Chapter 12
Chemical Kinetics
Stoichiometry

Allows us to calculate the theoretical amounts of reactants and products from a balanced chemical reaction
Thermodynamics

Allows us to predict whether a reaction will occur (is spontaneous) and how energy is exchanged with the surroundings.
What is missing?
The rate of a reaction!

Stoichiometry or thermodynamics tells us nothing about how fast a reaction proceeds!

A reaction may be spontaneous and very exothermic yet proceed at a very slow rate!
Example:

\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}) \]
\[ \Delta H_f = -92.22 \text{ kJmol}^{-1} \]

Even though spontaneous and exothermic, no reaction is observed at room temperature!

High temperatures and a catalyst are needed to make the reaction proceed at a measurable rate.
Chemical Kinetics

The study of the factors which determine the rates of chemical reactions
What does chemical kinetics tell us?
Gives information on the actual steps (mechanism) by which a reaction takes place (usually not the same as the balanced reaction).

Example: there is a very low probability that four molecules will simultaneously collide in the reaction:

\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}) \]

The actual reaction must therefore process by a number of simpler steps, which when combined give us the balanced reaction.

Chemical kinetics helps us deduce these steps!
Rate of Reaction

The change in the concentration of a reactant or product with time

\[ \text{rate} = \frac{\Delta [A]}{\Delta t} \]

Units are always \( \text{molL}^{-1}\text{s}^{-1} \)
Rates can be measured from concentration changes of reactants or products:

\[ aA \rightarrow bB + cC \]

Rates are always **positive** so for products:

\[ \text{rate} = \frac{\Delta[B]}{\Delta t} \text{ or } \frac{\Delta[C]}{\Delta t} \]

and for reactants:

\[ \text{rate} = -\frac{\Delta[A]}{\Delta t} \]
<table>
<thead>
<tr>
<th>Time (±1 s)</th>
<th>NO₂</th>
<th>NO</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>0.0079</td>
<td>0.0021</td>
<td>0.0011</td>
</tr>
<tr>
<td>100</td>
<td>0.0065</td>
<td>0.0035</td>
<td>0.0018</td>
</tr>
<tr>
<td>150</td>
<td>0.0055</td>
<td>0.0045</td>
<td>0.0023</td>
</tr>
<tr>
<td>200</td>
<td>0.0048</td>
<td>0.0052</td>
<td>0.0026</td>
</tr>
<tr>
<td>250</td>
<td>0.0043</td>
<td>0.0057</td>
<td>0.0029</td>
</tr>
<tr>
<td>300</td>
<td>0.0038</td>
<td>0.0062</td>
<td>0.0031</td>
</tr>
<tr>
<td>350</td>
<td>0.0034</td>
<td>0.0066</td>
<td>0.0033</td>
</tr>
<tr>
<td>400</td>
<td>0.0031</td>
<td>0.0069</td>
<td>0.0035</td>
</tr>
</tbody>
</table>

TABLE 12.1 Concentrations of Reactant and Products as a Function of Time for the Reaction $2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g)$ (at 300°C)
Plot of concentration vs. time
Average Rate

Change in concentration over a given time period

Example:

Rate between 50 and 100 s from $[\text{NO}_2]$:

\[
\text{rate} = -\frac{\Delta [\text{NO}_2]}{\Delta t} = -\frac{(0.0065 - 0.0079 \text{ molL}^{-1})}{(100 - 50. \text{ s})} = 2.8 \times 10^{-5} \text{ molL}^{-1}\text{s}^{-1}
\]
Rate decreases with time as reactant is consumed
**Instantaneous Rate**

Rate at a given instant obtained from slope of a line tangent to the curve at that time

Example:

Rate at 100 s from \([\text{NO}_2]\):

\[
\text{rate} = -\Delta[\text{NO}_2]/\Delta t \\
= -(-0.0026 \text{ molL}^{-1}/110. \text{ s}) \\
= 2.4 \times 10^{-5} \text{ molL}^{-1}\text{s}^{-1}
\]
Relative Rates depend on Stoichiometry

The coefficients in a balanced reaction relate the rate of disappearance of reactants to the rate of appearance of products

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

\[-\Delta\text{[NO}_2]/\Delta t = \Delta\text{[NO]}/\Delta t = 2(\Delta\text{[O}_2]/\Delta t)\]

Proof: slope of NO curve always double slope of O\(_2\) curve!

Therefore important to state which species the rate is defined by!
For the generic reaction:

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

\[
-(1/a)\Delta[A]/\Delta t = -(1/b)\Delta[B]/\Delta t = (1/c)\Delta[C]/\Delta t = (1/d)\Delta[D]/\Delta t
\]

From this it is possible to derive the rate relationships between any pair of reactants or products
Describe all the rate relationships in the gas phase combustion of benzene (hexacarbon hexahydride)
21. Consider the reaction

$$4\text{PH}_3(g) \rightarrow \text{P}_4(g) + 6\text{H}_2(g)$$

If, in a certain experiment, over a specific time period, 0.0048 mol \text{PH}_3 is consumed in a 2.0-L container each second of reaction, what are the rates of production of \text{P}_4 and \text{H}_2 in this experiment?
23. At 40°C, \( \text{H}_2\text{O}_2(aq) \) will decompose according to the following reaction:

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

The following data were collected for the concentration of \( \text{H}_2\text{O}_2 \) at various times.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>([\text{H}_2\text{O}_2]) (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.000</td>
</tr>
<tr>
<td>(2.16 \times 10^4)</td>
<td>0.500</td>
</tr>
<tr>
<td>(4.32 \times 10^4)</td>
<td>0.250</td>
</tr>
</tbody>
</table>

a. Calculate the average rate of decomposition of \( \text{H}_2\text{O}_2 \) between 0 and \(2.16 \times 10^4\) s. Use this rate to calculate the average rate of production of \( \text{O}_2(g) \) over the same time period.

b. What are these rates for the time period \(2.16 \times 10^4\) s to \(4.32 \times 10^4\) s?
(Differential) Rate Laws

Describes how rate varies with reactant concentration:

\[ aA \rightarrow bB + cC \]

\[ \text{rate} = \frac{-\Delta[A]}{\Delta t} = k[A]^n \]

\[ k = \text{rate constant} \]
\[ n = \text{order} \]

\( k \) and \( n \) are determined experimentally \textbf{not} from stoichiometry!

The rate always has units of m\text{olL}^{-1}\text{s}^{-1} while the units of the rate constant depend on the order.
Assumption

The rate of the reverse reaction is not significant so the overall rate of reaction only depends on the reactant concentrations and not on the product concentrations!
Form of Rate Law

Experimental determination of the power to which each reactant is raised in the rate law
<table>
<thead>
<tr>
<th>$[N_2O_5]$ (mol/L)</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>0.88</td>
<td>200</td>
</tr>
<tr>
<td>0.78</td>
<td>400</td>
</tr>
<tr>
<td>0.69</td>
<td>600</td>
</tr>
<tr>
<td>0.61</td>
<td>800</td>
</tr>
<tr>
<td>0.54</td>
<td>1000</td>
</tr>
<tr>
<td>0.48</td>
<td>1200</td>
</tr>
<tr>
<td>0.43</td>
<td>1400</td>
</tr>
<tr>
<td>0.38</td>
<td>1600</td>
</tr>
<tr>
<td>0.34</td>
<td>1800</td>
</tr>
<tr>
<td>0.30</td>
<td>2000</td>
</tr>
</tbody>
</table>
Plot of concentration vs. time

Rate at 0.45 M is half that at 0.90 M
When \([\text{N}_2\text{O}_5]\) is halved rate is halved so rate depends on \([\text{N}_2\text{O}_5]\) to the first power:

\[
\text{rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]^1 = k[\text{N}_2\text{O}_5]
\]

The reaction is 1\(^{st}\) order in \(\text{N}_2\text{O}_5\)

This is not the same as its coefficient!

