Coordination Chemistry

The Thermodynamics of Metal-Ligand Binding
Review of the Previous Lecture

1. Discuss Crystal Field Theory
2. Determined how to calculate Crystal Field Stabilization Energy (CFSE)
3. Evaluated the different factors that contribute to the magnitude of $\Delta$
4. Discussed different crystal field for different geometries
   - Introduced the Jahn Teller Effect
1. Metal-ligand complexation

\[ M + L \rightleftharpoons M-L \]
1. Metal-ligand complexation

Kinetic Standpoint:

- Tells how slow or fast the complexation event is
- Later we will discuss inertness (slow ligand exchange) vs lability (rapid ligand exchange)
- The $\Delta G^\neq$ values correspond to the activation barriers for the forward and reverse reactions and define the rate constants ($k$)

$$M + L \rightleftharpoons M-L$$

$\Delta G^\neq$ rate of the reaction
1. Metal-ligand complexation

\[
M + L \rightleftharpoons M-L
\]

\[
K = \frac{[M-L]}{[M][L]}
\]

**Thermodynamic Standpoint:**

- Tells about the relative ratio of product to reactants at equilibrium.
- The \( \Delta G^\circ \) values corresponds to the stability of the M-L complex.

\( \Delta G^\circ \), stability of the complex.
2. Defining Affinity

A. Single-step metal ligand interactions

When considering a single metal ligand interaction, we treat the interaction as a single ligand addition event regardless of the denticity of the ligand

\[ M + L \rightleftharpoons M-L \]

Formation (Stability) Constant = \[ K = \frac{[M-L]}{[M][L]} \]
Say a second ligand can coordinate, now we would have more than a single-step process...
2A. Single-step metal ligand interactions

The first ligand binding step:

\[ \text{M} + \text{L} \rightleftharpoons \text{M-L} \]

\[ K_1 = \frac{[\text{M-L}]}{[\text{M}][\text{L}]} \]

The second ligand binding step:

\[ \text{M-L} + \text{L} \rightleftharpoons \text{M-L}_2 \]

\[ K_2 = \frac{[\text{M-L}_2]}{[\text{M-L}][\text{L}]} \]
Let’s consider the metal ligand binding process in a cumulative manner.
2B. Cumulative M-L interactions

When considering metal ligand interaction in a cumulative process, we introduce the term $\beta$

$$\ce{M + L <=> M-L}$$

$$\beta_1 = \frac{[\text{M-L}]}{[\text{M}][\text{L}]}$$

Now consider both ligands binding to the metal:

$$\ce{M + 2L <=> M-L_2}$$

$$\beta_2 = \frac{[\text{M-L}_2]}{[\text{M}][\text{L}]^2}$$
2B. Cumulative M-L interactions

General expression for describing the cumulative process of metal ligand interactions:

\[ M + xL \rightleftharpoons M-L_x \]

\[ \beta_x = \frac{[M-L_x]}{[M][L]^x} \]
2C. Metal ions are never “free” in solution

I. In aqueous solutions, metal ions are water bound:

\[ M \overset{H_2O}{\longrightarrow} M(H_2O)_x \]

Some metals interact so strongly with water that they cause hydrolysis

\[ M(H_2O) \rightleftharpoons M(OH)^- + H^+ \]

Metal as Brønsted-Lowry Acid
2C. Metal ions are never “free” in solution

\[ M(H_2O) \iff M(OH)^{-} + H^{+} \]

Metal as Brønsted-Lowry Acid

**Brønsted-Lowry Acid Relative Acidity:**
- Alkali metal cations - Not acids
- Alkaline earth - Slight acidity
- 2+ Transition metals: Weak acidity
- 3+ Transition metals: Moderate acidity
- 4+ and higher: Strong acidity, typically oxygenated ions
  - Vanadium(V) usually exists as dioxovanadium (VO_2\(^+\))

*Metal ions lower the effective pK\(_{w}\) of water and pKa of ligands.*
2C. Metal ions are never “free” in solution

II. Ligand binding can be seen as a competition with solvent binding
- When you write formation constants (K) you ignore the bound water

\[ M(H_2O)_x + L \rightleftharpoons M(H_2O)_{x-1}L + H_2O \]
## 2D. Metal-ligand binding preferences

### I. Hard Soft Acid Base Theory

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>F$^-$</th>
<th>Cl$^-$</th>
<th>Br$^-$</th>
<th>I$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$ (aq)</td>
<td>6.04</td>
<td>1.41</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Hg$^{2+}$ (aq)</td>
<td>1.0</td>
<td>6.7</td>
<td>8.9</td>
<td>12.7</td>
</tr>
</tbody>
</table>
2D. Metal-ligand binding preferences

II. The Chelate Effect

When coordinating through the same type of atom, a chelating ligand will outcompete a monodentate ligand for metal binding.

- Chelates are favorable when they form five/six membered rings when metal bound

![Diagram of chelate structures]

- Smaller rings are strained
- Larger rings result in unfavorable ligand distortion
2D. Metal-ligand binding preferences

Let's consider thermodynamic factors for the stability afforded by chelators.

\[ \Delta G^0 = \Delta H^0 - T\Delta S^0 \]

**Enthalpy (\(\Delta H^0\)):** Bond breaking/bond forming

**Entropy (\(\Delta S^0\)):** Tendency toward “disorder”

Compare metal binding by:

\[ \text{CH}_3\text{NH}_2 \quad \text{vs} \quad \text{en} \]
2D. Metal-ligand binding preferences

Octahedral Cd\(^{2+}\) complexes:

A. \([\text{Cd(H}_2\text{O})_6]^{2+} + 4 \text{CH}_3\text{NH}_2 \rightleftharpoons [\text{Cd(CH}_3\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+} + 4 \text{H}_2\text{O}\) \(K (\text{M}) = 3.3 \times 10^6\)

