Chemical kinetics – rates of reactions and factors that influence rates

- rate of reaction = change in [X] / change in time; unit M•s\(^{-1}\)

  rates can be defined in terms of reactant consumption or product formation
  - as the reaction proceeds: [reactant] decreases
    - \([\text{reactant}]_{\text{final}} < [\text{reactant}]_{\text{initial}}\)
    - \(\Delta[\text{reactant}]\) is negative
  - as the reaction proceeds [product] increases
    - \([\text{product}]_{\text{final}} > [\text{product}]_{\text{initial}}\)
    - \(\Delta[\text{product}]\) is positive
  I use the absolute value of \(\Delta[X]\) (i.e. \(|\Delta[X]|\)) so that rates are always positive

- plots of [X] vs. time are generally curves (nonlinear)
  - profile of [reactant] vs time: starts at \(t = 0\) at high concentration (i.e. \([\text{reactant}]_{0}\)) and [react] decreases as \(t\) increases
  - profile of [product] vs. time: starts at \(t = 0\) at \([\text{product}] = 0\) and [product] increases as time increases

- reaction rates are dependent on concentration; this dependence is given by the rate law

  note: there is one class of reaction that we will discuss for which plot of [X] vs. time is linear, and rate is not dependent on concentration

- average vs. instantaneous reaction rates
  - average rate is the rate of reaction over some time interval; calculated using rate = \(\Delta[X] / \Delta t\)
  - ex. rate of reaction between 1200 and 1600 seconds
  - instantaneous rate is the rate of reaction at a specific time point; calculated as the slope of the line tangent to the concentration vs. time curve at the \(t\) of interest
  - ex. rate of reaction at \(t = 1400\) s
  - an initial rate of reaction is the instantaneous rate of reaction at \(t = 0\) s

- rates of consumption and formation of reactants and products within a reaction are related by stoichiometry
  - ex. \(4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightarrow 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g)\)

  Calculate the rate of consumption of \(\text{NH}_3\) if \([\text{NH}_3]_{0} = 4.000\) M, and \([\text{NH}_3] = 2.560\) M at \(t = 25\) s.
  \(\text{Rate}_{\text{NH}_3} = |\Delta[\text{NH}_3]| / \Delta t; \quad \text{Rate}_{\text{NH}_3} = 0.058\) M\(\cdot\)s\(^{-1}\)

  Calculate the rate of consumption of \(\text{O}_2\).
  \(\text{Rate}_{\text{O}_2} = (0.058\) mol \(\text{NH}_3/\text{Ls})(5\) mol \(\text{O}_2/4\) mol \(\text{NH}_3) = 0.072\) M\(\cdot\)s\(^{-1}\)

  Calculate the rate of formation of \(\text{H}_2\text{O}\).
  \(\text{Rate}_{\text{H}_2\text{O}} = (0.058\) mol \(\text{NH}_3/\text{Ls})(6\) mol \(\text{H}_2\text{O}/4\) mol \(\text{NH}_3) = 0.087\) M\(\cdot\)s\(^{-1}\)

  And . . . . \(\text{Rate}_{\text{NO}} = \text{Rate}_{\text{NH}_3}\)

Dependence of Reaction Rate on Concentration: Rate Laws

- for a given reaction the rate law defines the dependence of rate on concentration
  - consider the generic reaction: \(A + B \rightarrow C + D\)
the rate law is: \( \text{Rate} = k[A]^m[B]^n \)

where:
- \( k \) = rate constant; units depend on \( m \) and \( n \)
- \([A]\) and \([B]\) = concentration of reactants
- \( m \) and \( n \) = exponents define the order or reaction WRT reactants A and B

- a rate law must be experimentally determined
- \( m \) and \( n \) only relate directly to reaction stoichiometry for elementary processes
- more about \( k \):
  - dependent on specific reaction and temperature
  - independent of concentration
  - units depend on \( m \) and \( n \) (orders)
  - order of reaction; \( m \) and \( n \)
    - usually small + whole numbers; but could be ---, 0, or fractions
  - \([A]^m\); \( m \) = order with respect to reactant A
  - \([B]^n\); \( n \) = order with respect to reactant B
  - \( m + n \) = overall order of the reaction

How does rate change dependent on order? What is the factor of change?

