Announcements

Chem 11 Exam 1
December 18
Schmitt Hall 114 (Non-majors) C-109 (Majors)
6PM - 7:30PM
Chapter 12, 13 & 16
Format (40MC + 2 long questions)

Problem Set: Kinetics Chapter 16
3,4,5,11,14,16,18,20,21,22,26,28,29,31,33,36,38,41,50,59,67,72,74,76,78,79,80,82,87

Chapter 16
Kinetics: Rates and Mechanisms of Chemical Reactions

16.1 Factors that influence reaction rates
16.2 Expressing the reaction rate, average, instantaneous and initial rates
16.3 The rate law and its components
16.4 Integrated rate laws: Concentration changes over time
16.5 Reaction mechanisms: Steps in the overall reaction
16.6 Catalysis: Speeding up a chemical reaction

Different theories tell us different things.

Thermodynamic theory: gives information on the energetics of a reaction and whether a chemical reaction can occur, but no information on how fast a reaction can occur.

Kinetics gives information on how fast or slow a chemical reaction is, but it can not tell us the energetics or the extent a reaction will occur.

Equilibrium theory tells us the extent a chemical reaction occurs but not on how fast it will occur.

Kinetics Concept Map

Kinetics focus is “the rate” at which concentrations of reactants or products change with time.

Rate = k [A]^m [B]^n

Time: 0
Five factors affect the rate of a chemical reaction.

1. **Nature of Reactants**—bonds break and form during a reaction. Element and compounds have "inherent tendencies to react".

2. **Concentration**—molecules must collide to react; the more molecules there are—the faster the reaction.

3. **State or Phase of reacting molecules** must mix to collide, gas, liquids and solids have different surface area to volume ratios varying reactivity.

4. **Temperature**—molecules must collide with a minimum energy in order to react. Higher temperatures mean higher KE during a collision.

5. **Presence of a catalyst**: catalyst increase reaction rates without being consumed in the reaction itself.

A reaction rate is expressed as the change in the concentration (molarity) of a reactant or a product a change in time. By convention, rate is always a positive number with units of Molarity/sec.

For every 1 mol C₃H₈ (M) per unit time requires 5 mol O₂ per unit time
For every 1 mol C₃H₈ (M) per unit time produces 3 mol CO₂ per unit time
For every 1 mol C₃H₈ (M) per unit time produces 4 mol H₂O per unit time

\[
\text{rate} = -\frac{\Delta[A]}{\Delta t} = -5 \times \frac{\Delta[C₃H₈]}{\Delta t} = \frac{5}{3} \frac{\Delta[CO₂]}{\Delta t} = \frac{1}{4} \frac{\Delta[H₂O]}{\Delta t}
\]

We use a “unified rate” such that the stoichiometry is considered and a single positive value rate of reaction can be written.

\[
\text{rate} = \frac{\Delta[C₃H₈]}{\Delta t} = \frac{1}{5} \frac{\Delta[O₂]}{\Delta t} = \frac{1}{3} \frac{\Delta[CO₂]}{\Delta t} = \frac{1}{4} \frac{\Delta[H₂O]}{\Delta t}
\]

A balanced chemical equation relates the rates of disappearance of reactants to the rate of appearance of products.

\[
C₃H₈ (g) + 5O₂ (g) \longrightarrow 3CO₂ (g) + 4H₂O(g)
\]

To avoid the ambiguity in a reaction rate, we use a “scaled or unified rate” such that one number describes the rate of change of all reactants and all products.

\[
C₃H₈ (g) + 5O₂ (g) \longrightarrow 3CO₂ (g) + 4H₂O(g)
\]

Suppose you are given the following generalized reaction.

\[aA + bB \longrightarrow cC + dD\]

What is the rate of the chemical reaction written or expressed as a function of change in \([A]\), \([B]\), \([C]\) and \([D]?)
Suppose you are given the following generalized reaction.

\[ aA + bB \rightarrow cC + dD \]

What is the rate of reaction written as a function of change in \([A], [B], [C]\) and \([D]\)?

\[
\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}
\]

Suppose you are monitoring the reaction below. It is found that the rate of appearance of NO is measured and found to be 2 Molar sec\(^{-1}\). What is the rate of disappearance, \(\frac{\Delta[N_2O_5]}{\Delta t}\) and the rate of formation of \(O_2\)?

\[ 2 \text{N}_2\text{O}_5(g) \rightarrow 4 \text{NO}_2(g) + \text{O}_2(g) \]

Suppose you are given the following generalized reaction:

\[ aA + bB \rightarrow cC + dD \]

What is the rate of reaction written as a function of change in \([A], [B], [C], [D]\)?

\[
\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}
\]

Suppose we have drive to Alabang starting from White Plains.

(a) Express the reaction rate in terms of changes in \([H_2], [O_2], [H_2O]\) with time.

(b) If \([O_2]\) decreases at 0.23 mol O\(_2\)/L/s, at what rate is \([H_2O]\) increasing?

\[ 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) \]

Hydrogen gas is used for fuel aboard the space shuttle and may be used by automobile engines in the near future.

\[ 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) \]

Hydrogen gas is used for fuel aboard the space shuttle and may be used by automobile engines in the near future.

\[ 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) \]

We need to understand average, instantaneous and initial rates of a chemical reaction.

Suppose we have drive to Alabang starting from White Plains.

(a) Express the reaction rate in terms of changes in \([H_2], [O_2], [H_2O]\) with time.

(b) If \([O_2]\) decreases at 0.23 mol O\(_2\)/L/s, at what rate is \([H_2O]\) increasing?

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Hydrogen gas is used for fuel aboard the space shuttle and may be used by automobile engines in the near future.

\[ 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) \]
We can measure the distance from a point on Edsa by looking at the odometer of the car and noting the distance & time from the starting point.

rate of speed = \frac{\Delta \text{Distance}}{\Delta \text{time}} = \frac{\Delta D}{\Delta t} = \frac{D_f - D_i}{T_f - T_i}

<table>
<thead>
<tr>
<th>Place</th>
<th>Time (min)</th>
<th>Distance Traveled (km)</th>
<th>Rate of Speed (km/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ateneo</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sucat</td>
<td>20</td>
<td>25</td>
<td>1.25 km/min</td>
</tr>
<tr>
<td>Alabang</td>
<td>40</td>
<td>30</td>
<td>0.75 km/min</td>
</tr>
<tr>
<td>Canalubang</td>
<td>60</td>
<td>60</td>
<td>1.0 km/min</td>
</tr>
</tbody>
</table>

Note there are different rates or speeds depending on traffic and where we are.

We can choose any two data points to determine an average rate during the chemical reaction \( A \implies B \)?

What is the average rate of disappearance of \( A \) after 40 secs?

rate = \frac{\Delta [A]}{\Delta t} = \frac{[A_i] - [A_{t=0}]}{t - t_0}

\( = \frac{(12M - 40M)}{(40 s - 0 s)} = 11M/s \)

An Example: Reduction of Bromine to Bromide

\( \text{Br}_2(aq) + \text{HCOOH (aq)} \longrightarrow 2\text{Br}^- (aq) + 2\text{H}^+ (aq) + \text{CO}_2 (g) \)

We can easily monitor the change in \([\text{Br}]\) with an lab instrument.