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

rate = $k[A]^m$

<table>
<thead>
<tr>
<th>Order</th>
<th>Rate Law</th>
<th>[A]</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>$k[A]$</td>
<td>x2</td>
<td>x2</td>
</tr>
<tr>
<td>2nd</td>
<td>$k[A]^2$</td>
<td>x2</td>
<td>x4</td>
</tr>
<tr>
<td>3rd</td>
<td>$k[A]^3$</td>
<td>x2</td>
<td>x8</td>
</tr>
<tr>
<td>nth</td>
<td>$k[A]^n$</td>
<td>xa</td>
<td>$xa^n$</td>
</tr>
</tbody>
</table>

In practice we rarely see orders above 2, $1^{\text{st}}$ order reactions being most common.
Method of Initial Rates

Instantaneous rate measured close to $t=0$ before reactant concentrations have had time to change.

By varying initial concentrations we can determine the form by observing how rate depends on concentration.

For reactions with multiple reactants, only one concentration is changed at a time, the others being held constant.
From the measurements below determine the orders of each reactant and the rate constant for the reaction:

\[ \text{NH}_4^+(aq) + \text{NO}_2^-(aq) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l) \]

given:

\[ \text{rate} = -\Delta[\text{NH}_4^+]/\Delta t = k[\text{NH}_4^+]^n[\text{NO}_2^-]^m \]

**TABLE 12.4 Initial Rates from Three Experiments for the Reaction**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial Concentration of (\text{NH}_4^+)</th>
<th>Initial Concentration of (\text{NH}_2^-)</th>
<th>Initial Rate (mol/L \cdot s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100 (M)</td>
<td>0.0050 (M)</td>
<td>(1.35 \times 10^{-7})</td>
</tr>
<tr>
<td>2</td>
<td>0.100 (M)</td>
<td>0.010 (M)</td>
<td>(2.70 \times 10^{-7})</td>
</tr>
<tr>
<td>3</td>
<td>0.200 (M)</td>
<td>0.010 (M)</td>
<td>(5.40 \times 10^{-7})</td>
</tr>
</tbody>
</table>
27. The reaction

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

was studied at \(-10^\circ\text{C}\). The following results were obtained where

\[
\text{Rate} = -\frac{\Delta[\text{Cl}_2]}{\Delta t}
\]

<table>
<thead>
<tr>
<th>([\text{NO}]_0) (mol/L)</th>
<th>([\text{Cl}_2]_0) (mol/L)</th>
<th>Initial Rate (mol/L \cdot \text{min})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>0.18</td>
</tr>
<tr>
<td>0.10</td>
<td>0.20</td>
<td>0.36</td>
</tr>
<tr>
<td>0.20</td>
<td>0.20</td>
<td>1.45</td>
</tr>
</tbody>
</table>

a. What is the rate law?
b. What is the value of the rate constant?
Another approach useful for more complex cases...
The following data were obtained for the reaction:

\[
\text{BrO}_3^- (\text{aq}) + 5\text{Br}^- (\text{aq}) + 6\text{H}^+ (\text{aq}) \rightarrow 3\text{Br}_2 (\text{aq}) + 3\text{H}_2\text{O} (\text{l})
\]

where rate = \( k[\text{BrO}_3^-]^m[\text{Br}^-]^n[\text{H}^+]^p \)

<table>
<thead>
<tr>
<th>Exp</th>
<th>([\text{BrO}_3^-]_0) (molL(^{-1}))</th>
<th>([\text{Br}^-]_0) (molL(^{-1}))</th>
<th>([\text{H}^+]_0) (molL(^{-1}))</th>
<th>Rate(_0) (molL(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.178</td>
<td>0.563</td>
<td>0.299</td>
<td>5.78 x 10(^{-4})</td>
</tr>
<tr>
<td>2</td>
<td>0.356</td>
<td>0.563</td>
<td>0.299</td>
<td>1.16 x 10(^{-3})</td>
</tr>
<tr>
<td>3</td>
<td>0.356</td>
<td>1.126</td>
<td>0.299</td>
<td>2.31 x 10(^{-3})</td>
</tr>
<tr>
<td>4</td>
<td>0.178</td>
<td>0.563</td>
<td>0.598</td>
<td>2.31 x 10(^{-3})</td>
</tr>
</tbody>
</table>

What is the rate law and rate constant?
Divide by lowest value in each column:

<table>
<thead>
<tr>
<th>Exp</th>
<th>$[\text{BrO}_3^-]_0$ (mol L$^{-1}$)</th>
<th>$[\text{Br}^-]_0$ (mol L$^{-1}$)</th>
<th>$[\text{H}^+]_0$ (mol L$^{-1}$)</th>
<th>$\text{Rate}_0$ (mol L$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.178</td>
<td>0.563</td>
<td>0.299</td>
<td>$5.78 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>0.356</td>
<td>0.563</td>
<td>0.299</td>
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<tr>
<td>3</td>
<td>0.356</td>
<td>1.126</td>
<td>0.299</td>
<td>$2.31 \times 10^{-3}$</td>
</tr>
<tr>
<td>4</td>
<td>0.178</td>
<td>0.563</td>
<td>0.598</td>
<td>$2.31 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Divide by lowest value in each column:

<table>
<thead>
<tr>
<th>Exp</th>
<th>([\text{BrO}_3^-]_0) (molL(^{-1}))</th>
<th>([\text{Br}^-]_0) (molL(^{-1}))</th>
<th>([\text{H}^+]_0) (molL(^{-1}))</th>
<th>Rate(_0) (molL(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>
Divide by lowest value in each column:

<table>
<thead>
<tr>
<th>Exp</th>
<th>$[\text{BrO}_3^-]_0$ (molL$^{-1}$)</th>
<th>$[\text{Br}^-]_0$ (molL$^{-1}$)</th>
<th>$[\text{H}^+]_0$ (molL$^{-1}$)</th>
<th>Rate$_0$ (molL$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

Compare 1 and 2 ([Br$^-$] and [H$^+$] constant):
$[\text{BrO}_3^-] \times 2$, rate x2
1$^{st}$ order in $\text{BrO}_3^-$!
Divide by lowest value in each column:

<table>
<thead>
<tr>
<th>Exp</th>
<th>$[\text{BrO}_3^-]_0$ (molL$^{-1}$)</th>
<th>$[\text{Br}^-]_0$ (molL$^{-1}$)</th>
<th>$[\text{H}^+]_0$ (molL$^{-1}$)</th>
<th>Rate$_0$ (molL$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

Compare 1 and 2 ([Br$^-$] and [H$^+$] constant):
$[\text{BrO}_3^-]$ x2, rate x2
1$^{\text{st}}$ order in BrO$_3^-$!

Compare 2 and 3 ([BrO$_3^-$] and [H$^+$] constant):
$[\text{Br}^-]$ x2, rate x2
1$^{\text{st}}$ order in Br$^-$!
Divide by lowest value in each column:

<table>
<thead>
<tr>
<th>Exp</th>
<th>$[\text{BrO}_3^-]_0$ (molL$^{-1}$)</th>
<th>$[\text{Br}^-]_0$ (molL$^{-1}$)</th>
<th>$[\text{H}^+]_0$ (molL$^{-1}$)</th>
<th>Rate$_0$ (molL$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

Compare 1 and 2 ([Br$^-$] and [H$^+$] constant):
$[\text{BrO}_3^-]$ x2, rate x2
1$^{\text{st}}$ order in BrO$_3^-$!

Compare 2 and 3 ([BrO$_3^-$] and [H$^+$] constant):
[Br$^-$] x2, rate x2
1$^{\text{st}}$ order in Br$^-$!