B. \([\text{Cd(H}_2\text{O})_6]^{2+} + 2 \text{en} \rightleftharpoons [\text{Cd(en)}_2(\text{H}_2\text{O})_2]^{2+} + 4 \text{H}_2\text{O}\) \(K (\text{M}) = 4.0 \times 10^{10}\)
2D. Metal-ligand binding preferences

Octahedral Cd$^{2+}$ complexes:

A. $[\text{Cd(H}_2\text{O)}_6]^{2+}$ + 4 CH$_3$NH$_2$ $\rightleftharpoons$ $[\text{Cd(}\text{CH}_3\text{NH}_2)_4\text{(H}_2\text{O)}_2]^{2+}$ + 4 H$_2$O

5 molecules $\rightleftharpoons$ 5 molecules

K (M) $= 3.3 \times 10^6$

B. $[\text{Cd(H}_2\text{O)}_6]^{2+}$ + 2 en $\rightleftharpoons$ $[\text{Cd(en)}_2\text{(H}_2\text{O)}_2]^{2+}$ + 4 H$_2$O

3 molecules $\rightleftharpoons$ 5 molecules

K (M) $= 4.0 \times 10^{10}$

:: 2 more molecules
2D. Metal-ligand binding preferences

Octahedral Cd$^{2+}$ complexes:

A. $[\text{Cd(H}_2\text{O)}_6]^{2+} + 4 \text{CH}_3\text{NH}_2 \rightleftharpoons [\text{Cd(CH}_3\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+} + 4 \text{H}_2\text{O}$

\[ \text{K (M)} = 3.3 \times 10^6 \]

B. $[\text{Cd(H}_2\text{O)}_6]^{2+} + 2 \text{en} \rightleftharpoons [\text{Cd(en)}_2(\text{H}_2\text{O})_2]^{2+} + 4 \text{H}_2\text{O}$

\[ \text{K (M)} = 4.0 \times 10^{10} \]

<table>
<thead>
<tr>
<th>Rxn.</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (kJ/mol)</th>
<th>$\Delta G^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-57.3</td>
<td>-67.3</td>
<td>-37.2</td>
</tr>
<tr>
<td>B</td>
<td>-56.5</td>
<td>+47.1</td>
<td>-60.7</td>
</tr>
</tbody>
</table>
3. Redox Stability

The stability of the oxidation state of a metal ion in solution is highly dependent on the biochemical conditions and the coordination environment. Both can dictate the “preference” of M-L interactions.
3A. Definitions

**Oxidation**: Loss of one or more electrons

**Reduction**: Gain of one or more electrons

**Oxidation-reduction (Redox)** reactions are thermodynamically driven.

\[ \Delta G^0 = -nFE^0 \]

- \( n \) = # of electrons involved
- \( F \) = Faraday’s constant (96,485 C/mol or J/V)
- \( E^0 \) = Electromotive force: The potential energy for electron (or charge) movement

If \( E^0 \) is +, \( \Delta G^0 \) is -; Spontaneous reaction
3B. Ligand coordination shifts the $E^0$ of metal ions

**NOTE:** Oxidation-reduction (Redox) reactions are written from the reduction perspective.

Consider Fe$^{3+}$:

Half-reaction: $\text{Fe}^{3+}(\text{aq}) + e^- \rightarrow \text{Fe}^{2+}(\text{aq})$ $E^0 = +0.77 \text{ V vs Standard Hydrogen Electrode (SHE)}$

$P = 1 \text{ atm; } T = 25 \degree \text{C, pH } = 0$

- In a reducing environment, ligand-free Fe has an oxidation state of 2+
- But we live in an oxidizing environment, Fe$^{3+}$ dominates
3B. Ligand coordination shifts the $E^0$ of metal ions

NOTE: Oxidation-reduction (Redox) reactions are written from the reduction perspective.

Consider Fe$^{3+}$:

Half-reaction- Fe$^{3+}$(aq) + e$^-$ → Fe$^{2+}$(aq)  

$E^0 = +0.77$ V vs (SHE)

Fe(III)  

Fe(II)

The ligand stabilized the oxidation state of Fe(III).
3C. Redox potentials for metal ions can be found in tables or formatted in simplified diagrams.

**Latimer Diagram:** Summarizes a considerable amount of thermodynamic information about the oxidation states of an element.

- Diagrams are written for acidic, neutral, and basic conditions
- Omit $\text{H}_2\text{O}$, $\text{H}_3\text{O}^+$, $\text{OH}^-$
- Write oxidation state, highest to lowest, left to right

```
+0.77 V       -0.44 V
Fe^{3+}(aq) → Fe^{2+}(aq) → Fe(s)  Acidic solution (pH 0)
-0.04 V
```

3C. Redox potentials for metal ions can be found in tables or formatted in simplified diagrams.

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- Diagrams are written for acidic, neutral, and basic conditions
- Omit H₂O, H₃O⁺, OH⁻
- Write oxidation state, highest to lowest, left to right

\[
\begin{align*}
\text{Acidic solution (pH 0)} & \quad +0.77 \text{ V} & \quad -0.44 \text{ V} \\
\text{Fe}^{3+}(aq) & \quad \rightarrow & \quad \text{Fe}^{2+}(aq) & \quad \rightarrow & \quad \text{Fe}(s) \\
\text{Fe}^{2+}(aq) & \quad \rightarrow & \quad 2\text{e}^- & \quad \rightarrow & \quad \text{Fe}(s) \\
\text{Fe}^{3+}(aq) & \quad \rightarrow & \quad 3\text{e}^- & \quad \rightarrow & \quad \text{Fe}(s)
\end{align*}
\]