Structure of Water

- **sp³ hybridization**
  - 2 bonding and 2 non-bonding orbitals

- **Dipolar Character**

- **Origin of Water’s Unusual properties**
  - High melting and boiling point
  - High heat of vaporization
  - Expands upon freezing
  - High surface tension
  - Excellent polar solvent
Water’s intermolecular structure

- Dominated by Hydrogen Bonds
- Ice
  - Open tetrahedral structure
- Water
  - Flickering cluster model
    - 100 ps lifetime
    - 0.1 ps molecular vibration
  - Avg cluster size
    - 65 molecules @ 0°C
    - 12 molecules @ 100°C

Solutes in Water

- Great solvent for ionic or ionizable substances
- Ion-dipole bonds improves stability
  - Energy increases with charge of ion and decreases with size
- Solvent hole model
  - As solute-water bonding strengthens compared to water-water bonding, solubility goes up
    - Hydrophilic solute
  - Weak solute-water bonds reduce solubility
    - Hydrophobic solutes
**Activation Energy**

- Activation Energy must always be positive
  - Unlike $\Delta H$, which may be positive or negative
- Differing reaction rates

![Energy Reaction Coordinate Diagram](image)

**Encounter Theory I**

- Uncharged Solutes
  - Nature of diffusion in water
    - Encounter within a solvent cage
    - Random diffusion occurs through elementary jumps of distance
      \[ \lambda = 2r \]

  More appropriate for water

  - For a continuous medium:
    \[ D = \frac{x^2}{2\tau} \]
    or
    \[ \tau = \frac{x^2}{2D} \]
  - For a semi-crystalline structure:
    \[ D = \frac{x^2}{6\tau} \]
    or
    \[ \tau = \frac{x^2}{6D} \]

For water, $D \approx 1 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$, and $\lambda = 4 \times 10^{-8} \text{cm}$, so $\tau \approx 2.5 \times 10^{-11} \text{s}$.

If time between vibrations is $1.5 \times 10^{-13} \text{s}$, then the average water molecule vibrates 150 times ($2.5 \times 10^{-11}/1.5 \times 10^{-13}$) in its solvent cage before jumping to the next one.
Encounter Theory II

- **Probability of Encounter**
  - If A and B are the same size as water
    - They will have 12 nearest neighbors
  - Probability that “A” will encounter “B” in a solvent cage of 12 neighbors is:
    - Proportional to the mole fraction of “B”
    
    \[ P_{B/A} = 6X_B \]
    
    With each new jump, "A" has 6 new neighbors
    
    Where:
    
    \[ X_B = \frac{n_B}{\left(\frac{1}{\gamma^2}\right)} \]

- And combining the rate of movement with the probability of encountering “B”, we get an expression for the rate of encounter with “B”
  
  \[ \frac{1}{\tau_{AB}} = \frac{6D}{\lambda^2} P_{AB} \]

Encounter Theory III

- Then substituting in for the probability
  
  \[ \frac{1}{\tau_{AB}} = \frac{6D(6\gamma^2)}{\lambda^2} \]

  \[ = 36\gamma^2 n_B D \]

- For water, \( \gamma = 0.74 \), and the effective diffusion coefficient, \( D_{AB} = D_A + D_B \) and \( \lambda = r_{AB} \) the sum of the molecular radii

  - Then we get:
    
    \[ \frac{1}{\tau_{AB}} = 25r_{AB} D_{AB} n_B \]
Encounter Theory IV

- Now the total # of encounters between “A” and “B” per cm$^3$ per second is:

  \[ \frac{n_A}{r_{AB}} = 25r_{AB}D_{AB}n_An_B \]

- In terms of moles of encounters (encounter frequency) this becomes:

  \[ Z_{e,AB} = \frac{1000 \text{ cm}^3}{N_o \text{ molecule/Mole}} \left( \frac{n_A}{r} \right) = 25r_{AB}D_{AB} \left( \frac{1000 \text{ cm}^3}{N_o \text{ molecule/Mole}} \right) n_An_B \]

  \[ = 25r_{AB}D_{AB}[A][B] \]

Encounter Theory V

- Frequency Factor

  \[ Z_{e,AB} = 2.5 \times 10^{-2}r_{AB}D_{AB}N_o[A][B] \]

- When $E_a = 0$, $k=A$

  \[ k = Ae^{-E_a/RT} \]
Transition State Theory I

Consider the simple bimolecular reaction

\[ A + B \xrightarrow{k} C \]

