Chapter 17
Complexation
Reactions and Titrations

Complexation Titration
• Also known as complexometric titration, complexometry, or chelatometry
• One of the classical titrimetric methods developed for the rapid and quantitative chemical analysis of metal ions.
• Based on complex formation between metal ion (cation) and complexing agent (ligand).

Bronsted-Lowery vs Lewis Acid-Base Concept
• **Lewis base**: electron pair donor (ligand, can be molecules or ions)
• **Coordinate covalent bond**: a bond formed when both electrons of the bond are donated by one atom.

- **Lewis acid**: electron pair acceptor (metal cations, $M^{n+}$)

\[ A + B \rightarrow A \leftarrow B \]
**Complex ion:** A charged compound (+ or -) consisting of coordinate covalent bond.

**Complex (Coordinate compound):** a compound of neutral complex species.

\[
\text{Ag(NH}_3\text{)}_2^+ \text{ vs } \text{[Ag(NH}_3\text{)}_2\text{](OH)}
\]
• When there are three (four) groups, it is called tridentate (tetradentate) ligand, etc.

• When a bidentate (or higher number of donor groups present in the ligand) forms a complex with a metal cation, we call the resulting compound a metal chelate (“kee’late”-claw).

• As titrants, multidentate ligands, particularly those with 4 to 6 donor groups have the advantage that they usually react in a single step process, and their reactions with the metal cation are more complete than their unidentate counterparts.

Chelate Effect

• The ability of multidentate ligands to form more stable metal complexes than those formed by similar monodentate ligands

• Often results from the formation of 5-membered "ring" with metal and two atoms on the ligand

\[
\text{Complexation Equilibria} \\
\text{Cu}^{2+} + \text{NH}_3 \rightleftharpoons K_f \text{Cu(NH}_3)_2^{2+} \\
\text{Cu(NH}_3)_2^{2+} + \text{NH}_3 \rightleftharpoons K_2 \text{Cu(NH}_3)_3^{2+} \\
\text{Cu(NH}_3)_3^{2+} + \text{NH}_3 \rightleftharpoons K_3 \text{Cu(NH}_3)_4^{2+} \\
\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons K_f \text{Cu(NH}_3)_4^{2+} \\
K_f = K_1 K_2 K_3 K_4 = \beta_4 \\
K_f (\beta_4) - formation constant
• Complexation reactions occur in a stepwise fashion

\[ \text{M} + \text{L} \Leftrightarrow \text{ML} \quad K_1 = \frac{[\text{ML}]}{[\text{M}][\text{L}]} \]

\[ \text{ML} + \text{L} \Leftrightarrow \text{ML}_2 \quad K_2 = \frac{[\text{ML}_2]}{[\text{ML}][\text{L}]} \]

\[ \text{ML}_2 + \text{L} \Leftrightarrow \text{ML}_3 \quad K_3 = \frac{[\text{ML}_3]}{[\text{ML}_2][\text{L}]} \]

... 

\[ \text{ML}_{n-1} + \text{L} \Leftrightarrow \text{ML}_n \quad K_n = \frac{[\text{ML}_n]}{[\text{ML}_{n-1}][\text{L}]} \]

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**Formation Constants (\( \beta_i \))**

\( \text{M} + \text{L} \Leftrightarrow \text{ML} \quad \beta_1 = \frac{[\text{ML}]}{[\text{M}][\text{L}]} = K_1 \)

\( \text{M} + 2\text{L} \Leftrightarrow \text{ML}_2 \quad \beta_2 = \frac{[\text{ML}_2]}{[\text{M}][\text{L}]} = K_1 K_2 \)

\( \text{M} + 3\text{L} \Leftrightarrow \text{ML}_3 \quad \beta_3 = \frac{[\text{ML}_3]}{[\text{M}][\text{L}]} = K_1 K_2 K_3 \)

... 

\( \text{M} + n\text{L} \Leftrightarrow \text{ML}_n \quad \beta_n = \frac{[\text{ML}_n]}{[\text{M}][\text{L}]} = K_1 K_2 K_3 \ldots K_n \)

\( \beta_i \) : cumulated or collective formation constant with \( i \) \( \text{L} \).