- if \( m = 1 \) the reaction is 1st order overall
  - \( \text{rate} \propto [A]^1 \)
  - if \([A]\) doubles rate increases by \( 2^1 \)
    - if \([A]\)_1 = \( x \) M and \([A]\)_2 = \( 2x \) M
      - \( \frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]_2^1}{k[A]_1^1} \)
      - \( \frac{\text{rate}_2}{\text{rate}_1} = \frac{k(2x)^1}{k(x)^1} \)
      - \( \frac{\text{rate}_2}{\text{rate}_1} = 2 \)
      - \( \text{rate}_2 = (\text{rate}_1)(2) \)

- if \( m = 2 \) the reaction is 2nd order overall
  - \( \text{rate} \propto [A]^2 \)
  - if \([A]\) doubles rate increases by \( 2^2 \)
    - if \([A]\)_1 = \( x \) M and \([A]\)_2 = \( 2x \) M
      - \( \frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]_2^2}{k[A]_1^2} \)
      - \( \frac{\text{rate}_2}{\text{rate}_1} = \frac{k(2x)^2}{k(x)^2} \)
      - \( \frac{\text{rate}_2}{\text{rate}_1} = 2^2 \)
      - \( \text{rate}_2 = (\text{rate}_1)(4) \)

- if \( m = -1 \) the reaction is \(-1\) order overall
  - \( \text{rate} \propto [A]^{-1} \)
  - if \([A]\) doubles rate changes by a factor of \( 2^{-1} \)
    - if \([A]\)_1 = \( x \) M and \([A]\)_2 = \( 2x \) M
      - \( \frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]_2^{-1}}{k[A]_1^{-1}} \)
      - \( \frac{\text{rate}_2}{\text{rate}_1} = \frac{k(2x)^{-1}}{k(x)^{-1}} \)
      - \( \frac{\text{rate}_2}{\text{rate}_1} = 2^{-1} \)
      - \( \text{rate}_2 = (\text{rate}_1)(1/2) \)

- if \( m = 0 \) the reaction is 0 order overall
  - \( \text{rate} \propto [A]^0 \)
  - if \([A]\) doubles rate increases by \( 2^0 \)
    - if \([A]\)_1 = \( x \) M and \([A]\)_2 = \( 2x \) M
      - \( \text{rate}_1 = k[A]_1^0 \) and \( \text{rate}_2 = k[A]_2^0 \)
      - \( \text{rate}_1 = k(1) \) and \( \text{rate}_2 = k(1) \ldots \) rate is constant and does not depend on concentration as long as it is > 0
for a reaction with rate law of: \[ \text{rate} = k[A]^m \]
when \([A]\) increases by a factor of 2 (i.e. \(x\) M to \(2x\) M)

\[ \text{rate is multiplied by } 2^1 = 1/2 \]

\[ m = 1 \]

\[ 0 \]

\[ 1 \]

\[ 2 \]

\[ 3 \]

\[ 2^1 = 1 \]

\[ 2^1 = 2 \]

\[ 2^2 = 4 \]

\[ 2^3 = 8 \]

\[ (or \ rate = k[A]^n[B]^m \ when \ [B] \ is \ constant) \]
when \([A]\) increases by a factor of 3 (i.e. \(x\) M to \(3x\) M)

\[ \text{rate is multiplied by } 3^1 = 1/3 \]

\[ m = 1 \]

\[ 0 \]

\[ 1 \]

\[ 2 \]

\[ 3 \]

\[ 3^1 = 1 \]

\[ 3^1 = 3 \]

\[ 3^2 = 9 \]

\[ 3^3 = 27 \]

