Chapter 13
Rates of Reaction

Chemical Kinetics:
Rates of Chemical Reactions &
Factors that Affect Rates of Reactions

- How fast does a chemical reaction occur?
  rates of reactants consumed
  rates of products formed
  define and calculate rates

- relationship between rate & concentration
  rate law & experimental determination of rate law

- relationship between concentration & time
  integrated rate law & half-life of reaction

- dependence of rate on temperature & catalyst
  Arrhenius equation

- reaction mechanisms

Reaction Rates
rate of chemical reaction = \( \frac{\Delta\text{ concentration}}{\Delta\text{ time}} \)
rate = \( \frac{\Delta[X]}{\Delta t} = \frac{[X]_2 - [X]_1}{t_2 - t_1} \)

- \([X]\) = molar concentration of reactant or product
  - if reactant: \([X]_2 < [X]_1\)
    - rate of consumption of reactant
  - if product: \([X]_2 > [X]_1\)
    - rate of formation of product

- typically a plot of \([X]\) vs. time will not yield a straight line, but instead a curve;
  concentration vs. time curve

- consider the difference in shape of concentration vs. time curve for reactants & products
example:

Consider the decomposition of hydrogen peroxide:

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

If the initial concentration of \( \text{H}_2\text{O}_2 \) is 1.000 M, and the concentration of \( \text{H}_2\text{O}_2 \) decreases to 0.983 M after 10 seconds of reaction, calculate the rate of decomposition of \( \text{H}_2\text{O}_2 \) over this time interval.

\[
\begin{align*}
[H_2O_2]_0 &= 1.000 \text{ M at } t = 0 \text{ s} \\
[H_2O_2] &= 0.983 \text{ M at } t = 10 \text{ s}
\end{align*}
\]

- [H_2O_2] decreases over time b/c it is a reactant ∴ consumed
- rate of reaction is not constant over time as [H_2O_2] decreases, so does rate

example:

Consider the reaction:

\[ 4 \text{NH}_3 \text{(g)} + 5 \text{O}_2 \text{(g)} \rightarrow 4 \text{NO} \text{(g)} + 6 \text{H}_2\text{O (g)} \]

The initial concentration of \( \text{NH}_3 \) is 4.000 M; after 25 seconds, \([\text{NH}_3]\) has decreased to 2.560 M.

Determine the following:

a. the rate of consumption of \( \text{NH}_3 \)
b. the rate of consumption of \( \text{O}_2 \)
c. the rate of formation of \( \text{H}_2\text{O} \)

\[ \text{Concentration vs. Time Curve for Decomposition of H}_2\text{O}_2 \]

<table>
<thead>
<tr>
<th>Time, s</th>
<th>[H2O2], M</th>
<th>Change in [H2O2], M</th>
<th>Rate, M/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>2.3200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400.00</td>
<td>1.7200</td>
<td>0.6000</td>
<td>0.001500</td>
</tr>
<tr>
<td>800.00</td>
<td>1.3000</td>
<td>0.4200</td>
<td>0.001050</td>
</tr>
<tr>
<td>1200.00</td>
<td>0.9800</td>
<td>0.3200</td>
<td>0.000800</td>
</tr>
<tr>
<td>1600.00</td>
<td>0.7300</td>
<td>0.2500</td>
<td>0.000630</td>
</tr>
<tr>
<td>2000.00</td>
<td>0.5400</td>
<td>0.1900</td>
<td>0.000480</td>
</tr>
<tr>
<td>2400.00</td>
<td>0.3900</td>
<td>0.1500</td>
<td>0.000380</td>
</tr>
<tr>
<td>2800.00</td>
<td>0.2800</td>
<td>0.1100</td>
<td>0.000280</td>
</tr>
</tbody>
</table>
Average vs. Instantaneous Reaction Rates

- **average rate of reaction** - rate of reaction over some time interval
  
ex. What is the rate of decomposition of $\text{H}_2\text{O}_2$ between 1200 and 1600 seconds?

- **instantaneous rate of reaction** - rate of reaction at a specific time point
  
ex. What is the rate of decomposition of $\text{H}_2\text{O}_2$ at 1400 seconds?

