EDTA Titrations

Metal Chelate Complexes – complexes formed between a Lewis acid and a Lewis base.

Metals ions are *Lewis acids*, because they accept electrons from Lewis bases. When metal cations combine with Lewis bases, the resulting species is called a *complex ion*, and the base is called a *ligand*.

The coordination number is the number of covalent bonds that the metal cation tends to form with the electron donor.

**Ligands**: monodentate, bidentate, multidentate  [dentate = “toothed”]
**Tetradentate ligand**: ATP (adenosine triphosphate)
**Chelate effect** - ability of multidentate ligands to form more stable metal compounds than those formed by monodentate ligands.

\[
K = \beta_2 = 8 \times 10^9
\]
EDTA, $\text{H}_6\text{Y}^{2+}$, is a hexaprotic system; it has six acidic hydrogens that are lost upon metal-complex formation. The first four $pK$ values apply to carboxyl protons, and the last two are for the ammonium protons.

**Hexaprotic system: $\text{H}_6\text{Y}^{2+}$**

\[
\begin{align*}
\text{COOH} & \quad \text{H}_6\text{Y}^{2+} \leftrightarrow \text{H}^+ + \text{H}_5\text{Y}^+ \quad pK_1 = 0.0 \\
\text{COOH} & \quad \text{H}_5\text{Y}^+ \leftrightarrow \text{H}^+ + \text{H}_4\text{Y} \quad pK_2 = 1.5
\end{align*}
\]

**Tetraprotic system: $\text{H}_4\text{Y}$**

\[
\begin{align*}
\text{COOH} & \quad \text{H}_4\text{Y} \leftrightarrow \text{H}^+ + \text{H}_3\text{Y}^- \quad pK_3 = 2.0 \\
\text{COOH} & \quad \text{H}_3\text{Y}^- \leftrightarrow \text{H}^+ + \text{H}_2\text{Y}^{2-} \quad pK_4 = 2.69
\end{align*}
\]

**Commonly used: $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$**

\[
\begin{align*}
\text{NH}^+ & \quad \text{H}_2\text{Y}^{2-} \leftrightarrow \text{H}^+ + \text{HY}^+ \quad pK_5 = 6.13 \\
\text{NH}^+ & \quad \text{HY}^+ \leftrightarrow \text{H}^+ + \text{Y}^{4-} \quad pK_6 = 10.37
\end{align*}
\]

**Note:** $pK$ values are at $25^\circ\text{C}$ and $\mu = 0.1\text{ M}$ except $pK_1$ applies at $\mu = 1.0\text{ M}$

**Complexometric titration:** a titration based on a complex formation.

The pH of an EDTA solution affects the equilibrium constant of complex formation. Solutions of high pH used in analytical procedures do not significantly effect the stability of a complex.

The fraction of EDTA in each of its protonated forms is shown in the figure below:
We define $\alpha$ for each species as the fraction of EDTA at that form:

$$[\text{EDTA}] = [\text{H}_6\text{Y}^{2+}] + [\text{H}_5\text{Y}^+] + [\text{H}_4\text{Y}] + [\text{H}_3\text{Y}^-] + [\text{H}_2\text{Y}^{2-}] + [\text{HY}^3] + [\text{Y}^4^-]$$

$$\alpha_{Y^4^-} = \frac{[Y^4^-]}{[\text{EDTA}]} \quad \text{← this is the concentration of “free” EDTA, not complexed to metal ions. The $\alpha$ fraction is a function of pH. (Equation 12-4 of Harris)}$$

$$\alpha_{Y^4^-} = \frac{K_1K_2K_3K_4K_5K_6}{\{[H^+]^6 + [H^+]^5K_1 + [H^+]^4K_1K_2 + [H^+]^3K_1K_2K_3 + [H^+]^2K_1K_2K_3K_4 + [H^+]K_1K_2K_3K_4K_5 + K_1K_2K_3K_4K_5K_6\}}$$

(Equation 12-4 of Harris)

**Reaction with a Metal Ion**

$$\text{Formation constant: } M^{a+} + Y^{4-} \rightleftharpoons MY^{a-4} \quad K_f = \frac{[MY^{a-4}]}{[M^{a+}][Y^{4-}]} \quad \text{(12-5)}$$

This $K_f$ is defined only for $Y^{4-}$ This is a **problem**!!!

