1. What’s in a solution? How far does a reaction “go”?  
2. What factors influence how far a reaction “goes” and how fast it gets there?  
3. How do atomic and molecular structure influence observed properties of substances?

**Big Question #2**
What factors influence how far a reaction “goes” and how fast it gets there?

**CHAPTER 16**

**CHEMICAL KINETICS**

the study of rates of chemical reactions. *How fast* is a reaction? The kinetics of a reaction must be determined experimentally.

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

\[\text{Temp. 40°C (104°F)}\]

\begin{array}{|c|c|c|c|c|c|}
\hline
\text{time (s)} & \text{[H}_2\text{O}_2] & \Delta\text{[H}_2\text{O}_2] & \text{[H}_2\text{O}] & \Delta\text{[H}_2\text{O}] & \text{[O}_2] & \Delta\text{[O}_2] \\
\hline
0 & 1.000 & & 0.000 & & 0.000 & \\
6h & > & -0.500 & > & +0.500 & > & +0.250 \\
21600 & 0.500 & & 0.500 & & 0.250 & \\
6h & > & -0.250 & > & +0.250 & > & +0.125 \\
43200 & 0.250 & & 0.750 & & 0.375 & \\
& 0.125 & & 0.875 & & 0.437 & \\
64800 & > & -0.0625 & > & +0.0625 & > & +0.0312 \\
86400 & 0.0625 & & 0.938 & & 0.469 & \\
\hline
\end{array}

---

**egm.**
$$Rate = k(\text{ClO}_2)^2(\text{OH}^-)$$

Using:

$$2.32 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} = k(0.100 \text{ mol} \cdot \text{L}^{-1})^2(0.100 \text{ mol} \cdot \text{L}^{-1})$$

$$k = \frac{2.32 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}}{1.00 \times 10^{-3} \text{ mol}^3 \cdot \text{L}^{-3}} \frac{L}{L^3} \frac{L^3}{L^3} \frac{1}{L^3} \text{L}$$

$$k = 2.32 \times 10^2 \text{ mol}^{-2} \cdot \text{L}^2 \cdot \text{s}^{-1}$$

$$\text{units of } k \text{ for 3rd order overall}$$

$$A + B \rightarrow \text{products}$$

<table>
<thead>
<tr>
<th>Initial</th>
<th>Change</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0 M</td>
<td>-0.01</td>
<td>9.99 M</td>
</tr>
<tr>
<td>0.01 M</td>
<td>-0.01</td>
<td>0</td>
</tr>
</tbody>
</table>

Flood with A to find order for B

0.1% change in (A)
reaction rate = \frac{\text{change in concentration}}{\text{change in time}}

rate = \frac{\Delta(A)}{\Delta t} = \frac{d(A)}{dt}

The differential form of the rate shows that the rate = the slope of the tangent line to the curve in a graph of concentration vs. time. (Rates are always described as positive numbers.)

So, for \(2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2\), rate of appearance of \(\text{H}_2\text{O}\) = \(\frac{\Delta(\text{H}_2\text{O})}{\Delta t}\)

rate of appearance of \(\text{O}_2\) = \(\frac{\Delta(\text{O}_2)}{\Delta t}\)

rate of disappearance of \(\text{H}_2\text{O}_2\) = \(\frac{-\Delta(\text{H}_2\text{O}_2)}{\Delta t}\)

The rate of reaction changes during the course of the reaction. Looking at the \(\text{H}_2\text{O}_2\) data:

\[
\begin{align*}
\text{rate}_1 &= \frac{-\Delta(\text{H}_2\text{O}_2)}{\Delta t} = \frac{(0.500) \text{mol L}^{-1}}{2.16 \times 10^4 \text{s}} = 2.31 \times 10^{-5} \text{mol L}^{-1} \text{s}^{-1} \\
\text{rate}_2 &= \frac{-\Delta(\text{H}_2\text{O}_2)}{\Delta t} = \frac{(-0.250) \text{mol L}^{-1}}{2.16 \times 10^4 \text{s}} = 1.16 \times 10^{-5} \text{mol L}^{-1} \text{s}^{-1} \\
\text{rate}_3 &= \frac{-\Delta(\text{H}_2\text{O}_2)}{\Delta t} = \frac{(-0.125) \text{mol L}^{-1}}{2.16 \times 10^4 \text{s}} = 0.58 \times 10^{-5} \text{mol L}^{-1} \text{s}^{-1} \\
\text{rate}_4 &= \frac{-\Delta(\text{H}_2\text{O}_2)}{\Delta t} = \frac{(-0.0625) \text{mol L}^{-1}}{2.16 \times 10^4 \text{s}} = 0.29 \times 10^{-5} \text{mol L}^{-1} \text{s}^{-1}
\end{align*}
\]