*initial rate of reaction* - instantaneous rate of reaction at $t = 0$ s

- to calculate an *initial rate of reaction*, draw a line tangent to the concentration vs. time curve at $t = 0$
  
slope of tangent line = initial rate of reaction; units $\text{M} \cdot \text{s}^{-1}$

Rate Laws

- **rate law** - equation that shows the dependence of a reaction’s rate on concentration
  
  for a reaction: $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$
  
  $\text{Rate} = k[\text{A}]^m[\text{B}]^n$

  *** for a reaction, the rate law must be determined experimentally ***
Rate = $k[A]^m[B]^n$

- $m$ and $n$ – order of reaction with respect to A & B
  - typically small, positive, whole numbers
  - negative numbers and fractions are possible
- $k$ – rate constant
  - dependent on specific reaction
  - dependent on temperature
  - independent of concentration
  - units are variable; depend on orders of reaction

- some rate law terminology:
  - if $m = 1$, the reaction is 1st order in A
  - if $n = 2$, the reaction is 2nd order in B
  - overall order of the reaction = $m + n$
- reactions of the same overall order will have similar characteristics
  - specifically we will discuss 0, 1st, and 2nd order overall reactions

Reaction Order & Rate Change with Concentration

consider the reaction: $A \rightarrow B + C$

- if 1st order overall:
  - Rate = $k[A]^1$
  - if [A] increases by factor of 2, rate will increase by factor of $2^1$ OR rate will double
- if 2nd order overall:
  - Rate = $k[A]^2$
  - if [A] increases by factor of 3, rate will increase by factor of $3^2$ OR rate will increase 9x

- if $-1$ order overall:
  - Rate = $k[A]^{-1}$
  - if [A] increases by factor of 2, rate will change by factor of $2^{-1}$ OR rate will decrease by half
- if 0 order overall:
  - Rate = $k[A]^0$
  - rate is constant; changes in [A] have no effect on the rate as long as some A is present
Reaction Order & Rate Change with Concentration

- in general, for the reaction: \( A \rightarrow B + C \)
  \[ \text{Rate} = k[A]^m \]

if \([A]\) changes by a factor of \(x\), the rate will change by a factor of \(x^m\)

- when \([A]\) is doubled:
- when \([A]\) is tripled:

<table>
<thead>
<tr>
<th>(m)</th>
<th>rate multiplied by</th>
<th>(m)</th>
<th>rate multiplied by</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-1)</td>
<td>(2^{-1} = \frac{1}{2})</td>
<td>(-1)</td>
<td>(3^{-1} = \frac{1}{3})</td>
</tr>
<tr>
<td>(0)</td>
<td>(2^0 = 1)</td>
<td>(0)</td>
<td>(3^0 = 1)</td>
</tr>
<tr>
<td>(1)</td>
<td>(2^1 = 2)</td>
<td>(1)</td>
<td>(3^1 = 3)</td>
</tr>
<tr>
<td>(2)</td>
<td>(2^2 = 4)</td>
<td>(2)</td>
<td>(3^2 = 9)</td>
</tr>
<tr>
<td>(3)</td>
<td>(2^3 = 8)</td>
<td>(3)</td>
<td>(3^3 = 27)</td>
</tr>
</tbody>
</table>

Reaction Order & Units of \(k\)

<table>
<thead>
<tr>
<th>order</th>
<th>rate law</th>
<th>(k = )</th>
<th>(k) units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{\text{st}})</td>
<td>(\text{Rate} = k[A])</td>
<td>(\text{Rate}/[A])</td>
<td>(\text{s}^{-1})</td>
</tr>
<tr>
<td>2(^{\text{nd}})</td>
<td>(\text{Rate} = k[A]^2)</td>
<td>(\text{Rate}/[A]^2)</td>
<td>(\text{M}^{-1}\text{•s}^{-1})</td>
</tr>
<tr>
<td>3(^{\text{rd}})</td>
<td>(\text{Rate} = k[A]^3)</td>
<td>(\text{Rate}/[A]^3)</td>
<td>(\text{M}^{-2}\text{•s}^{-1})</td>
</tr>
</tbody>
</table>

Determination of Rate Law from Experimental Data: Method of Initial Rates

- reaction run multiple times at the same temperature (\(\therefore\) same \(k\)) with different initial concentrations
- initial rates of reaction are determined
- analyze how rate changes as concentration changes
- determine order with respect to each reactant
- write rate law
- do calculations

a simple example:

