Thermodynamics and kinetics

- Thermodynamics
  - Observe relative stability of states
  - Energy differences
  - Static comparisons of states
- Kinetics
  - Observe changes of state over time
  - Several different topics
    - Empirical description of the rate of reaction
    - Determination of experimental parameters
    - Microscopic theories

Rates

- A chemical reaction is described by an equation of the type

\[ H_2 \text{(gas)} + \frac{1}{2} O_2 \text{(gas)} \rightarrow H_2O \text{(liquid)} \]

- Rates:
  - Rate of change of [H₂O]: \( \frac{d[H₂O]}{dt} \)
  - Rate of change of [H₂]: \( \frac{d[H₂]}{dt} \)
  - Rate of change of [O₂]: \( \frac{d[O₂]}{dt} \)

- Rates related by the overall equation
  - 1 oxygen molecule disappears for every 2 hydrogen molecules in the above reaction

Reaction velocity

- The rates of appearance of products and disappearance of reactants are related by stoichiometry of the reaction

Define the reaction velocity, \( v \), in terms of "normalized" rates of appearance of products and disappearance of reactants

\[ v = \frac{1}{v} \frac{d[i]}{dt} \]

Example of the production of water:

\[ v = -\frac{d[H₂]}{dt} = -2 \frac{d[O₂]}{dt} = \frac{d[H₂O]}{dt} \]

Rate laws

- Description of how the reaction velocity depends on parameters such as concentrations, temperature, pressure, etc.

\[ v = f(A_\text{react}, B_\text{prod}, T, P) \]

- May be simple or complex
- Gives insight into the manner in which the reaction occurs
  - Reactions do not necessarily occur in the manner indicated by the overall reaction equation

Order

- In many situations, one may write the functional form of the reaction velocity approximately as

\[ v = k[A]^a[B]^b[C]^c \cdots \]

- \( a, b, c \) are the orders of reaction under the conditions examined
- Many reaction velocities are more complicated functions than the simple one above
- Example: Production of HBr over a wide range

\[ v_{\text{net}} = k \frac{[H_2]^2[Br_2]}{[HBr]^2} \]

- Orders are often determined over a limited range
  - Initial order of reaction
Determining initial order
- Measure initial velocity as a function of the amount of reactants in the mixture
- Example: \( \text{OCl}^- + \text{I}^- \rightarrow \text{OI}^- + \text{Cl}^- \)

<table>
<thead>
<tr>
<th>[\text{OCl}^-]</th>
<th>[\text{I}^-]</th>
<th>[\text{OH}^-]</th>
<th>Initial velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0037</td>
<td>0.0017</td>
<td>1.00</td>
<td>1.75 \times 10^{-4}</td>
</tr>
<tr>
<td>0.0034</td>
<td>0.0017</td>
<td>1.00</td>
<td>3.50 \times 10^{-4}</td>
</tr>
<tr>
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</tr>
</tbody>
</table>

By comparison, one finds the initial rate equation

\[
\nu_{initial} = k(\text{OCl}^-)[\text{I}^-][\text{OH}^-]^{-1}
\]

Integrated rate laws - first order in a reactant
- For simple chemical reactions, integrate the rate laws to determine how the reactant concentration changes with time
- First-order rate law
  - Exponential in time
  - Linear form is the logarithm

\[
\ln([A(t)]) = \ln([A(0)]) - kt
\]

First-order rate law
- Example: decomposition of di-tert-butyl peroxide
  - Line slope \( = 1.04 \)
  - Order with respect to DTBP is close to 1 under these conditions (and probably is 1)

\[
\text{rate} = k \cdot [\text{DTBP}]^{-1}
\]

Reactant or Product?
- What if one can only measure a product concentration with time?
- Sometimes one can derive an equation for the reactant concentration with time
- Can solve for the concentration of B exactly

First-order Product
- Rely on conservation of matter

\[
\frac{[B(t)]}{[A(0)]} = \frac{[A(0)] - [A(t)]}{[A(0)]} = 1 - e^{-kt}
\]

Rearrange to find the linear form

\[
\ln\left(\frac{[B(t)]}{[A(0)]}\right) = -kt
\]
Integrated rate law – second order in reactant

- Second-order rate law may be integrated
- Linear plot of $1/[A(t)]$ versus $t$
- Often see reported rate constant for disappearance of $A$
  \[ k_{\text{eff}} = 2k_2 \]
  - Exercise caution in assessing reported rate constants

Example:
- Collision-induced decomposition of diacetylene, DA
- Hou and Palmer, 1965
- Linear plot of $[DA]^{-1}$ versus $t$
  \[ k_{\text{eff}} = 6.79 \times 10^7 \text{ cm}^3/\text{mol} \cdot \text{sec} \]

Integrated rate laws for other reactant orders

- Integration gives a general form for all orders (except 1)
- The power of the function of concentration linear in time is related to order of reaction for the conditions under which the system is observed

\[ \frac{d[A]}{dt} = -k[A]^n \]
\[ \frac{1}{[A(t)]^n} = \frac{1}{[A(0)]^n} + k_1t \]

Half life

- Can describe time dependence in several different ways
  - Rate constant, $k$
  - Half life, $t_{1/2}$, time for one half of reactant to disappear
  - Other times that describe the amount left

First order
\[ t_{1/2} = \frac{\ln 2}{k} \]

Second order
\[ t_{1/2} = \frac{1}{k_{\text{eff}}[A(0)]} \]

Determining kinetic parameters

- Two conceptual steps
  - Find parameter proportional to concentration
  - Find appropriate function of time to allow evaluation of time course

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameter often measured</th>
<th>Parameter needed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>$P$, total pressure</td>
<td>$P_1$, partial pressure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>of reaction</td>
</tr>
<tr>
<td>Solution</td>
<td>Total optical absorption</td>
<td>Absorption of a single component</td>
</tr>
<tr>
<td></td>
<td>Total conductance</td>
<td>Conductance of a single component</td>
</tr>
<tr>
<td></td>
<td>Total volume</td>
<td>Volume change of a single component</td>
</tr>
<tr>
<td></td>
<td>Titration</td>
<td>Concentration of a single component</td>
</tr>
</tbody>
</table>
Summary

- Chemical change quantified by the mathematics of chemical kinetics
- Rate constant and order characterize a reaction
- Determining rates and velocities
  - Differential method
  - Integrated-rate-law method
- Results often limited to a particular time scale or situation
  - Initial reaction
  - With some materials in excess