units of \(k\) dependent on order

<table>
<thead>
<tr>
<th>overall order</th>
<th>rate law</th>
<th>(k)</th>
<th>units of (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(\text{rate} = k[A]^0)</td>
<td>(k = \text{rate})</td>
<td>(\text{M} \cdot \text{s}^{-1})</td>
</tr>
<tr>
<td>1(^{\text{st}})</td>
<td>(\text{rate} = k[A]^1)</td>
<td>(k = \text{rate}[A])</td>
<td>(\text{s}^{-1})</td>
</tr>
<tr>
<td>2(^{\text{nd}})</td>
<td>(\text{rate} = k[A]^2)</td>
<td>(k = \text{rate}[A]^2)</td>
<td>(\text{M}^1 \cdot \text{s}^{-1})</td>
</tr>
<tr>
<td>3(^{\text{rd}})</td>
<td>(\text{rate} = k[A]^3)</td>
<td>(k = \text{rate}[A]^3)</td>
<td>(\text{M}^2 \cdot \text{s}^{-1})</td>
</tr>
</tbody>
</table>

Determination of Rate Law from experimental data:

- Method of Initial Rates
  - reaction repeated with different initial concentrations
  - initial rates measured
  - interpret how rate varies with concentration

- several examples – determine the rate law for the following reactions based on experimental data

  **ex.** \(2\ \text{N}_2\text{O}_5\) (g) \(\rightleftharpoons 4\ \text{NO}_2\) (g) + \(\text{O}_2\) (g)

<table>
<thead>
<tr>
<th>exp’t</th>
<th>([\text{N}_2\text{O}<em>5]</em>{\text{i}}), M</th>
<th>initial rate, (\text{M} \cdot \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.010</td>
<td>(4.8 \times 10^{-5})</td>
</tr>
<tr>
<td>2</td>
<td>0.020</td>
<td>(9.6 \times 10^{-6})</td>
</tr>
</tbody>
</table>

  2 approaches:
  - by inspection: \([\text{N}_2\text{O}_5]\) doubles, rate doubles \(\therefore 1^{\text{st}}\) order with respect to \(\text{N}_2\text{O}_5\)

  set up rate law ratio, plug in data, solve for \(m\)

  \[
  \frac{\text{rate}_2}{\text{rate}_1} = \frac{k[N_2O_5]^m_{\text{2}}}{k[N_2O_5]^m_{\text{1}}} = \frac{9.6 \times 10^{-6} \text{Ms}^{-1}}{4.8 \times 10^{-6} \text{Ms}^{-1}} = \frac{k(0.020)^m}{k(0.010)^m} \]

  \[ m = 1; \quad \text{rate} = k[N_2O_5] \]

  **ex.** \(2\ \text{HgCl}_2\) (aq) + \(\text{C}_2\text{O}_4^{2-}\) (aq) \(\rightleftharpoons 2\ \text{Cl}^-\) (aq) + \(2\ \text{CO}_2\) (g) + \(\text{Hg}_2\text{Cl}_2\) (s)

<table>
<thead>
<tr>
<th>exp’t</th>
<th>([\text{HgCl}<em>2]</em>{\text{i}}), M</th>
<th>([\text{C}_2\text{O}<em>4^{2-}]</em>{\text{i}}), M</th>
<th>initial rate, (\text{M} \cdot \text{min}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.105</td>
<td>0.15</td>
<td>(1.8 \times 10^{-3})</td>
</tr>
<tr>
<td>2</td>
<td>0.105</td>
<td>0.30</td>
<td>(7.1 \times 10^{-5})</td>
</tr>
<tr>
<td>3</td>
<td>0.052</td>
<td>0.30</td>
<td>(3.5 \times 10^{-5})</td>
</tr>
</tbody>
</table>

  compare exp’ts 1 and 2 to determine the order with respect to \(\text{C}_2\text{O}_4^{2-}\) (b/c \([\text{HgCl}_2]\) held constant)

  compare exp’ts 2 and 3 to determine the order with respect to \(\text{HgCl}_2\) (b/c \([\text{C}_2\text{O}_4^{2-}]\) held constant)

  \[
  \frac{\text{rate}_2}{\text{rate}_1} = \frac{k[\text{HgCl}_2]^2_{\text{2}}[\text{C}_2\text{O}_4^{2-}]_{\text{n}}^2}{k[\text{HgCl}_2]^2_{\text{1}}[\text{C}_2\text{O}_4^{2-}]_{\text{n}}^2} = \frac{7.1 \times 10^{-5} \text{Mmin}^{-1}}{1.8 \times 10^{-5} \text{Mmin}^{-1}} = \frac{k(0.105)^m(0.30)^n}{k(0.105)^m(0.15)^n} \]

  \[ m = 1, n = 2; \quad \text{rate} = k[\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2 \]
Determine the value of $k$ (with appropriate units). 