Compare 1 and 4 ([BrO$_3^-$] and [Br$^-$] constant):
[H$^+$] x2, rate x4
2$^{\text{nd}}$ order in H$^+$!
Divide by lowest value in each column:

<table>
<thead>
<tr>
<th>Exp</th>
<th>([\text{BrO}_3^-]_0) (molL(^{-1}))</th>
<th>([\text{Br}^-]_0) (molL(^{-1}))</th>
<th>([\text{H}^+]_0) (molL(^{-1}))</th>
<th>Rate(_0) (molL(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

Compare 1 and 2 (\([\text{Br}^-]\) and \([\text{H}^+]\) constant):
\([\text{BrO}_3^-]\) x2, rate x2
1\(^{st}\) order in \text{BrO}_3^-!

Compare 2 and 3 (\([\text{BrO}_3^-]\) and \([\text{H}^+]\) constant):
\([\text{Br}^-]\) x2, rate x2
1\(^{st}\) order in \text{Br}^-!

Compare 1 and 4 (\([\text{BrO}_3^-]\) and \([\text{Br}^-]\) constant):
\([\text{H}^+]\) x2, rate x4
2\(^{nd}\) order in \text{H}^+!

rate = \(k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2\)
31. The reaction

\[ \text{I}^- (aq) + \text{OCl}^- (aq) \rightarrow \text{IO}^- (aq) + \text{Cl}^- (aq) \]

was studied, and the following data were obtained:

<table>
<thead>
<tr>
<th>([I^-]_0 ) (mol/L)</th>
<th>([\text{OCl}^-]_0 ) (mol/L)</th>
<th>Initial Rate (mol/L \cdot s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.18</td>
<td>(7.91 \times 10^{-2})</td>
</tr>
<tr>
<td>0.060</td>
<td>0.18</td>
<td>(3.95 \times 10^{-2})</td>
</tr>
<tr>
<td>0.030</td>
<td>0.090</td>
<td>(9.88 \times 10^{-3})</td>
</tr>
<tr>
<td>0.24</td>
<td>0.090</td>
<td>(7.91 \times 10^{-2})</td>
</tr>
</tbody>
</table>

a. What is the rate law?

b. Calculate the value of the rate constant.

c. Calculate the initial rate for an experiment where both \(\text{I}^-\) and \(\text{OCl}^-\) are initially present at 0.15 mol/L.
Integrated Rate Laws

Describe how reactant concentrations vary with time

Related to the differential rate law mathematically – know one, know the other

The type of rate law determined by experiment depends on which data is easiest to collect
1st Order Rate Laws

\[ aA \rightarrow \text{products} \]

\[
\text{Rate} = -\Delta[A]/\Delta t = k[A]^1 = k[A]
\]

The rate constant of a 1st order reaction has units of s\(^{-1}\) and hence is independent of concentration.
Integrating the 1st Order Rate Law

\[-\Delta[A]/\Delta t = k[A]\]

\[-\Delta[A]/[A] = k\Delta t\]

In the limit \(\Delta[A] \to 0\) and \(\Delta t \to 0\), \(\Delta[A] \to d[A]\) and \(\Delta t \to dt\)

\[-\frac{d[A]}{[A]} = kdt\]

Integrating between \(t = 0\), \([A] = [A]_0\) and \(t = t\), \([A] = [A]\):

\[-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = k\int_0^t dt\]

\[-(\ln[A] - \ln[A]_0) = kt\]

\(\ln[A] = -kt + \ln[A]_0\)

\(y = mx + b\)

A linear equation!
\[ \ln[A] = -kt + \ln[A]_0 \]

Plot of \( \ln[A] \) vs. \( t \) will give a straight line with slope \(-k\) and intercept \( \ln[A]_0 \)
Measurements of concentration vs. time were collected for the reaction:

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

<table>
<thead>
<tr>
<th>[N$_2$O$_5$] (molL$^{-1}$)</th>
<th>t (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1000</td>
<td>0</td>
</tr>
<tr>
<td>0.0707</td>
<td>50.</td>
</tr>
<tr>
<td>0.0500</td>
<td>100.</td>
</tr>
<tr>
<td>0.0250</td>
<td>200.</td>
</tr>
<tr>
<td>0.0125</td>
<td>300.</td>
</tr>
<tr>
<td>0.00625</td>
<td>400.</td>
</tr>
</tbody>
</table>

Verify that the rate law is first order in N$_2$O$_5$ and calculate the rate constant.

What is the value of [N$_2$O$_5$] 150 s after the start of the reaction?
<table>
<thead>
<tr>
<th>$t$ (s)</th>
<th>$\ln[N_2O_5]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-2.303</td>
</tr>
<tr>
<td>50</td>
<td>-2.649</td>
</tr>
<tr>
<td>100</td>
<td>-2.996</td>
</tr>
<tr>
<td>200</td>
<td>-3.689</td>
</tr>
<tr>
<td>300</td>
<td>-4.382</td>
</tr>
<tr>
<td>400</td>
<td>-5.075</td>
</tr>
</tbody>
</table>
1st Order Plot

\[ y = -6.930526316 \times 10^{-3} - 2.302824561 \]
\[ R^2 = -0.9999999846 \]
33. The decomposition of hydrogen peroxide was studied, and the following data were obtained at a particular temperature:

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>([\text{H}_2\text{O}_2]) (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
</tr>
<tr>
<td>120 ± 1</td>
<td>0.91</td>
</tr>
<tr>
<td>300 ± 1</td>
<td>0.78</td>
</tr>
<tr>
<td>600 ± 1</td>
<td>0.59</td>
</tr>
<tr>
<td>1200 ± 1</td>
<td>0.37</td>
</tr>
<tr>
<td>1800 ± 1</td>
<td>0.22</td>
</tr>
<tr>
<td>2400 ± 1</td>
<td>0.13</td>
</tr>
<tr>
<td>3000 ± 1</td>
<td>0.082</td>
</tr>
<tr>
<td>3600 ± 1</td>
<td>0.050</td>
</tr>
</tbody>
</table>

Assuming that

\[
\text{Rate} = -\frac{\Delta [\text{H}_2\text{O}_2]}{\Delta t}
\]

determine the rate law, the integrated rate law, and the value of the rate constant. Calculate \([\text{H}_2\text{O}_2]\) at 4000. s after the start of the reaction.
<table>
<thead>
<tr>
<th>t(s)</th>
<th>$[H_2O_2]$ (molL$^{-1}$)</th>
<th>$\ln[H_2O_2]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
<td>0.000</td>
</tr>
<tr>
<td>120</td>
<td>0.91</td>
<td>-0.094</td>
</tr>
<tr>
<td>300.</td>
<td>0.78</td>
<td>-0.25</td>
</tr>
<tr>
<td>600.</td>
<td>0.59</td>
<td>-0.53</td>
</tr>
<tr>
<td>1200.</td>
<td>0.37</td>
<td>-0.99</td>
</tr>
<tr>
<td>1800.</td>
<td>0.22</td>
<td>-1.51</td>
</tr>
<tr>
<td>2400.</td>
<td>0.13</td>
<td>-2.04</td>
</tr>
<tr>
<td>3000.</td>
<td>0.082</td>
<td>-2.50</td>
</tr>
<tr>
<td>3600.</td>
<td>0.050</td>
<td>-3.00</td>
</tr>
</tbody>
</table>
1st Order Plot

\[ y = -8.352360858 \times 10^{-4} - 4.358462591 \times 10^{-3} \]

\[ R^2 = -0.999886085 \]
Normally, you should always perform linear regression analysis on the data!

However, in this class you can assume that the data will always be correlated well enough that the slope can be determined from two points on the line.
Half-Life of a 1st Order Reaction ($t_{\frac{1}{2}}$)

The time for a reactant to reach half its original concentration is $t_{\frac{1}{2}} = 100$ s.