---

**Alpha (\( \alpha \)) Values**

Fraction of the Total Metal Concentration

\[ \alpha_M = \frac{[\text{M}]}{c_M} \]

\[ \alpha_{\text{ML}_i} = \frac{[\text{ML}_i]}{c_M} \]

\[ c_M = [\text{M}] + [\text{ML}] + [\text{ML}_2] + \ldots + [\text{ML}_n] \]

\[ = [\text{M}] + \beta_1[M][L] + \beta_2[M][L]^2 + \ldots + \beta_n[M][L]^n \]

\[ = [\text{M}][1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n] \]
\[
\alpha_M = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n}
\]

\[
\alpha_{ML} = \frac{\beta_1[L]}{1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n}
\]

\[
\alpha_{ML_2} = \frac{\beta_1[L]^2}{1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n}
\]

\[
\alpha_{ML_3} = \frac{\beta_1[L]^3}{1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n}
\]

\[
\alpha_i = f(\beta_i[L]) \quad [\text{vs. } \alpha_i = f(K_\alpha[H^+])] 
\]

**Titration Curves of ML\textsubscript{n}**

(A) Tetradentate ligand, 1:1  
(B) Bidentate ligand 2:1  
(C) Unidentate ligand, 4:1

Tetradentate or hexadentate ligands are more satisfactory as titrants than ligands with a lesser number of donor groups because their reactions with cations are more complete and they tend to form 1:1 complexes.

**Ethylenediaminetetraacetic Acid (EDTA)**

Most widely used complexometric titrant, Hexadentate ligand (4 –COOH+2 amino groups)
EDTA

- It forms 1:1 complexes with most metals. (Not with Group 1A metals – Na, K, Li)
- Forms stable water soluble complexes.
- High formation constants.
- A primary standard material – a highly purified compound that serves as a reference material.

Octahedron Structure of EDTA-M

![Octahedron Structure of EDTA-M](image)

5 – five membered rings

<table>
<thead>
<tr>
<th>Cation</th>
<th>$K_{MY}$</th>
<th>log $K_{MY}$</th>
<th>Cation</th>
<th>$K_{MY}$</th>
<th>log $K_{MY}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$^{+}$</td>
<td>$1.9 \times 10^{7}$</td>
<td>7.59</td>
<td>Cu$^{2+}$</td>
<td>$6.3 \times 10^{4}$</td>
<td>4.88</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>$4.9 \times 10^{8}$</td>
<td>8.69</td>
<td>Zn$^{2+}$</td>
<td>$3.2 \times 10^{5}$</td>
<td>5.50</td>
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<tr>
<td>Ca$^{2+}$</td>
<td>$5.0 \times 10^{9}$</td>
<td>9.70</td>
<td>Cd$^{2+}$</td>
<td>$2.9 \times 10^{7}$</td>
<td>7.46</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>$4.3 \times 10^{10}$</td>
<td>10.39</td>
<td>Hg$^{2+}$</td>
<td>$6.3 \times 10^{5}$</td>
<td>5.10</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>$5.8 \times 10^{11}$</td>
<td>11.76</td>
<td>Pd$^{2+}$</td>
<td>$1.1 \times 10^{7}$</td>
<td>6.04</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>$6.2 \times 10^{12}$</td>
<td>12.79</td>
<td>Ag$^{+}$</td>
<td>$1.3 \times 10^{10}$</td>
<td>8.23</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>$2.3 \times 10^{14}$</td>
<td>14.33</td>
<td>Zn$^{2+}$</td>
<td>$1.3 \times 10^{12}$</td>
<td>10.11</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>$2.0 \times 10^{16}$</td>
<td>16.31</td>
<td>Cu$^{2+}$</td>
<td>$7.9 \times 10^{14}$</td>
<td>15.99</td>
</tr>
<tr>
<td>K$^{+}$</td>
<td>$4.2 \times 10^{19}$</td>
<td>19.72</td>
<td>Ag$^{+}$</td>
<td>$1.6 \times 10^{15}$</td>
<td>15.22</td>
</tr>
</tbody>
</table>

*Constants are valid at 20°C and ionic strength of 0.1.
Acid-Base Properties ($H_6Y^{2+}$)

The first four values apply to carboxyl protons, and the last two are for the ammonium protons. The neutral acid is tetraprotic, with the formula $H_4Y$. A commonly used reagent is the disodium salt, $Na_2H_2Y$.2H_2O.