\[\frac{1}{2}(\frac{-\Delta(\text{H}_2\text{O}_2)}{\Delta t}) = \frac{\Delta(\text{O}_2)}{\Delta t}\]

In general, for \(a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}\),

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

\(\Delta(\text{A}), \Delta(\text{B}), \Delta(\text{C}), \Delta(\text{D})\) are relationships between/among rates in terms of different reactants and products

e.g., hydrogen peroxide disappears at twice the rate at which oxygen appears:

\[-\frac{\Delta(\text{H}_2\text{O}_2)}{\Delta t} = 2\frac{\Delta(\text{O}_2)}{\Delta t}\]

**Differential Rate Laws**

A general relationship between species concentration and reaction rate is called a rate law.

**Assumptions:**
1. only forward reactions (i.e., write rate laws in terms of reactants)
2. equilibrium avoided

We observed that the rate of reaction depended on \((\text{H}_2\text{O}_2)^n\), but how exactly?

\[
\begin{align*}
\text{rate} &\propto (\text{H}_2\text{O}_2)^n & n = \text{order of reaction} \\
\text{rate} &= k (\text{H}_2\text{O}_2)^n & k = \text{rate constant} \\
\text{rate} &= \frac{-\Delta(\text{H}_2\text{O}_2)}{\Delta t} = k (\text{H}_2\text{O}_2)^n & \text{a differential rate law: rate as a function of concentration}
\end{align*}
\]

**CAUTIONS!**
1. \(n\) not necessarily equal to stoichiometric coefficient.
2. \(n\) and \(k\) are experimentally determined.
3. rates vary for each product/reactant. Must specify.
Method of Initial Rates

\[ \text{Rate} = k(\text{ClO}_2^-)^x(\text{OH}^-)^y \]

e.g., Consider this reaction: \(2\text{ClO}_2\text{(aq)} + 2\text{OH}^- \text{(aq)} \rightarrow \text{ClO}_3^- \text{(aq)} + \text{ClO}_2^- \text{(aq)} + \text{H}_2\text{O(l)}\)

and the following initial rate data:

<table>
<thead>
<tr>
<th>((\text{ClO}_2^-)_0/\text{mol}\cdot\text{L}^-1)</th>
<th>((\text{OH}^-)_0/\text{mol}\cdot\text{L}^-1)</th>
<th>initial rate/\text{mol}\cdot\text{L}^-1\cdot\text{s}^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0500</td>
<td>0.100</td>
</tr>
<tr>
<td>2</td>
<td>0.100</td>
<td>0.100</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>0.050</td>
</tr>
</tbody>
</table>

Determine the rate law for the reaction and the value of \(k\) (with units).

1 & 2: double \((\text{ClO}_2^-)_0\): rate quadruples \(\therefore x = 2\)

\[
\frac{\text{rate}_2}{\text{rate}_1} = \left(\frac{0.100 \text{m}}{0.0500 \text{m}}\right)^x \left(\frac{0.100 \text{m}}{0.0500 \text{m}}\right)^y = 4 = \left(\frac{0.100 \text{m}}{0.0500 \text{m}}\right)^x
\]

3 & 2: double \((\text{OH}^-)_0\): rate doubles \(\therefore y = 1\)

\[\log 4 = x \log 2\]

\[x = \frac{\log 4}{\log 2} = 2\]

Integrated Rate Laws

Differential rate laws give information about rate as a function of concentration, but what about concentrations as a function of time? We need to integrate the differential rate law.

The calculus involved for orders 0, 1, and 2 is below…it’s only necessary to use the final results and not worry about the derivation.