We saw from the fraction plot and Table 12-1 that most of the EDTA is not in the form of $Y^{4-}$ below a pH $\sim$10.
**Solution to the problem: Conditional formation constant, $K_f$**

- We can derive a more useful equilibrium equation by rearranging the fraction relationship:

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[EDTA]} \Rightarrow [Y^{4-}] = \alpha_{Y^{4-}}[EDTA]$$

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]} = \frac{[MY^{n-4}]}{[M^{n+}][\alpha_{Y^{4-}}][EDTA]}$$

- If we fix the pH of the titration with a buffer, then $\alpha_{Y^{4-}}$ is a constant that can be combined with $K_f$.

$$K'_f = \alpha_{Y^{4-}}K_f = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

$$M^{n+} + EDTA \Leftrightarrow MY^{n-4} \quad K'_f = \alpha_{Y^{4-}}K_f$$

**Example**

Calculate the concentration of free Ca$^{2+}$ in a solution of 0.10 M CaY$^{2-}$ at pH 10 and pH 6. $K_f$ for CaY$^{2-}$ is $4.5 \times 10^{10}$ (Table 12-2)

$$Ca^{2+} + EDTA \Leftrightarrow CaY^{2-} \quad K'_f = \alpha_{Y^{4-}}K_f$$

at pH = 10.00, $K'_f = \alpha_{Y^{4-}}K_f = (0.30)(4.5 \times 10^{10}) = 1.34 \times 10^{10}$

at pH = 6.00, $K'_f = \alpha_{Y^{4-}}K_f = (1.8 \times 10^{-5})(4.5 \times 10^{10}) = 8.0 \times 10^{5}$

$$Ca^{2+} + EDTA \Leftrightarrow CaY^{2-}$$

<table>
<thead>
<tr>
<th>Conc$_i$</th>
<th>0</th>
<th>0</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc$_f$</td>
<td>$x$</td>
<td>$x$</td>
<td>0.1 - $x$</td>
</tr>
</tbody>
</table>

$$K'_f = \frac{[CaY^{2-}]}{[Ca^{2+}][EDTA]} = \frac{0.1 - x}{x^2}$$
We solve w/r/t \( x \) and at pH 10: \([Ca^{2+}] = 2.7 \times 10^{-6}\)
and at pH 6: \([Ca^{2+}] = 3.5 \times 10^{-4}\)

Note: At low pH, the metal-complex is less stable

**Calcium/EDTA Titration Curve**

For calcium, the end point becomes hard to detect below \( \sim \text{pH}=8 \). The formation constant is too small below this point. This can be used to separate metals. At pH=4, Ca\(^{2+}\) does not perform significant complexation with EDTA.

**Generic Titration Curve**

We’ll consider a titration where we have 50.0 mL of 0.040 M Ca\(^{2+}\) (buffered at pH=10) with 0.080 M EDTA

\[
Ca^{2+} + \text{EDTA} \leftrightarrow CaY^{2-} \quad K_f' = \alpha_{Y^+} K_f
\]

\[
(50.0 \text{ mL})(0.040 \text{ M}) = V_e (0.080 \text{ M}) \Rightarrow V_e = 25.0 \text{ mL}
\]

From the previous example at pH 10.00

\[
K_f' = 1.34 \times 10^{10}
\]

- **Before the Equivalence Point:** What is pCa\(^{2+}\) when we have added 5.0 mL of EDTA?
\[ [\text{Ca}^{2+}] = \left( \frac{25.0 - 5.0}{25.0} \right) (0.040) \left( \frac{50.0}{55.0} \right) = 0.0291 \text{ M} \]

\[ \frac{\text{Fraction remaining}}{\text{initial dilution factor concentration}} \]

\[ \text{pCa}^{2+} = -\log(1.2 \times 10^{-6}) = 5.91 \]

- At the Equivalence Point: What is \( \text{pCa}^{2+} \) when we have added 25.0 mL of EDTA?