<table>
<thead>
<tr>
<th>$[\text{N}_2\text{O}_5]_0$ (mol/L)</th>
<th>$t$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1000</td>
<td>0</td>
</tr>
<tr>
<td>0.0707</td>
<td>50</td>
</tr>
<tr>
<td>0.0500</td>
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<tr>
<td>0.0250</td>
<td>200</td>
</tr>
<tr>
<td>0.0125</td>
<td>300</td>
</tr>
<tr>
<td>0.00625</td>
<td>400</td>
</tr>
</tbody>
</table>
Derivation of the Half-Life of a 1\textsuperscript{st} Order Reaction

\[ aA \rightarrow \text{products} \]

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

Rearranging:

\[ \ln([A]/[A]_0) = kt \]

When \( t = t_{\frac{1}{2}} \):

\[ [A] = [A]_0/2 \]

Substituting:

\[ \ln([A]_0/[A]_0/2) = kt_{\frac{1}{2}} \]

\[ \ln(2) = kt_{\frac{1}{2}} \]

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

For a 1\textsuperscript{st} order reaction, \( t_{\frac{1}{2}} \) is constant and independent of concentration!
Given that a 1st order reaction has a half-life of 12 s, calculate the rate constant and the time required for the reaction to be 85% complete.

47. A first-order reaction is 75.0% complete in 320. s.
   a. What are the first and second half-lives for this reaction?
   b. How long does it take for 90.0% completion?
2\textsuperscript{nd} Order Rate Laws

\[ aA \rightarrow \text{products} \]

\[ \text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2 \]
Integrating the 2\textsuperscript{nd} Order Rate Law

\(-\Delta[A]/\Delta t = k[A]^2\)

\(-\Delta[A]/[A]^2 = k\Delta t\)

In the limit \(\Delta[A] \rightarrow 0\) and \(\Delta t \rightarrow 0\), \(\Delta[A] \rightarrow d[A]\) and \(\Delta t \rightarrow dt\)

\[-\frac{d[A]}{[A]^2} = kdt\]

Integrating between \(t = 0, [A] = [A]_0\) and \(t = t, [A] = [A]\):

\[-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = k\int_{0}^{t} dt\]

\[-(-\frac{1}{[A]} - (-\frac{1}{[A]_0})) = kt\]

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

\[y = mx + b\]
\[
\frac{1}{[A]} = kt + \frac{1}{[A]_0}
\]

Plot of \(1/[A]\) vs. \(t\) will give a straight line with slope \(k\) and intercept \([A]_0\)
35. The rate of the reaction

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

depends only on the concentration of nitrogen dioxide below 225°C. At a temperature below 225°C, the following data were collected:

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[NO(_2)] (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.500</td>
</tr>
<tr>
<td>1.20 \times 10^3</td>
<td>0.444</td>
</tr>
<tr>
<td>3.00 \times 10^3</td>
<td>0.381</td>
</tr>
<tr>
<td>4.50 \times 10^3</td>
<td>0.340</td>
</tr>
<tr>
<td>9.00 \times 10^3</td>
<td>0.250</td>
</tr>
<tr>
<td>1.80 \times 10^4</td>
<td>0.174</td>
</tr>
</tbody>
</table>

a. Verify the reaction is 2\(^{nd}\) order by plotting the appropriate graph
b. Calculate the value of the rate constant
c. Calculate [NO\(_2\)] 2.70 \times 10^4 s after the start of the reaction
<table>
<thead>
<tr>
<th>t(s)</th>
<th>[NO₂] (M)</th>
<th>1/[NO₂] (M⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.500</td>
<td>2.00</td>
</tr>
<tr>
<td>1.20 x 10³</td>
<td>0.444</td>
<td>2.25</td>
</tr>
<tr>
<td>3.00 x 10³</td>
<td>0.381</td>
<td>2.62</td>
</tr>
<tr>
<td>4.50 x 10³</td>
<td>0.340</td>
<td>2.94</td>
</tr>
<tr>
<td>9.00 x 10³</td>
<td>0.250</td>
<td>4.00</td>
</tr>
<tr>
<td>1.80 x 10⁴</td>
<td>0.174</td>
<td>5.75</td>
</tr>
</tbody>
</table>
Derivation of the Half-Life of a 2nd Order Reaction

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

When \( t = t_{1/2} \):

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

Substituting:

\[ \frac{1}{\left(\frac{[A]_0}{2}\right)} = kt_{1/2} + \frac{1}{[A]_0} \]

\[ \frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2} \]

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

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

For a 2nd order reaction, \( t_{1/2} \) depends on both \( k \) and \( [A]_0 \)!

Each successive half-life is double the preceding one since after each half-life \( [A]_0 \) halves!
51. For the reaction $A \rightarrow \text{products}$, successive half-lives are observed to be 10.0, 20.0, and 40.0 min for an experiment in which $[A]_0 = 0.10 \, M$. Calculate the concentration of $A$ at the following times.

a. 80.0 min  
b. 30.0 min
0\textsuperscript{th} Order Rate Laws

\[ aA \rightarrow \text{products} \]

\[
\text{Rate} = -\Delta[A]/\Delta t = k[A]^0 = k
\]

The rate is constant and doesn’t depend on concentration

Commonly seen when reactions occur on a surface or in biological systems involving enzymes
Integrating the 0th Order Rate Law

\[-\Delta[A]/\Delta t = k\]

\[-\Delta[A] = k\Delta t\]

In the limit \(\Delta[A] \to 0\) and \(\Delta t \to 0\), \(\Delta[A] \to d[A]\) and \(\Delta t \to dt\)

\[-d[A] = kdt\]

Integrating between \(t = 0\), \([A] = [A]_0\) and \(t = t\), \([A] = [A]\):

\[-\int_{[A]_0}^{[A]} dA = k\int_0^{t} dt\]

\[-([A] - [A]_0) = kt\]

\([A] = -kt + [A]_0\]

\(y = mx + b\)
\[ [A] = -kt + [A]_0 \]

Plot of \([A]\) vs. \(t\) will give a straight line with slope \(-k\) and intercept \([A]_0\)
Derivation of the Half-Life of a 0th Order Reaction

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

When \( t = t_{1/2} \):

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

Substituting:

\[ \frac{[A]_0}{2} = -kt_{1/2} + [A]_0 \]

\[ \frac{[A]_0}{2} - [A]_0 = -kt_{1/2} \]

\[ -\frac{[A]_0}{2} = -kt_{1/2} \]

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

For a 0th order reaction, \( t_{1/2} \) again depends on both \( k \) and \( [A]_0 \)!

Each successive half-life is half the preceding one since after each half-life \([A]_0\) halves!
Measurements of concentration vs. time were collected for the reaction:

\[ aA \rightarrow \text{products} \]

<table>
<thead>
<tr>
<th>[A] (molL^{-1})</th>
<th>t (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.48</td>
<td>0.0</td>
</tr>
<tr>
<td>3.82</td>
<td>114.6</td>
</tr>
<tr>
<td>2.40</td>
<td>355.4</td>
</tr>
<tr>
<td>0.575</td>
<td>672.0</td>
</tr>
</tbody>
</table>

Verify that the rate law is \( 0^{th} \) order in [A] and calculate the rate constant and half-life.

