EDTA Titrations

We already used metal complexation in Week 2 for the Fe Colorimetry Experiment:

$$\text{Fe}^{2+} + 3 \text{Fz}^{2-} \rightarrow \text{Fe(Fz)}_3^{4-}$$

Ferrozine ($\text{Fz}^{2-}$) is a metal ligand

Three Ferrozine will form a metal-ligand complex with $\text{Fe}^{2+}$
Metal Complex Formation Constants

Weak Metal Complex Formation Constants have similar values of $K_1$ to $K_n$. Therefore, many species co-exist in solution!

Zinc Complexation

1. Zinc-ammonia complexation

\[
\begin{align*}
\text{Zn}^{2+} + \text{NH}_3 &= \text{Zn(NH}_3)_2^{2+} & K_1 &= 180 & \beta_1 &= K_1 = 180 \\
\text{Zn(NH}_3)_2^{2+} + \text{NH}_3 &= \text{Zn(NH}_3)_3^{2+} & K_2 &= 220 & \beta_2 &= K_1 K_2 = 3.96 \times 10^4 \\
\text{Zn(NH}_3)_3^{2+} + \text{NH}_3 &= \text{Zn(NH}_3)_4^{2+} & K_3 &= 250 & \beta_3 &= K_1 K_2 K_3 = 9.90 \times 10^6 \\
\text{Zn(NH}_3)_4^{2+} + \text{NH}_3 &= \text{Zn(NH}_3)_5^{2+} & K_4 &= 110 & \beta_4 &= K_1 K_2 K_3 K_4 = 1.09 \times 10^9 \\
\end{align*}
\]

\[
\alpha_{\text{Zn}^{2+}} = \frac{1}{1 + K_1 [\text{NH}_3] + K_1 K_2 [\text{NH}_3]^2 + K_1 K_2 K_3 [\text{NH}_3]^3 + K_1 K_2 K_3 K_4 [\text{NH}_3]^4}
\]

Therefore, many species co-exist in solution!
2. Zinc-tren complexation

\[ \text{Zn}^{2+} + \text{tren} = \text{Zn(tren)}^{2+} \]

\[ K_f = \beta_1 = 4.5 \times 10^{14} \]

\[ \text{tren} = \text{triaminotriethylamine} \]

\[ \alpha_{\text{Zn}^{2+}} = \frac{1}{1 + K_f[\text{tren}]} \]
EDTA Metal Ion Complexation Equilibria

Ethylene Diamine Tetra-acetic Acid (H₄Y)

EDTA - the world’s best metal ion chelator

Metal complexation reactions with Y⁴⁻:

Mⁿ⁺ + Y⁴⁻ ⇌ MnYⁿ⁻⁴₄

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>log K_f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>7.32</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>8.69</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>10.70</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>16.31</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>16.46</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>15.89</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>25.10</td>
</tr>
<tr>
<td>V³⁺</td>
<td>25.90</td>
</tr>
</tbody>
</table>

Conditional formation constant: \( K'_f = \alpha_{Y^4-} K_f \)
Most EDTA titrations are performed at pH $\geq 10$. 

$\alpha_{Y^{4-}}$
EDTA-Metal ion Complexation.

EDTA is a polyprotic acid - Ethylenediaminetetraacetic Acid. $H_4^+Y$.

$pK_1 = 1.99$; $pK_2 = 2.67$; $pK_3 = 6.16$; $pK_4 = 10.26$.

Alpha fraction for $Y^{4-}$:

$$\alpha_{Y^{4-}} = \frac{K_1K_2K_3K_4}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4}$$

$\alpha_{Y^{4-}}$ is equal to 0.35 at a pH of 10.

**EDTA titrations are always run in basic solutions to insure that there is enough $Y^{4-}$ species**
EDTA titrations for metal ions

\[ \text{Ca}^{2+} + Y^{4-} \rightarrow \text{CaY}^{2-} \quad K_f = 5.01 \times 10^{10} \]
\[ \text{Mg}^{2+} + Y^{4-} \rightarrow \text{MgY}^{2-} \quad K_f = 4.90 \times 10^8 \]

\text{pCa or pMg can be used to determine the titration endpoint.}

\text{pCa}

\text{Sadly, we cannot measure pCa directly in our M3LC lab. 😞}
We must use an indicator to detect the endpoint of the EDTA titration.

EDTA will displace weaker ligands -- you will use this process with calmagite to determine the endpoint of an EDTA titration for Mg$^{2+}$.

\[ In^{3-} \rightleftharpoons HIn^{2-} \rightleftharpoons H_2In^- \rightleftharpoons H_3In \]

(orange) (blue)

*what you see will depend on pH

\[ MgIn^- + Y^{4-} \rightleftharpoons MgY^{2-} + In^{3-} \]

(wine-red) (colorless) (??)*
Zn-EDTA Titration: Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a 1.00 x 10^{-4} M Zn^{2+} solution with a 1.00 x 10^{-4} M EDTA solution.