Beer's Law

\( \text{Absorbance} = \epsilon \text{C} \)

\( 393 \text{ nm light} \)

Detector

Suppose we monitor the color change and we plot the reaction data:

\( \text{Br}_2(aq) + \text{HCOOH (aq)} \longrightarrow 2\text{Br}^- (aq) + 2\text{H}^+ (aq) + \text{CO}_2 (g) \)

**Lab Data**

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>([\text{Br}]) (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>12.0 mM</td>
</tr>
<tr>
<td>50.0</td>
<td>10.0 mM</td>
</tr>
<tr>
<td>100.0</td>
<td>8.46 mM</td>
</tr>
<tr>
<td>150.0</td>
<td>7.10 mM</td>
</tr>
<tr>
<td>200.0</td>
<td>5.96 mM</td>
</tr>
<tr>
<td>250.0</td>
<td>5.00 mM</td>
</tr>
<tr>
<td>300.0</td>
<td>4.20 mM</td>
</tr>
<tr>
<td>350.0</td>
<td>3.55 mM</td>
</tr>
<tr>
<td>400.0</td>
<td>2.96 mM</td>
</tr>
</tbody>
</table>

average rate of disappearance = \frac{\Delta [\text{Br}]_i}{\Delta t} = \frac{[\text{Br}]_{\text{final}} - [\text{Br}]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>([\text{Br}]) (mM)</th>
<th>(\Delta [\text{Br}])</th>
<th>Avg Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>12.0 mM</td>
<td>2.00</td>
<td>0.04</td>
</tr>
<tr>
<td>50.0</td>
<td>10.0 mM</td>
<td>1.54</td>
<td>0.031</td>
</tr>
<tr>
<td>100.0</td>
<td>8.46 mM</td>
<td>1.36</td>
<td>0.027</td>
</tr>
<tr>
<td>150.0</td>
<td>7.10 mM</td>
<td>1.14</td>
<td>0.023</td>
</tr>
<tr>
<td>200.0</td>
<td>5.96 mM</td>
<td>0.96</td>
<td>0.019</td>
</tr>
<tr>
<td>250.0</td>
<td>5.00 mM</td>
<td>0.80</td>
<td>0.016</td>
</tr>
<tr>
<td>300.0</td>
<td>4.20 mM</td>
<td>0.65</td>
<td>0.013</td>
</tr>
<tr>
<td>350.0</td>
<td>3.55 mM</td>
<td>0.59</td>
<td>0.01</td>
</tr>
<tr>
<td>400.0</td>
<td>2.96 mM</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Just like driving in a car and sometimes going fast, then slow, then fast again—the average rate of a chemical reaction also varies over time!
The average rate of disappearance of \( \text{Br}_2 \) is the slope of the line between any two points on the curve. We can pick any two points and get an average rate.

\[
\text{rate} = -\frac{[\text{Br}_2]_{\text{final}} - [\text{Br}_2]_{\text{initial}}}{\Delta t} = -\frac{[3]_{\text{final}} - [12]_{\text{initial}}}{400 - 0}
\]

The instantaneous rate of disappearance of \( \text{Br}_2 \) is the slope of the line tangent at any point along the curve.

\[
\text{Instantaneous Rate of Change} = \frac{[\text{Br}_2]_{\text{final}} - [\text{Br}_2]_{\text{initial}}}{\Delta t} = \frac{-\Delta [\text{Br}_2]}{\Delta t}
\]

There are an infinite number of instantaneous rate along the curve but not all are relevant in chemistry!

Because chemical reactions are reversible as we move away from \( t = 0 \), chemists are interested in the “initial” instantaneous rate.

\[
\text{O}_2(g) + 2\text{NO}(g) \rightleftharpoons 2\text{NO}_2(g)
\]

Use method of initial rates (i.e. measure rates close to \( t=0 \) sec) and we avoid \( k_{\text{reverse}} \) and convolution of kinetic data!

One goal of a kinetic experiment is to measure data to determine an equation that “summarizes” the “rate” at which a particular reaction occurs.

Consider: \( a \text{A} + b \text{B} \rightarrow c \text{C} + d \text{D} \)

\[
\text{Rate} = k [\text{A}]^m [\text{B}]^n
\]

- \( k \) is the temperature dependent “rate constant”.
- \( m \) and \( n \) are experimentally determined, and indicate how sensitive the chemical reaction is to changes in [A] and [B].
- We call the sum of \( m + n \) the “order of the reaction”.
- Rate Units are always (M/sec) so units of \( k \) change!
**Connecting Dots: Rate law vernacular and usage.**

Suppose we do a kinetic study of the reaction of \( \text{H}_2 \) and \( \text{ICl} \)

\[
\text{H}_2 + \text{ICl} \rightarrow \text{I}_2 + 2\text{HCl}
\]

The rate law containing unknown variables can be written immediately with unknowns \( k, m \) and \( n \).

\[
\text{Rate} = k [\text{H}_2]^m [\text{ICl}]^n
\]

Obtaining (or be provided with) experimental data allows us to calculate the unknowns \( k, m \) and \( n \).

**Rate** = \( k [\text{H}_2]^2 [\text{ICl}]^1 = k [\text{H}_2] [\text{ICl}] \)

Chemists then say "the reaction is 2nd order with respect to \( \text{H}_2 \) and 1st order with respect to \( \text{ICl} \)." The **overall reaction order** \( m + n = 3 \) (3rd order).

---

**Reaction rates** always have units of \( \text{M/sec} \). The units of the rate constant, \( k \), in the rate law therefore depend on the exponents in the rate law.

Consider a **simple reaction**:

\[
\text{A} \rightarrow \text{C}
\]

\[
\text{rate (M/sec)} = k [\text{A}]^n
\]

1. If \( m = 0 \) then \( [\text{A}]^0 = 1 \) rate is a constant = \( k \) must have units of \( \text{M/sec} \)
2. If \( m = 1 \) \( [\text{A}]^1 = [\text{A}] \) means rate depends linearly on concentration of \( \text{A} \), \( k \) must have units of \( \text{s}^{-1} \)
3. If \( m = 2 \) \( [\text{A}]^2 \) the rate quadruples when \( \text{A} \) is doubled and \( k \) must have units of \( 1/\text{M} \cdot \text{s}^{-1} \)

---

**The Method of Initial Rates** is used to determine the reaction "rate" by choosing a time very close to \( t = 0 \) where we can rid the \( k_{\text{reverse}} \) from the rate.

\[
\text{O}_2 (\text{g}) + 2\text{NO (g)} \xrightarrow{k_{\text{forward}}} 2\text{NO}_2 (\text{g})
\]

\[
\text{O}_2 (\text{g}) + 2\text{NO (g)} \xrightarrow{k_{\text{forward}}} 2\text{NO}_2 (\text{g})
\]

Our math is simplified greatly in this regime.

---

For each of the following reactions, determine the reaction order with respect to each reactant and the **overall reaction order** from the given rate law.