What is the value of [A] 223s after the start of the reaction?
43. The reaction

\[ A \longrightarrow B + C \]

is known to be zero order in A and to have a rate constant of \( 5.0 \times 10^{-2} \) mol/L \( \cdot \) s at 25\(^\circ\)C. An experiment was run at 25\(^\circ\)C where \([A]_0 = 1.0 \times 10^{-3} \) M.

a. Write the integrated rate law for this reaction.

b. Calculate the half-life for the reaction.

c. Calculate the concentration of B after \( 5.0 \times 10^{-3} \) s has elapsed.
### Summary

<table>
<thead>
<tr>
<th>Order</th>
<th>Zero</th>
<th>First</th>
<th>Second</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:</td>
<td>( [A] = -kt + [A]_0 )</td>
<td>( \ln[A] = -kt + \ln[A]_0 )</td>
<td>( \frac{1}{[A]} = kt + \frac{1}{[A]_0} )</td>
</tr>
<tr>
<td>Plot Needed to Give a Straight Line:</td>
<td>( [A] ) versus ( t )</td>
<td>( \ln[A] ) versus ( t )</td>
<td>( \frac{1}{[A]} ) versus ( t )</td>
</tr>
<tr>
<td>Relationship of Rate Constant to the Slope of Straight Line:</td>
<td>Slope = ( -k )</td>
<td>Slope = ( -k )</td>
<td>Slope = ( k )</td>
</tr>
<tr>
<td>Half-Life:</td>
<td>( t_{1/2} = \frac{[A]_0}{2k} )</td>
<td>( t_{1/2} = \frac{0.693}{k} )</td>
<td>( t_{1/2} = \frac{1}{k[A]_0} )</td>
</tr>
</tbody>
</table>
Determining Rate Laws

Given a set of data of reactant concentration, $[A]$ vs. time it is possible to determine the rate law by plotting graphs of $\ln[A]$ vs. $t$, $1/[A]$ vs. $t$ and $[A]$ vs. $t$ to see which is linear.

$1^{st}$ and $2^{nd}$ order reactions are most common so it’s a good idea to plot these first!
The data below were collected for the following reaction:

\[ 2\text{C}_4\text{H}_6(\text{g}) \rightarrow \text{C}_8\text{H}_{12}(\text{g}) \]

<table>
<thead>
<tr>
<th>[\text{C}_4\text{H}_6] (\text{molL}^{-1})</th>
<th>t (\text{s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01000</td>
<td>0</td>
</tr>
<tr>
<td>0.00625</td>
<td>1000.</td>
</tr>
<tr>
<td>0.00476</td>
<td>1800.</td>
</tr>
<tr>
<td>0.00370</td>
<td>2800.</td>
</tr>
<tr>
<td>0.00313</td>
<td>3600.</td>
</tr>
<tr>
<td>0.00270</td>
<td>4400.</td>
</tr>
<tr>
<td>0.00241</td>
<td>5200.</td>
</tr>
<tr>
<td>0.00208</td>
<td>6200.</td>
</tr>
</tbody>
</table>

Determine the order of the reaction, the value of the rate constant and the half-life.
<table>
<thead>
<tr>
<th>( \ln[C_4H_6] )</th>
<th>( \frac{1}{[C_4H_6]} ) (mol(^{-1})L)</th>
<th>([C_4H_6]) (molL(^{-1}))</th>
<th>( t ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-4.605</td>
<td>100</td>
<td>0.01000</td>
<td>0</td>
</tr>
<tr>
<td>-5.075</td>
<td>160</td>
<td>0.00625</td>
<td>1000</td>
</tr>
<tr>
<td>-5.348</td>
<td>210</td>
<td>0.00476</td>
<td>1800</td>
</tr>
<tr>
<td>-5.599</td>
<td>270</td>
<td>0.00370</td>
<td>2800</td>
</tr>
<tr>
<td>-5.767</td>
<td>320</td>
<td>0.00313</td>
<td>3600</td>
</tr>
<tr>
<td>-5.915</td>
<td>370</td>
<td>0.00270</td>
<td>4400</td>
</tr>
<tr>
<td>-6.028</td>
<td>415</td>
<td>0.00241</td>
<td>5200</td>
</tr>
<tr>
<td>-6.175</td>
<td>481</td>
<td>0.00208</td>
<td>6200</td>
</tr>
</tbody>
</table>
1st Order Plot

\( \ln[C_4H_6] \)

\( t(s) \)

0 1000 2000 3000 4000 5000 6000 7000

-6.6 -6.4 -6.2 -6.0 -5.8 -5.6 -5.4 -5.2 -5.0 -4.8 -4.6 -4.4
2\textsuperscript{nd} Order Plot

![Diagram showing a 2nd order plot with time (t(s)) on the x-axis and 1/[C\textsubscript{4}H\textsubscript{6}] (Lmol\textsuperscript{-1}) on the y-axis. The plot is a straight line passing through the points at t = 0, 1000, 2000, 3000, 4000, 5000, 6000, and 7000 seconds.]
41. Experimental data for the reaction

\[ A \rightarrow 2B + C \]

have been plotted in the following three different ways (with concentration units in mol/L):

What is the order of the reaction with respect to A and what is the initial concentration of A?
42. Consider the data plotted in Exercise 41 when answering the following questions.
   a. What is the concentration of A after 9 s?
   b. What are the first three half-lives for this experiment?
Shortcut
In some data sets it is possible to determine the order by inspection without drawing any graphs!

Remember how half-lives differ for different orders:

1\textsuperscript{st} order: half-life is constant

2\textsuperscript{nd} order: each successive half-life doubles

0\textsuperscript{th} order: each successive half-life halves

If you can find two pairs of concentrations each roughly half of the other you can look to see how the half-life varies and hence determine the order!

This does not work for all data sets but if it does it can save you some time!
Look at the data from the previous example again:

<table>
<thead>
<tr>
<th>$[\text{C}_4\text{H}_6]$ (molL$^{-1}$)</th>
<th>t (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01000</td>
<td>0</td>
</tr>
<tr>
<td>0.00625</td>
<td>1000</td>
</tr>
<tr>
<td>0.00476</td>
<td>1800</td>
</tr>
<tr>
<td>0.00370</td>
<td>2800</td>
</tr>
<tr>
<td>0.00313</td>
<td>3600</td>
</tr>
<tr>
<td>0.00270</td>
<td>4400</td>
</tr>
<tr>
<td>0.00241</td>
<td>5200</td>
</tr>
<tr>
<td>0.00208</td>
<td>6200</td>
</tr>
</tbody>
</table>

The concentration roughly halves between $t = 0$ and $t = 1800$ s giving a half-life of approximately 1800 s
Look at the data from the previous example again:

<table>
<thead>
<tr>
<th>[C₄H₆] (mol/L)</th>
<th>t (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01000</td>
<td>0</td>
</tr>
<tr>
<td>0.00625</td>
<td>1000</td>
</tr>
<tr>
<td><strong>0.00476</strong></td>
<td><strong>1800</strong></td>
</tr>
<tr>
<td>0.00370</td>
<td>2800</td>
</tr>
<tr>
<td>0.00313</td>
<td>3600</td>
</tr>
<tr>
<td>0.00270</td>
<td>4400</td>
</tr>
<tr>
<td><strong>0.00241</strong></td>
<td><strong>5200</strong></td>
</tr>
<tr>
<td>0.00208</td>
<td>6200</td>
</tr>
</tbody>
</table>

The concentration roughly halves between t = 0 and t = 1800 s giving a half-life of approximately 1800 s.

The concentration also roughly halves between t = 1800 and t = 5200 s giving a half-life of 3400 s.
Look at the data from the previous example again:

<table>
<thead>
<tr>
<th>$[C_4H_6]$ (molL$^{-1}$)</th>
<th>t (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01000</td>
<td>0</td>
</tr>
<tr>
<td>0.00625</td>
<td>1000</td>
</tr>
<tr>
<td><strong>0.00476</strong></td>
<td>1800</td>
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<tr>
<td>0.00370</td>
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<tr>
<td>0.00313</td>
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<tr>
<td>0.00270</td>
<td>4400</td>
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<tr>
<td><strong>0.00241</strong></td>
<td>5200</td>
</tr>
<tr>
<td>0.00208</td>
<td>6200</td>
</tr>
</tbody>
</table>

The concentration roughly halves between $t = 0$ and $t = 1800$ s giving a half-life of approximately 1800 s.

The concentration also roughly halves between $t = 1800$ and $t = 5200$ s giving a half life of 3400 s.