use any one of the exp’ts data; plug rate and concentrations into rate law 

using exp’t 2: 

\[ 7.1 \times 10^{-5} \text{ M s}^{-1} = k(0.105 \text{ M})(0.030 \text{ M})^2 \]

\[ k = 7.5 \times 10^{-3} \text{ M}^2 \text{ s}^{-1} \]

Determine the rate of this reaction when $[\text{HgCl}_2] = 0.050 \text{ M}$ and $[\text{C}_2\text{O}_4^{2-}] = 0.025 \text{ M}$. 

rate = \(7.5 \times 10^{-3} \text{ M}^2 \text{ s}^{-1})(0.050 \text{ M})(0.025 \text{ M})^2\)

rate = \(2.4 \times 10^{-7} \text{ M} \text{ s}^{-1}\)

ex. Consider the reaction of iodide oxidized by \(\text{H}_2\text{O}_2\) in an acidic solution: 

\(\text{H}_2\text{O}_2 + 3 \text{ I}^- + 2 \text{ H}^+ \rightarrow \text{I}_2 + 2 \text{ H}_2\text{O}\)

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{exp’t} & [\text{H}_2\text{O}_2]_0, \text{M} & [\text{I}^-]_0, \text{M} & [\text{H}^+]_0, \text{M} & \text{initial rate, M s}^{-1} \\
\hline
1 & 0.010 & 0.010 & 0.00050 & 1.15 \times 10^{-9} \text{M} \\
2 & 0.020 & 0.010 & 0.00050 & 2.30 \times 10^{-9} \text{M} \\
3 & 0.010 & 0.020 & 0.00050 & 2.30 \times 10^{-9} \text{M} \\
4 & 0.010 & 0.010 & 0.00100 & 1.15 \times 10^{-9} \text{M} \\
\hline
\end{array}
\]

\textbf{note:} in comparing exp’ts 1 and 4, $[\text{H}_2\text{O}_2]$ and $[\text{I}^-]$ are held constant and only $[\text{H}^+]$ is varied, but the rate does not change. Therefore, the order with respect to $\text{H}^+$ is 0.

\[\text{answer: rate} = k[\text{H}_2\text{O}_2][\text{I}^-]\]

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

\[
\begin{array}{|c|c|c|c|}
\hline
\text{exp’t} & [\text{NO}]_0, \text{M} & [\text{O}_2]_0, \text{M} & \text{initial rate, M s}^{-1} \\
\hline
1 & 0.0010 & 0.0010 & 7.10 \text{M s}^{-1} \\
2 & 0.0010 & 0.0040 & 28.4 \text{M s}^{-1} \\
3 & 0.0030 & 0.0040 & 255.6 \text{M s}^{-1} \\
\hline
\end{array}
\]

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

Characteristics of 1\textsuperscript{st}, 2\textsuperscript{nd}, and 0 order reactions

\textbullet For reactions of the general type: \(A \rightarrow \) products

\textbullet integrated rate law

\textbullet half-life equation

\textbullet experimental data plot to support order determination

\textbullet 1\textsuperscript{st} order reactions; rate = \(k[A]\)

\textbf{integrated rate law: use to answer questions relating [A] to time}

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

\[\text{OR} \quad \ln[A]_t = -k t + \ln[A]_0\]

for a 1\textsuperscript{st} order reaction a plot of $\ln[A]$ vs time yields a straight line with slope $= -k$, y int. $= \ln[A]_0$

\textbf{ex.} The decomposition of $\text{H}_2\text{O}_2$ is a 1\textsuperscript{st} order reaction with $k = 7.30 \times 10^{-4} \text{ s}^{-1}$.

