Complexation Equilibria

- Typically Lewis Acid-Base reactions
  Metal + Ligand = Complex Defined by formation constant, $K$

- Many metals form more complex coordination compounds, containing several ligands. These may occur in a stepwise fashion

\[
\begin{align*}
M + L &= ML & K_1 \\
ML + L &= ML_2 & K_2 \\
ML_2 + L &= ML_3 & K_3 \\
ML_{n-1} + L &= ML_n & K_n
\end{align*}
\]

- Multiple steps of these reactions can be combined using overall formation constants ($\beta$)

\[
M + 3L = ML_3 & \quad \beta =
\]

Formation Constants for EDTA

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\log K_1$</th>
<th>Ion</th>
<th>$\log K_2$</th>
<th>Ion</th>
<th>$\log K_3$</th>
<th>Ion</th>
<th>$\log K_4$</th>
</tr>
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<tbody>
<tr>
<td>Li$^+$</td>
<td>2.95</td>
<td>V$^{3+}$</td>
<td>23.4</td>
<td>Ti$^{3+}$</td>
<td>35.3</td>
<td>Na$^+$</td>
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<td>K$^+$</td>
<td>0.8</td>
<td>Cr$^{3+}$</td>
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<td>Ba$^{2+}$</td>
<td>15.9</td>
<td>Mg$^{2+}$</td>
<td>8.79</td>
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<td>Fe$^{2+}$</td>
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<td>Co$^{3+}$</td>
<td>41.4</td>
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<td>15.9</td>
<td>Ca$^{2+}$</td>
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<tr>
<td>Zn$^{2+}$</td>
<td>8.72</td>
<td>Hg$^{2+}$</td>
<td>29.5</td>
<td>Hg$^{2+}$</td>
<td>17.0</td>
<td>Sr$^{2+}$</td>
<td>6.79</td>
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<td>Ba$^{2+}$</td>
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<td>VO$^{2+}$</td>
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<td>Ba$^{2+}$</td>
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<td>Ra$^{2+}$</td>
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<tr>
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<td>Zn$^{2+}$</td>
<td>21.3</td>
<td>Zn$^{2+}$</td>
<td>21.3</td>
</tr>
</tbody>
</table>

Note: The stability constant is the equilibrium constant for the reaction $M^{2+} + 2\text{EDTA}^2- \rightarrow M\text{ EDTA}_2^{3-}$. Values in table apply at 25°C and 0.1 M unless otherwise indicated.
Complexation Equilibria

- In predicting the completeness of a reaction (complexation, precipitation...), we need to account for all equilibria involving M and L.
  - Often specify conditions for a given system - Conditional Formation Constants (K')

- Conditional Formation Constant for EDTA
  EDTA = ethylendiaminetetraacetic acid, hexaprotic acid!

  \[
  \begin{align*}
  H_6Y^{2+} & = H^+ + H_5Y^+ & K_{a1} = 1 \\
  H_5Y^+ & = H^+ + H_4Y & K_{a2} = 3.16 \times 10^{-2} \\
  H_4Y & = H^+ + H_3Y^- & K_{a3} = 1.02 \times 10^{-2} \\
  H_3Y^- & = H^+ + H_2Y^{2-} & K_{a4} = 2.14 \times 10^{-3} \\
  H_2Y^{2-} & = H^+ + HY^3- & K_{a5} = 6.92 \times 10^{-7} \\
  HY^3- & = H^+ + Y^4- & K_{a6} = 5.50 \times 10^{-11}
  \end{align*}
  \]

- Predominant forms depend on pH (Fig 11-7).
pH Dependence of EDTA Formation Constant

• Typically focus on fully deprotonated form (Y\(^{4-}\)):
  \[M^{n+} + Y^{4-} = MY^{n-4}\]
  
  \[K'_f = \alpha_y, \quad K_f = \frac{[MY^{n-4}]}{[M^{n+}]_{EDTA}}\]

  This is just like \(M^{n+} + \text{EDTA} = MY^{n-4}\), or looking at all forms of EDTA
  • We can calculate \(K'_f\) at any pH
  • We’d like to work where \(K'_f\) is large, where is this?

If it were only that easy!

What do we need to be concerned with when working with metal ions and high pH?

\[M^{n+} + n\text{OH}^- = M(\text{OH})_n (s)\]

How do we avoid this? Two options:

1. Work at low pH.

2. Add something to prevent hydroxide formation. Characteristics?
   • Must bind more strongly than OH\(^-\)
   • Must bind less strongly than EDTA
   • Will keep \(M^{n+}\) in solution until it can be complexed by EDTA
     • Most commonly used auxiliary complexing agent is ammonia, serves two purposes:
How Do We Handle Complexing Agents?

- Many metals form more than one complex with ammonia (and other complexing agents)
  \[
  M + L = ML \\
  M + 2L = ML_2
  \]
  \[
  \beta_1 = K_1 = \frac{[ML]}{[M][L]} \\
  \beta_2 = K_2 = \frac{[ML_2]}{[M][L]}
  \]

- Since EDTA only binds with free \( M^{n+} \), need to know fraction of \( M \) present in the solution
  \[
  \alpha_{M^{n+}} = \frac{[M]}{C_M} = \frac{[M]}{[M]+[ML]+[ML_2]}
  \]

- Use \( \beta \) equilibria to simplify:
  \[
  \alpha_{M^{n+}} = \frac{[M]}{[M]+\beta_1[M][L]+\beta_2[M][L]^2} = \frac{1}{1+\beta_1[L]+\beta_2[L]^2}
  \]

- Now we arrive at a new conditional formation constant for a given pH and \([NH_3]\) (or \([L]\)):
  \[
  K_f = \alpha_{M^{n+}} \cdot \alpha_{\beta} \cdot K_f
  \]

EDTA Titration Curves

Much like strong acid/base titration
(Figure 12-10)

Before adding titrant:

Before equivalence point:

At equivalence point:

After equivalence point:
EDTA Titration Considerations

Requirements for indicators for complexometric titrations:

1. Must bind metal ion of interest
2. Must have different properties (color) in the bound and unbound state
3. Must bind less strongly than the complexing agent (EDTA)

EDTA titration techniques: READ this section carefully.

- Direct titration
- Back titration
- Displacement Titration
- Indirect Titration