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

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

<table>
<thead>
<tr>
<th>experiment</th>
<th>([\text{N}_2\text{O}_5]_0)</th>
<th>initial rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.010 M</td>
<td>(4.8 \times 10^{-6} \text{M}\text{•s}^{-1})</td>
</tr>
<tr>
<td>2</td>
<td>0.020 M</td>
<td>(9.6 \times 10^{-6} \text{M}\text{•s}^{-1})</td>
</tr>
</tbody>
</table>

- \([\text{N}_2\text{O}_5]\) increase by factor of 2
- rate increases by factor of 2
  \(\therefore\) reaction is 1\(^{\text{st}}\) order in \(\text{N}_2\text{O}_5\)
  \(m = 1\)
example:

\[2 \text{HgCl}_2 (aq) + \text{C}_2\text{O}_4^{2-} (aq) \rightarrow 2 \text{Cl}^- (aq) + 2 \text{CO}_2 (g) + \text{Hg}_2\text{Cl}_2 (s)\]

Rate = \(k[\text{HgCl}_2]^m[\text{C}_2\text{O}_4^{2-}]^n\)

<table>
<thead>
<tr>
<th>experiment</th>
<th>([\text{HgCl}_2]_0)</th>
<th>([\text{C}_2\text{O}_4^{2-}]_0)</th>
<th>initial rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.105 M</td>
<td>0.15 M</td>
<td>1.8 \times 10^{-5} M\cdot\text{min}^{-1}</td>
</tr>
<tr>
<td>2</td>
<td>0.105 M</td>
<td>0.30 M</td>
<td>7.1 \times 10^{-5} M\cdot\text{min}^{-1}</td>
</tr>
<tr>
<td>3</td>
<td>0.052 M</td>
<td>0.30 M</td>
<td>3.5 \times 10^{-5} M\cdot\text{min}^{-1}</td>
</tr>
</tbody>
</table>

- compare experiments 1 & 2 to determine order with respect to \(\text{C}_2\text{O}_4^{2-}\); i.e. determine \(n\)
- compare experiments 2 & 3 to determine order with respect to \(\text{HgCl}_2\); i.e. determine \(m\)

example (continued):

- comparing experiments 1 & 2:
  determination of \(n\)

\[
\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{HgCl}_2]^2[\text{C}_2\text{O}_4^{2-}]^2}{k[\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2} = \frac{k(0.105)^m(0.30)^2}{k(0.052)^m(0.30)^2}
\]

\[
\frac{7.1 \times 10^{-5}}{3.5 \times 10^{-5}} = \frac{k(0.105)^m(0.30)^2}{k(0.052)^m(0.30)^2}
\]

\[
4 = 2^n
\]

so: \(n = 2\)

- the reaction is 2\(^{nd}\) order in \(\text{C}_2\text{O}_4^{2-}\)

example (continued):

- comparing experiments 2 & 3:
  determination of \(m\)

\[
\frac{\text{Rate}_2}{\text{Rate}_3} = \frac{k[\text{HgCl}_2]^2[\text{C}_2\text{O}_4^{2-}]^2}{k[\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^3} = \frac{k(0.105)^m(0.30)^2}{k(0.052)^m(0.30)^3}
\]

\[
\frac{7.1 \times 10^{-5}}{3.5 \times 10^{-5}} = \frac{k(0.105)^m(0.30)^2}{k(0.052)^m(0.30)^3}
\]

\[
2 = 2^m
\]

so: \(m = 1\)

- the reaction is 1\(^{st}\) order in \(\text{HgCl}_2\)

example (continued):

\[2 \text{HgCl}_2 (aq) + \text{C}_2\text{O}_4^{2-} (aq) \rightarrow 2 \text{Cl}^- (aq) + 2 \text{CO}_2 (g) + \text{Hg}_2\text{Cl}_2 (s)\]

Rate = \(k[\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2\)

<table>
<thead>
<tr>
<th>experiment</th>
<th>([\text{HgCl}_2]_0)</th>
<th>([\text{C}_2\text{O}_4^{2-}]_0)</th>
<th>initial rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.105 M</td>
<td>0.15 M</td>
<td>1.8 \times 10^{-5} M\cdot\text{min}^{-1}</td>
</tr>
<tr>
<td>2</td>
<td>0.105 M</td>
<td>0.30 M</td>
<td>7.1 \times 10^{-5} M\cdot\text{min}^{-1}</td>
</tr>
<tr>
<td>3</td>
<td>0.052 M</td>
<td>0.30 M</td>
<td>3.5 \times 10^{-5} M\cdot\text{min}^{-1}</td>
</tr>
</tbody>
</table>