Determine the $[\text{H}_2\text{O}_2]$ after 1200 s of reaction if the initial concentration of $\text{H}_2\text{O}_2$ is 2.32 M.

\[\text{answer: 0.967 M}\]

Determine the percent $\text{H}_2\text{O}_2$ that has decomposed after 500 s of reaction.

\[\text{answer: 30.6 % decomposed}\]
Half-life of a reaction; $t_{1/2}$
- time at which 50% of the reactant has been consumed; time req’d for [reactant] to decrease to $1/2$ of its initial value
- at $t_{1/2}$: $t = t_{1/2}$
  $[A] = 1/2[A]_0$
substitute these into the integrated rate law
for a 1$^{st}$ order reaction: $t_{1/2} = \ln2/k = 0.693/k$

**note:** for a 1$^{st}$ order reaction the half-life is constant; dependent on $k$ but not of $[A]_0$

ex. Consider a first-order reaction $A \rightarrow B + C$ with $t_{1/2} = 200$ s.
    if $[A]_0 = 1.0$ M: $[A] 1.0$ M $\rightarrow$ $0.50$ M $[A] 100\% \rightarrow 50\%$ $t = 200$ s
    $[A] 0.50$ M $\rightarrow$ $0.25$ M $[A] 50\% \rightarrow 25\%$ $t = 200$ s
    $[A] 0.25$ M $\rightarrow$ $0.125$ M $[A] 25\% \rightarrow 12.5\%$ $t = 200$ s
etc.
Total time required for $[A]$ to decrease to 6.25% of its initial value? $t = 4 \cdot t_{1/2} = 4(200) = 800$ s

ex. Calculate the half-life for the decomposition of $H_2O_2$. $k = 7.3 \times 10^{-4}$ s$^{-1}$
    $t_{1/2} = 0.693/k = 0.693/7.3 \times 10^{-4}$ s$^{-1} = 950$ s

2$^{nd}$ order reactions
- rate = $k[A]^2$
- integrated rate law:
  $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
- plot of $1/[A]$ vs. $t$ will yield a straight line; slope = $k$ (units M$^{-1}$s$^{-1}$); y int = $1/[A]_0$
- half-life equation
  $t_{1/2} = \frac{1}{k[A]_0}$

**note:** for a 2$^{nd}$ order reaction each successive half-life is 2x as long as the one before it; dependent on $[A]_0$

ex. Consider a first-order reaction $A \rightarrow B + C$ with $t_{1/2} = 200$ s.
    if $[A]_0 = 1.0$ M: $[A] 1.0$ M $\rightarrow$ $0.50$ M $[A] 100\% \rightarrow 50\%$ $t = 200$ s
    $[A] 0.50$ M $\rightarrow$ $0.25$ M $[A] 50\% \rightarrow 25\%$ $t = 400$ s
    $[A] 0.25$ M $\rightarrow$ $0.125$ M $[A] 25\% \rightarrow 12.5\%$ $t = 800$ s
etc.
Total time required for $[A]$ to decrease to 6.25% of its initial value? $t = 200 + 400 + 800 + 1600 = 3000$ s

Zero-order reactions
- rate = $k[A]^0$; rate = $k$
  **note:** rate is not dependent on concentration; rate is constant (as long as there is some $A$ present)
  once the reaction starts it will continue at the same rate until $[A] = 0$
- integrated rate law:
  $[A]_t = -kt + [A]_0$
- plot of $[A]$ vs $t$ will yield a straight line; slope = $-k$ (units M$\cdot$s$^{-1}$); y int = $[A]_0$
half-life equation:

\[ t_{1/2} = \frac{[A]_0}{2k} \]