Note that the rate laws were determined experimentally not from the equations given.

(a) \( 2\text{NO(g)} + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \); rate = \( k[\text{NO}]^2[\text{O}_2] \)

(b) \( \text{CH}_3\text{CHO(g)} \rightarrow \text{CH}_4(g) + \text{CO}(g) \); rate = \( k[\text{CH}_3\text{CHO}]^{3/2} \)

(c) \( \text{H}_2\text{O}_2(l) + 3\text{I}^- + 2\text{H}^+(aq) \rightarrow 2\text{I}_2 + 2\text{H}_2\text{O}(l) \); rate = \( k[\text{H}_2\text{O}_2][\text{I}^-] \)

---

Connecting the Kinetic Dots

**Suppose we are asked to determine the rate law, \( k \) the rate constant, and the order of the reaction. How do we do it?**

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

1. Write a balanced chemical equation ✓
2. Write the generic rate law expression with all unknowns (you don’t need any data to do this just a balanced equation) ✓

\[
\text{rate} = k [\text{O}_2]^m [\text{NO}]^n
\]

3. To solve the equation with needed experimental data either from a lab measurement or in Chem 11 from data provided. There are many unknowns \( (k, m \text{ and } n) \) but we devise ways to simplify. ✓

4. Analyze the data using mathematics that we must get comfortable with. Not hard once you get use to it.
Given the experimental data on the production of nitrogen dioxide from oxygen and nitrogen monoxide: determine the rate law, the total order of the reaction and the rate constant $k$.

$$\text{O}_2 (g) + 2\text{NO} (g) \rightarrow 2\text{NO}_2 (g)$$

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$[\text{O}_2]$ (mol/L)</th>
<th>$[\text{NO}]$ (mol/L)</th>
<th>Measured Rate $\text{rate}$ (mol/L s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.10 \times 10^{-2}$</td>
<td>$1.30 \times 10^{-2}$</td>
<td>$3.21 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>$2.20 \times 10^{-2}$</td>
<td>$1.30 \times 10^{-2}$</td>
<td>$6.40 \times 10^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>$1.10 \times 10^{-2}$</td>
<td>$2.60 \times 10^{-2}$</td>
<td>$12.8 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Use data ratios to eliminate unknowns in the rate law

Experiment | Initial reactant concentrations (mol/L) | Initial rate $\text{rate}$ (mol/L s) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.10 \times 10^{-2}$  $1.30 \times 10^{-2}$</td>
<td>$3.21 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>$2.20 \times 10^{-2}$  $1.30 \times 10^{-2}$</td>
<td>$6.40 \times 10^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>$1.10 \times 10^{-2}$  $2.60 \times 10^{-2}$</td>
<td>$12.8 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k [\text{O}_2]^n [\text{NO}]^m}{k [\text{O}_2]^1 [\text{NO}]^1} = \left( \frac{[\text{O}_2]^3}{[\text{NO}]} \right)^n$$

$$\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{6.40 \times 10^{-3} \, M \, s^{-1}}{3.21 \times 10^{-3} \, M \, s^{-1}} = \left( \frac{2.20 \times 10^{-2} \, mol/L}{1.10 \times 10^{-2} \, mol/L} \right)^m$$

$$\frac{\text{Rate}_3}{\text{Rate}_1} = 4 = (2.00)^m \quad m = 2$$

$$\text{rate} = k [\text{O}_2]^2 [\text{NO}]^2$$

We can summarize our answer:

$$\text{O}_2 (g) + 2\text{NO} (g) \rightarrow 2\text{NO}_2 (g)$$

**Rate Law:** rate = $k [\text{O}_2]^1 [\text{NO}]^2$

**Total Order:** $(1 + 2)$ third order overall.

**Rate constant $k$** (from any of the data set)

$$k = \frac{\text{rate}}{[\text{O}_2][\text{NO}]^2} = \frac{3.21 \times 10^{-3} \, M/\text{sec}}{1.10 \times 10^{-2} \, M \times (1.30 \times 10^{-2} \, M)^2}$$

$$k = 1.73 \times 10^3 \, M^{-2} \, \text{sec}^{-1}$$

In many instances we can determine the order of the reaction by inspection of the data.

$$aA + bB \rightarrow cC + dD \quad \text{Rate} = k \, [A]^n \, [B]^m$$

Ratio of Rates

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[A]^n [B]^m}{k[A]^1 [B]^1}$$

Many gaseous reactions occur in a car engine and exhaust system. One such reaction is as follows:

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

Use the following data to determine the individual and overall reaction orders.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial rate (M/s)</th>
<th>Initial $[\text{NO}_2]$ (M)</th>
<th>Initial $[\text{CO}]$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.005</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>0.40</td>
<td>0.10</td>
</tr>
<tr>
<td>3</td>
<td>0.0050</td>
<td>0.10</td>
<td>0.20</td>
</tr>
</tbody>
</table>
The rate law is nice--as it ties the rate of reaction to reactant concentration, but it would be better to have a function that can tell us the concentration of [A] at anytime, t.

\[
rate = k \ [\text{NO}_2]^m[\text{CO}]^n
\]

First, choose any two experiments in which [CO] remains constant and [NO\textsubscript{2}] varies.

\[
\frac{rate_2}{rate_1} = \frac{k \ [\text{NO}_2]^m[\text{CO}]^n}{k \ [\text{NO}_2]^m[\text{CO}]^n} = \left(\frac{[\text{CO}]}{[\text{CO}]_1}\right)^n = \left(\frac{[S]}{[S]_1}\right)^n
\]

The reaction is 2nd order in NO\textsubscript{2}.

\[
\frac{rate_3}{rate_1} = \frac{k \ [\text{NO}_2]^m[\text{CO}]^n}{k \ [\text{NO}_2]^m[\text{CO}]^n} = \left(\frac{[\text{CO}]}{[\text{CO}]_1}\right)^n = \left(\frac{[I]}{[I]_1}\right)^n
\]

The reaction is zero order in CO.

**Rate Law:** rate = \(k \ [\text{NO}_2]^2[\text{CO}]^0 = k \ [\text{NO}_2]^2\)

The reaction is second order overall.

---

**A Summary So Far and A Transition......**

1. Rate of Disappearance = \(-\frac{1}{\bar{a}} \frac{\Delta[A]}{\Delta t} = \frac{1}{\bar{b}} \frac{\Delta[B]}{\Delta t}\)

2. Rate Law: Rate = \(k \ [A]^m \ [B]^n\) Order of A Reaction = \(m+n\)

3. Rate Constant: \(k\): temperature and reaction dependent and determined from experimental data

4. We use the method of initial rates (and ratios of data) to determine rate law, order of reaction and rate constant.

**Integrated rate laws** are functions derived by solving the differential form of the rate law using integral calculus. The new functions link reactant concentration with time.