- Determine the value of \(k\).
- Determine the rate of reaction when \([\text{HgCl}_2] = 0.050 \text{ M and } [\text{C}_2\text{O}_4^{2-}] = 0.025 \text{ M.}\)
example:

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

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

<table>
<thead>
<tr>
<th>experiment</th>
<th>[NO]_0</th>
<th>[O}_2]_0</th>
<th>initial rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0010 M</td>
<td>0.0010 M</td>
<td>7.10 M•s(^{-1})</td>
</tr>
<tr>
<td>2</td>
<td>0.0010 M</td>
<td>0.0040 M</td>
<td>28.4 M•s(^{-1})</td>
</tr>
<tr>
<td>3</td>
<td>0.0030 M</td>
<td>0.0040 M</td>
<td>255.6 M•s(^{-1})</td>
</tr>
</tbody>
</table>

- compare experiments 1 & 2 to determine order with respect to \(\text{O}_2\); i.e. determine \(n\)
- compare experiments 2 & 3 to determine order with respect to \(\text{NO}\); i.e. determine \(m\)

example (continued):

- comparing experiments 1 & 2:
  determination of \(n\)

\[
\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{NO}]^2[\text{O}_2]^n}{k[\text{NO}]^m[\text{O}_2]^n}
\]

\[
\frac{28.4}{7.10} = \frac{k(0.0010)^m(0.0040)^n}{k(0.0010)^m(0.0010)^n}
\]

\[ 4 = 4^n \]

so: \(n = 1\)

- the reaction is 1\(^{st}\) order in \(\text{O}_2\)

example (continued):

- comparing experiments 2 & 3:
  determination of \(m\)

\[
\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{k[\text{NO}]^3[\text{O}_2]^3}{k[\text{NO}]^2[\text{O}_2]^2}
\]

\[
\frac{255.6}{28.4} = \frac{k(0.0030)^m(0.0040)}{k(0.0010)^m(0.0040)}
\]

\[ 9 = 3^m \]

so: \(m = 2\)

- the reaction is 2\(^{nd}\) order in \(\text{NO}\)

\(1^{st}\) Order Overall Reactions

- for a reaction: \(A \rightarrow \text{products}\)
- rate law: \(\text{Rate} = k[A]\)
  rate law provides information about how rate changes relative to changes in \([A]\)

- Other questions we’d like to answer?
  What is \([A]\) at some time, \(t\)?
  What \% of \(A\) has been consumed after \(t\)?
  How much time elapses before the reaction is 50\% complete?

these questions all probe the relationship between \([A]\) and time

- use the Integrated Rate Law to answer these questions
1st Order Overall Reactions:
Integrated Rate Law

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

\[
\ln [A]_t - \ln[A]_0 = -kt
\]

\[
\ln [A]_t = -kt + \ln[A]_0
\]

- look at this as an equation for a straight line:
  - plot of \(\ln[A]\) vs. \(t\) will yield a straight line
  - slope = \(-k\)
  - y intercept = \(\ln[A]_0\)

example:

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

The decomposition of hydrogen peroxide is a 1st order reaction with \(k = 7.30 \times 10^{-4} \text{ s}^{-1}\).

If \([\text{H}_2\text{O}_2]_0 = 2.32 \text{ M}\), determine \([\text{H}_2\text{O}_2]\) after 1200 seconds of reaction.

Half-Life of a Reaction, \(t_{1/2}\)

- The half-life \((t_{1/2})\) of a reaction is the time required for the [reactant] to decrease to half of its initial value.

\[
t = t_{1/2}
\]

\[
[A]_t = \frac{1}{2}[A]_0
\]

- for a 1st order reaction:

\[
t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}
\]

- note: for a 1st order reaction, \(t_{1/2}\) is constant
  \(t_{1/2}\) is dependent on \(k\) but not on \([A]_0\)
Half-Life of a 1\textsuperscript{st} Order Reaction

