Fractional distillation: If a solution contains two volatile liquids, then the vapor pressure is the average of the two pure liquid vapor pressures weighted by the mole fraction of each component.

\[ P_{\text{total}} = P_A + P_B = P_A X_A + P_B X_B \]

The mixture boils at the temperature where \( P_{\text{total}} = 1 \text{ atm} \). The vapor is enriched with the more volatile component (lower boiling point); hence, the condensed liquid is also enriched. Repetition of the evaporation and condensation generally causes the condensed liquid to contain mainly the lower boiling liquid.


**III. Chemical Kinetics.**

There are 3 crucial questions about every chemical reaction: (a) What is the reaction stoichiometry (amount of reactants and products)? (b) What is the rate of the reaction (chemical kinetics)? (c) How far does the reaction go to products (chemical equilibria)? In this section, we focus on chemical kinetics.

Dr. Finklea’s research asks the questions: what is the rate of electron transfer between an electrode and a redox molecule pinned near the electrode surface? What factors affect that rate? Answers to these questions are relevant to areas such as electron transfer between proteins in living systems.

\[ \text{Au/S(CH}_2\text{)}_n\text{-Ox} + e^- \rightleftharpoons \text{Au/S(CH}_2\text{)}_n\text{-Red} \quad (\text{Ox} = \text{oxidized molecule; Red} = \text{reduced molecule}) \]

A. Reaction rates.

A reaction rate is expressed as the change in concentration of a substance per unit time. The substance can be a reactant or a product.

Ex. In the reaction \( A \rightarrow B \), the rate can be expressed as \( -\Delta[A]/\Delta t \) or \( +\Delta[B]/\Delta t \), where \([A]\) and \([B]\) are the molar concentrations of \( A \) and \( B \). (\( \Delta = \text{change in }.. \)). Note the \( - \) sign for the reaction rate in terms of reactant loss, + sign (or no sign) for reaction rate in terms of product gain.

The rate of product gain or reactant loss in a given reaction can be related to the reaction stoichiometry.
Ex. Given: $3\text{I}^- + \text{H}_3\text{AsO}_4 + 2\text{H}^+ \rightarrow \text{I}_3^- + \text{H}_2\text{AsO}_4 + \text{H}_2\text{O}$ (a net ionic redox reaction)
If $-\Delta[\text{I}^-]/\Delta t = 4.8 \times 10^{-4}$ M/s (note units), what are $\Delta[\text{I}_3^-]/\Delta t$ and $-\Delta[\text{H}^+]/\Delta t$ over the same time interval?

$(4.8 \times 10^{-4}$ mol I/L/s)(1 mol I$_3^-$/3 mol I$^-$) = 1.6$ \times 10^{-4}$ mol I$_3^-$/L/s
Similarly, $-\Delta[\text{H}^+]/\Delta t = (4.8 \times 10^{-4}$ M I$^-$/s)(2 mol H$^+$/3 mol I$^-$) = 3.2$ \times 10^{-4}$ M H$^+$/s

B. Rate laws and reaction order.

Several factors affect reaction rates: concentration, time, temperature, and the presence/absence of catalysts. A rate law describes the instantaneous rate as a function of instantaneous concentrations. Consider a generic reaction:

$$\text{aA} + \text{bB} \rightarrow \text{cC} + \text{dD}$$

The rate law might be: \[ \text{rate} = -\frac{\Delta[\text{I}^-]}{\Delta t} = k[A]^m[B]^n \]
where $k$ is the rate constant - a number which is independent of concentration and time (but is temperature-dependent). The units of $k$ depend on the rate law.
The exponents $m$ and $n$ are the reaction orders with respect to A and B, respectively. Generally (but not always), reaction orders are integers. The sum of all reaction orders is overall reaction order.

Ex. For the rate law $-\Delta[\text{BrO}_3^-]/\Delta t = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$, the rate is 1$^{\text{st}}$ order in BrO$_3^-$, 1$^{\text{st}}$ order in Br$^-$, 2$^{\text{nd}}$ order in H$^+$, and 4$^{\text{th}}$ order overall.

