Chemical Kinetics

- Kinetics is a study of the rate at which a chemical reaction occurs.
- The study of kinetics may be done in steps:
  - Determination of reaction mechanism
  - Prediction of rate law
  - Measurement of reaction rates
  - Comparison of predicted and measured rates

Reaction Mechanisms

- Up to now, we have written chemical reactions as “net” reactions—a balanced chemical equation that shows the initial reactants and final products.
- A “reaction mechanism” shows the “elementary” reactions that must occur to produce the net reaction.
- An “elementary” reaction is a chemical reaction that actually takes place.
Every September since the early 80s, an “ozone hole” has developed over Antarctica which lasts until mid-November.
Reaction Mechanisms

The net reaction for this process is:
\[ 2 \text{O}_3(g) \rightarrow 3 \text{O}_2(g) \]

If this reaction were an elementary reaction, then two ozone molecules would need to collide with each other in such a way to form a new O-O bond while breaking two other O-O bonds to form products:

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\hline
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\rightarrow 3 \text{O}_2
\]
It is hard to imagine this process happening based on our current understanding of chemical principles.

The net reaction must proceed via some other set of elementary reactions:

One possibility is:

\[
\begin{align*}
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{ClO} & \rightarrow \text{ClOOCl} \\
\text{ClOOCl} & \rightarrow \text{Cl} + \text{ClOO} \\
\text{ClOO} & \rightarrow \text{Cl} + \text{O}_2 \\
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\end{align*}
\]

net: \(2 \text{O}_3 \rightarrow 3 \text{O}_2\)
Reaction Mechanisms

- In this mechanism, each elementary reaction makes sense chemically:

\[
\text{Cl} \cdots \text{O} - \text{O} \rightarrow \text{Cl-O} + \text{O-O}
\]

- The chlorine atom abstracts an oxygen atom from ozone leaving ClO and molecular oxygen.

Reaction Mechanisms

- Why does this chemistry occur over Antarctica producing an ozone hole?
  - During the Antarctic winter, a polar vortex forms in which air from lower latitudes no longer enters the south polar region—the air mass within the polar vortex is trapped.
  - There is no sunlight during winter, so no “photochemistry” takes place—reactions initiated by sunlight.
During this period of darkness, molecules form, assisted by polar stratospheric clouds, containing chlorine atoms. These species absorb light and dissociate, but the absence of sunlight eliminates this process.

When the sun rises in mid-September, the chlorine containing species now dissociate to release a flood of chlorine atoms which react with ozone through the mechanism given.
When we examine a reaction mechanism, we can identify the chemical species in one of four ways: reactants, intermediates, catalysts, or products.

- **Reactants** are necessary for the reaction to proceed and appear in the net reaction.
- **Intermediates** are species formed in the mechanism that undergo further reaction, but do not appear in the net reaction.
Catalysts are required to initiate the reaction. A catalyst does not appear in the net reaction and is regenerated in the reaction mechanism.

Products are the final chemical species formed and appear in the net reaction.
Reaction Mechanisms

- Each elementary reaction has a rate coefficient associated with it.
- The rate coefficient, given the symbol k, is a measure of how fast that specific elementary reaction occurs.
- k is often referred to as the rate constant, but this is a misnomer because k frequently changes with temperature or pressure.
- The rate coefficients are usually included in the reaction mechanism:

\[
\begin{align*}
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 & k_1 \\
\text{ClO} + \text{ClO} & \rightarrow \text{ClOOCl} & k_2 \\
\text{ClOOCl} + h\nu & \rightarrow \text{Cl} + \text{ClOO} & k_3 \\
\text{ClOO} & \rightarrow \text{Cl} + \text{O}_2 & k_4 \\
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 & k_1
\end{align*}
\]