2\textsuperscript{nd} Order Overall Reactions

- for a reaction: A $\rightarrow$ products
- rate law: \( \text{Rate} = k[A]^2 \)
  rate law provides information about how rate changes relative to changes in [A]
- integrated rate law:
  \[ \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \]
- plot of 1/[A] vs. t will give a straight line
  \( \text{slope} = k \)
  \( \text{y intercept} = 1/[A]_0 \)
- half-life equation:
  \[ t_{\frac{1}{2}} = \frac{1}{k[A]_0} \]

Zero (0) Order Overall Reactions

- for a reaction: A $\rightarrow$ products
- rate law: \( \text{Rate} = k[A]^0; \text{ Rate} = k \)
  the rate of a 0 order reaction is constant and does not depend on [A]
- integrated rate law:
  \[ [A]_t = -kt + [A]_0 \]
- plot of [A] vs. t will give a straight line
  \( \text{slope} = -k \)
  \( \text{y intercept} = [A]_0 \)
- half-life equation:
  \[ t_{\frac{1}{2}} = \frac{[A]_0}{2k} \]
Collision Theory of Reactions

- reactions occur when particles collide
- not all collisions result in the formation of product
- 2 factors influence whether or not product forms:
  - energy of collision
  - orientation of particle at collision

Energy Considerations

- molecular collisions are successful (i.e. result in the formation of product) when they occur with enough energy to break bonds
- minimum amount of E required for reaction to occur is the activation energy, $E_a$, for the reaction
  $$E_{\text{collision}} > E_a \text{ required for product formation}$$
- in general, the larger the $E_a$ for a reaction, the slower the rate
  a smaller fraction of molecular collisions will occur with sufficient energy to form products
Energy Considerations

- energy of molecular collision is affected by temperature
- at higher T's:
  - kinetic energy of particles is greater
  - speed is greater
  - force of collisions will be greater
  - frequency of collisions will be higher

∴ fraction of collisions with $E > E_a$ is greater

Orientation of Collisions

consider the reaction: $A_2 + B_2 \rightarrow 2AB$

favorable orientation:

unfavorable orientation:

$NO (g) + Cl_2 (g) \rightarrow NOCl (g) + Cl (g)$

favorable orientation:

unfavorable orientation:
- consider the species in the middle of this reaction:

  ![Reaction Diagram]

  - a short-lived, transient species formed in between reactants and products can be called:
    - transition state
    - activated complex
    - reaction intermediate

- track how energy changes as the reaction progresses from reactant → transition state → products

  ![Reaction Profile Diagram]

- reaction rates almost always increase with increasing temperature

  - if rate increases while \([A]\) is held constant, \(k\) must also increase

  - temperature dependence of \(k\) is given by the Arrhenius equation:

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

    OR

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

    \(E_a = \text{activation energy, kJ/mol}\)

    \(A = \text{frequency factor, s}^{-1}\)

    \(R = 8.314 \text{ J/K\cdotmol}\)
Arrhenius Equation

- look at the logarithmic form of the Arrhenius equation as a straight line equation:
  \[ \ln k = -\frac{E_a}{RT} + \ln A \]
- plot of \( \ln k \) vs. \( 1/T \) yields a straight line with:
  \[ \text{slope} = -\frac{E_a}{R} \quad \text{y intercept} = \ln A \]
- this is called an Arrhenius plot
- you can derive a 2-point equation:
  \[ \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \]

example:
Consider the following 1st order reaction:

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

For this reaction at 50°C, \( A = 4.0 \times 10^{13} \text{ s}^{-1} \) and \( E_a = 88 \text{ kJ/mol} \).

Determine the rate of this reaction at 50°C if \([\text{N}_2\text{O}_5]_0 = 2.68 \text{ M}\).

Determine the value of \( k \) at 30°C.

Catalysts

A catalyst is a substance that increases the rate of a chemical reaction without being consumed by it.