**Differential Form**

<table>
<thead>
<tr>
<th>Oth</th>
<th>1st</th>
<th>2nd</th>
</tr>
</thead>
</table>

**Integrated rate laws**

\[
[A]_t = -kn + [A]_{t=0}
\]

\[
\ln[A]_t = -kt + \ln[A]_{t=0}
\]

\[
\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}
\]
For each differential form we can separate the variables and integrate each giving 3 new functions.

\[ \text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt} = k[A] \]

\[ \int \frac{d[A]}{[A]} = -k \int dt \]

\[ \ln[A]_t = -k t + \ln[A]_{t=0} \]

This equation links \([A]\) with any time \(t\) during the reaction. \(k\) and \([A]_0\) must be known.

### Summary of Kinetic Reaction Equations

<table>
<thead>
<tr>
<th></th>
<th>(0th) Order</th>
<th>(1st) Order</th>
<th>(2nd) Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate law</td>
<td>(rate = k)</td>
<td>(rate = k[A])</td>
<td>(rate = k[A]^2)</td>
</tr>
<tr>
<td>Integrated rate law in straight-line form</td>
<td>([A]_0 = -k t + [A]_0)</td>
<td>(\ln[A]_t = -k t + \ln[A]_0)</td>
<td>(1/[A]_0 = -k t + 1/[A]_0)</td>
</tr>
<tr>
<td>Straight line plot</td>
<td>([A]_t) vs (t)</td>
<td>(\ln[A]_t) vs (t)</td>
<td>(1/[A]_0) vs (t)</td>
</tr>
<tr>
<td>Slope, y-intercept</td>
<td>(-k, [A]_0)</td>
<td>(-k, \ln[A]_0)</td>
<td>(k, 1/[A]_0)</td>
</tr>
<tr>
<td>Units for (k)</td>
<td>mol/L·s</td>
<td>1/s</td>
<td>1/M·s</td>
</tr>
</tbody>
</table>

### 0th Order Reaction: Deriving the Integral Form

\[ -\frac{\Delta[A]}{\Delta t} = \frac{d[A]}{dt} = k \]

\[ d[A] = -k \, dt \]

\[ \int_{A_i}^{A_t} dA = -k \int_{0}^{t} dt \]

\[ [A]_t - [A]_{t=0} = -k t \]

\[ [A]_t = -k t + [A]_{t=0} \]

Plotting \([A]\) vs time gives a line with \(-k = \text{slope}\).  

\[ y = m x + b \]

### 1st Order Reaction: Deriving the Integral Form

\[ -\frac{\Delta[A]}{\Delta t} = \frac{d[A]}{dt} = k[A] \]

\[ \frac{d[A]}{[A]} = -k \, dt \]

\[ \int_{A_i}^{A_t} \frac{d[A]}{[A]} = \int_{0}^{t} -k \, dt \]

\[ \ln[A]_t - \ln[A]_{t=0} = -k t \]

\[ \ln[A]_t = -k t + \ln[A]_{t=0} \]

\[ y = m x + b \]

Plotting \(\ln[A]_t\) vs time gives a line with \(-k = \text{slope}\).  

### 2nd Order Reaction: Deriving the Integral Form

\[ -\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt} = k[A]^2 \]

\[ \frac{d[A]}{[A]^2} = -k \, dt \]

\[ \int_{A_i}^{A_t} \frac{d[A]}{[A]^2} = \int_{0}^{t} -k \, dt \]

\[ \frac{1}{[A]_t} + \frac{1}{[A]_0} = -kt \]

\[ \frac{1}{[A]_t} = -kt + \frac{1}{[A]_0} \]

\[ y = m x + b \]

Plotting \(1/[A]_t\) vs time gives a line with \(+k = \text{slope}\).  

<table>
<thead>
<tr>
<th></th>
<th>(0th) order</th>
<th>(1st) order</th>
<th>(2nd) order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate law</td>
<td>(rate = k)</td>
<td>(rate = k[A])</td>
<td>(rate = k[A]^2)</td>
</tr>
<tr>
<td>Units for (k)</td>
<td>mol/L·s</td>
<td>1/s</td>
<td>1/M·s</td>
</tr>
<tr>
<td>Integrated rate law in straight-line form</td>
<td>([A]_0 = -k t + [A]_0)</td>
<td>(\ln[A]_t = -k t + \ln[A]_0)</td>
<td>(1/[A]_0 = -k t + 1/[A]_0)</td>
</tr>
<tr>
<td>Straight line plot</td>
<td>([A]_t) vs (t)</td>
<td>(\ln[A]_t) vs (t)</td>
<td>(1/[A]_0) vs (t)</td>
</tr>
<tr>
<td>Slope, y-intercept</td>
<td>(-k, [A]_0)</td>
<td>(-k, \ln[A]_0)</td>
<td>(k, 1/[A]_0)</td>
</tr>
</tbody>
</table>
Suppose the following data was given for the decomposition of N₂O₅. Determine the order of the reaction and the rate constant.

\[
2\text{N}_2\text{O}_5 \rightarrow 2\text{N}_2 + 5\text{O}_2
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[N₂O₅]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0165</td>
</tr>
<tr>
<td>10</td>
<td>0.0124</td>
</tr>
<tr>
<td>20</td>
<td>0.0093</td>
</tr>
<tr>
<td>30</td>
<td>0.0071</td>
</tr>
<tr>
<td>40</td>
<td>0.0053</td>
</tr>
<tr>
<td>50</td>
<td>0.0039</td>
</tr>
<tr>
<td>60</td>
<td>0.0029</td>
</tr>
</tbody>
</table>

First, we transform the original data in Excel as shown below in the table.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[N₂O₅]</th>
<th>ln[N₂O₅]</th>
<th>1/[N₂O₅]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0165</td>
<td>-4.104</td>
<td>60.6</td>
</tr>
<tr>
<td>10</td>
<td>0.0124</td>
<td>-4.390</td>
<td>80.6</td>
</tr>
<tr>
<td>20</td>
<td>0.0093</td>
<td>-4.68</td>
<td>1.1 \times 10^2</td>
</tr>
<tr>
<td>30</td>
<td>0.0071</td>
<td>-4.95</td>
<td>1.4 \times 10^2</td>
</tr>
<tr>
<td>40</td>
<td>0.0053</td>
<td>-5.24</td>
<td>1.9 \times 10^2</td>
</tr>
<tr>
<td>50</td>
<td>0.0039</td>
<td>-5.55</td>
<td>2.6 \times 10^2</td>
</tr>
<tr>
<td>60</td>
<td>0.0029</td>
<td>-5.84</td>
<td>3.4 \times 10^2</td>
</tr>
</tbody>
</table>

Then we plot the Excel data

The graph that gives a straight line shows us the order of the reaction.

- \( k = \text{slope of the line} = -4.68 - (-4.104)/(20 \text{ s} - 0 \text{ s}) = 0.0288 \text{ sec}^{-1} \)

The linear ln plot shows that the reaction is 1st order

Rate = \( k [\text{N}_2\text{O}_5]^m \)

Plot shows that the order m = 1

Rate = \( k [\text{N}_2\text{O}_5] \)

Now pick any two points from the 1st order data and determine k.

\( -k = \text{slope of the line} = -4.68 - (-4.104)/(20 \text{ s} - 0 \text{ s}) = -0.0288 \text{ sec}^{-1} \)

The half-life, \( t_{1/2} \), is the time for the initial concentration \([A]_{t=0}\) to reduce to 1/2 \([A]_{t=0}\).