Question: What does it mean when a rate is zero-order with respect to a substance? The rate does not depend on the concentration of that substance.

C. Experimental determination of a rate law.

Important point: The rate law expression and reaction orders must be determined by experiment; they are generally not given by the coefficients of the reaction.

One method: measure initial rates (near $t = 0$) as a function of differing concentrations of substances (reactants, products, ...). (measuring initial rates ensures that there is no significant back-reaction to confuse the results)

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>$[\text{H}_2\text{O}_2]_i$</th>
<th>$[\text{I}^-]_i$</th>
<th>Initial rate (M/s) ($[A]_i$ = initial conc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100</td>
<td>0.100</td>
<td>1.15$\times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>0.100</td>
<td>0.200</td>
<td>2.30$\times 10^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>0.200</td>
<td>0.100</td>
<td>2.30$\times 10^{-4}$</td>
</tr>
</tbody>
</table>
Look at exp. # 1 & 2. \([H_2O_2]_i\) is constant, \([I^-]_i\) doubles. Since the initial rate doubles, the reaction is 1st order in \(I^-\). Likewise, from exp. # 1 & 3, \([I^-]_i\) is constant and \([H_2O_2]_i\) doubles. The rate doubles, so the reaction is 1st order in \(H_2O_2\). The rate law is:

\[
rate = k [H_2O_2][I^-] \quad (2\text{nd order overall})
\]

Pick any experiment to evaluate the rate constant. From exp. 1:

\[
1.15 \times 10^{-4} \text{ M/s} = k(0.100 \text{ M})(0.100 \text{ M}); \quad k = 1.15 \times 10^{-2} \text{ M}^{-1} /\text{s} \quad \text{(note units!)}
\]

Ex. What is the reaction rate if \([H_2O_2] = 0.300 \text{ M} \) and \([I^-] = 0.400 \text{ M}\)?

\[
rate = (1.15 \times 10^{-2} \text{ M}^{-1} /\text{s})(0.300 \text{ M})(0.400 \text{ M}) = 1.38 \times 10^{-3} \text{ M/s}
\]

In general, a reaction order \(n\) can be determined by solving this equation:

\[
\left(\frac{[A]_i}{[A]_o}\right)^n = \left(\frac{rate_{i,1}}{rate_{i,2}}\right)
\]

D. Integrated rate law for a first order reaction.

Many important reactions (and processes) obey a 1st order rate law: \(rate = -\Delta[A]/\Delta t = k[A]\).

The integrated rate law for a 1st order reaction is:

\[
[A]_t = [A]_0 e^{-kt} \quad \text{or} \quad \log([A]/[A]_0) = -kt/2.303 \quad \text{(will use the latter form)}
\]

where \([A]_i\) is the conc. of A at any time \(t\), and \([A]_0\) is the initial conc. of A. 2.303 = ln(10). The units of \(k\) are reciprocal time (e.g., /s or s\(^{-1}\)).

A plot of \([A] \) vs \(t\) exhibits exponential decay (see Fig. 12.6 in M&F). A plot of \(\log[A] \) (or \(\log([A]/[A]_0)\)) vs \(t\) is a straight line whose slope is \(-k/2.303\). A linear \(\log[A] \) plot vs \(t\) is a good diagnostic for a 1st order reaction.

Ex. Given \(\text{Co(NH}_3\text{)}_5\text{Br}^{2+} + \text{H}_2\text{O} \rightarrow \text{Co(NH}_3\text{)}_5\text{(H}_2\text{O})^{3+} + \text{Br}^-\)

The reaction is 1st order in \(\text{Co(NH}_3\text{)}_5\text{Br}^{2+}\); \(k = 6.3 \times 10^{-6} /\text{s}\). If \([\text{Co(NH}_3\text{)}_5\text{Br}^{2+}]_i = 0.100 \text{ M}\), what is \([\text{Co(NH}_3\text{)}_5\text{(H}_2\text{O})^{3+}]\) after 10. hours?

Convert to a common time unit: (10. h)(60 min/h)(60 s/min) = 36000 s (2 sig. fig.)

\[
\log([\text{Co}]_i/(0.100 \text{ M})) = -(6.3 \times 10^{-6} /\text{s})(36000 \text{ s}) /2.303 = -0.098
\]

\[
[\text{Co}]_i/(0.100 \text{ M}) = 10^{-0.098} = 0.80; \quad [\text{Co}]_i = 0.080 \text{ M}
\]

Ex. How many hours are required for 75% of the Co complex to react? 25% of Co complex is left, so \([\text{Co}] / [\text{Co}]_0 = 0.25.\)

\[
\log(0.25) = -0.60 = -(6.3 \times 10^{-6} /\text{s})t /2.303; \quad t = (2.2 \times 10^5 \text{ s})(1 \text{ min}/60 \text{ s})(1 \text{ h}/60 \text{ min}) = 61 \text{ h}
\]

Another characteristic of 1st order rate law and exponential decay of the reactant is a constant half-life \(t_{1/2}\) - the time required for the reactant conc. to decrease by a factor of 2. Two important equations:
\[
\frac{[A]}{[A]_0} = (1/2)^N \quad \text{where } N \text{ (the number of half lives that have passed)} = \frac{t}{t_{1/2}}
\]

And: \( t_{1/2} = \frac{0.693}{k} \) which is independent of the conc. of A. \((\ln(2) = 0.693)\)

Ex. The decomposition of \( \text{H}_2\text{O}_2 \) in dilute base is 1st order, with \( k = 1.8 \times 10^{-5}/\text{s} \). What is the half-life in hours?

\[
t_{1/2} = \frac{(0.693)}{(1.8 \times 10^{-5}/\text{s})} = (3.8 \times 10^4 \text{ s})(1 \text{ h}/3600 \text{ s}) = 11 \text{ h}
\]

Ex. If the initial conc. of \( \text{H}_2\text{O}_2 \) is 0.30 M, what is the conc. after 4 half-lives?

\[
[\text{H}_2\text{O}_2] = \left(\frac{1}{2}\right)^4 = 1/16 = 0.0625; \quad [\text{H}_2\text{O}_2]_t = 0.019 \text{ M}
\]

E. Integrated rate law for a second order reaction.

If \( \text{rate} = k[A]^2 \), then: \( 1/[A] = kt + 1/[A]_0 \) and \( t_{1/2} = 1/(k[A]_0) \)

A plot of \( 1/[A] \) vs \( t \) is linear with slope \( k \) and intercept \( 1/[A]_0 \) (diagnostic for a 2nd order reaction).

Ex. The decomposition of \( \text{HI}(g) \) at 410°C is second order in \( \text{HI} \):

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

Given the following conc.-time date, calculate the rate constant:

<table>
<thead>
<tr>
<th>time (min):</th>
<th>0</th>
<th>20.0</th>
<th>40.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HI] (M):</td>
<td>0.500</td>
<td>0.382</td>
<td>0.310</td>
</tr>
</tbody>
</table>

\[
1/(0.310 \text{ M}) = k(40 \text{ min}) + 1/(0.500 \text{ M})
\]

\[
k(40 \text{ min}) = 3.23/\text{M} - 2.00/\text{M} = 1.23/\text{M}; \quad k = (1.23/\text{M})/(40.0 \text{ min}) = 0.0306/(\text{M} \cdot \text{min})
\]

Note the units of \( k \) (reciprocal conc.-reciprocal time).

Ex. When does the conc. of \( \text{HI} \) reach 0.100 M?

\[
1/(0.100 \text{ M}) = (0.0306/(\text{M} \cdot \text{min}))t + 1/(0.500 \text{ M}); \quad t = 260 \text{ min}
\]

Ex. How many minutes does it take for \( [\text{HI}] \) to drop from 0.400 to 0.200 M? One half-life.

\[
t_{1/2} = 1/((0.0306/(\text{M} \cdot \text{min})(0.400 \text{ M})) = 81.6 \text{ min}
\]