Chapter 12
EDTA Titrations

Acids and Bases
• Definitions: Lewis – Electrons (acid: electron pair acceptor);
  Brønsted-Lowry (acid: proton donor)

Lewis acid-base concept in Metal-Chelate Complexes
Metal ions (electron pair acceptor) → Lewis acid
Ligand (electron pair donor) → Lewis base

Coordination Number
• The atom of the ligand that supplies the nonbonding electrons for the metal-ligand bond is the donor atom.
• The number of these atoms is the coordination number.

Complex Formation
Formation of coordinate bonds between Lewis Acids/Bases
\[
\begin{align*}
Ag^+ (aq) + NH_3 (aq) &\rightleftharpoons K_f \cdot Ag(NH_3)^+ (aq) \\
Ag(NH_3)^+ (aq) + NH_3 (aq) &\rightleftharpoons K_f \cdot Ag(NH_3)_2^+ (aq)
\end{align*}
\]

Formation constants (Kf) are the equilibrium constants for complex ion formation. The overall, or cumulative, formation constants are denoted \( \beta_i \).

\[
Ag^+ (aq) + 2NH_3 (aq) = K_f \cdot Ag(NH_3)_2^+ (aq)
\]

Geometries
There are two common geometries for metals with a coordination number of four:
- Tetrahedral & Square planar

By far the most-encountered geometry, when the coordination number is six, is octahedral.

Ligands
• Monodentate ligand: binds to a metal ion through only one atom, e.g., CN-
• Multidentate ligand or chelating ligand: has more than one ligand donor atoms.
  - In ethylenediamine, \( \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \) (i.e., en), each N is a donor atom. \( \rightarrow \) en is bidentate.
Chelating Effect
A multidentate ligand to form more stable metal complexes than those formed by similar monodentate ligand

Chelating Agents
- Porphyrins (tetradeinate ligands, in heme and chlorophyll)
- Adenosine triphosphate (ATP)

EDTA
Ethylenediaminetetraacetic acid (H$_4$EDTA or H$_4$Y)
Ethylenediaminetetraacetate anion (EDTA$^-$ or Y$^-$)
Ethylenediaminetetraacetate, mercifully abbreviated EDTA, has six donor atoms.
EDTA is a primary standard material.

Some Metals Form 7 or 8 Coordinate Complexes

EDTA Complexes
- EDTA forms 1:1 complexes with most metals (Not with Group 1A metals)
- EDTA complexes are usually stable water soluble complexes with high formation constants
- Formation constant, $K_f$, (or stability constant):
  $M^{n+} + Y^{n-} \leftrightarrow MY^{n-}$
  $K_f = \frac{[MY^{n-}]}{[M^{n+}][Y^{n-}]}$
- $K_f$ could have been defined for any form of EDTA
pH affects EDTA titration

Acid-Base Properties of EDTA:

EDTA is a hexaprotic system \((H_y^{2+})\) with 4 carboxylic acids and 2 ammoniums

\[
H_y^{2+} \\
pK_1 = 0.0 \quad pK_2 = 1.5 \quad pK_3 = 2.0 \quad pK_4 = 2.66 \\
pK_5 = 6.16 \quad pK_6 = 10.24 \\
\]

\[
\text{pH:} \quad \frac{M^{n+} + Y^{n-}}{M^{n+} Y^{n-}} \\
H_y^{2+} \\
\]

Fraction of EDTA in the form \(Y^{4-}\):

\[
\alpha_{Y^4^-} = \frac{[H_y Y^{2-}][H_y Y^-][H_y Y][H_y Y^+] + [H_y^+][Y^{3-}]}{[\text{EDTA}]} \\
\alpha_{Y^4^-} = \frac{[Y^{4-}]}{[\text{EDTA}]} \\
\alpha_{Y^4^-} = \frac{[M^{n+} + Y^{n-}]}{[M^{n+}] [\text{EDTA}]} \\
\]