The half-life, \( t_{1/2} \), depends on the order of the reaction.

\[
2\text{N}_2\text{O}_5 \rightarrow 2\text{N}_2 + 5\text{O}_2
\]

Half-lives, \( t_{1/2} \), can be obtained for all the integrated rate laws by substituting 1/2 \([A]_{t=0}\) for \([A]_{t=0}\) in each integrated equation.

\[
\begin{align*}
0\text{th Order} & \quad [A]_{t} - [A]_{0} = -kt \\
& \quad \frac{1}{2}[A]_{0} - [A]_{t} = -kt \\
& \quad \frac{1}{2}[A]_{0} = kt \\
& \quad \frac{1}{2} = \frac{[A]_{0}}{2k} \\
t_{1/2} = \frac{[A]_{0}}{2k} \\
1\text{st Order} & \quad \ln[A]_{t} - \ln[A]_{0} = -kt \\
& \quad \ln(\frac{1}{2}[A]_{0}) - \ln[A]_{t} = -kt \\
& \quad \ln(1/2) = -kt \\
& \quad \ln(1/2) = \frac{1}{t_{1/2}} \\
& \quad t_{1/2} = 0.693/k \\
2\text{nd Order} & \quad \frac{1}{[A]_{t}} - \frac{1}{[A]_{0}} = kt \\
& \quad \frac{1}{[A]_{0}} - \frac{1}{[A]_{t}} = -kt \\
& \quad \frac{1}{[A]_{0}} = kt \\
& \quad t_{1/2} = 1/k[A]_{0}
\end{align*}
\]
Transforming the integrated rate laws into exponential form is useful for time-dependent questions.

\[
[A]_t = [A]_{t=0} \exp(-kt)
\]

\[
\ln[A]_t = -k t + \ln[A]_{t=0}
\]

We can use the logarithmic form or the exponential form of the integrated rate law.

\[
\ln[A]_t = -k t + \ln[A]_0
\]

\[
\ln[A]_t - \ln[A]_0 = -k t
\]

\[
\frac{\ln[A]_t}{[A]_0} = -k t
\]

\[
\exp\left(\frac{\ln[A]_t}{\ln[A]_0}\right) = \exp(-k t)
\]

\[
[A]_t = A_0 \exp(-k t)
\]

\[
\frac{[A]_t}{[A]_0} = \exp(-k t)
\]

Fractional Form useful for problems

Radioactive decay is a well known first order kinetic process. Suppose the half-life of radioactive I-132 is 2.295h. What percentage remains after 24 hours?

For a 1st order reaction \( t_{1/2} = 0.693/k \)

Rearranging: 

\( k = \frac{0.693}{2.295} \text{ hr} = 0.302 \text{ h}^{-1} \)

Use 1st order integrated law: 

\[ \ln[A]_t = -k t + \ln[A]_0 \]

\[ \ln[A]_t - \ln[A]_0 = -k t \]

\[ \ln \left( \frac{[A]_t}{[A]_0} \right) = \ln(\frac{[A]_t}{[A]_0}) - kt \]

\[ \exp(\ln(\frac{[A]_t}{[A]_0})) = \exp(-kt) \]

\[ \frac{[A]_t}{[A]_0} = \exp(-k t) = \exp(-0.302 \, 24) = 0.000711 \]

\[ \%A_{\text{remaining}} = 0.000711 \times 100 = 0.0711 \%

Imagine that the rate law for the reaction of \( A \rightarrow B \) is zero order in reactant \( A \) and that the rate constant, \( k \), is known to be 0.02 M/s. If the reaction begins with 1.50 M \( A \), what is \([A]\) 15 seconds after the reaction starts?

The problem states it is 0th Order so we must use the 0th Order Integrated Rate Law to determine \([A]\) after 15 seconds elapses.

\[ [A]_t = -k t + [A]_0 \]

\[ = -(0.02 \text{M/sec}) (15 \text{ sec}) + 1.50 \text{M} \]

\[ [A]_t = 1.3 \text{M} \]
The rate law for the reaction of A → 2B is zero order in A and has a rate constant of 0.12 M/s.

If the reaction starts with 1.50 M A, after what time will the concentration of A be 0.90 M?

In this case the problem gives us:

\[ [A]_0 = 1.50 \text{M} \]
\[ [A]_t = 0.90 \text{M} \]
\[ k = 0.12 \text{M/sec} \]

It zero order so:

\[ [A]_t = -k \cdot t \cdot [A]_0 \]

Rearrange:

\[ t = \frac{-(A)_t - [A]_0)}{k} \]

\[ t = (1.50 \text{M} - 0.90 \text{M})/0.12 \text{M/sec} \]

\[ t = 5 \text{sec} \]

The reaction 2A → B is first order in A with a rate constant of 2.8 \times 10^{-2} \text{s}^{-1} at 80^\circ \text{C}. How long will it take for A to decrease from 0.88 \text{M} to 0.14 \text{M}?

Given:

1st order process and time = t

\[ [A]_0 = 0.88 \text{M} \]
\[ [A]_t = 0.14 \text{M} \]
\[ k = 0.028 \text{sec}^{-1} \]

\[ \ln[A]_t - \ln[A]_0 = -k \cdot t \]

\[ k \cdot t = \ln[A]_0 - \ln[A]_t \]

\[ t = \frac{\ln[A]_0 - \ln[A]_t)}{k} = \frac{0.88 \text{M}}{0.14 \text{M}} \cdot \frac{\ln[0.88 \text{M}]}{\ln[0.14 \text{M}]} \cdot 2.8 \times 10^{-2} \text{s}^{-1} = 66 \text{s} \]

### Summary of Kinetic Reaction Equations

<table>
<thead>
<tr>
<th>( \text{A} \rightarrow \text{C} )</th>
<th>zero order</th>
<th>first order</th>
<th>second order</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate law</td>
<td>rate = k</td>
<td>rate = k[A]</td>
<td>rate = k[A]^2</td>
</tr>
<tr>
<td>integrated rate law in straight-line form</td>
<td>([A]_t = -k \cdot t \cdot [A]_0 )</td>
<td>( \ln[A]_t = -k \cdot t \cdot \ln[A]_0 )</td>
<td>( 1/[A]_t = k t + 1/[A]_0 )</td>
</tr>
<tr>
<td>straight line plot</td>
<td>([A]_t \text{ vs } t )</td>
<td>( \ln[A]_t \text{ vs } t )</td>
<td>( 1/[A]_t \text{ vs } t )</td>
</tr>
<tr>
<td>slope, y-intercept</td>
<td>-k, [A]_0</td>
<td>-k, \ln[A]_0</td>
<td>k, 1/[A]_0</td>
</tr>
<tr>
<td>( t_{1/2} \text{ half-life} )</td>
<td>([A]_0/2k )</td>
<td>0.693/k</td>
<td>1/k[A]_0</td>
</tr>
<tr>
<td>units for ( k )</td>
<td>mol/L \cdot s</td>
<td>1/s</td>
<td>L/mol \cdot s</td>
</tr>
</tbody>
</table>
The first order rate constant is $1.87 \times 10^{-3}$ min$^{-1}$ at 37°C for a reaction of cisplatin (a cancer drug) with water. Suppose that the concentration of cisplatin in the blood stream in a cancer patient after injection is $4.73 \times 10^{-4}$ mol/L. What will be the concentration of cisplatin 24 hours later?