EDTA ($H_4Y$) Disassociation

$H_4Y^{2+} \rightleftharpoons H_3Y^{+} \rightleftharpoons H_2Y^- \rightleftharpoons HY^2^- \rightleftharpoons Y^{4-}$

$\alpha_0 \quad \alpha_1 \quad \alpha_2 \quad \alpha_3 \quad \alpha_4$ (or $\alpha_{iv}$)

$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n+4)}_T \quad K_{MY} = \frac{[MY^{(n+4)}]}{[M^{n+}][Y^{4-}]}$

$\alpha_4 = \frac{[Y^{4-}]}{[EDTA]} = \frac{[Y^{4-}]}{[H_4Y^{2+} + H_3Y^+ + H_2Y^- + HY^2^- + Y^{4-}]}$

$K_{MY} = \frac{[MY^{(n+4)}]}{[M^{n+}][Y^{4-}]} = \frac{[MY^{(n+4)}]}{[M^{n+}][Y^{4-}]} \alpha_4 c_T$

Conditional formation constant:

$K'_{MY} = \frac{[MY^{(n+4)}]}{[M^{n+}]c_T} = \alpha_4 K_{MY}$

$K'_{MY} \leq K_{MY} \quad as \quad \alpha_4 \leq 1.0$

$K'_{MY}$ is pH dependent!
Example 17-4 Use spreadsheet to construct the titration curve of pCa versus volume of EDTA for 50.0 mL of 0.00500 M Ca²⁺ being titrated with 0.0100 M EDTA in a solution buffered to a constant pH of 10.0

(1) pH = 10.0, \( \alpha_4 = 0.35 \), \( K_{\text{CaY}} = 5.0 \times 10^9 \), \( K'_{\text{CaY}} = \alpha_4 K_{\text{CaY}} = 1.75 \times 10^9 \)

(2) Equivalence point: 
\( V_{\text{EDTA}} = 50 \times 0.00500/0.0100 = 25.0 \) mL

(3) Initial pCa: \([\text{Ca}^{2+}] = 0.00500 \) M, pCa = 2.30
(4) Pre-equivalence point: 
\[
\text{Ca (excess) + Y} \rightleftharpoons \text{CaY (disassociation negligible)}
\]

\[
[\text{Ca}] = \frac{50.00 \times 0.00500 - V_{\text{EDTA}} \times 0.0100}{50.00 + V_{\text{EDTA}}}
\]

<table>
<thead>
<tr>
<th>(V_{\text{EDTA}}) (mL)</th>
<th>[Ca]</th>
<th>(p\text{Ca})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>3.64e-3</td>
<td>2.44</td>
</tr>
<tr>
<td>10.00</td>
<td>2.46e-3</td>
<td>2.61</td>
</tr>
<tr>
<td>20.00</td>
<td>7.14e-4</td>
<td>3.15</td>
</tr>
<tr>
<td>24.00</td>
<td>1.35e-4</td>
<td>3.87</td>
</tr>
</tbody>
</table>

(5) At equivalence point: 
\[
\text{CaY} \rightleftharpoons \text{Ca} + \text{Y}, \quad [\text{Ca}] = [\text{Y}]
\]

\[
[\text{CaY}] / [\text{Ca}]^2 = K'_{\text{MY}}, \quad [\text{Ca}] = ([\text{CaY}] / K'_{\text{MY}})^{1/2}
\]

\[
[\text{Ca}] = \left(\frac{50.00 \times 0.00500 / (50.00 + 25.00)}{1.75 \times 10^{10}}\right)^{0.5} = 4.36 \times 10^{-7} \text{M}, \quad p\text{Ca} = 6.36
\]

(6) Post-equivalence point: 
\[
\text{Ca} + \text{Y} \rightleftharpoons \text{CaY}
\]

\[
\times \quad \text{excess} \quad -\text{equivalence concentration}
\]

\[
(50.00 \times 0.00500) / (50.00 + V_{\text{EDTA}})^2 /
\frac{[\text{Ca}][0.0100 \times V_{\text{EDTA}} - 0.25 \times 50.00 + 0.00500] / (50.00 + V_{\text{EDTA}})}{K'_{\text{MY}}} = [\text{Ca}]
\]

\[
[\text{Ca}] = [0.25 / (0.0100 \times V_{\text{EDTA}} - 0.25) \times K'_{\text{MY}}]^{1.43 \times 10^{-11} / (0.0100 \times V_{\text{EDTA}} - 0.25)}
\]