- a catalyst provides an alternate path from reactant to product
- path with lower \( E_a \)
- frequently multiple step path
- a catalyst participates in one step of the mechanism, and is regenerated in a later step
**Catalysts**

*heterogeneous* catalyst – catalyst is in a different phase than the reacting species

- usually a solid catalyst in contact with liquid or gas phase reaction mixture
- reactants *adsorb* onto catalyst surface
  - physical adsorption
  - chemisorption

*homogeneous* catalyst – catalyst in the same phase as reacting species

---

**Catalytic Hydrogenation - Heterogeneous Catalysis**

\[
\text{C} = \text{C} + \text{H}_2 \xrightarrow{\text{Pt}} \text{H} - \text{C} = \text{C} - \text{H}
\]

- 
  - Ethylene
  - Hydrogen (H₂)
  - Ethane (C₂H₆)
  - Ethene (C₂H₄)
  - Catalyst surface

- C₂H₄ and H₂ molecules diffuse to the catalyst.
- The molecules form bonds to the catalyst surface. (The H₂ molecules dissociate to atoms in the process.)
- H atoms migrate to the C₂H₄ molecule, where they react to form C₂H₆.
- C₂H₆ diffuses away from the catalyst.

---

**Catalytic Converters - Heterogeneous Catalysis**

- conversion of CO (g), NO (g), and O₂ (g) to CO₂ (g) and N₂ (g) released into atmosphere
Enzymes - Biochemical Catalysts

Arrhenius Equation and Catalyst Considerations

- for a reaction, the addition of a catalyst causes:
  - rate increase: \( \text{rate}_{\text{cat}} > \text{rate}_{\text{uncat}} \)
  - \( k \) increase: \( k_{\text{cat}} > k_{\text{uncat}} \)
  - \( E_a \) decrease: \( E_{a-\text{cat}} < E_{a-\text{uncat}} \)

- consider writing the Arrhenius equation in terms of both a catalyzed and uncatalyzed reaction:

\[
\frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{A e^{-E_{a-\text{cat}}/RT}}{A e^{-E_{a-\text{uncat}}/RT}}
\]

Reaction Mechanisms

- a collection of elementary steps that describe the path from reactants to products in a chemical reaction
- for a mechanism to be plausible, it must meet 2 criteria:
  - match the overall or net chemical reaction after steps are added together
  - produce a rate law that is consistent with the experimentally determined rate law

Elementary Processes

- individual steps in reaction mechanism
- rate law can be written by inspection; orders equivalent to stoichiometric coefficients
- identified by their \textit{molecularity}
  - may be \textit{unimolecular}, \textit{bimolecular}, \textit{termolecular}
- may be fast, reversible (equilibrium) steps
  \( \text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}} \)
- may be slow
  - rate determining step (RDS)
  - largest \( E_a \)
    - \( \textbf{** determines the overall rate of reaction} \)
    \[ \text{Rate}_{\text{rxn}} = \text{Rate}_{\text{RDS}} \]
Reaction Intermediates & Catalysts in Mechanisms

- reaction intermediates and catalysts are both species that may be involved in a mechanism but not appear in the overall chemical equation or its rate law

- *reaction intermediate* – generated in one step, then consumed in a later step

- *catalyst* – consumed in one step, then regenerated in a later step

Consider the following reaction:

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

The experimentally determined rate law is:

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

Is this a plausible mechanism?

step 1: \( \text{H}_2(g) + \text{ICl}(g) \rightarrow \text{HI}(g) + \text{HCl}(g) \) (slow)

step 2: \( \text{HI}(g) + \text{ICl}(g) \rightarrow \text{I}_2(g) + \text{HCl}(g) \) (fast)

Consider the following reaction:

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2 \text{ICl}(g) + \text{H}_2(g) \rightarrow \text{I}_2(g) + 2 \text{HCl}(g)
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The experimentally determined rate law is:

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

Is this a plausible mechanism?

step 1: \( \text{H}_2(g) + \text{ICl}(g) \rightarrow \text{HI}(g) + \text{HCl}(g) \) (RDS)

step 2: \( \text{HI}(g) + \text{ICl}(g) \rightarrow \text{I}_2(g) + \text{HCl}(g) \) (fast)

overall rxn: \( \text{H}_2(g) + 2 \text{ICl}(g) \rightarrow \text{I}_2(g) + 2 \text{HCl}(g) \)

rate law from mechanism: \( \text{Rate}_{\text{rxn}} = \text{Rate}_{\text{RDS}} \)

\[ \therefore \text{Rate} = k[\text{H}_2][\text{ICl}] \]
Consider the following reaction:

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

The experimentally determined rate law is:

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

Is this a plausible mechanism?