At 1000°C, cyclobutane ($C_4H_8$) decomposes in a first-order reaction to two molecules of ethylene ($C_2H_4$) with a known rate constant, $k$, of 87 s$^{-1}$.

(a) If the initial $C_4H_8$ concentration is 2.00M, what is the concentration after 0.010 s?

(b) What fraction of $C_4H_8$ has decomposed in this time?

$$\ln[A]_t = -(87 \text{ s}^{-1})(0.010 \text{ s})$$

$$[A]_t = 2.00 \text{ M} \times \exp(-87 \text{ s}^{-1})(0.010 \text{ s}) = 0.837 \text{ M}$$

At 1000°C, cyclobutane ($C_4H_8$) decomposes in a first-order reaction to two molecules of ethylene ($C_2H_4$) with a known rate constant, $k$, of 87 s$^{-1}$.

(a) If the initial $C_4H_8$ concentration is 2.00M, what is the concentration after 0.010 s?

(b) What fraction of $C_4H_8$ has decomposed in this time?

$$\ln[A]_t = -k t + \ln[A]_0$$

$$\ln[A]_t = -k t$$

$$\exp \left( \frac{\ln[A]_t}{\ln[A]_0} \right) = \exp(-k t)$$

$$[A]_t = A_0 \exp(-k t)$$

$$[A]_t = (4.73 \times 10^{-4}) \exp(-1.87 \times 10^{-3} \text{ min}^{-1} \times 24 \text{ hr} \times 60 \text{ min/hr}) = 3.20 \times 10^{-5} \text{ M}$$

Given: $[A]_0 = 4.73 \times 10^{-4} \text{ M}$ and $k = 1.87 \times 10^{-3} \text{ min}^{-1}$.

At 1000°C, cyclobutane ($C_4H_8$) decomposes in a 2nd-order reaction, with the very high rate constant of 87 L/mol s, to two molecules of ethylene ($C_2H_4$).

(a) If the initial $C_4H_8$ concentration is 2.00M, what is the concentration after 0.010 s?

(b) What fraction of $C_4H_8$ has decomposed in this time?

Fraction decomposed = ($[A]_0 - [A]_t$) / $[A]_0$

Fraction decomposed = (2M - 0.7299) / 2M = 0.635 ~ 0.64

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[0.35]} - \frac{1}{[A]_0} = 5.3 \times 10^{-5} \text{ M}^{-1} \text{s}^{-1} \times 7200 \text{ s}$$

$$A_0 = 0.40 \text{ M}$$

The rate constant for the second order reaction $2A \rightarrow B$ is $5.3 \times 10^{-5}$ M$^{-1}$s$^{-1}$. What is the original amount present if, after 2 hours, there is 0.35M available?

The rate constant for the second order reaction $2A \rightarrow B$ is $5.3 \times 10^{-5}$ M$^{-1}$s$^{-1}$. What is the original amount present if, after 2 hours, there is 0.35M available?

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[0.35]} - \frac{1}{[A]_0} = 5.3 \times 10^{-5} \text{ M}^{-1} \text{s}^{-1} \times 7200 \text{ s}$$

$$A_0 = 0.40 \text{ M}$$
The rate constant for a second order reaction $B \rightarrow C$ is $4.5 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1}$. What is the half-life of this reaction if the reactions begins with a reactant concentration of 5.0 M?

The rate constant for a second order reaction is $4.5 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1}$. What is the half-life if we start with a reactant concentration of 5.0 M?

$$t_{1/2} = \frac{1}{k[A_0]} = \frac{1}{4.5 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1} \times 5 \text{ M}} = 440 \text{ s}$$

$$= 7.4 \text{ min}$$

---

The Chernobyl nuclear reactor accident occurred in 1986. The reactor exploded some 2.4 M Ci of radioactive $^{137}$Cs into the atmosphere (1000 Ci received over a period of several minutes is deadly). Assuming first-order kinetics and knowing that the half-life of $^{137}$Cs is 30.1 years, what year will the amount of $^{137}$Cs released from Chernobyl finally decrease to 100 Ci? A Ci is a unit of radioactivity called the Curie.

We have to know that the half-life for second order is:

$$\frac{1}{k[A_0]} = t_{1/2}$$

$$\frac{1}{4.5 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1} \times 5 \text{ M}} = t_{1/2}$$

$$t_{1/2} = 440 \text{ s}$$

$$= 7.4 \text{ min}$$

---

Cyclopropane is the smallest cyclic hydrocarbon. Because its 60° bond angles allow poor orbital overlap, its bonds are weak. As a result, it is thermally unstable and rearranges to propene at 1000 °C via the following first-order reaction:

$$\text{CH}_3\text{-CH=CH}_2(g) \rightarrow \text{CH}_3\text{CH} = \text{CH}_2$$

Suppose the rate constant $k = 9.2 \text{ s}^{-1}$.

(a) How long will it take for 1/2 of cyclopropane to rearrange to propene (ie. what is the half-life--$t_{1/2}$) ?

(b) How long does it take for [cyclopropane] to reach one-quarter of its initial value?

Suppose the rate constant $k = 9.2 \text{ s}^{-1}$.

(a) How long will it take for 1/2 of cyclopropane to rearrange to propene (ie. what is the half-life--$t_{1/2}$) ?

$$t_{1/2} = \frac{0.693}{k} \cdot \frac{0.693}{30.1 \text{ y}} = \frac{0.693}{9.2 \text{ s}^{-1}} = 0.075 \text{ s}$$

(b) How long does it take for [cyclopropane] to reach one-quarter of its initial value?

It takes 1 half-life to get to 1/2 $[A]_0$ another to get to 1/4 of $[A]_0 = 2 \cdot t_{1/2} = 2 \cdot (0.075 \text{ s}) = 0.15 \text{ s}$
Experiments show that reaction rate increases when temperature increases.

\[ \text{R-COOR'} + \text{H}_2\text{O} \rightarrow \text{R-COOH} + \text{R'}\text{OH} \]

Note both reactant concentrations are held constant.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[Ester]</th>
<th>[H(_2)O]</th>
<th>T (K)</th>
<th>Rate (mol/L(\cdot)sec)</th>
<th>(k) (L/mol(\cdot)sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100</td>
<td>0.200</td>
<td>288</td>
<td>1.64\times10^{-3}</td>
<td>0.0521</td>
</tr>
<tr>
<td>2</td>
<td>0.100</td>
<td>0.200</td>
<td>298</td>
<td>2.02\times10^{-3}</td>
<td>0.101</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>0.200</td>
<td>308</td>
<td>3.68\times10^{-3}</td>
<td>0.184</td>
</tr>
<tr>
<td>4</td>
<td>0.100</td>
<td>0.200</td>
<td>318</td>
<td>6.64\times10^{-3}</td>
<td>0.332</td>
</tr>
</tbody>
</table>

If we plot \(k\) vs T data we observe that \(k\) increases exponentially as T increases.

Temperature alters the rate constant, \(k\) of a chemical reaction!

Physicist Svante Arrhenius showed that the rate constant, \(k\), varies with temperature according to:

\[ k = A \exp(-\frac{E_a}{RT}) \]

- \(k\): reaction rate constant
- \(E_a\): Activation energy (specific for any given reaction)
- \(A\): Frequency factor (related to geometry and # of collisions for any given reaction)
- \(T\): temperature in Kelvin
- \(R\): gas constant (\(R = 8.314\) J/mol \(\cdot\) K)

Plotting \(\ln k\) vs 1/T, we get a straight line with a slope \(-\frac{E_a}{R}\). It’s called an Arrenhius Plot.

\[ \ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A \]

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>(k) (M(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>3.52E-07</td>
</tr>
<tr>
<td>356</td>
<td>3.02E+05</td>
</tr>
<tr>
<td>393</td>
<td>2.19E-04</td>
</tr>
<tr>
<td>427</td>
<td>1.16E-03</td>
</tr>
<tr>
<td>508</td>
<td>3.95E-02</td>
</tr>
</tbody>
</table>

Temperature (K\(^{-1}\))

The Arrenhius equation links the macroscopic rate constant, \(k\), to the fraction of molecular collisions with proper spatial orientation and \(E_a\) of collision theory at a molecular level.

\[ k = A e^{-\frac{E_a}{RT}} \]

\(A\): Activation Energy
\(E_a\): Gas Constant
\(T\): Temperature (K)

Because the rate of a chemical reaction depends on the temperature, different temperatures give different rate constants (\(k\)).

Consider the first order reaction and pretend someone finds that the experimental rate law is first order:

\[ A \rightarrow C \quad \text{rate} = k(T) [A]^1 \]

What is the molecular origin of the temperature dependence?
If we plug the Arrhenius factor into our "rate law expression" we can see the temperature dependence that we could not see before.

\[ aA + bB \rightarrow cC + dD \quad \text{rate} = k \ [A]^m [B]^n \]

We can transform the Arrhenius equation to useful graphical form by taking the natural logarithm (ln) of each side.

\[ \ln k = \ln (A e^{-E_a/RT}) \]

By expanding and simplifying,

\[ \ln k = \ln A + \ln(e^{-E_a/RT}) = \ln A - E_a/RT \]

We can also transform the Arrhenius equation into something more useful using ratios of two different rate constants at two different temps.

\[ \frac{k_2}{k_1} = \frac{A e^{-E_a/RT_2}}{A e^{-E_a/RT_1}} = e^{-E_a/RT_2} - e^{-E_a/RT_1} \]

\[ \frac{k_2}{k_1} = \exp \left( \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right) \]

\[ \ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

The decomposition reaction of hydrogen iodide, \( 2\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g) \)

has a rate constant of \( 9.51 \times 10^{-9} \text{L/mol s} \) at 500. K and one of \( 1.10 \times 10^{-5} \text{L/mol s} \) at 600. K. Find the activation energy, \( E_a \).

\[ E_a = -\left( \frac{8.314 \text{ J/mol K}}{1.10 \times 10^{-5} \text{ L/mol s} / 9.51 \times 10^{-5} \text{ L/mol s}} \right) \left( \frac{1}{600 \text{ K}} - \frac{1}{500 \text{ K}} \right) \]

\[ E_a = 1.76 \times 10^5 \text{ J/mol} = 176 \text{ kJ/mol} \]

There are unanswered questions using the equations of kinetics which are largely macroscopic.

1) Why does the reaction rate depend on temperature but yet there is no T in the rate law equation?

2) Why are \([A]\) and \([B]\) multiplied in the rate law equations?

3) What is happening at the molecular level?

4) Why does the reaction rate depend on concentration of reactants to varying degrees?

Two models help chemists understand what is happening at a molecular level: 1) collision theory and 2) transition state theory.
The framework of the kinetic models.

1. **Collision Theory**—is like Kinetic Molecular theory of gases. Chemical reactions occur only when reactant molecules collide. Those molecules with a certain minimum activation energy ($E_a$), temperature and correct spatial orientation will transform into products.

2. **Transition State Theory**—graphical model used to describe the thermodynamics of a reaction while postulating what reactants and products look like in transforming reactants to products. We get “reaction mechanisms” that useful in organic chemistry.

**Collision Theory** provides the “microscopic basis” of the rate law, and explains the following:

- **Why Concentrations Are Multiplied in the Rate Law**
- **How Temperature affects a Reaction Rate** by linking $k$, the rate constant to temperature, molecule collision frequency, molecule spatial orientation and fraction of molecules that have sufficient energy to react (the Activation Energy, $E_a$)
- **Spatial Orientation of Reactants**
  - Molecules must be oriented in a certain way called “effective collisions” in 3-D space in order for a collision to lead to a chemical reaction.

The reactants are multiplied in the rate law because a product must collide to transform to a product. Multiplying gives # collisions.

\[
A + B \rightarrow C \quad \text{rate} = k \ [A][B] \quad \text{Why Multiplication?}
\]

Reactants must be collide with the proper spatial orientation in order to transform from reactant to product.

**Activation energy, $E_a$,** is the minimum kinetic energy needed for a reaction to occur. Higher $T$ results in greater fraction of molecules with critical energy $> E_a$

\[
\text{fraction} = e^{-E_a/RT}
\]

called the Boltzmann factor

The Arrehenius equation links the macroscopic rate constant to fraction of molecular collisions with proper spatial orientation and $E_a$ of collision theory.

\[
k = Ae^{-E_a/RT}
\]
The reaction rate constant, $k$, increases when either the activation energy ($E_a$) decreases or the temperature increases.

$$k = A e^{-E_a/RT} = A \exp(-E_a/RT)$$

<table>
<thead>
<tr>
<th>$E_a$ (kJ/mol)</th>
<th>$f$ (at $T = 298$ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>$1.70 \times 10^{-9}$</td>
</tr>
<tr>
<td>75</td>
<td>$7.03 \times 10^{-14}$</td>
</tr>
<tr>
<td>100</td>
<td>$2.90 \times 10^{-18}$</td>
</tr>
</tbody>
</table>

Same information as preceding slide but shown in a more “chemistry-like” way. Formal.

Is this reaction exothermic or endothermic?

**Transition State Theory** explains the energetics and postulate what substances look like as they are transforming from reactants to products.

**Reaction energy diagrams** are used to depict the energetics and events that occur as reactants are transformed to products.

**Key Points of Collision Theory**

1. increased $T$ $\rightarrow$ increased average speed and KE of particles $\rightarrow$ increased collision frequency $\rightarrow$ increased fraction of reacting molecule $\rightarrow$ increase reaction rate

2. Significance of Activation Energy, $E_a$: only molecular collisions with energy $\geq E_a$ can yield products.

3. Reactants must collide with the “correct” spatial orientation $E_a$ to react and give products.

4. Either decreasing $E_a$ and/or increasing $T$ enhances the fraction of productive collisions, $f$ increases and through the Arrhenius equation $k$ and the reaction rate increases.
**Reaction energy diagrams** include the energetics for enthalpies and levels of activation energy.

\[ \Delta H > 0 \quad \Delta H < 0 \quad \Delta H < 0 \]

2 NOCl(g) → 2 NO(g) + Cl₂(g)

---

**Example:** Consider the proposed transition state for the reaction:

\[ \text{CH}_3\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Br}^- \]

The postulated transition state is **NOT** TETRAHEDRAL but rather trigonal bipyramidal, note the elongated forming C---Br and the breaking C---O bonds.

---

**Example:** Consider the proposed transition state for the reaction:

\[ \text{CH}_3\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Br}^- \]

Transition state theory says that every step in a reaction goes through a transition state from which it continues in either the forward or reverse directions.

---

**The activation energy,** \( E_a \) **can be viewed as the energy required to stretch and deform bonds forming an activated complex or transition state.**
A key reaction in the upper atmosphere is

$$O_3(g) + O(g) \rightarrow 2O_2(g)$$

The $E_{a(fwd)}$ is 19 kJ, and $\Delta H_{rxn}$ for the reaction is -392 kJ.

Draw a reaction energy diagram for this reaction, a transition state, and calculate $E_{a(rev)}$.

$$E_{a(rev)} = (392 + 19) \text{ kJ} = 411 \text{ kJ}$$

**Reaction Mechanisms--Why and What For**

A balanced chemical equation tells us what reactants react and what products are made. It does not tell us how the transformation occurs on a molecular level.

$$2A + B \rightarrow E + F \quad \text{Rate} = k[A][B]$$

A reaction mechanism is a series of postulated chemical equations or events called "elementary steps" which are posited "molecular events" for reactant molecules.

Elementary step 1: $A + B \rightarrow C$ intermediates

Elementary step 2: $C + A \rightarrow D$

Elementary step 3: $D \rightarrow E + F$

Overall reaction: $2A + B \rightarrow E + F$

An intermediate is formed in an early elementary step and consumed in a later elementary step.

**Correlating A Reaction Mechanism with the Rate Law**

1. The sum of the elementary steps must give the overall balanced equation for the reaction.
2. The rate law for each elementary step is given by the equation stoichiometry and must be reasonable.
3. The rate limiting step (slowest step) determines the rate law of the overall reaction! See below

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g) \quad \text{Rate} = k[NO_2]^2$$

Here is the postulated mechanism intermediate

Elementary step: $NO_2 + NO_2 \rightarrow NO_3 + NO$ Rate $= k[NO_2]^2$

Elementary step: $NO_3 + CO \rightarrow NO_2 + CO_2$ Rate $= k_1[NO_3][CO]$ Overall reaction: $NO_2 + CO \rightarrow NO + CO_2$ Rate $= k[NO_2]^2$

**Each elementary step** is characterized by its molecularity, which is the number of molecules reacting in the elementary step. This also is the order of the reaction for that elementary step.

| Table 16.6 Rate Laws for General Elementary Steps |
|----------------|----------------|-------------|
| Elementary Step | Molecularity   | Rate Law    |
| $A \rightarrow$ product | Unimolecular | $k[A]$     |
| $2A \rightarrow$ product | Bimolecular | $k[A]^2$    |
| $A + B \rightarrow$ product | Termolecular | $k[A][B]$  |

Elementary step: $NO_2 + NO_2 \rightarrow NO_3 + NO$ bimolecular

Elementary step: $NO_3 + CO \rightarrow NO_2 + CO_2$ bimolecular

Overall reaction: $2NO_2 + CO \rightarrow NO + CO_2$

The experimental rate law for the reaction between NO$_2$ and CO to produce NO and CO$_2$ is $k[NO_2]^2$. The reaction is believed to occur via two steps:

Step 1: $NO_2 + NO_2 \rightarrow NO + NO_3$

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$

What is the equation for the overall reaction?

What is the intermediate?

What is the molecularity and order of each step?

What can you say about the relative rates of steps 1 and 2?
The experimental rate law for the reaction between NO$_2$ and CO to produce NO and CO$_2$ is rate = k[NO$_2$]$^2$. The reaction is believed to occur via two steps:

Step 1: NO$_2$ + NO$_2$ → NO + NO$_3$
Step 2: NO$_3$ + CO → NO$_2$ + CO$_2$

What is the equation for the overall reaction?
NO$_2$ + CO → NO + CO$_2$

What is the intermediate?
NO$_3$

What can you say about the relative rates of steps 1 and 2?
rate = k[NO$_2$]$^2$ is the rate law for step 1 and rate$_2$ = k[NO$_3$][CO].
Therefore, step 1 must be rate limiting (it matches the experiment).

The following elementary steps are proposed as the mechanism of an overall reaction:

(1) NO$_2$Cl(g) → NO$_2$(g) + Cl(g)
(2) NO$_2$Cl(g) + Cl(g) → NO$_2$(g) + Cl$_2$(g)

(a) Write the overall balanced equation.
(b) Determine the molecularity of each step.
(c) Is there an intermediate?
(d) What is the rate law for each step?
(e) If the experimental rate law is found to be 1st order which reaction is rate-limiting?

The following elementary steps are proposed as the mechanism of an overall reaction:

(1) NO$_2$Cl(g) → NO$_2$(g) + Cl(g)
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(a) Write the overall balanced equation.
(b) Determine the molecularity of each step.
(c) Is there an intermediate?
(d) What is the rate law for each step?
(e) If the experimental rate law is found to be 1st order which reaction is rate-limiting?

SOLUTION:

(a) Step(1) is unimolecular.
Step(2) is bimolecular.
(b) rate$_1$ = $k_1$ [NO$_2$Cl]
rate$_2$ = $k_2$ [NO$_2$Cl][Cl]

Summary

• The overall chemical reaction is a sequence of elementary steps called the reaction mechanism.

• The rate law of each elementary step can be determined from stoichiometry and determines the molecularity.

• Therefore, the experimentally observed rate law for an overall reaction must depend on the reaction mechanism.

• The slowest elementary step in a multistep reaction is called the rate-determining step—it determined by the rate of the rate-determining step.

• The overall reaction cannot occur faster than the speed of the rate-determining step.

A catalyst is any substance that increases the rate of a chemical reaction without itself being consumed in the reaction.

--increases reaction rate in both directions by increasing k via lowering the activation energy, $E_a$ of the reaction.

--The reaction thermodynamics (enthalpy, entropy) are unaffected!

--No change in the yield of the reaction!

--The catalyzed reaction proceeds via a different reaction mechanism than the uncatalyzed reaction.
A catalyst increases $k$ by lowering the activation energy, $E_a$, relative to an uncatalyzed reaction.

Both reactions have the same enthalpy, $\Delta H$.

Catalyst does not alter the yield of the reaction relative to uncatalyzed pathway.

The reaction pathway (mechanism) is different in a catalyzed reaction.

The reaction pathway (mechanism) is different in a catalyzed reaction.