<table>
<thead>
<tr>
<th>(V_{\text{EDTA}}) (mL)</th>
<th>[Ca]</th>
<th>(p\text{Ca})</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.00</td>
<td>1.42e-9</td>
<td>8.85</td>
</tr>
<tr>
<td>30.00</td>
<td>2.86e-10</td>
<td>9.54</td>
</tr>
<tr>
<td>40.00</td>
<td>9.53e-11</td>
<td>10.02</td>
</tr>
<tr>
<td>50.00</td>
<td>5.71e-11</td>
<td>10.24</td>
</tr>
</tbody>
</table>

Ca-EDTA Titration Curve at pH 10
EDTA Titration Curves for Ca (K'2.75e10) and Mg (K'1.72e8) at pH 10

Larger the K'MY, Larger the pM change

Eriochrome Black T

Typical Metal Ion Indicator--Eriochrome Black T (EBT)

A Weak Acid and azo dye

Indicators for EDTA Titrations

Compounds changing colour when binding to metal ion.

$K_f$ for Metal-In < $K_f$ for Metal-EDTA

**Before Titration:**

$\text{Mg}^{2+} + \text{In} \rightarrow \text{MgIn}$

(colorless) (blue) (red)

**During Titration:** Before the end point

$\text{Mg}^{2+} + \text{EDTA} \rightarrow \text{MgEDTA}$

(free Mg$^{2+}$ ions) (Solution red due to MgIn complex)

**At the end point:**

$\text{MgIn} + \text{EDTA} \rightarrow \text{MgEDTA} + \text{In}$

(red) (colorless) (colorless) (Blue)
EDTA Titration Solution pH must be Controlled for EBT Indicator

Factors Influencing Chemical Specification of Eriochrome Black T (EBT):

1. pH, as EBT is a weak acid, color varies on pH:
   \[ \text{HIn}^\text{blue} \quad \text{and} \quad \text{HIn}^\text{red} \]
   
   \[ K_1 = 5 \times 10^{-7} \]

2. \[ \text{M-In} \text{complex}, \]

3. Mg\(^{2+}\) + In (blue) \[ \rightarrow \text{MgIn (red)} \]

4. \[ K_{\text{M-In}} \approx 1.0 \times 10^{-7} \]

5. \[ K_{\text{MY}} \text{ must be smaller than } K_{\text{M-In}} \]

Influence of pH on Titration Curves of Ca-EDTA

The higher pH, the larger pCa change, pH should > 8 for Ca-EDTA titrations

Lower pHs OK for Large \( K_{\text{MY}} \) Complexes

\[ K_{\text{MY}} = \begin{cases} 1.3 \times 10^{25} \\ 6.3 \times 10^2 \\ 3.2 \times 10^{14} \\ 2.1 \times 10^{14} \\ 5.0 \times 10^{12} \end{cases} \]
Minimum pH needed for satisfactory titration of various cations with EDTA.

Effect of Other Complexing Agents on EDTA Titration Curves

- A second complexing agent added to maintain the analyte metal ion in solution (many metal ions form insoluble hydroxides or oxides at slightly high pH).
- To "mask" or remove interfering ions present in the sample matrix.
- The second complexing agent ("masking agent") usually has a higher affinity for the interfering ion than the EDTA to prevent it from reacting with the EDTA.
- Most buffers will complex metal ions because they also contain functional groups (-OH, -COOH, -NH₂) which can form coordinate covalent bonds and their effect on the free metal ion concentration must be considered.

Ammonia decreases the change in pZn in the equivalence-point region.
**EDTA Titration Techniques**

1. **Direct Titration**
   * Buffer analyte to pH where $K_f'$ for MY is large,
   * and M-In color distinct from free In color.
   * Auxiliary complexing agent may be used.

2. **Back Titration**
   * Known excess std EDTA added.
   * Excess EDTA then titrated with a std sol'n of a second metal ion.
   * Note: Std metal ion for back titration must not displace analyte from MY complex.