Even though it is an elementary reaction, we can break it down into two steps

\[ A + B \leftrightarrow \text{AB}^* \xrightarrow{k^*} C \]

Where the first “equilibrium” is:

\[ K^* = \frac{[\text{AB}^*]}{[A][B]} \]

So the forward rate is:

\[ \frac{d[C]}{dt} = k^*[\text{AB}^*] = k^*K^*[A][B] \]

Transition State Theory II

Now the transition state is just one bond vibration away from conversion to products

- Plank’s Law:
  \[ E_{vib} = h\nu \]
  where \( h \) is Planck’s constant (6.62 x 10^-27 ergs·s)

- Bond energy must be in the thermal region:
  \[ E_{\text{bond}} \approx kT \]
  where \( k \) is Boltzmann constant (1.3807 x 10^-23 ergs·K)

- So equating, we get:
  \[ h\nu = kT \]
  \[ \nu = \frac{kT}{h} \]

- And since conversion occurs on the next vibration:
  \[ k^* = \nu \quad \text{and} \quad k = k^*K^* = \frac{kT}{h}K^* \]
Transition State Theory III

- Now from basic thermodynamics:
  \[ \Delta G^\circ = -RT \ln K \quad \text{or} \quad K = e^{-\Delta G^\circ / RT} \]
  - And also \[ \Delta G^\circ = \Delta H - T \Delta S \]
  - So:
    \[ K = e^{\Delta S^*/R} e^{-\Delta H^*/RT} \]
  - And combining:
    \[ k = \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \]
- Recall:
  \[ \Delta E = \Delta H - P \Delta V \approx \Delta H \]
- And substituting back in:
  \[ k = \left(\frac{kT}{h} e^{\Delta S^*/R}\right) e^{-E_a/RT} \]

Activation Energy

- Activation Energy must always be positive
  - Unlike \( \Delta H \), which may be positive or negative
- Differing reaction rates
Temperature Effects

**Arrhenius Equation**

\[ \frac{d \ln k}{dT} = \frac{E_a}{RT^2} \]

\[ k = Ae^{-E_a/RT} \]

\[ \ln \frac{k_2}{k_1} = \frac{(T_2 - T_1)E_a}{RT_1T_2} \]

\[ \ln \frac{K_2}{K_1} = \frac{(T_2 - T_1)\Delta H_a}{RT_1T_2} \]

Analogous to Van’t Hoff Equation for Equilibria

Ionic Strength Effects

**Ion-ion Reactions**

- Based on activated complex theory

\[ A + B \leftrightarrow AB^z \xrightarrow{k^*} C \]

\[ \frac{d[C]}{dt} = k^*[AB^z] = k^*[A][B] \]

- So let’s look at the equilibrium constant

\[ K^* = \frac{[AB^z]}{[A][B]} = \frac{[AB^z]n_{AB^z}}{[A]n_A[B]n_B} \]

\[ \text{or } [AB^z] = K^*[A][B]\left(\frac{n_{AB^z}}{n_{AB^z}}\right) \]

- Which means:

\[ \frac{d[C]}{dt} = kT \frac{K^*[A][B]\left(\frac{n_{AB^z}}{n_{AB^z}}\right)}{h} \]

\[ K_{2}^{\circ} \text{ (for I=0)} \]
Reactions with charged ions

- Using the Debye-Huckel Equation
  - \( I < 0.005 \)
  - \( \log k_2 = \log k_2^0 + \left\{ -0.51z_i^2 + 0.51z_i^2 + 0.5\left(z_i + z_a\right)^2 \right\} I^{0.5} \)
  - \( k_2 = k_2^0 + 1.02z_i z_a I^{0.5} \)

- Using the Guntelberg Approximation
  - \( I < 0.01 \)
  - \( \log k_2 = \log k_2^0 + 1.02z_i z_a I^{0.5} + \left( k_2^0 + 2z_i z_a + z_a^2 \right) \frac{f^{0.5}}{(1 + f^{0.5})} \)

I corrections (cont.)

- Neutral species
  - \( \log k_2 = \log k_2^0 + \left( \rho_A + b_A - b_{\text{diff}} \right) I \)

- Some case studies:
Case Study: TCP

- Observed loss of 1,1,1-trichloropropanone in distribution systems
  - Lab studies show that chloroform is the product
  - Logically presumed to be a simple hydrolysis

Reckhow & Singer, 1985
"Mechanisms of Organic Halide Formation During Fulvic Acid Chlorination and Implications with Respect to Preozonation", In Jolley et al., Water Chlorination; Chemistry, Environmental Impact and Health Effect, Volume 5, Lewis.