The half-life is clearly not constant so the reaction cannot be 1$^{st}$ order but you can see that it roughly doubles so it must be 2$^{nd}$ order!
88. Sulfuryl chloride ($SO_2Cl_2$) decomposes to sulfur dioxide ($SO_2$) and chlorine ($Cl_2$) by reaction in the gas phase. The following pressure data were obtained when a sample containing $5.00 \times 10^{-2}$ mol sulfuryl chloride was heated to 600. K in a $5.00 \times 10^{-1}$-L container.

<table>
<thead>
<tr>
<th>Time (hours):</th>
<th>0.00</th>
<th>1.00</th>
<th>2.00</th>
<th>4.00</th>
<th>8.00</th>
<th>16.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{SO_2Cl_2}$ (atm):</td>
<td>4.93</td>
<td>4.26</td>
<td>3.52</td>
<td>2.53</td>
<td>1.30</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Defining the rate as $\frac{\Delta [SO_2Cl_2]}{\Delta t}$,

a. determine the value of the rate constant for the decomposition of sulfuryl chloride at 600. K.
b. what is the half-life of the reaction?
c. what fraction of the sulfuryl chloride remains after 20.0 h?
The Isolation Method

Reactions with more than one reactant require simplification since it is generally not possible to simultaneously measure the concentrations of multiple reactants

\[
aA + bB + cC \rightarrow \text{products}
\]

where rate = \( k[A]^m[B]^n[C]^p \)

In cases like this we study (isolate) one reactant at a time by arranging that the concentration of one reactant be small compared to the others

If \([B]_0\) and \([C]_0\) \(>>\) \([A]_0\) then their concentrations remain approximately constant: \([B] \approx [B]_0\) and \([C] \approx [C]_0\)

so the rate law simplifies to the **pseudo rate law**:

\[
\text{rate} = k_{obs}[A]^m
\]

where the observed pseduo rate constant, \( k_{obs} = k[B]^n[C]^p \)
Once $k_{obs}$ is determined from the slope of a plot, knowing $[B]_0$ and $[C]_0$, the true rate constant, $k$ can be calculated

$$k_{obs} = k[B]^n[C]^p$$

$$k = \frac{k_{obs}}{[B]^n[C]^p}$$

By arranging for $[A]_0$ and $[B]_0 >> [C]_0$ we can determine $p$

By arranging for $[A]_0$ and $[C]_0 >> [B]_0$ we can determine $n$

This technique allows the determination of the rate laws for complex reactions
93. Consider the reaction

\[ 3A + B + C \rightarrow D + E \]

where the rate law is defined as

\[ \frac{\Delta[A]}{\Delta t} = k[A]^2[B][C] \]

An experiment is carried out where \([B]_0 = [C]_0 = 1.00 \text{ M}\) and \([A]_0 = 1.00 \times 10^{-4} \text{ M}\).

a. If after 3.00 min, \([A] = 3.26 \times 10^{-5} \text{ M}\), calculate the value of \(k\).

b. Calculate the half-life for this experiment.

c. Calculate the concentration of B and the concentration of A after 10.0 min.
The following data were collected in two studies of the reaction

\[ 2A + B \rightarrow C + D \]

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Experiment 1 [A] (mol/L) \times 10^{-2}</th>
<th>Experiment 2 [A] (mol/L) \times 10^{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>20.</td>
<td>6.67</td>
<td>5.00</td>
</tr>
<tr>
<td>40.</td>
<td>5.00</td>
<td>3.33</td>
</tr>
<tr>
<td>60.</td>
<td>4.00</td>
<td>2.50</td>
</tr>
<tr>
<td>80.</td>
<td>3.33</td>
<td>2.00</td>
</tr>
<tr>
<td>100.</td>
<td>2.86</td>
<td>1.67</td>
</tr>
<tr>
<td>120.</td>
<td>2.50</td>
<td>1.43</td>
</tr>
</tbody>
</table>

In Experiment 1, \([B]_0 = 5.0 \text{ M}\).
In Experiment 2, \([B]_0 = 10.0 \text{ M}\).

\[
\text{Rate} = \frac{-\Delta[A]}{\Delta t}
\]

a. Why is \([B]\) much greater than \([A]\)?
b. Give the rate law and value for \(k\) for this reaction.
Reaction Mechanisms

Chemical reactions rarely occur exactly as shown in the balanced chemical equation.

Rather they occur as a number of simpler **elementary steps** which constitute the **reaction mechanism**

Elementary steps often include **intermediates**, species which are both created and consumed in the reaction.

Combination of the elementary steps produce the overall balanced chemical equation.
Reaction of Nitrogen Dioxide and Carbon Monoxide

Balanced equation:

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

Elementary steps of reaction mechanism:

\[ \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g) \]

\[ \text{NO}_3(g) + \text{CO}(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g) \]

\textbf{NO}_3 is an intermediate since it is both created and consumed in the elementary steps

Sum of elementary steps:

\[ \begin{align*}
\text{NO}_2(g) + \text{NO}_2(g) & \rightarrow \text{NO}_3(g) + \text{NO}(g) \\
\text{NO}_3(g) + \text{CO}(g) & \rightarrow \text{NO}_2(g) + \text{CO}_2(g)
\end{align*} \]

\[ \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \]
Rate Laws for Elementary Steps

Since elementary steps cannot be simplified further, the rate law is related directly to their stoichiometry.

Elementary steps are classified according to their **molecularity**, or the number of species that must collide to produce that step.

The molecularity of an elemental step can be unimolecular, bimolecular, or termolecular depending on the number of species which collide.

<table>
<thead>
<tr>
<th>Elementary Step</th>
<th>Molecularity</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>A → products</td>
<td>Unimolecular</td>
<td>Rate = $k[A]$</td>
</tr>
<tr>
<td>A + A → products (2A → products)</td>
<td>Bimolecular</td>
<td>Rate = $k[A]^2$</td>
</tr>
<tr>
<td>A + B → products</td>
<td>Bimolecular</td>
<td>Rate = $k[A][B]$</td>
</tr>
<tr>
<td>A + A + B → products (2A + B → products)</td>
<td>Termolecular</td>
<td>Rate = $k[A]^2[B]$</td>
</tr>
<tr>
<td>A + B + C → products</td>
<td>Termolecular</td>
<td>Rate = $k[A][B][C]$</td>
</tr>
</tbody>
</table>

Termolecular steps are rare since the probability of three species colliding simultaneously is low.
Rate-determining Step

Generally one of the elementary steps in a reaction is slower than the others

Since a reaction cannot proceed faster than the slowest elementary step, this step determines the rate of the overall reaction and hence is referred to as the rate-determining step

The rate law for the overall reaction is the same as the rate law for the rate-determining step

This is why the rate law for a balanced reaction rarely corresponds to its stoichiometry
Reaction of Nitrogen Dioxide and Carbon Monoxide

Balanced equation:

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

Elementary step 1 is slower than step 2:

\[ \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g) \text{ slow} \]

\[ \text{NO}_3(g) + \text{CO}(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g) \text{ fast} \]

Step 1 is therefore the rate-determining step and so the rate law for the overall reaction is:

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

Notice that this not what we would expect from the balanced reaction alone!

This is why kinetics gives us information an how a reaction actually proceeds
Procedure for Deducing Reaction Mechanisms

The experimental rate law is always determined first

Reaction mechanism are then proposed which must meet two requirements in order to be considered viable:

1. The sum of elementary steps must give the overall balanced equation

2. Any proposed mechanism must agree with the experimentally determined rate law

We can never be totally certain that a viable mechanism is the correct mechanism, only that it is a possible mechanism

If several proposed mechanisms are viable then additional experimental work is needed to determine the most probable mechanism
The balanced equation for the reaction of the gases nitrogen dioxide and fluorine is

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

The experimentally determined rate law is

\[
\text{Rate} = k[\text{NO}_2][\text{F}_2]
\]

A suggested mechanism for this reaction is

\[\text{NO}_2 + \text{F}_2 \xrightarrow{k_1} \text{NO}_2\text{F} + \text{F} \quad \text{Slow}\]
\[\text{F} + \text{NO}_2 \xrightarrow{k_2} \text{NO}_2\text{F} \quad \text{Fast}\]

Is this an acceptable mechanism? That is, does it satisfy the two requirements?
For the reaction

$$2\text{H}_2(g) + 2\text{NO}(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g)$$

the observed rate law is

$$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$$

Which of the following are acceptable mechanisms? Explain.

