Physical Chemistry

Lecture 4
Introduction to chemical kinetics

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 \([H_2O]\): \(\frac{d[H_2O]}{dt}\)
  - Rate of change of \([H_2]\): \(\frac{d[H_2]}{dt}\)
  - Rate of change of \([O_2]\): \(\frac{d[O_2]}{dt}\)
- 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:
  \[ v = -\frac{d[H_2]}{dt} = -2 \frac{d[O_2]}{dt} = \frac{d[H_2O]}{dt} \]

Rate laws
- Describe of how reaction velocity depends on parameters such as concentrations, temperature, pressure, etc.
  \[ v = f([A]_\text{initial},[B]_\text{initial},T,P) \]
- 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
  \[ v = k[A]^a[B]^b[C]^c \ldots \]
- \(a, b, c\) 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
    \[ v_{\text{HBR}} = k \frac{[H_2]^2[Br_2]}{1+k^\lambda[Br_2]} \]
- 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}^-] ) mol dm(^{-3})</th>
<th>(\text{[I}^-] ) mol dm(^{-3})</th>
<th>(\text{[OH}^-] ) mol dm(^{-3})</th>
<th>Initial velocity (\nu) mol dm(^{-3}) sec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0003</td>
<td>0.0017</td>
<td>1.00</td>
<td>1.75 \times 10(^{-6})</td>
</tr>
<tr>
<td>0.0004</td>
<td>0.0017</td>
<td>1.00</td>
<td>3.50 \times 10(^{-6})</td>
</tr>
<tr>
<td>0.0005</td>
<td>0.0034</td>
<td>1.00</td>
<td>3.50 \times 10(^{-6})</td>
</tr>
<tr>
<td>0.0007</td>
<td>0.30</td>
<td>1.00</td>
<td>3.50 \times 10(^{-6})</td>
</tr>
</tbody>
</table>

By comparison, one finds the initial rate equation:

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

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
  \[ \ln(\text{[A]}_t) = \ln(\text{[A]}_0) - kt \]

First-order rate law

- Example: decomposition of di-tert-butyl peroxide
- Line slope = 1.04
- Rate constant for this reaction is determined to be \( k_1 = 0.0193 \text{ min}^{-1} \) from the slope of the line

Reactant or Product?

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

First-order Product

- Rely on conservation of matter
  \[ \text{[B]}(t) = \text{[A]}(0) - \text{[A]}(t) \]
  \[ = \text{[A]}(0) - \text{[A]}(0)e^{-kt} \]
  \[ = \text{[A]}(0)(1 - e^{-kt}) \]
- Rearrange to find the linear form
  \[ \ln\left(\frac{\text{[A]}(0) - \text{[B]}(t)}{\text{[A]}(0)}\right) = -kt \]
Integrated rate law – second order in reactant (Case I)

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

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

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

Second-order rate law

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

Second-order rate law (Case II)

- Previously considered
  - Homomolecular reaction (A + A)
  - If other species affected reaction, they were held constant
- Consider second-order heteromolecular
  - Second order overall
  - First order in each reactant
- \( \text{Does not work for } [A]_0 = [B]_0 \)

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_i, partial pressure of reactant</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>Titration</td>
<td>Concentration of a single component</td>
<td></td>
</tr>
</tbody>
</table>
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