Or

\[
\begin{align*}
\text{Cl} + \text{O}_3 & \overset{k_1}{\rightarrow} \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{ClO} & \overset{k_2}{\rightarrow} \text{ClOOCl} \\
\text{ClOOCl} + h\nu & \overset{k_3}{\rightarrow} \text{Cl} + \text{ClOO} \\
\text{ClOO} & \overset{k_4}{\rightarrow} \text{Cl} + \text{O}_2 \\
\text{Cl} + \text{O}_3 & \overset{k_1}{\rightarrow} \text{ClO} + \text{O}_2
\end{align*}
\]
The Reaction Rate Law

- Based on the reaction mechanism, we can now derive a rate law.
- The rate law of a reaction expresses the speed of the reaction in terms of the concentrations of reactants and/or intermediates or catalysts and the rate coefficients of the elementary reactions.
- The overall rate law is given by:
  \[ \text{rate} = K [A]^y[B]^z \]
  
  \( K \) is a collection of constants

The Reaction Rate Law

- The powers of concentrations in the rate law express the **order** of the reaction.

**Example**

If the rate law is

- \( \text{rate} = K [A]^2[B]^1 \)
- the reaction is \( 2\text{nd} \) order in A, \( 1\text{st} \) order in B, and \( 3\text{rd} \) order overall.

If the rate law is

- \( \text{rate} = K [A]^3[B]^{1/2} \)
- the reaction is \( 3\text{rd} \) order in A, \( 1/2 \) order in B, and \( 3\frac{1}{2} \) order overall.
The Reaction Rate Law

- The rate of a reaction is measured by monitoring the concentration of a chemical species as a function of time.
  \[ \alpha A + \beta B \rightarrow \gamma C + \delta D \]

  \[ \text{rate} = -\frac{1}{\alpha} \frac{d[A]}{dt} = -\frac{1}{\beta} \frac{d[B]}{dt} = \frac{1}{\gamma} \frac{d[C]}{dt} = \frac{1}{\delta} \frac{d[D]}{dt} \]

- The rate is negative for reactants because the concentration is decreasing, positive for products because the concentration is increasing.

The Reaction Rate Law

- The rate law for a specific *elementary* reaction,
  \[ \alpha A + \beta B \rightarrow^k \gamma C + \delta D \]
  is given by:
  \[ \text{rate} = k[A]^{\alpha}[B]^{\beta} \]

- Note that the rate of a specific elementary reaction depends only on the concentration of reactants, not products.

- The overall rate law is derived by combining rate laws for each elementary reaction in the mechanism.
The Reaction Rate Law

Example: For the O₃ cycle over Antarctica, determine the rate law for the formation of oxygen.

\[
\begin{align*}
\text{Cl} + \text{O}_3 &\rightarrow \text{ClO} + \text{O}_2 \quad k_1 \\
\text{ClO} + \text{ClO} &\rightarrow \text{ClOOCl} \quad k_2 \\
\text{ClOOCl} + \text{hv} &\rightarrow \text{Cl} + \text{ClOO} \quad k_3 \\
\text{ClOO} &\rightarrow \text{Cl} + \text{O}_2 \quad k_4 \\
\text{Cl} + \text{O}_3 &\rightarrow \text{ClO} + \text{O}_2 \quad k_1
\end{align*}
\]

The Reaction Rate Law

Example (con’t.):

Oxygen is formed in reactions 1 (repeated in last step of mechanism) and 4. We write a rate for each of these reactions and sum them to get a total rate of oxygen formation:

\[
\begin{align*}
\frac{d[\text{O}_2]}{dt} &= k_1[\text{Cl}][\text{O}_3] + k_4[\text{ClOO}] + k_1[\text{Cl}][\text{O}_3] \\
&= 2k_1[\text{Cl}][\text{O}_3] + k_4[\text{ClOO}]
\end{align*}
\]
The Reaction Rate Law

Example (con’t.):
Note that oxygen is a product in each of these elementary reactions, so the sign of each term is positive.

\[
\frac{d[O_2]}{dt} = k_1[Cl][O_3] + k_4[ClOO] + k_1[Cl][O_3] \\
= 2k_1[Cl][O_3] + k_4[ClOO]
\]