What is $pZn$ at the equivalence point?

Log $K_f$ for the ZnY^{2-} complex is 16.5. Both solutions are buffered to a pH of 10.0. The alpha fraction for $Y^{4-}$ is 0.355 at a pH of 10.0.
Zn-EDTA Titration: Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a 1.00 x 10^{-4} M Zn^{2+} solution with a 1.00 x 10^{-4} M EDTA solution.

Total moles of Zinc = (1.00 x 10^{-4} M)(0.050L)

= 5.0 x 10^{-6} moles
Zn-EDTA Titration: Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a 1.00 x 10^{-4} M Zn^{2+} solution with a 1.00 x 10^{-4} M EDTA solution.

Total moles of Zinc = 5.0 x 10^{-6} moles

Equivalence point volume = 0.100L
Total moles of Zinc = $5.0 \times 10^{-6}$ moles

Equivalence point volume = $0.100$ L

$[\text{ZnY}^{2-}] = 5.0 \times 10^{-5}$ M

We first assume a stoichiometric reaction.
Zn-EDTA Titration: Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a 1.00 x 10^{-4} M Zn^{2+} solution with a 1.00 x 10^{-4} M EDTA solution.

Total moles of Zinc = 5.0 x 10^{-6} moles

Equivalence point volume = 0.100L

\[ [ZnY^{2-}] = 5.0 \times 10^{-5} \text{ M} \]

\[ [Zn^{2+}] = ?? \]

\[ K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]} \]

Then we assume a little bit of free Zinc is formed as required by \( K_f \).
Zn-EDTA Titration: Equivalence Point Calculation

You would like to perform a titration of 50.00 mL of a 1.00 x 10^{-4} M Zn^{2+} solution with a 1.00 x 10^{-4} M EDTA solution.

Total moles of Zinc = 5.0 x 10^{-6} moles

Equivalence point volume = 0.100L

\[ [\text{ZnY}^2-] = 5.0 \times 10^{-5} \text{ M} \]

\[ K_f = \frac{[\text{ZnY}^2-]}{[\text{Zn}^{2+}][\text{Y}^{4-}]} \]

\[ [\text{Zn}^{2+}] = C_{EDTA}^{tot} \]

For every free Zn^{2+}, there is a free EDTA species

\[ [\text{Y}^{4-}] = \alpha_{Y^{4-}}C_{EDTA}^{tot} \]

\[ Y^{4-} \text{ concentration is obtained from the alpha fraction.} \]
**Zn-EDTA Titration: Equivalence Point Calculation**

You would like to perform a titration of 50.00 mL of a 1.00 x 10^{-4} M Zn^{2+} solution with a 1.00 x 10^{-4} M EDTA solution.

Total moles of Zinc = 5.0 x 10^{-6} moles

Equivalence point volume = 0.100L

\[ [\text{ZnY}^{2-}] = 5.0 \times 10^{-5} \text{ M} \]

\[ [\text{Zn}^{2+}] = ?? \]

\[ [\text{Zn}^{2+}] = \sqrt{\frac{[\text{ZnY}^{2-}]}{\alpha_{Y^4-}K_f}} \]

*Plug everything in and solve for Zn^{2+}...*
**Zn-EDTA Titration: Equivalence Point Calculation**

You would like to perform a titration of 50.00 mL of a 1.00 x 10^{-4} M Zn^{2+} solution with a 1.00 x 10^{-4} M EDTA solution.

Total moles of Zinc = 5.0 x 10^{-6} moles

Equivalence point volume = 0.100L

\[
[ZnY^{2-}] = 5.0 \times 10^{-5} \text{ M}
\]

\[
[Zn^{2+}] = 6.67 \times 10^{-11} \text{ M}
\]

\[
pZn = 10.2
\]

And we are done!

conditional formation constant
Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

You would like to perform a titration of 50.00 mL of a 1.00 x \(10^{-4}\) M \(\text{Zn}^{2+}\) solution with a 1.00 x \(10^{-4}\) M EDTA solution.