**Zero-Order**

\[\frac{\Delta (A)}{\Delta t} = k(A)^0 = k\]

or \(\frac{d(A)}{dt} = k\)

\[-d(A) = k dt\]

\[\int d(A) = -k \int_0^t dt\]

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

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

an integrated rate law; concentration as a function of time

**First-Order**

\[\frac{\Delta (A)}{\Delta t} = k(A)^1\] or \(\frac{d(A)}{dt} = k(A)\)

\[\int d(A) = -k \int_{(A)_0}^{(A)} dt\]

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

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

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

**Half-Life**

let \((A) = \frac{(A)_0}{2}\) at \(t = t_{1/2}\)

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

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

**Big Question 2**

\[\int_1^x \frac{1}{x} dx = \ln x\]
### Second-Order

Rate formula: 
\[
\begin{align*}
\text{Rate} &= -\frac{\Delta (A)}{\Delta t} = k(A)^2 \\
\text{Rate} &= -\frac{d(A)}{dt} = k(A)^2 \\
-\frac{d(A)}{(A)^2} &= k \ dt \\
\int_{(A)_o}^{(A)} \frac{d(A)}{(A)^2} &= -k \int_0^t dt \\
\frac{1}{(A)} &= kt + \frac{1}{(A)_o}
\end{align*}
\]

Half-Life

- \(t_{1/2} = \frac{1}{k(\frac{1}{2})}\)

\[
\begin{align*}
\frac{1}{(A)_o} &= k t_{1/2} + \frac{1}{(A)_o} \\
2 - k t_{1/2} &= \frac{1}{(A)_o} \\
\frac{1}{(A)_o} &= t_{1/2}
\end{align*}
\]

### Summary of Rate Laws

<table>
<thead>
<tr>
<th>Order</th>
<th>Differential Rate Law</th>
<th>Integrated Rate Law (straight-line form)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Rate = (-\frac{d(A)}{dt}) = k</td>
<td>((A) = -kt + (A)_o)</td>
</tr>
<tr>
<td>1</td>
<td>Rate = (-\frac{d(A)}{dt}) = k(A)</td>
<td>(\ln(A) = -kt + \ln(A)_o)</td>
</tr>
<tr>
<td>2</td>
<td>Rate = (-\frac{d(A)}{dt}) = k(A)^2</td>
<td>(\frac{1}{(A)} = kt + \frac{1}{(A)_o})</td>
</tr>
</tbody>
</table>

### Using the Integrated Rate Laws

**Example:** What are the order and rate constant at 25 °C for the decomposition of \(N_2O_5\)?

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

Experimental method: place 0.1000 mol of \(N_2O_5\) in a 1.000 L flask and measure \((N_2O_5)\) as a function of time.

Experimental data:

<table>
<thead>
<tr>
<th>time/s</th>
<th>((N_2O_5)/\text{mol L}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1000</td>
</tr>
<tr>
<td>50</td>
<td>0.0707</td>
</tr>
<tr>
<td>100</td>
<td>0.0500</td>
</tr>
<tr>
<td>200</td>
<td>0.0250</td>
</tr>
<tr>
<td>300</td>
<td>0.0125</td>
</tr>
<tr>
<td>400</td>
<td>0.00625</td>
</tr>
</tbody>
</table>

Approach: Make a guess at the reaction order, \(n\). Plot the experimental data using the corresponding integrated rate law. The integrated rate law that gives a straight line will give the values of \(n\) and \(k\).

\[
\ln(N_2O_5) \text{ vs. time is linear} \Rightarrow 1^{st} \text{ order}
\]

\[
\text{slope} = -0.0069 \text{ s}^{-1}, \quad k = -\text{slope} = 0.0069 \text{ s}^{-1}
\]
Integrated rate law plots and reaction orders.

**Half-Life** \( t_{1/2} \)

- the amount of time required for the reactant concentration to decrease to half its initial value
  - i.e., the amount of time to reach \( [A] = \frac{1}{2}[A]_0 \)

You can derive the formulas for half-life from the integrated rate laws; see above.

Only the first-order half-life formula is independent of the initial concentration.

**Radioactive decay:** first order

*(other orders: half-life not commonly used)*
Zero Order Plot

\[ y = -0.0002x + 0.0831 \]

\[ R^2 = 0.8871 \]
Second Order Plot

\[ y = 0.3535x - 7.8441 \]

\[ R^2 = 0.8841 \]
First Order Plot

\[ y = -0.0069x - 2.3026 \]

\[ R^2 = 1 \]