The Reaction Rate Law

Example (con’t.):
Let’s assume that reaction 4 occurs much faster than reaction 1, i.e., as soon as the ClOO intermediate is formed, it immediately decomposes to Cl and O₂, but the Cl + O₃ reaction takes more time to proceed. In this case, reaction 1 is called the “rate-limiting” step because it determines the overall rate at which the net reaction can occur.
The Reaction Rate Law

Example (con’t.):
This simplifies the rate law:

\[
\frac{d[O_2]}{dt} = 2k_1[Cl][O_3] + k_4[ClOO] \equiv 2k_1[Cl][O_3]
\]

This rate law predicts that the formation of oxygen depends only on the concentration of atomic chlorine and ozone.

As [Cl] increases, the rate of oxygen formation from the reaction of ozone increases.

Experimental Determination of Rate Law

- If we measure the rate of a reaction under different concentration conditions, we can determine the order of the reaction.
- Experimentally, we design the measurements to change only one variable at a time:
Experimental Determination of Rate Law

Example:
For the reaction $A + B \rightarrow C + D$, the following data were measured:

<table>
<thead>
<tr>
<th></th>
<th>[A]</th>
<th>[B]</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>1.0 M</td>
<td>1.0 M</td>
<td>25.0 M s$^{-1}$</td>
</tr>
<tr>
<td>#2</td>
<td>0.5 M</td>
<td>2.0 M</td>
<td>12.5 M s$^{-1}$</td>
</tr>
<tr>
<td>#3</td>
<td>0.5 M</td>
<td>1.0 M</td>
<td>6.25 M s$^{-1}$</td>
</tr>
<tr>
<td>#4</td>
<td>1.0 M</td>
<td>2.0 M</td>
<td>50.0 M s$^{-1}$</td>
</tr>
</tbody>
</table>

Determine the rate law for this reaction.

Experimental Determination of Rate Law

Example (con’t.):
We need to find $K$, $y$, and $z$ in:
rate = $K [A]^y[B]^z$

Compare #1 and #3: $[A]$ is halved and the rate decreases by a factor of 4
$\Rightarrow y = 2$

Compare #1 and #4: $[B]$ is doubled and the rate increases by a factor of 2
$\Rightarrow z = 1$
Example (con’t.):
We need to find $K$, $y$, and $z$ in:
\[
\text{rate} = K [A]^2[B]^1
\]
We can take any run and determine the value of the constant $K$:
\[
12.5 \text{ M s}^{-1} = K [0.5 \text{ M}]^2[2.0 \text{ M}]
\]
\[
\Rightarrow K = 25 \text{ M}^{-2} \text{ s}^{-1}
\]
Rate law is:
\[
\text{rate} = 25 \text{ M}^{-2} \text{s}^{-1} [A]^2[B]
\]
Experimental Determination of Rate Law

- If we take the natural log of both side of this expression, we get
  \[ \ln[A(t)] = \ln[A_0] - k \cdot t \]
- If we now plot \( \ln[A(t)] \) versus time, we get a straight line with a slope equal to \(-k\).

Experimental Determination of Rate Law

- If a reaction is 2\(^{nd}\) order in some reactant \(A\), the rate can be expressed as
  \[ \frac{d[A]}{dt} = -k[A]^2 \]
- Rearrangement and integration of this expression yields:
  \[ \frac{1}{[A(t)]} = \frac{1}{[A_0]} + k \cdot t \]
Experimental Determination of Rate Law

- If we now plot $1/\left[A(t)\right]$ versus time, we get a straight line with a slope equal to $k$.
- One way of determining if a reaction is $1^{\text{st}}$ or $2^{\text{nd}}$ order is to plot the natural log of the measured concentration versus time or the inverse of the measured concentration versus time—which ever plot results in a straight line indicates the order of the reaction for that species.