*Mechanism I:*

$$2\text{H}_2(g) + 2\text{NO}(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g)$$

*Mechanism II:*

$$\text{H}_2(g) + \text{NO}(g) \longrightarrow \text{H}_2\text{O}(g) + \text{N}(g) \quad \text{Slow}$$

$$\text{N}(g) + \text{NO}(g) \longrightarrow \text{N}_2(g) + \text{O}(g) \quad \text{Fast}$$

$$\text{H}_2(g) + \text{O}(g) \longrightarrow \text{H}_2\text{O}(g) \quad \text{Fast}$$

*Mechanism III:*

$$\text{H}_2(g) + 2\text{NO}(g) \longrightarrow \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g) \quad \text{Slow}$$

$$\text{N}_2\text{O}(g) + \text{H}_2(g) \longrightarrow \text{N}_2(g) + \text{H}_2\text{O}(g) \quad \text{Fast}$$
55. A proposed mechanism for a reaction is

\[ \text{C}_4\text{H}_9\text{Br} \rightarrow \text{C}_4\text{H}_9^+ + \text{Br}^- \quad \text{Slow} \]
\[ \text{C}_4\text{H}_9^+ + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH}_2^+ \quad \text{Fast} \]
\[ \text{C}_4\text{H}_9\text{OH}_2^+ + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{H}_3\text{O}^+ \quad \text{Fast} \]

Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction? What are the intermediates in the proposed mechanism?
A Model for Chemical Kinetics
So far we have seen that the rates of reaction depend on the concentrations of one or more of the reactants.

For the reaction:

\[ aA + bB + cC \rightarrow \text{products} \]

the rate law can be written as:

\[ \text{rate} = k[A]^m[B]^n[C]^p \]

assuming that A, B and C all appear in the rate-determining step.

The orders \( m \), \( n \) and \( p \) depend on the detailed mechanism (the coefficients in the rate-determining step).

What other factors affect the rate of reaction?

In other words, what determines the value of the rate constant, \( k \)?
The Collision Model

For a chemical reaction to take place, the reactant molecules must collide
Effect of Temperature

According to kinetic theory, the higher the temperature, the faster the reactant molecules move (higher kinetic energy). The faster the reactant molecules move, the greater the number of collisions that can lead to a reaction.

\[
\text{temperature} \uparrow \quad \text{rate constant} \uparrow \quad \text{reaction rate} \uparrow
\]
In order for a chemical reaction to occur, chemical bonds have to be broken.

This requires a certain minimum collision energy.

Collisions with energies below this minimum will not result in a reaction.

**sufficient energy 😊**

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

**insufficient energy 😞**

\[ \text{N}_2 + \text{O}_2 \rightarrow \text{NO} + \text{NO} \]
sufficient energy

insufficient energy
Activation Energy, $E_a$

The minimum collision energy required to break the bonds between reactants.

The arrangement of atoms at the top of the “energy barrier” is called the transition state where reactants transition into products.

The rate of reaction does not depend on whether it is exothermic or endothermic but rather on the size of the activation energy.
59. The activation energy for the reaction

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

is 125 kJ/mol, and \( \Delta E \) for the reaction is \(-216 \) kJ/mol. What is the activation energy for the reverse reaction \([\text{NO}(g) + \text{CO}_2(g) \rightarrow \text{NO}_2(g) + \text{CO}(g)]\)?
67. Which of the following reactions would you expect to proceed at a faster rate at room temperature? Why? (Hint: Think about which reaction would have the lower activation energy.)

\[ \begin{align*}
2\text{Ce}^{4+}(aq) + \text{Hg}_2^{2+}(aq) &\rightarrow 2\text{Ce}^{3+}(aq) + 2\text{Hg}^{2+}(aq) \\
\text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) &\rightarrow 2\text{H}_2\text{O}(l)
\end{align*} \]
The Maxwell-Boltzmann Distribution

At a given temperature molecules have a distribution of velocities

Only those molecules with velocities that result in collisions with energies greater than the activation energy will be able to climb the energy barrier and react

As temperature increases the fraction of collisions with energies greater that the minimum activation energy increases exponentially
According to the Maxwell-Boltzmann distribution, the number of collisions with minimum energy, $E_a$ is given by:

$$ze^{-Ea/RT}$$

where:

- $z =$ the collision frequency ($s^{-1}$)
- $E_a =$ activation energy ($Jmol^{-1}$)
- $R =$ universal gas constant ($8.3145$ JK$^{-1}$mol$^{-1}$)
- $T =$ temperature ($K$)
Effect of Molecular Orientation

In addition to having the minimum activation energy, the reactants must collide with the correct alignment in order to break and form bonds.

**Correct Orientation**: 🌞

**Incorrect Orientation**: ☹️
The effect of molecular orientation is taken into account by the **steric factor**, $p$ which is the fraction of collisions with the correct orientation.

This number is always greater than 0 (no collisions with the correct orientation) but less than 1 (all collisions have the correct orientation).
Summary

1. Reactants must collide

2. The collision energy must be equal to or greater than the activation energy

3. Reactants must be correctly aligned to break and form bonds
Svante Arrhenius (1859-1927)
The Arrhenius Equation

An equation relating the rate constant, $k$ to the collision frequency, $z$, steric factor, $p$, activation energy, $E_a$ and the temperature, $T$:

$$k = zpe^{-Ea/RT}$$

It is most commonly written in the form:

$$k = Ae^{-Ea/RT}$$

where $A$ is the frequency factor which replaces the term $zp$

Taking the natural logarithm of each side of this equation gives:

$$\ln(k) = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln(A)$$

$$y = mx + b$$

Another linear equation!!!!

Note that $A$ has the same units as $k$
\[ \ln(k) = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln(A) \]

Plot of \( \ln(k) \) vs. \( 1/T \) will give a straight line with slope \(-E_a/R\) and intercept \(\ln(A)\).

If we can measure \( k \) at different temperatures we can determine \( E_a \) and \( A! \)
The reaction

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

was studied at several temperatures, and the following values of $k$ were obtained:

<table>
<thead>
<tr>
<th>$k \ (s^{-1})$</th>
<th>$T \ (^\circ\ C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.0 \times 10^{-5}$</td>
<td>20</td>
</tr>
<tr>
<td>$7.3 \times 10^{-5}$</td>
<td>30</td>
</tr>
<tr>
<td>$2.7 \times 10^{-4}$</td>
<td>40</td>
</tr>
<tr>
<td>$9.1 \times 10^{-4}$</td>
<td>50</td>
</tr>
<tr>
<td>$2.9 \times 10^{-3}$</td>
<td>60</td>
</tr>
</tbody>
</table>

Calculate the value of $E_a$ for this reaction.
To obtain the value of $E_a$, we need to construct a plot of $\ln(k)$ versus $1/T$. First, we must calculate values of $\ln(k)$ and $1/T$, as shown below:

