2 \quad \text{fast}
\end{align*}
\]

1. Rate = \(k[N_2O_5][NO_2][NO][NO_3]^2\)
2. Rate = \(k[NO_2][NO][NO_3]^2\)
3. Rate = \(k[N_2O_5]\)
4. Rate = \(k[NO_2][NO_3]\)
5. Rate = \(k[NO][NO_3]\)
Kinetics distinguishes mechanisms

• Recall the $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ reaction

First reaction is slow (rate-determining) so Mechanism I predicts:

$\text{Rate}_I = k[\text{NO}_2]$
Kinetics distinguishes mechanisms

Again, first reaction is slow (rate-determining)
Mechanism II predicts:
\[ \text{Rate}_{II} = k[\text{NO}_2]^2 \]

Measuring rate law experimentally can rule out one of the proposed mechanisms
Today

• Seminar 4:00 Schaap 1000
  – Molecular electronics & single-molecule spectroscopy
• Go out!

Monday

• CAPA #7

• Exam I two weeks from today!