TCP (cont.)

- Ionic strength effects
  \[ \ln k_H = -4.81 - 1.4\sqrt{I} \]
  \[ \log k_H = -2.08 - 0.6\sqrt{I} \]

- Rate with chlorine
  - Increases greatly
  - High intercept
  \[ k_f = 0.024 + 32[HOCI] \]

Note: both TCP and TCAC refer to the 1,1,1-trichloropropanone.

---

Figure 6. Chlorination of 1,1,1-trichloropropanone (TCP). Conditions: 20.4 mg/L applied HOCI, [PO₄]₃₋ = 0.0145 M, pH 7.0, 30°C.

Figure 7. Pseudo-first-order reaction rate constants for the hydrolysis of 1,1,1-trichloropropanone as a function of ionic strength. Conditions: pH 7.0, 30°C, no added chlorine.

Figure 8. Pseudo-first-order reaction rate constants for the disappearance of 1,1,1-trichloropropanone as a function of chlorine dose. Conditions: pH 7.0, 30°C, [PO₄]₃₋ = 0.0145 M.
Disagreement with prior study

- Gurol & Suffet showed 10x higher rate constants
- Phosphate?

Figure 7. Pseudo-first-order reaction rate constants for the chlorination of 1,1,1-trichloro-
propane as a function of phosphate concentration at pH 7.6.

Putting it together

Figure 12. Hypothetical mechanism for the decomposition of trichloroacetone to chloral in the presence of intermediate concentrations of phosphate at pH 7.
Homogeneous Catalysis

Definition

Liquid-phase substances which react with the main reactants or intermediates thereby providing an alternative pathway to products with a lower activation energy or a higher frequency factor. Catalysts are often regenerated over the course of the reaction.

\[ 2A^{2+} + B^+ \rightarrow 2A^+ + B^{3+} \]

termolecular reaction? – be skeptical

What really happens:

\[ A^{2+} + C^+ \rightarrow A^+ + C^{2+} \]

\[ A^{2+} + C^{2+} \rightarrow A^+ + C^+ \]

\[ C^{3+} + B^+ \rightarrow C^+ + B^{3+} \]

\[ 2A^{2+} + B^+ \rightarrow 2A^+ + B^{3+} \]

“C” serves as a sort of charge-transfer facilitator, since “B” does not exist in a divalent state.

Table 4-1. Mechanisms of Acid-Base Catalysis

<table>
<thead>
<tr>
<th>Type</th>
<th>Mechanism</th>
<th>Rate expression</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Specific</td>
<td>[ S + HA \rightarrow SH^- + A^- ]</td>
<td>[ k_3 \cdot [SH^-][A^-] ]</td>
<td>For protolytic cases, expression applies when ( k_3 \ll k_1 ), where the general form is independent of the specific acid-base pair.</td>
</tr>
<tr>
<td>II. General acid</td>
<td>[ S + HA \rightarrow SH^- + A^- ]</td>
<td>[ k_3 \cdot [SH^-][A^-] ]</td>
<td>Protolytic mechanism yields general acid catalysts regardless of relative sizes of ( k_1 ) and ( k_2 ).</td>
</tr>
<tr>
<td>III. General acid</td>
<td>[ SH + B \rightarrow S^- + B^+ ]</td>
<td>[ k_4 \cdot [SH][B^+] ]</td>
<td>For protolytic cases, expression applies when ( k_4 \gg k_3 ), regardless of nature of proton acceptor in final step.</td>
</tr>
<tr>
<td>IV. Specific OH-</td>
<td>[ HS + B \rightarrow S^- + BH^+ ]</td>
<td>[ k_5 \cdot [HS][BH^+] ]</td>
<td>Protolytic cases yield general acid catalysts regardless of relative sizes of ( k_2 ) and ( k_3 ).</td>
</tr>
<tr>
<td>V. General base</td>
<td>[ HS + B \rightarrow S^- + BH^+ ]</td>
<td>[ k_5 \cdot [HS][BH^+] ]</td>
<td>Protolytic cases yield general base catalysts regardless of relative sizes of ( k_2 ) and ( k_3 ).</td>
</tr>
</tbody>
</table>

☐ To next lecture