Non-Liquid Solutions

- Gas-gas e.g., air
  all gases are infinitely soluble in other gases.
- Solid-solid e.g., alloys, waxes
  o substitutional alloy vs. interstitial alloy

Beyond Solutions: Colloids & Suspensions

**Suspension**
- heterogeneous mixture
- settles out eventually
- suspended particles visible to naked eye

**Colloid**
- Dispersed substance larger than simple molecules, but small enough to not settle out (sizes 1–1000 nm, includes the range of visible wavelengths) \(\therefore\) colloids scatter light beams

**Solution**
- homogeneous mixture
- does not separate
- visually uniform

---

### Types of Colloids

<table>
<thead>
<tr>
<th>Colloid Type</th>
<th>Dispersed Substance</th>
<th>Dispersing Medium</th>
<th>Example(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol</td>
<td>Liquid</td>
<td>Gas</td>
<td>Fog</td>
</tr>
<tr>
<td>Aerosol</td>
<td>Solid</td>
<td>Gas</td>
<td>Smoke</td>
</tr>
<tr>
<td>Foam</td>
<td>Gas</td>
<td>Liquid</td>
<td>Whipped cream</td>
</tr>
<tr>
<td>Solid foam</td>
<td>Gas</td>
<td>Solid</td>
<td>Marshmallow</td>
</tr>
<tr>
<td>Emulsion</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Milk</td>
</tr>
<tr>
<td>Solid emulsion</td>
<td>Liquid</td>
<td>Solid</td>
<td>Butter</td>
</tr>
<tr>
<td>Sol</td>
<td>Solid</td>
<td>Liquid</td>
<td>Paint, cell fluid</td>
</tr>
<tr>
<td>Solid sol</td>
<td>Solid</td>
<td>Solid</td>
<td>Opal</td>
</tr>
</tbody>
</table>
Chapter 14
Chemical Kinetics

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

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

\[(\text{H}_2\text{O}_2) = 1.000 \text{ M}\]

Temp. 40°C (104°F)

<table>
<thead>
<tr>
<th>time (s)</th>
<th>[H₂O₂]</th>
<th>Δ[H₂O₂]</th>
<th>[H₂O]</th>
<th>Δ[H₂O]</th>
<th>[O₂]</th>
<th>Δ[O₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21600</td>
<td>0.500</td>
<td>-0.500</td>
<td>0.500</td>
<td>+0.500</td>
<td>+0.250</td>
<td></td>
</tr>
<tr>
<td>43200</td>
<td>0.250</td>
<td>-0.250</td>
<td>0.750</td>
<td>+0.250</td>
<td>+0.125</td>
<td></td>
</tr>
<tr>
<td>64800</td>
<td>0.125</td>
<td>-0.125</td>
<td>0.875</td>
<td>+0.125</td>
<td>+0.0625</td>
<td></td>
</tr>
<tr>
<td>86400</td>
<td>0.0625</td>
<td>-0.0625</td>
<td>0.938</td>
<td>+0.0625</td>
<td>+0.0312</td>
<td></td>
</tr>
</tbody>
</table>

The differential form of the rate shows that the rate = the slope of the tangent line to the curve.

\[\text{reaction rate} = \frac{\text{change in concentration}}{\text{change in time}}\]

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

The differential form of the rate shows that the rate = the slope of the tangent line to the curve.
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:

rate$_1 = -\frac{\Delta(\text{H}_2\text{O}_2)}{\Delta t} = \frac{-0.500 \text{ mol L}^{-1}}{2.16 \times 10^4 \text{ s}^{-1}} = 2.31 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$

rate$_2 = -\frac{\Delta(\text{H}_2\text{O}_2)}{\Delta t} = \frac{-0.250 \text{ mol L}^{-1}}{2.16 \times 10^4 \text{ s}^{-1}} = 1.16 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$

rate$_3 = -\frac{\Delta(\text{H}_2\text{O}_2)}{\Delta t} = \frac{-0.125 \text{ mol L}^{-1}}{2.16 \times 10^4 \text{ s}^{-1}} = 0.58 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$

rate$_4 = -\frac{\Delta(\text{H}_2\text{O}_2)}{\Delta t} = \frac{-0.0625 \text{ mol L}^{-1}}{2.16 \times 10^4 \text{ s}^{-1}} = 0.29 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$

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

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

relationships between/among rates in terms of different reactants and products

e.g., hydrogen peroxide disappears at twice the rate at which oxygen appears: $-\frac{\Delta(\text{H}_2\text{O}_2)}{\Delta t} = 2\left(\frac{\Delta(\text{O}_2)}{\Delta t}\right)$

**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 $(\text{H}_2\text{O}_2)$, but how exactly?

rate $\propto (\text{H}_2\text{O}_2)^n$ \hspace{1cm} n = order of reaction

rate $= k (\text{H}_2\text{O}_2)^n$ \hspace{1cm} k = rate constant

rate $= -\frac{\Delta(\text{H}_2\text{O}_2)}{\Delta t} = k (\text{H}_2\text{O}_2)^n$ \hspace{1cm} \text{a differential rate law}: rate as a function of concentration

**\textbf{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.

e.g., Consider this reaction:

$2\text{ClO}_2(\text{aq}) + 2\text{OH}^- (\text{aq}) \rightarrow \text{ClO}_3^- (\text{aq}) + \text{ClO}_2^- (\text{aq}) + \text{H}_2\text{O}(\text{l})$

and the following initial rate data:

<table>
<thead>
<tr>
<th>(ClO$_2$)$_o$/mol·L$^{-1}$</th>
<th>(OH$^-$)$_o$/mol·L$^{-1}$</th>
<th>initial rate/mol·L$^{-1}$·s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0500</td>
<td>0.100</td>
<td>$5.77 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.100</td>
<td>$2.32 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.100</td>
<td>0.050</td>
<td>$1.15 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

Determine the rate law for the reaction and the value of k (with units).
Rate = \( k \cdot (\text{ClO}_2)^x \cdot (\text{OH}^-)^y \)

**Trials 1 & 2:** double \((\text{ClO}_2)_o\), \((\text{OH}^-)_o\) constant: rate quadruples \(\uparrow 4x\)
\[ \therefore x = 2 \]

**Trials 3 & 2:** double \((\text{OH}^-)_o\), \((\text{ClO}_2)_o\) constant: rate doubles
\[ \therefore y = 1 \]

\[ \text{Rate} = k \cdot (\text{ClO}_2)^2 \cdot (\text{OH}^-) \]

\(3\text{rd order overall}\)

Using Trial 2 to calculate \(k\):

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

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

\[ \frac{\text{mol} \cdot \text{L}^2}{\text{L} \cdot \text{s} \cdot \text{mol} \cdot \text{mol}} \]

\[ k = \frac{1}{\text{mol} \cdot \text{L}^2 \cdot \text{s}^{-1} \cdot \text{mol}^2 \cdot \text{L}^2 \cdot \text{mol}^{-1} \cdot \text{k}} \]