3. **Displacement Titration**
   * Metal ions with no satisfactory indicator.
   * Analyte treated with excess Mg(EDTA)

\[ M + MgY \rightarrow MY + Mg \]

* $K_f'$ for MY > $K_f'$ for MgY

\[ M + nL \rightleftharpoons ML_n \text{ (second complexing agent)} \]

\[ K_{MY} = \frac{[MY]}{[M][Y]} \text{ ([M],[Y]–free concentration)} \]

\[ K_{MY} = \frac{[MY]}{(\alpha_M)c_M(\alpha_Y)c_Y} = \frac{[MY]}{(\alpha_M)c_M(c_Y)} \]

Conditional formation constant:

\[ K''_{MY} = \alpha_M\alpha_Y K_{MY} = \frac{[MY]}{c_Mc_Y} \]

Where \( \alpha_M = \frac{[M]}{c_M} = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3} \)
4. Indirect Titration

- Anions analyzed: CO$_3^{2-}$, CrO$_4^{2-}$, S$_2^-$, and SO$_4^{2-}$.
- Precipitate SO$_4^{2-}$ with excess Ba$_2^+$ at pH 1.
- BaSO$_4$(s) was washed & boiled with excess EDTA at pH 10.

\[ \text{BaSO}_4(\text{s}) + \text{EDTA(aq)} \rightarrow \text{BaY}_2^-(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \]

Excess EDTA titrated:

\[ \text{EDTA(aq)} + \text{Mg}^{2+} \rightarrow \text{MgY}_2^-(\text{aq}) \]

Alternatively:

- Precipitate SO$_4^{2-}$ with excess Ba$_2^+$ at pH 1.
- Filter & wash precipitate.
- Treat excess metal ion in filtrate with EDTA.

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5. Masking

- Masking Agent: Protects some component of analyte from reacting with EDTA.
- F$^-$ masks Hg$^{2+}$, Fe$^{3+}$, Ti$^{4+}$, and Be$^{2+}$.
- CN$^-$ masks Cd$^{2+}$, Zn$^{2+}$, Hg$^{2+}$, Co$^{2+}$, Cu$^+$, Ag$^+$, Ni$^{2+}$, Pd$^{2+}$, Pt$^{2+}$, Hg$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$.
- but not Mg$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, Pb$^{2+}$.
- Triethanolamine: Al$^{3+}$, Fe$^{3+}$, and Mn$^{2+}$.
- 2,3-dimercapto-1-propanol: Bi$^{3+}$, Cd$^{2+}$, Cu$^{2+}$, Hg$^{2+}$, and Pb$^{2+}$.

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*Demasking:* Releasing masking agent from analyte.

- Oxidation with H$_2$O$_2$ releases Cu$^{2+}$ from Cu$^+$-Thiourea complex.
- Thus, analyte selectivity:
  1. pH control
  2. Masking
  3. Demasking
Chapter 17 Summary

- Stepwise formation of complexes
- Complexation equilibria
- Calculate alpha values for complexes
- Types of complexometric titrations.
- Species in EDTA solutions
- Structure of EDTA complexes
- Determine conditional formation constants
- Apply EDTA titrations, titration curves, water hardness
- Indicators for EDTA titrations
- Use masking agents for EDTA titrations

Important Equations

Overall reaction:
\[ M + d = M_d \]
\[ \beta_k = \frac{[M_d]_k}{[M][d]^k} \]

Alpha values:
\[ \alpha_0 = \frac{[M]}{[M]} \]
\[ \alpha_1 = \frac{[M_d]}{[M][d]} \]
\[ \alpha_2 = \frac{[M_d][d]}{[M][d]^2} \]
\[ \alpha_k = \frac{[M_d][d]_k}{[M][d]^k} \]

Conditional formation constants:
\[ K_m = \frac{[M_d][d]_m}{[M][d]^m} \]
\[ K_a = \frac{[M_d][d]_a}{[M][d]^a} \]

Equation for EDTA in NaOH buffer:
\[ K_m = \frac{Za^{2+}}{a^{3+}} \]

Equation for EDTA in buffer:
\[ K_a = \frac{Za^{2+}}{a^{3+}} \]

Equation for EDTA in water:
\[ K_a = \frac{Za^{2+}}{a^{3+}} \]

Equation for EDTA in solution:
\[ K_a = \frac{Za^{2+}}{a^{3+}} \]