<table>
<thead>
<tr>
<th>Order</th>
<th>Rate Law</th>
<th>Integrated Rate Law</th>
<th>Half-life Equation</th>
<th>Graph</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Rate = ( k[A]^0 )</td>
<td>([A] = -kt + [A]_0 )</td>
<td>( t_{1/2} = [A]_0/2k )</td>
<td>([A] ) vs ( t ); slope = (-k)</td>
</tr>
<tr>
<td>1</td>
<td>Rate = ( k[A]^1 )</td>
<td>( \ln[A] = -kt + \ln[A]_0 )</td>
<td>( t_{1/2} = 0.693/k )</td>
<td>( \ln[A] ) vs ( t ); slope = (-k)</td>
</tr>
<tr>
<td>2</td>
<td>Rate = ( k[A]^2 )</td>
<td>( 1/[A] = kt + 1/[A]_0 )</td>
<td>( t_{1/2} = 1/[A]_0 )</td>
<td>( 1/[A] ) vs ( t ); slope = ( k)</td>
</tr>
</tbody>
</table>

d a few examples:

ex. For a certain reaction \( k = 0.0217 \text{ s}^{-1} \). Calculate half-life, and determine the time when 5% of the reactant remains.

units of \( k \) are \text{ s}^{-1} \:

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

\[ \text{answer: } t_{1/2} = 32.0 \text{ s} \]

use integrated rate law to determine \( t \) corresponding to 5% \( A \) remaining.

\[ [A]/[A]_0 = 0.05 \]

\[ \text{answer: } 138 \text{ s} \]

ex. For a certain reaction \( 2A \rightarrow B \) the rate law is: \( \text{rate} = k[A]^2 \) and \( k = 0.0250 \text{ M}^{-1} \cdot \text{s}^{-1} \). If \([A]_0 = 1.1 \text{ M}\), determine \([A] \) at 45.0 s. What is \([B] \) at this time?

use the integrated rate law for a 2\text{nd} order reaction to determine \([A]_t\)

\[ \text{answer: } 0.493 \text{ M} \]

\([B] \) formed depends stochiometrically on how much \( A \) is consumed: 1 mol \( B \): 2 mol \( A \)

if \([A]_0 = 1.1 \text{ M} \), and \([A] \) at 45 s = 0.493 M:

\[ [A]_{\text{consumed}} = (1.1 - 0.493) \text{M} = 0.61 \text{molA/L} \]

\( (0.61 \text{molA/L})(1 \text{ molB/2 molA}) = 0.31 \text{ M B present at 45 s} \)

ex. Consider the following data collected for the reaction \( A \rightarrow \) products:

<table>
<thead>
<tr>
<th>Time, min</th>
<th>([A] ), M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>5.00</td>
<td>0.63</td>
</tr>
<tr>
<td>10.0</td>
<td>0.46</td>
</tr>
<tr>
<td>15.0</td>
<td>0.36</td>
</tr>
<tr>
<td>25.0</td>
<td>0.25</td>
</tr>
</tbody>
</table>

a. Calculate the average rate of reaction of \( A \) between 10.0 and 15.0 min. Be sure your units on rate are correct.

b. Determine the order of this reaction (by graphing).

c. From your graph, determine the value of the rate constant (include appropriate units).

d. What is the rate of reaction when \([A] = 0.85 \text{ M}\)?

e. Calculate \( t_{1/2} \) for this reaction.

f. What percent of reactant \( A \) remains after 32.5 min of reaction?

You can find the answer to this problem online on the Handouts page (Answer to Kinetics Practice Problem)
Collision Theory – How do reactions occur?

→ Reactions occur when molecules collide with appropriate orientation and sufficient energy. not all molecular collisions result successfully in the formation of product

→ molecular orientation
consider A\(_2\) + B\(_2\) \(\rightarrow\) 2 AB

![Molecular Collision Diagram]

2 possible orientations:

VS:

energy of collision
molecular collisions are successful when they occur with enough energy to break bonds
minimum energy required for a reaction to occur = activation energy (E\(_a\)) of the reaction
E\(_a\) is dependent on the numbers and types of bonds present; units kJ/mol
if E\(_{\text{collision}}\) > E\(_a\) \(\rightarrow\) product
E\(_{\text{collision}}\) is dependent on temperature; frequency of collision is dependent on concentration and temperature

Temperature Dependence of Rate and k; Arrhenius Equation

→ Reaction rates almost always increase with temperature

→ temperature dependence of k given by the Arrhenius equation:
\[
k = A e^{E_a/R T}
\]

A = frequency factor (NOT concentration of reactant A) \hspace{1cm} R = 8.314 \text{ J/K} \cdot \text{mol}
E\(_a\) = activation energy, kJ/mol \hspace{1cm} T = \text{temp in K}
A and E\(_a\) are called the Arrhenius parameters