At the equivalence point almost all the metal is in the form \( \text{CaY}^{2-} \):

\[ [\text{CaY}^{2-}] = (0.040) \left( \frac{50.0}{75.0} \right) = 0.0267 \text{ M} \]

\[ \frac{\text{initial dilution factor concentration}}{\text{Ca}^{2+}} \]

Free \( \text{Ca}^{2+} \) is small and can be found:

\[
\begin{align*}
\text{Ca}^{2+} + \text{EDTA} &\leftrightarrow \text{CaY}^{2-} \\
\text{Conc}_i &\quad 0 \quad 0 \quad 0.0267 \\
\text{Conc}_f &\quad x \quad x \quad 0.0267 - x
\end{align*}
\]

\[ K_f' = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{EDTA}]} = \frac{0.0267 - x}{x^2} = 1.34 \times 10^{10} \]

\[ x = 1.4 \times 10^{-6} \text{ M} \quad \text{pCa}^{2+} = -\log(1.4 \times 10^{-6}) = 5.85 \]

- After the Equivalence Point: What is \( \text{pCa}^{2+} \) when we have added 26.0 mL of EDTA?

We have 1 mL excess of EDTA.

\[ [\text{EDTA}] = (0.080) \left( \frac{1.0}{76.0} \right) = 1.05 \times 10^{-3} \text{ M} \]

\[ \frac{\text{Initial dilution factor}}{\text{EDTA}} \]
\[
\left[CaY^{2-}\right] = (0.040) \left(\frac{50.0}{76.0}\right) = 2.63 \times 10^{-2} \text{ M}
\]

\[
\uparrow \quad \text{Initial } [Ca^{2+}] \quad \uparrow \quad \text{dilution factor}
\]

\[
K_f' = \frac{\left[CaY^{2-}\right]}{[Ca^{2+}][EDTA]} = \frac{2.63 \times 10^{-2}}{[Ca^{2+} \left(1.05 \times 10^{-3}\right)]} = 1.34 \times 10^{10}
\]

\[
[Ca^{2+}] = 1.9 \times 10^{-9} \text{ M} \quad \text{pCa}^{2+} = 8.73
\]

**Auxiliary Complexing Agent**

This is a ligand that binds strongly enough to the metal to prevent hydroxide precipitation, but weak enough to be displaced by EDTA. Ammonia is a common auxiliary complex for transition metals like Zn.

**Metal Ion Indicators**

To detect the end point of EDTA titrations, we usually use a metal ion indicator or an ion-selective electrode (chapter in Electrochemistry).

Metal ion indicators change color when the metal ion is bound to EDTA:

\[
\text{MgEbT + EDTA} \leftrightarrow \text{MgEDTA + EbT}
\]

(Red) (Clear) (Clear) (Blue)

The indicator must bind less strongly than EDTA.

**EDTA Titration Techniques**

- **Direct titration**: analyte is titrated with standard EDTA with solution buffered at a pH where \(K_f'\) is large.
- **Back titration**: known excess of EDTA is added to analyte. Excess EDTA is titrated with 2nd metal ion.
• **Displacement titration**: For metals without a good indicator ion, the analyte can be treated with excess Mg(EDTA)$^{2-}$. The analyte displaces Mg$^{2+}$, and then Mg$^{2+}$ can be titrated with standard EDTA.

• **Indirect titration**: Anions can be analyzed by precipitation with excess metal ion and then titration of the metal in the dissolved precipitate with EDTA.

Example 25.0 mL of an unknown Ni$^{2+}$ solution was treated with 25.00 mL of 0.05283 M Na$_2$EDTA. The pH of the solution was buffered to 5.5 and then back-titrated with 17.61 mL of 0.02299 M Zn$^{2+}$. What was the unknown Ni$^{2+}$ M?

\[
\text{Zn}^{2+} + \text{Y}^{4-} \leftrightarrow \text{ZnY}^{2-}
\]
\[
\text{mol EDTA} = (25.00 \text{ mL})(0.05283 \text{ M}) = 1.32 \text{ mmol EDTA}
\]
\[
\text{mol Zn}^{2+} = (17.61 \text{ mL})(0.02299 \text{ M}) = 0.4049 \text{ mmol Zn}^{2+}
\]
\[
\text{mol Ni}^{2+} = 1.321 \text{ mmol EDTA} - 0.4049 \text{ mmol Zn}^{2+} = 0.916 \text{ mmol}
\]
\[
\text{M Ni}^{2+} = (0.916 \text{ mmol})(25.00 \text{ mL}) = 0.0366 \text{ M}
\]