Example: For the reaction $\text{ClO} + \text{ClO} \rightarrow \text{ClOOCI}$, the following data were obtained:

<table>
<thead>
<tr>
<th>[ClO] (molecule cm$^{-3}$)</th>
<th>time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.00 \times 10^{12}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$6.45 \times 10^{11}$</td>
<td>0.1</td>
</tr>
<tr>
<td>$4.87 \times 10^{11}$</td>
<td>0.2</td>
</tr>
<tr>
<td>$3.73 \times 10^{11}$</td>
<td>0.3</td>
</tr>
<tr>
<td>$2.81 \times 10^{11}$</td>
<td>0.5</td>
</tr>
<tr>
<td>$1.62 \times 10^{11}$</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Experimental Determination of Rate Law

Example: For the reaction ClO + ClO $\rightarrow$ ClOOCl, the following data were obtained:

\[
\begin{align*}
\text{Time (s)} & \quad 0.0 & 0.2 & 0.4 & 0.6 & 0.8 & 1.0 \\
25.5 & \quad 26.0 & 26.5 & 27.0 & 27.5 & 28.0
\end{align*}
\]

Experimental Determination of Rate Law

Example: For the reaction Cl + H$_2$CO $\rightarrow$ HCl + HCO, the following data were obtained:

<table>
<thead>
<tr>
<th>[Cl] (molecule cm$^{-3}$)</th>
<th>time ($\mu$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.00 \times 10^{14}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$4.75 \times 10^{13}$</td>
<td>1.0</td>
</tr>
<tr>
<td>$2.27 \times 10^{13}$</td>
<td>2.0</td>
</tr>
<tr>
<td>$5.52 \times 10^{12}$</td>
<td>4.0</td>
</tr>
<tr>
<td>$6.09 \times 10^{11}$</td>
<td>7.0</td>
</tr>
<tr>
<td>$6.71 \times 10^{10}$</td>
<td>10.0</td>
</tr>
</tbody>
</table>
**Experimental Determination of Rate Law**

**Example:** For the reaction $\text{Cl} + \text{H}_2\text{CO} \rightarrow \text{HCl} + \text{HCO}$, the following data were obtained:

![Graph](image)

**Experimental Determination of Rate Law**

**Example:** For the reaction $\text{CH}_3\text{CHO}(g) \rightarrow \text{CH}_4(g) + \text{CO}(g)$ at 1000 K, the following data were obtained:

<table>
<thead>
<tr>
<th>$[\text{CH}_3\text{CHO}]_0$</th>
<th>$d[\text{CH}_4]/dt$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \times 10^{14}$</td>
<td>$1.47 \times 10^{12}$ s$^{-1}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{13}$</td>
<td>$4.65 \times 10^{10}$ s$^{-1}$</td>
</tr>
<tr>
<td>$2.0 \times 10^{12}$</td>
<td>$4.16 \times 10^{9}$ s$^{-1}$</td>
</tr>
<tr>
<td>$5.0 \times 10^{11}$</td>
<td>$5.20 \times 10^{8}$ s$^{-1}$</td>
</tr>
</tbody>
</table>
Experimental Determination of Rate Law

Example: For the reaction $\text{CH}_3\text{CHO}(g) \rightarrow \text{CH}_4(g) + \text{CO}(g)$ at 1000 K:

Part I. Determine the rate law for the formation of $\text{CH}_4$.