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$T$ (K)</th>
<th>$1/T$ (K)</th>
<th>$k$ (s$^{-1}$)</th>
<th>$\ln(k)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>293</td>
<td>$3.41 \times 10^{-3}$</td>
<td>$2.0 \times 10^{-5}$</td>
<td>$-10.82$</td>
</tr>
<tr>
<td>30</td>
<td>303</td>
<td>$3.30 \times 10^{-3}$</td>
<td>$7.3 \times 10^{-5}$</td>
<td>$-9.53$</td>
</tr>
<tr>
<td>40</td>
<td>313</td>
<td>$3.19 \times 10^{-3}$</td>
<td>$2.7 \times 10^{-4}$</td>
<td>$-8.22$</td>
</tr>
<tr>
<td>50</td>
<td>323</td>
<td>$3.10 \times 10^{-3}$</td>
<td>$9.1 \times 10^{-4}$</td>
<td>$-7.00$</td>
</tr>
<tr>
<td>60</td>
<td>333</td>
<td>$3.00 \times 10^{-3}$</td>
<td>$2.9 \times 10^{-3}$</td>
<td>$-5.84$</td>
</tr>
</tbody>
</table>
The plot of $\ln(k)$ versus $1/T$ is shown in Fig. 12.14, where the slope

\[
\frac{\Delta \ln(k)}{\Delta \left(\frac{1}{T}\right)}
\]

is found to be $-1.2 \times 10^4 \text{ K}$. The value of $E_a$ can be determined by solving the following equation:

\[
\text{Slope} = -\frac{E_a}{R}
\]

\[
E_a = -R(\text{slope}) = -(8.3145 \text{ J/K \cdot mol})(-1.2 \times 10^4 \text{ K})
\]

\[= 1.0 \times 10^5 \text{ J/mol} \]

Thus the value of the activation energy for this reaction is $1.0 \times 10^5 \text{ J/mol}$. 
61. The rate constant for the gas-phase decomposition of N\textsubscript{2}O\textsubscript{5},

\[
N\text{\textsubscript{2}}O\text{\textsubscript{5}} \rightarrow 2\text{NO} \text{\textsubscript{2}} + \frac{1}{2}\text{O} \text{\textsubscript{2}}
\]

has the following temperature dependence:

<table>
<thead>
<tr>
<th>T (K)</th>
<th>k (s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>338</td>
<td>4.9 \times 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>318</td>
<td>5.0 \times 10\textsuperscript{-4}</td>
</tr>
<tr>
<td>298</td>
<td>3.5 \times 10\textsuperscript{-5}</td>
</tr>
</tbody>
</table>

Make the appropriate graph using these data, and determine the activation energy for this reaction.
Decomposition of $N_2O_5$

\[ y = -12447x + 31.519 \]
\[ R^2 = 0.9999 \]
Shortcut
$E_a$ can also be calculated from the values of $k$ at only two temperatures, $T$ if we assume that $A$ is independent of $T$:

At temperature $T_1$, where the rate constant is $k_1$,

$$\ln(k_1) = -\frac{E_a}{RT_1} + \ln(A)$$

At temperature $T_2$, where the rate constant is $k_2$,

$$\ln(k_2) = -\frac{E_a}{RT_2} + \ln(A)$$

Subtracting the first equation from the second gives

$$\ln(k_2) - \ln(k_1) = \left[ -\frac{E_a}{RT_2} + \ln(A) \right] - \left[ -\frac{E_a}{RT_1} + \ln(A) \right]$$

$$= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

And

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$
63. The activation energy for the decomposition of HI(g) to H₂(g) and I₂(g) is 186 kJ/mol. The rate constant at 555 K is \(3.52 \times 10^{-7}\) L/mol \cdot s. What is the rate constant at 645 K?
65. A certain reaction has an activation energy of 54.0 kJ/mol. As the temperature is increased from 22°C to a higher temperature, the rate constant increases by a factor of 7.00. Calculate the higher temperature.
Catalysis

A **catalyst** is a substance that speeds up a reaction without being consumed itself.

Many reactions only occur at high temperatures so by using a catalyst, the reaction can proceed at much lower temperatures saving energy. This is very important in industrial applications.

Catalysts are also vital in biological systems where reactions can only occur over a narrow range of temperatures (the human body functions at an almost constant temperature of 98.6 °F). Biological catalysts are called **enzymes**.
How does a catalyst work?

A catalyst works by providing an alternative reaction pathway with lower activation energy.
Heterogeneous Catalysts

A heterogeneous catalyst is one that is present in a different phase to the reactants.

The most common heterogeneous catalysts are solids which bring reactants together by adsorbing them on their surfaces.

**Adsorption** is NOT the same as **absorption** (which involves the penetration of one substance into another, e.g. a sponge).
Hydrogenation of Unsaturated Hydrocarbons on a Metal Surface

The surface of the catalyst helps break the strong H-H bonds thus lowering the activation energy of the reaction.
Catalytic Converters

$2\text{NO}(g) \rightarrow \text{N}_2(g) + \text{O}_2(g)$
NO absorbed on catalyst

Surface of metal (Pt, Pd) catalyst

$2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$
CO and $\text{O}_2$ absorbed on catalyst

Surface of metal (Pt, Pd) catalyst

$\text{O}_2$ dissociates
Homogeneous Catalysts

A homogeneous catalyst is one that is present in the same phase as the reactants.

They most commonly occur in gas and liquid phases.
Destruction of Ozone in the Stratosphere

Freons are stable, volatile compounds once used as refrigerants and aerosol repellants (more commonly known as chlorofluorocarbons or CFC’s)

When released into the atmosphere they migrate up into the stratosphere where they are photodissociated by UV-light from the Sun to form chlorine atoms:

\[
CCl_2F_2(g) \xrightarrow{\text{Light}} CClF_2(g) + Cl(g)
\]

The chlorine atoms then catalyze the destruction of ozone:

\[
\begin{align*}
Cl(g) + O_3(g) & \rightarrow ClO(g) + O_2(g) \\
O(g) + ClO(g) & \rightarrow Cl(g) + O_2(g) \\
O(g) + O_3(g) & \rightarrow 2O_2(g)
\end{align*}
\]

Ozone protects the Earth’s surface from high-energy UV-radiation so Freons have now been banned and alternatives are being used.
The Difference between Homogeneous Catalysts and Intermediates

Many homogenous catalytic reactions contain intermediates in their elementary steps which can be difficult to distinguish from the catalyst.

This is the way to distinguish them:

1. A catalyst first appears as a reactant and is then regenerated as a product.

2. An intermediate first appears as a product (since it is formed in one of the elementary steps) and is then later removed as a reactant.

\[
\begin{align*}
\text{Cl}(g) + \text{O}_3(g) & \longrightarrow \text{ClO}(g) + \text{O}_2(g) \\
\text{O}(g) + \text{ClO}(g) & \longrightarrow \text{Cl}(g) + \text{O}_2(g) \\
\text{O}(g) + \text{O}_3(g) & \longrightarrow 2\text{O}_2(g)
\end{align*}
\]

In the above reaction, Cl is the catalyst and ClO is an intermediate.
69. One mechanism for the destruction of ozone in the upper atmosphere is

\[
\begin{align*}
O_3(g) + NO(g) & \rightarrow NO_2(g) + O_2(g) \quad \text{Slow} \\
NO_2(g) + O(g) & \rightarrow NO(g) + O_2(g) \quad \text{Fast}
\end{align*}
\]

Overall reaction \( O_3(g) + O(g) \rightarrow 2O_2(g) \)

a. Which species is a catalyst?

b. Which species is an intermediate?

c. \( E_a \) for the uncatalyzed reaction

\[
O_3(g) + O(g) \rightarrow 2O_2
\]

is 14.0 kJ. \( E_a \) for the same reaction when catalyzed is 11.9 kJ. What is the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25°C? Assume that the frequency factor \( A \) is the same for each reaction.
A popular chemical demonstration is the “magic genie” procedure, in which hydrogen peroxide decomposes to water and oxygen gas with the aid of a catalyst. The activation energy of this (uncatalyzed) reaction is 70.0 kJ/mol. When the catalyst is added, the activation energy (at 20.°C) is 42.0 kJ/mol. Theoretically, to what temperature (°C) would one have to heat the hydrogen peroxide solution so that the rate of the uncatalyzed reaction is equal to the rate of the catalyzed reaction at 20.°C? Assume the frequency factor A is constant and assume the initial concentrations are the same.