→ 2 other forms of the Arrhenius equation:
\[
\ln k = \ln A - \frac{E_a}{RT} \hspace{1cm} \ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

→ Arrhenius plot of experimental data: plot ln k vs 1/T; slope = \(-E_a/R\); y int = ln A

→ examples
ex. 2 \(\text{N}_2\text{O}_5\) (g) \(\rightarrow\) 4 \(\text{NO}_2\) (g) + \(\text{O}_2\) (g) is a 1\(^{st}\) order reaction. If [\(\text{N}_2\text{O}_5\)]\(_0\) = 2.68 M, and at 50° C E\(_a\) = 88 kJ/mol, and A = 4.0 \times 10^{13} \text{ s}^{-1} determine the rate of reaction at 50°C and the value of k at 30°C.

3 step process:
1\(^{st}\) use the Arrhenius equation to determine k at 50°C

\[
\text{answer: } 0.19 \text{ s}^{-1}
\]
2nd use the rate law to determine rate at 50°C  

Answer: 0.51 Ms⁻¹

3rd use the Arrhenius equation to determine k at 30°C  

Answer: 0.021 s⁻¹

ex. The half-life of a 1st order reaction triples when temperature decreases from 25°C to 0°C. Calculate the activation energy for this reaction.

2 T’s:  

\[ T_1 = 25°C (298 K); T_2 = 0°C (273 K) \]

\[ k_1 = 0.693/t_{1/2}; \quad k_2 = 0.693/t_{1/2} \]

but \( (t_{1/2})_2 = 3 \cdot (t_{1/2})_1 \)

so \( k_1 = 3 \cdot k_2 \), and then \( \ln(k_2/k_1) = \ln(1/3) \)

Answer: 29.8 kJ/mol

Catalysis

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

catalysts can be recovered and used again

catalysts are typically required in only small amounts

catalysts are reaction specific

a catalyst provides an alternate path from reactant to product (alternative mechanism); path with lower \( E_a \)

\( k_{cat} > k_{uncat} \)

can use the Arrhenius equation to determine the factor of rate change (= \( k_{cat}/k_{uncat} \)) if you know \( E_{a\,cat} \) vs. \( E_{a\,uncat} \)

can use the Arrhenius equation to determine the catalyzed reaction’s \( E_a \) if you know factor of rate change (or \( k’s \))

homogeneous vs. heterogeneous catalysis

homogeneous catalyst is in the same phase as the reacting species

i.e.  
\[ 2 \text{H}_2\text{O}_2 (aq) \rightarrow 2 \text{H}_2\text{O} (l) + \text{O}_2 (g); \text{catalyzed by HBr (aq)} \]

heterogeneous catalyst is in a different phase than the reacting species

usually catalyst is (s) and reactants are (aq) or (g)

typical heterogeneous catalysts have a high surface area are

i.e. finely divided powders or metals

Raney-Ni, Pd, Pt, SiO₂, Al₂O₃

i.e. catalytic hydrogenation of ethylene: \( \text{C}_2\text{H}_4 (g) + \text{H}_2 (g) \rightarrow \text{C}_2\text{H}_6 (g); \text{catalyzed by SiO}_2 \)

i.e. catalytic converter in cars; converts CO \( \rightarrow \text{CO}_2 \) and NO \( \rightarrow \text{N}_2 \) and \( \text{O}_2 \); poisoned by Pb

Good catalysts will:

- have high selectivity
- have high turnover rate and number
- be required in only small quantity
- be easily regenerated

have low probability of side reactions

not be easily poisoned

be easily regenerated
Reaction Profiles:
- plot of energy vs. reaction coordinate for a chemical reaction
- reactants at some initial energy level
  energy increases as reactants come together to form reaction intermediate
  transition state (intermediate) corresponds to energy maximum in profile (activation barrier of reaction, $E_a$)
  energy decreases as the intermediate goes on to form products at some final energy level
  can identify $E_a$ and $\Delta E$ for the both the forward and reverse reaction; $E_a$ – kinetics vs. $\Delta E$ – thermodynamics
- single step profile vs. multi-step profile