rate = $K [\text{CH}_3\text{CHO}]^y$

$\ln(\text{rate}) = \ln(K) + y \ln[\text{CH}_3\text{CHO}]$

plot $\ln(\text{rate})$ versus $\ln[\text{CH}_3\text{CHO}]$

slope = $y$

$y$-int = $\ln(K)$

Experimental Determination of Rate Law

Example: For the reaction $\text{CH}_3\text{CHO}(g) \rightarrow \text{CH}_4(g) + \text{CO}(g)$ at 1000 K:

plot $\ln(\text{rate})$ versus $\ln[\text{CH}_3\text{CHO}]$

Slope = 1.50

Y-int = -20.33
Experimental Determination of Rate Law

Example: For the reaction CH$_3$CHO(g) $\rightarrow$ CH$_4$(g) + CO(g) at 1000 K:
Part I. Determine the rate law for the formation of CH$_4$.
\[
\text{rate} = K \left[\text{CH}_3\text{CHO}\right]^y
\]
\[
y = 1.50
\]
\[
\ln(K) = -20.33 \quad \Rightarrow K = 1.48 \times 10^{-9}
\]
\[
\text{rate} = 1.48 \times 10^{-9} \left[\text{CH}_3\text{CHO}\right]^{3/2}
\]

Experimental Determination of Rate Law

Example (con’t.): For the reaction CH$_3$CHO(g) $\rightarrow$ CH$_4$(g) + CO(g) at 1000 K:
Part II. If we assume the reaction
\[
\text{CH}_3\text{CHO}(g) \rightarrow \text{CH}_4(g) + \text{CO}(g) \quad k_1
\]
is an elementary reaction, does this mechanism predict the correct rate law?
\[
\frac{d[\text{CH}_4]}{dt} = k_1 \left[\text{CH}_3\text{CHO}\right]
\]
This is not the measured rate law!
**Experimental Determination of Rate Law**

Example (con’t.): For the reaction \( \text{CH}_3\text{CHO}(g) \rightarrow \text{CH}_4(g) + \text{CO}(g) \) at 1000 K:

Part II. A reaction mechanism that correctly predicts the measured rate law is:

- \( \text{CH}_3\text{CHO} \rightarrow \text{CH}_3 + \text{CHO} \quad k_1 \)
- \( \text{CH}_3\text{CHO} + \text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_3\text{CO} \quad k_2 \)
- \( \text{CH}_3\text{CO} \rightarrow \text{CH}_3 + \text{CO} \quad k_3 \)
- \( \text{CH}_3 + \text{CH}_3 \rightarrow \text{CH}_3\text{CH}_3 \quad k_4 \)

\[
\frac{d[\text{CH}_4]}{dt} = k_2 \left( \frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}
\]

---

**Experimental Determination of Rate Law**

- A reaction mechanism can not be proven correct, it can only be proven incorrect
- If a proposed mechanism correctly predicts the observed rate law, it is possibly the “true” mechanism, but there may be other proposed mechanisms that also correctly predict the observed behavior.
**Rate Coefficients**

- The rate coefficient, \( k \), of an elementary reaction is a measure of how fast that reaction occurs.
- For a 1\(^{st} \) order reaction, the expression relating the concentration of reactant A and the rate coefficient is:
  \[
  [A(t)] = [A]_0 \exp\{-kt\}
  \]
- This can be manipulated to the form:
  \[
  \ln([A(t)]/[A]_0) = -kt
  \]

**Rate Coefficients**

- The half-life of a reaction is the time required for the reactants to be reduced to \( \frac{1}{2} \) their initial concentration:
  \[
  [A(t_{1/2})] = \frac{1}{2} [A]_0
  \]
- If we substitute these values into the 1\(^{st} \) order expression, we get
  \[
  \ln\left(\frac{1/2[A]_0}{[A]_0}\right) = -kt_{1/2} \quad \Rightarrow \quad \ln\left(\frac{1}{2}\right) = -kt_{1/2}
  \]
  \[
  \ln(1) - \ln(2) = -kt_{1/2} \quad \Rightarrow \quad t_{1/2} = \frac{\ln(2)}{k}
  \]
Rate Coefficients

- Examples of 1\textsuperscript{st} order kinetics include radioactive decay—the half-life of a radio-isotope is the time it takes for the amount of that isotope to be decreased by a factor of two.
- Because 1\textsuperscript{st} order half-lives are constant (half-life does not depend on concentration of isotope) this can be used to date materials containing radioactive elements.