step 1: \[ \text{H}_2 (g) + \text{ICl (g)} \rightarrow \text{HI (g)} + \text{HCl (g)} \] \text{(RDS)}
step 2: \[ \text{HI (g)} + \text{ICl (g)} \rightarrow \text{I}_2 (g) + \text{HCl (g)} \] \text{(fast)}

overall rxn: \[ \text{H}_2 (g) + 2 \text{ICl (g)} \rightarrow \text{I}_2 (g) + 2 \text{HCl (g)} \]

rate law from mechanism: \[ \text{Rate}_{\text{rxn}} = \text{Rate}_{\text{RDS}} \]
\[ \therefore \text{Rate} = k[\text{H}_2][\text{ICl}] \]

Yes – this is a plausible mechanism.

example:

Ozone reacts with nitrogen dioxide to produce oxygen and dinitrogen pentoxide by the following proposed mechanism:

step 1: \[ \text{O}_3 (g) + \text{NO}_2 (g) \rightarrow \text{NO}_3 (g) + \text{O}_2 (g) \] \text{(slow)}
step 2: \[ \text{NO}_2 (g) + \text{NO}_3 (g) \rightarrow \text{N}_2\text{O}_5 (g) \] \text{(fast)}

Determine the overall reaction & rate law consistent with this mechanism.

example:

Consider the following proposed mechanism for the reaction between \( \text{F}_2 \) and \( \text{N}_2\text{O}_4 \):

\[ \begin{array}{c|c|c}
\text{step 1:} & \text{N}_2\text{O}_4 (g) & \rightleftharpoons 2 \text{NO}_2 (g) \quad E_a, \text{kJ/mol} \\
\text{step 2:} & \text{NO}_2 (g) + \text{F}_2 (g) & \rightarrow \text{F} (g) + \text{FNO}_2 (g) \quad 83 \\
\text{step 3:} & \text{F} (g) + \text{NO}_2 (g) & \rightarrow \text{FNO}_2 (g) \quad 9 \\
\end{array} \]

- What is the overall reaction predicted by this mechanism?
- Identify any reaction intermediates or catalysts.
example:

Consider the following proposed mechanism for the reaction between F₂ and N₂O₄:

\[
\text{E}_a, \text{kJ/mol} \\
\text{step 1: } \text{N}_2\text{O}_4 (g) \rightleftharpoons 2 \text{NO}_2 (g) \quad 59 \\
\text{step 2: } \text{NO}_2 (g) + \text{F}_2 (g) \rightarrow \text{F} (g) + \text{FNO}_2 (g) \quad 83 \\
\text{step 3: } \text{F} (g) + \text{NO}_2 (g) \rightarrow \text{FNO}_2 (g) \quad 9 \\
\text{overall rxn: } \text{N}_2\text{O}_4 (g) + \text{F}_2 (g) \rightarrow 2 \text{FNO}_2 (g)
\]

NO₂ and F are reaction intermediates

example:

Consider the following proposed mechanism for the reaction between F₂ and N₂O₄:

\[
\begin{align*}
\text{E}_a, \text{kJ/mol} \\
\text{step 1: } & \text{N}_2\text{O}_4 (g) \rightleftharpoons 2 \text{NO}_2 (g) & 59 \\
\text{step 2: } & \text{NO}_2 (g) + \text{F}_2 (g) \rightarrow \text{F} (g) + \text{FNO}_2 (g) & 83 \\
\text{step 3: } & \text{F} (g) + \text{NO}_2 (g) \rightarrow \text{FNO}_2 (g) & 9 \\
\text{overall rxn: } & \text{N}_2\text{O}_4 (g) + \text{F}_2 (g) \rightarrow 2 \text{FNO}_2 (g)
\end{align*}
\]

Which step \{1, 2, or 3\} is the fastest step?

\[\text{step 3 because smallest } E_a\]

Which step \{1, 2, or 3\} is the rate-determining step?

\[\text{step 2 because largest } E_a\]

example:

For the proposed mechanism for the reaction between F₂ and N₂O₄, consider both the Eₐ values and ΔH values for steps 1 – 3, and the overall reaction to sketch the reaction profile.

\[
\begin{align*}
\text{E}_a, \text{kJ/mol} & \quad \Delta H, \text{kJ} \\
\text{step 1: } & 59 \quad +55.6 \\
\text{step 2: } & 83 \quad -20.0 \\
\text{step 3: } & 9 \quad -207 \\
\text{overall rxn: } & --- \quad -171
\end{align*}
\]