Fractional Composition Diagram for EDTA

pH Dependence of \(\alpha_{Y^4^-}\)

<table>
<thead>
<tr>
<th>pH</th>
<th>(\alpha_{Y^4^-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(1.3 \times 10^{-3})</td>
</tr>
<tr>
<td>1</td>
<td>(1.4 \times 10^{-3})</td>
</tr>
<tr>
<td>2</td>
<td>(2.6 \times 10^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>(2.1 \times 10^{-5})</td>
</tr>
<tr>
<td>4</td>
<td>(3.0 \times 10^{-6})</td>
</tr>
<tr>
<td>5</td>
<td>(2.9 \times 10^{-7})</td>
</tr>
<tr>
<td>6</td>
<td>(1.8 \times 10^{-8})</td>
</tr>
<tr>
<td>7</td>
<td>(3.6 \times 10^{-9})</td>
</tr>
<tr>
<td>8</td>
<td>(4.2 \times 10^{-10})</td>
</tr>
<tr>
<td>9</td>
<td>0.001</td>
</tr>
<tr>
<td>10</td>
<td>0.30</td>
</tr>
<tr>
<td>11</td>
<td>0.81</td>
</tr>
<tr>
<td>12</td>
<td>1.00</td>
</tr>
<tr>
<td>13</td>
<td>1.00</td>
</tr>
<tr>
<td>14</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Conditional Formation Constant

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

Fixing the pH by buffering, then \(\alpha_{Y^4^-}\) is a constant.

At any fixed pH, find \(\alpha_{Y^4^-}\) and evaluate \(K_f\)
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 10\(^{10.65}\) (Table 12-2).

\[
\text{Ca}^{2+} + \text{EDTA} \leftrightarrow \text{CaY}^{2-} \quad K_{f} = \alpha_{Ca} K_{f}\]

at pH = 10.00, \(K_f = \alpha_{Ca} K_{f} = (0.30)(10^{10.65}) = 1.3 \times 10^6\)

at pH = 6.00, \(K_f = \alpha_{Ca} K_{f} = (1.8 \times 10^{-4})(10^{10.65}) = 8.0 \times 10^2\)

\[
\text{Ca}^{2+} + \text{EDTA} \leftrightarrow \text{CaY}^{2-}
\]

<table>
<thead>
<tr>
<th>Conc.</th>
<th>(x)</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.1 x</td>
</tr>
<tr>
<td>(x)</td>
<td>(x)</td>
<td>0.1 x</td>
</tr>
</tbody>
</table>

\[K_f = \frac{[\text{Ca}^{2+}][\text{EDTA}]}{[\text{CaY}^{2-}]} = \frac{0.1 - x}{x^2} \]

\[x = [\text{Ca}^{2+}] = 2.7 \times 10^{-6} \text{ M at pH} = 10\]

\[x = 3.5 \times 10^{-4} \text{ M at pH} = 6\]

EDTA Titration Curve

1. Excess M\(^{n+}\) left after each addition of EDTA. Conc. of free metal equal to conc. of unreacted M\(^{n+}\).

2. Equivalence point: [M\(^{n+}\)] = [EDTA] Some free M\(^{n+}\) generated by MY\(^{n-4}\) \(\rightleftharpoons\) M\(^{n+}\) + EDTA

3. Excess EDTA. Virtually all metal in MY\(^{n-4}\) form.

EDTA Titration Curve

EXAMPLE: Derive a titration curve for the titration of 50.0 mL of 0.040 M Ca\(^{2+}\) (buffered at pH=10) with 5.00, 25.00, and 26.00 mL of 0.080 M EDTA.

\[
\text{Ca}^{2+} + \text{EDTA} \rightarrow \text{CaY}^{2-} \quad K_{f} = \alpha_{Ca} K_{f} = 0.30 \times 10^{10.65} = 1.3 \times 10^6
\]

At equivalence point, Vol. of EDTA = 25.0 mL

5.00 mL Before the equivalence point
25.00 mL At the equivalence point
26.00 mL After the equivalence point

EDTA Titration Curve

EXAMPLE: Derive a titration curve for the titration of 50.0 mL of 0.040 M Ca\(^{2+}\) (buffered at pH=10) with 5.00, 25.00, and 26.00 mL of 0.080 M EDTA.