Rate Coefficients

- The half-life of a 2\textsuperscript{nd} order reaction is given by:
  \[ t_{1/2} = \frac{1}{k[A]_0} \]
- For second order kinetics, the half-life depends on the initial concentration of the reactant, so the half-life get longer as the concentration decreases.
Temperature Dependence of Rate Coefficients

- The value of the rate coefficient, $k$, usually changes with temperature.
- The Arrhenius Equation expresses the temperature dependence of the rate coefficient:
  \[ k(T) = A \exp\left\{-\frac{E_a}{RT}\right\} \]
  where
  - $A$ is called the pre-exponential factor or frequency factor
  - $E_a$ is the activation energy

For the reaction:

\[
\text{O} + \text{O}_3 \rightarrow 2 \text{O}_2
\]

the rate coefficient has an Arrhenius expression of

\[ k(T) = 8.0 \times 10^{-12} \exp\{-17.1 \text{ kJ}/RT\} \]

in units of cm$^3$ molecule$^{-1}$ s$^{-1}$

- The reaction has an activation barrier of 17.1 kJ mol$^{-1}$—this means that the reactants must collide with at least that much energy in order proceed to products.
The $O + O_3 \rightarrow 2 O_2$ reaction is very exothermic:

$$\Delta H_{\text{rxn}}^0 = -391.9 \text{ kJ mol}^{-1}$$

but at room temperature, the rate coefficient is only

$$8.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This is very slow, indicating that only one in every 40,000 collisions between O and $O_3$ results in reaction. The inefficiency of reaction is due to the large activation barrier.
Temperature Dependence of Rate Coefficients

- To determine the activation barrier of a reaction, we must measure the rate coefficient at a number of different temperatures:
  \[ k(T) = A \exp\{-E_a/RT\} \]
  \[ \ln(k) = \ln(A) - E_a/RT \]
- If we plot \( \ln(k) \) vs \( 1/T \), the graph has:
  slope = \(-E_a/R\)
  y-int = \( \ln(A) \)

Arrhenius plot for the reaction:
HO₂ + ClO
slope = 312.1
y-int = -26.58
\( E_a = -R \cdot \text{slope} \)
\( = -(8.314)(312.1) \)
\( = -2.59 \text{ kJ mol}^{-1} \)
\( A = \exp\{y\text{-int}\} \)
\( = \exp\{-26.82\} \)
\( = 2.9 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1}\text{s}^{-1} \)

A catalyst is a species that participates in a reaction, is regenerated in the reaction mechanism, and has the effect of increasing the net rate of reaction relative to the absence of the catalyst.

Catalytic destruction of ozone:
The reaction $O + O_3 \rightarrow 2 O_2$ occurs naturally in the stratosphere, but the rate coefficient at stratospheric temperatures is

$$k(220 \text{ K}) = 7.0 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

This is very slow and does not account for very much ozone loss in the “natural” stratosphere.
There is a catalytic reaction mechanism involving chlorine atoms that accomplishes the same thing chemically:

\[
\begin{align*}
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \quad k_1 \\
\text{ClO} + \text{O} & \rightarrow \text{Cl} + \text{O}_2 \quad k_2 \\
\text{net:} \quad \text{O} + \text{O}_3 & \rightarrow 2 \text{O}_2
\end{align*}
\]

The rate coefficients for these two reactions are:

\[
\begin{align*}
k_1(T) &= 2.9 \times 10^{-11} \exp\{-2.16 \text{ kJ/RT}\} \\
k_2(T) &= 3.0 \times 10^{-11} \exp\{+0.58 \text{ kJ/RT}\}
\end{align*}
\]
This chlorine catalytic cycle has the same net reaction as the $O + O_3$ reaction, but forms products about 200 times faster than the direct $O + O_3$ reaction.

This is due to the much smaller activation barrier in the catalytic mechanism—it is much easier for $O_3$ to react with chlorine atoms than with oxygen atoms, so the overall process is faster.