Reaction Mechanism
- step by step path from reactants to products
  each individual step is an elementary process
  $\text{m A + n B } \rightarrow \text{ product; so the rate law: rate } = k[A]^m[B]^n$
- Is a proposed mechanism plausible?
  hard to prove a mechanism (requires isolating and identifying intermediates; usually unstable)
  a proposed mechanism is plausible if:
  1. it is consistent with the overall stoichiometry of the reaction
  2. it accounts for the experimentally determined rate law
- molecularity
  each step in a mechanism can be described by its molecularity; number of molecules interacting
  unimolecular: 1 molecule; i.e $A_2 \rightarrow 2 A$
  bimolecular: 2 molecules; $A_2 + B_2 \rightarrow 2 AB$
  termolecular and beyond: 3 or more molecules; not very likely
- each step may be reversible
  $A \leftrightarrow B$; rate $\text{for} = \text{ rate }\text{ rev}$
- steps may be fast or slow
  the rate-determining step (RDS) in a mechanism is the slow step; rate law of mechanism = rate law of RDS
- use mechanisms to identify reaction intermediate and catalyst
  a reaction intermediate is produced in one step and consumed in a later step
  a catalyst is consumed in one step and re-formed in a later step
  note: neither catalysts nor intermediates can appear in the net reaction or the rate law
- ex. consider the proposed mechanism for the depletion of ozone by chlorine atoms in the stratosphere
  step 1: \[ \text{Cl (g) + O}_3 \text{(g)} \rightarrow \text{ClO (g) + O}_2 \text{(g)}; \quad \text{bimolecular; rate law: rate } = k[\text{Cl}][\text{O}_3] \]
  step 2: \[ \text{ClO (g) + O (g)} \rightarrow \text{Cl (g) + O}_2 \text{(g)} \quad \text{bimolecular; rate law: rate } = k[\text{ClO}][\text{O}] \]
  net rxn: \[ \text{O}_3 \text{(g) + O (g)} \rightarrow 2 \text{O}_2 \text{(g)} \quad \text{Cl (g) catalyst; ClO (g) reaction intermediate} \]
Consider the 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 the following proposed mechanism plausible?

**step 1 (SLOW):** \[ \text{H}_2 + \text{ICl} \rightarrow \text{HI} + \text{ICl} \]

**step 2 (FAST):** \[ \text{HI} + \text{ICl} \rightarrow \text{HCl} + \text{I}_2 \]

**net rxn:** \[ \text{H}_2 + 2 \text{ICl} \rightarrow 2 \text{HCl} + \text{I}_2 \]

The net reaction and rate law from the mechanism suggest that this is a plausible mechanism.

**note:** rate law determined experimentally can often provide clues to the reaction mechanism

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

\[ \Delta H^\circ \text{data: } \text{N}_2\text{O}_4:8.8 \text{ kJ/mol; } \text{NO}_2:32.3 \text{ kJ/mol; } 93.5 \text{ kJ/mol; } \text{FNO}_2:-81.3 \text{ kJ/mol} \]

**mechanism:**

1. \[ \text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2 \quad E_a = 59 \text{ kJ/mol} \quad \Delta H_1 = +55.6 \text{ kJ} \]
2. \[ \text{NO}_2 + \text{F}_2 \rightarrow \text{F} + \text{FNO}_2 \quad E_a = 83 \text{ kJ/mol} \quad \Delta H_2 = -20 \text{ kJ} \]
3. \[ \text{F} + \text{NO}_2 \rightarrow \text{FNO}_2 \quad E_a = 9 \text{ kJ/mol} \quad \Delta H_3 = -207 \text{ kJ} \]

**net rxn:** \[ \text{N}_2\text{O}_4 + \text{F}_2 \rightarrow 2 \text{FNO}_2 \quad \Delta H_{\text{rxn}} = -171.4 \text{ kJ} \]

step 2 is the RDS because it has the largest \( E_a \) and will therefore be the slowest

\( \text{NO}_2 \) and \( \text{F} \) are reaction intermediates

putting this all together construct a reaction profile: