Physical Chemistry

Lecture 8
Reactions in solution and relaxation methods in fast kinetics

The cage effect
- In solution, solvent is a major factor in kinetics
- Limited proximity of reactants
- Molecules must diffuse into reaction zone

Diffusion control
- Limiting behavior
  - EVERY molecule entering the cage reacts
  - Diffusive motions control the time it takes to enter the cage
  - Simple bimolecular reaction with diffusion control
- Typical size of diffusion-controlled rate constant
  \[ k_{\text{eff}} = 4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \]

Rate constants for bimolecular reactions in solution

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( k ) (298 K) ( (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1^+ + 2^- \rightarrow \text{products} )</td>
<td>( 1 \times 10^{-12} )</td>
</tr>
<tr>
<td>( \text{H}_2 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH}_2^+ )</td>
<td>( 1 \times 10^9 )</td>
</tr>
<tr>
<td>( \text{OH}^- + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}^- + \text{H}_2\text{O} )</td>
<td>( 6 \times 10^8 )</td>
</tr>
<tr>
<td>( \text{OH}^- + \text{p-C}_6\text{H}_4(\text{COOC}_2\text{H}_5)_2 \rightarrow \text{p-C}_6\text{H}_5\text{OOCC}_6\text{H}_4\text{COO}^- + \text{H}_2\text{O} )</td>
<td>( 5.4 \times 10^{-2} )</td>
</tr>
</tbody>
</table>

Ionic reactions in solution

- The charge on an ion affects the reaction rate
- Can be understood with activated complex theory and Debye-Hückel theory

\[ \ln k(T) = \ln k_0(T) + 2\alpha |z_A z_B| \sqrt{I} \]

Ionic reactions in solution

- Dependence of rate constant on
  - Ionic strength
  - Product of charges
- Example reactions

\( \text{CH}_3\text{CO}_2^- + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H}^- + \text{OH}^- \)
\( \text{Cu}^{+2} + \text{OH}^- \rightarrow \text{Cu}^{+} + \text{OH}_2^- \)
Perturbation-relaxation methods

- For reactions that happen very fast
  - It is not possible to mix reactants uniformly before the reaction is substantially done
  - One cannot use typical methods of kinetics
- Alternative is the perturbation-relaxation method
  - Move the system from equilibrium quickly
  - Observe the return to equilibrium
- Types of relaxation methods
  - T-jump
  - P-jump
  - E-jump
  - Laser-pump

Example relaxation method

- Refolding of a decanucleotide at 32.4°C
- Determined optically through absorption of UV light
- Slope of line = -τ⁻¹
- Time scale of milliseconds

Examples of fast reactions

- Recombinations
  \[ H^+ + OH^- \leftrightarrow H_2O \]
  \[ OH^- + NH_4^+ \leftrightarrow NH_3OH \]
- Substitution reactions
  \[ Ca^{2+}(H_2O)_6 + NH_3 \leftrightarrow Ca^{2+}(H_2O)_2NH_3 + H_2O \]
- Dimerizations
  \[ 2 \text{proflavin} \leftrightarrow (\text{proflavin})_2 \]

Summary

- Solution reactions are complicated because of the interaction with the solvent
- Diffusion control gives an estimate of the cage effect
  - Reactive species such as HS show reaction rate constants that imply total diffusion control
  - Other reactions show slower reaction rates
- Ionic reactions show a dependence on
  - Ionic strength
  - Charge on ions
  - Debye-Hückel theory prediction
- Fast reactions studied by relaxation techniques
  - Can determine rate constants for fast processes
  - Modern techniques allow study processes on scales of picoseconds and femtoseconds

Example relaxation calculation

- Perturbation changes concentrations from equilibrium values
- Concentrations return to equilibrium values with time constant \( \tau \), which is measured
- That, plus the equilibrium constant, gives \( k_1 \) and \( k_2 \) uniquely