Both solutions are buffered to a pH of 10.0 using a 0.100M ammonia buffer.

a) How much total free Zn is left in solution?

b) What is the \(\text{Zn}^{2+}\) concentration?
Zinc Hydroxide

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2(s) \]

Solubility product \( K_{sp} = 3.0 \times 10^{-17} \)

\[ K_{sp} = [\text{Zn}^{2+}][\text{OH}^-]^2 \]

At pH=10, [Zn\(^{2+}\)] = ??
**Zinc Hydroxide**

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2(s)
\]

Solubility product \( K_{sp} = 3.0 \times 10^{-17} \)

\[
K_{sp} = [\text{Zn}^{2+}][\text{OH}^-]^2
\]

At pH=10, \( [\text{Zn}^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2} \)
Zinc Hydroxide

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2(s) \]

Solubility product \( K_{sp} = 3.0 \times 10^{-17} \)

\[ K_{sp} = [\text{Zn}^{2+}][\text{OH}^-]^2 \]

At pH=10, \([\text{Zn}^{2+}] = K_{sp} /[\text{OH}^-]^2 \)

\[ = (3.0 \times 10^{-17}) / (1.0 \times 10^{-4})^2 \]

\[ = 3.0 \times 10^{-9} \text{ M} \]

This is the maximum free Zinc concentration.
Ammonia Buffer Solution

\[ \text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad \text{pK}_b = 4.74 \]

\[ [\text{NH}_3]_{\text{total}} = 0.100\text{M} \]

At pH=10, \[ [\text{NH}_3] = ?? \]
Ammonia Buffer Solution

\[ \text{At pH}=10: \]

\[ \text{NH}_3 + \text{H}_2\text{O} \leftrightharpoons \text{NH}_4^+ + \text{OH}^- \quad \text{pK}_b = 4.74 \]

\[ [\text{NH}_3]_{\text{total}} = 0.100\text{M} \]

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

At pH=10:

\[ [\text{NH}_3] = 0.0846\text{M} \]

\[ \alpha_{\text{NH}_3} = \left[1 + \frac{K_b}{[\text{OH}^-]}\right]^{-1} \]
Zinc Complexation

1. Zinc-ammonia complexation

\[ \text{Zn}^{2+} + \text{NH}_3 = \text{Zn(NH}_3)^{2+} \quad \quad K_1 = 180 \quad \quad \beta_1 = K_1 = 180 \]

\[ \text{Zn(NH}_3)^{2+} + \text{NH}_3 = \text{Zn(NH}_3)^2{2+} \quad \quad K_2 = 220 \quad \quad \beta_2 = K_1K_2 = 3.96 \times 10^4 \]

\[ \text{Zn(NH}_3)^2{2+} + \text{NH}_3 = \text{Zn(NH}_3)^3{2+} \quad \quad K_3 = 250 \quad \quad \beta_3 = K_1K_2K_3 = 9.90 \times 10^6 \]

\[ \text{Zn(NH}_3)^3{2+} + \text{NH}_3 = \text{Zn(NH}_3)^4{2+} \quad \quad K_4 = 110 \quad \quad \beta_4 = K_1K_2K_3K_4 = 1.09 \times 10^9 \]

\[ \alpha_{\text{Zn}^{2+}} = \frac{1}{1 + K_1[\text{NH}_3] + K_1K_2[\text{NH}_3]^2 + K_1K_2K_3[\text{NH}_3]^3 + K_1K_2K_3K_4[\text{NH}_3]^4} \]

At \([\text{NH}_3] = 0.0846 \text{M}, \quad \alpha_{\text{Zn}^{2+}} = 1.61 \times 10^{-5} \]
Zinc - Ammonia Complexation

At a TOTAL Zinc concentration of $1.00 \times 10^{-4}$ M:

$$[\text{Zn}^{2+}] = \alpha_{\text{Zn}^{2+}} [\text{Zn}^{2+}]_{\text{tot}}$$

$$[\text{Zn}^{2+}] = (1.61 \times 10^{-5})(1.00 \times 10^{-4})$$

$$[\text{Zn}^{2+}] = 1.61 \times 10^{-9} \text{ M}$$

Therefore: no precipitation!
Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

You would like to perform a titration of 50.00 mL of a 1.00 × 10^{-4} M Zn^{2+} solution with a 1.00 × 10^{-4} M EDTA solution.

Both solutions are buffered to a pH of 10.0 using a 0.100M ammonia buffer.

a) How much total free Zn is left in solution?

b) What is the Zn^{2+} concentration?
Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

You would like to perform a titration of 50.00 mL of a $1.00 \times 10^{-4}$ M Zn$^{2+}$ solution with a $1.00 \times 10^{-4}$ M EDTA solution.

Both solutions are buffered to a pH of 10.0 using a 0.100M ammonia buffer.

At pH=10: \[ \alpha_{Y^{4-}} = 0.355 \]
\[ \alpha_{Zn^{2+}} = 1.61 \times 10^{-5} \]

For ZnY$^{4-}$ \[ \log K_f = 16.5 \]
Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

You would like to perform a titration of 50.00 mL of a $1.00 \times 10^{-4}$ M Zn$^{2+}$ solution with a $1.00 \times 10^{-4}$ M EDTA solution.

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$$\alpha_{Y^{4-}} = 0.355$$
$$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$$
$$\log K_f = 16.5$$

We assume a stoichiometric reaction.