At equivalence point, Vol. of EDTA = 25.0 mL

almost all the metal is in the form, CaY\(^{2-}\)

\[
[\text{Ca}^{2+}][\text{EDTA}]^0 = \frac{50.0}{25.0+50.0} = 0.2027 \text{ M}
\]

\[
\text{Ca}^{2+} + \text{EDTA} \leftrightarrow \text{CaY}^{2-}
\]

<table>
<thead>
<tr>
<th>Conc.</th>
<th>0</th>
<th>0.0267</th>
<th>0.267 - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc.</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[x = 1.2 \times 10^{-4} \text{ M} \quad \text{pCa}^{2+} = -\log(1.2 \times 10^{-4}) = 5.91\]
**EDTA Titration Curve**

**EXAMPLE:** Derive a titration curve for the titration of 50.0 mL of 0.040 M Ca\(^{2+}\) (buffered at pH=10) with 5.00, 25.00, and 26.00 mL of 0.080 M EDTA.

At equivalence point, Vol. of EDTA = 25.0 mL.

\[
26.00 \text{ mL} \rightarrow 1.0 \text{ mL excess EDTA, after the equivalence point}
\]

\[
\left[\text{EDTA}\right] = (0.080) \left(\frac{26.00}{50.0 + 26.00}\right) = 1.05 \times 10^{-2} \text{ M}
\]

\[
\left[\text{CaY}^{3-}\right] = (0.040) \left(\frac{50.0}{50.0 + 26.00}\right) = 2.63 \times 10^{-3} \text{ M}
\]

\[
K_f' = \frac{\left[\text{CaY}^{3-}\right]}{\left[\text{Ca}^{2+}\right] \left[\text{EDTA}\right]} = \frac{2.63 \times 10^{-3}}{1.05 \times 10^{-2}} = 1.8 \times 10^2 \quad \text{Ca}^{2+} = 1.4 \times 10^{-4} \text{ M}
\]

\[
p\text{Ca}^{2+} = 8.86
\]

---

**pH affects the titration of Ca\(^{2+}\) with EDTA**

- pH affects the titration of Ca\(^{2+}\) with EDTA.

---

**Auxiliary Complexing Agents**

- A ligand that binds strongly enough to the metal to prevent hydroxide precipitation, but weak enough to be displaced by EDTA (e.g., ammonia, tartrate, citrate, or trithanolamine).

Ammonia is a common auxiliary complex for transition metals like zinc (p. 239)

\[
K_f'' = \alpha_{\text{NH}_3} \alpha_{f-} K_f
\]

\(K_f''\) is the effective formation constant at a fixed concentration of auxiliary complexing agent.
Metal Ion Indicators

• To detect the end point of EDTA titrations, we usually use a metal ion indicator or an ion-selective electrode (Ch. 15)

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

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

- Eriochrome black T is an organic ion

• 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.

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\(^{2+}\) in M?

\[
\text{mol EDTA} = (25.00 \text{ mL})(0.05283 \text{ M}) = 1.32 \text{ mmol EDTA}
\]

\[
\text{mol Zn}^{2+} = (17.61 \text{ mL})(0.02299 \text{ M}) = 0.4049 \text{ mmol Zn}^{2+}
\]

\[
\text{mol Ni}^{2+} = 1.321 \text{ mmol EDTA} - 0.4049 \text{ mmol Zn}^{2+} = 0.916 \text{ mmol}
\]

\[
M \text{ Ni}^{2+} = (0.916 \text{ mmol})(25.00 \text{ mL}) = 0.0366 \text{ M}
\]