Total moles of Zinc = $5.0 \times 10^{-6}$ moles

Equivalence point volume = 0.100L

$$[ZnY^{2-}] = 5.0 \times 10^{-5} \text{ M}$$
You would like to perform a titration of 50.00 mL of a 1.00 x $10^{-4}$ M Zn$^{2+}$ solution with a 1.00 x $10^{-4}$ M EDTA solution.

\[ K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]} \]

$\alpha_{Y^{4-}} = 0.355$

$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$

\[ \log K_f = 16.5 \]

$[ZnY^{2-}] = 5.0 \times 10^{-5}$ M

a) How much total free Zn is left in solution?
Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

You would like to perform a titration of 50.00 mL of a $1.00 \times 10^{-4} \text{ M Zn}^{2+}$ solution with a $1.00 \times 10^{-4} \text{ M EDTA}$ solution.

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$$
$$\alpha_{Y^{4-}} = 0.355$$
$$\log K_f = 16.5$$
$$[ZnY^{2-}] = 5.0 \times 10^{-5} \text{ M}$$

a) How much total free Zn is left in solution?

$$C_{Zn}^{tot} = C_{EDTA}^{tot}$$
$$[Zn^{2+}] = \alpha_{Zn^{2+}} C_{Zn}^{tot}$$
$$[Y^{4-}] = \alpha_{Y^{4-}} C_{EDTA}^{tot}$$

$$C_{Zn}^{tot} = \sqrt{\frac{[ZnY^{2-}]}{\alpha_{Zn^{2+}}+\alpha_{Y^{4-}}K_f}}$$
Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

You would like to perform a titration of 50.00 mL of a $1.00 \times 10^{-4}$ M Zn$^{2+}$ solution with a $1.00 \times 10^{-4}$ M EDTA solution.

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

$\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}$

$\alpha_{Y^{4-}} = 0.355$

$\log K_f = 16.5$

$[ZnY^{2-}] = 5.0 \times 10^{-5}$ M

\[\alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f = K_f'\]

\[K_f'' = \frac{1}{\alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f}\]

\[C_{Zn}^{tot} = 1.66 \times 10^{-8} \text{ M}\]

\[C_{Zn}^{tot} = \sqrt{\frac{[ZnY^{2-}]}{\alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f}}\]

\[\alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f = K_f''\]

*a) How much total free* Zn is left in solution?*

*free means not in the ZnY$^{2-}$ complex

double conditional formation constant
**Zinc-EDTA Titration Calculation #2 (with ammonia buffer)**

You would like to perform a titration of 50.00 mL of a $1.00 \times 10^{-4}$ M $\text{Zn}^{2+}$ solution with a $1.00 \times 10^{-4}$ M EDTA solution.

$$K_f = \frac{[\text{ZnY}^{2-}]}{[\text{Zn}^{2+}][Y^{4-}]}$$

b) **What is the $\text{Zn}^{2+}$ concentration?**

- $\alpha_{\text{Y}^{4-}} = 0.355$
- $\alpha_{\text{Zn}^{2+}} = 1.61 \times 10^{-5}$
- $\log K_f = 16.5$
- $[\text{ZnY}^{2-}] = 5.0 \times 10^{-5} \text{ M}$
- $C_{\text{Zn}}^{\text{tot}} = 1.66 \times 10^{-8} \text{ M}$
Zinc-EDTA Titration Calculation #2 (with ammonia buffer)

You would like to perform a titration of 50.00 mL of a $1.00 \times 10^{-4}$ M Zn$^{2+}$ solution with a $1.00 \times 10^{-4}$ M EDTA solution.

\[
K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}\]

b) What is the Zn$^{2+}$ concentration?

\[
[Zn^{2+}] = \alpha_{Zn^{2+}}C_{Zn}^{tot} = (1.61 \times 10^{-5})(1.66 \times 10^{-8} \text{ M})
\]

\[
[Zn^{2+}] = 2.67 \times 10^{-13} \text{ M} \quad pZn = 12.6
\]

\[
\alpha_{Y^{4-}} = 0.355
\]

\[
\alpha_{Zn^{2+}} = 1.61 \times 10^{-5}
\]

\[
\log K_f = 16.5
\]

\[
[ZnY^{2-}] = 5.0 \times 10^{-5} \text{ M}
\]

\[
C_{Zn}^{tot} = 1.66 \times 10^{-8} \text{ M}
\]
Hydroxyquinoline: a metal chelator that fluoresces upon binding!

8-hydroxyquinoline

Trivalent Cations

Divalent Cations
Hydroxyquinoline: a metal chelator that fluoresces upon binding!

8-hydroxyquinoline-5-sulfonic Acid

Fluorometric Detection of $\text{Mg}^{2+}$ in Seawater

Figure 1. pH dependence of the fluorescence intensities of group II metal-HQS chelates: Cd, 2 µM; all other metals in this and following figures, 20 µM; HQS, 1 mM.