Acid-base Titration
Titration diprotic base using HCl

- Titration of 10.00 mL of 0.100 M base B with 0.100 M HCl:

\[ B + H_2O \rightleftharpoons BH^+ + OH^- \quad K_{b1} = \frac{K_w}{K_{a1}} \]

\[ BH^+ + H_2O \rightleftharpoons BH^{2+} + OH^- \quad K_{b2} = \frac{K_w}{K_{a2}} \]
Before acid is added – point A

- The weak diprotic base dissolves in the water and can be treated as monoprotic base

\[ \text{B} + \text{H}^+ \leftrightarrow \text{BH}^+ \]

\[ K_{b1} = \frac{K_w}{K_{a1}} \]

\[ \frac{0.100-x}{x} \times x = K_{b1} \]

pH = 11.49
Before the first equivalence point (point A-C)

• The majority ions are B and BH⁺, the solution can be treated as buffer between the two ions.

\[
pH = pK_{a2} + \log\left\{\frac{[B]}{[BH^+]}\right\}
\]

\[
K_{a2} = \frac{K_w}{K_{b1}}
\]
The amount of NaOH needed

- For the first equivalence point:
  \[ V_e \times 0.100 = 10.00 \times 0.1000 \]
  \[ V_e = 10.00 \text{ mL} \]

- To reach the second equivalence point, another 10.00 mL is needed.
First equivalence point

- B has totally converted into BH\(^+\), which is the intermediate form of the diprotic acid.

\[
[H^+]=\sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}
\]

F = total mole of BH\(^+\)/total volume
mole of BH\(^+\)= mole of B = 0.01000 x 0.1000=1.000 x 10\(^{-3}\) mole
total volume is 10.00 + 10.00 mL = 20 mL
Between 1st and 2nd equivalence points

- Buffer solution based on equation:

\[\text{BH}^+ + \text{H}^+ \rightleftharpoons \text{BH}^2+ \quad K_{b2} = \frac{K_w}{K_{a1}}\]

\[\text{pH} = pK_{a1} + \log\left\{\frac{[\text{BH}^+]}{[\text{BH}^2+]}\right\}\]
2\textsuperscript{nd} equivalence point and beyond

• At the second equivalence point B is all converted into BH\textsubscript{2}\textsuperscript{2+}:\
\[ \text{BH}_2\textsuperscript{2+} \rightleftharpoons \text{BH}^+ + \text{H}^+ \quad K_{a1} = K_w / K_{b2} \]

• Beyond 2\textsuperscript{nd} point: control by the excess amount HCl added
Determine the end point

- The end point is determined by the pH changes.
- Using derivatives to find the end point.

![Graphs showing pH changes and derivative analysis to determine end points.](https://via.placeholder.com/150)
Determine the end point

- Using a Gran Plot to find end point

weak acid is titrated by strong acid

\[ V_b \cdot 10^{-pH} = \frac{\gamma_{HA}}{\gamma_{A^-}} K_a (V_e - V_b) \]

weak base is titrated by strong base

\[ V_a \cdot 10^{-pH} \Leftrightarrow \left( \frac{1}{K_a} \cdot \frac{\gamma_B}{\gamma_{BH^+}} \right) (V_e - V_a) \]

\( V_e \): the volume of titrant needed to reach equivalence.

\( V_a, V_b \): the amount of titrant added
Using indicator

- An acid-base indicator itself is a weak acid or base, the color changes at different stages of protonation.

\[
R \rightleftharpoons Y^- + H^+ \quad \text{pH} = pK_1 + \log \frac{[Y^-]}{[R]}
\]

<table>
<thead>
<tr>
<th>pH</th>
<th>$[Y^-]:[R]$</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>1:10</td>
<td>red</td>
</tr>
<tr>
<td>1.7</td>
<td>1:1</td>
<td>orange</td>
</tr>
<tr>
<td>2.7</td>
<td>10:1</td>
<td>yellow</td>
</tr>
</tbody>
</table>
Complexometric Titration
Terminologies

- Complexometric titration: A titration based on complex formation.
- Lewis acid: accepting electron pairs from electron donating ligands.
- Lewis base: donating electrons to Lewis acid.
- Monodentate ligand: the ligand binds to a metal ion through only one atom e.g. Cyanide (CN⁻).

• Multidentate Ligand: a ligand attaches to a metal ion through more than one ligand atoms: chelating ligand.
The Chelate effect

- The ability of chelate ligands to form more stable metal complex than those formed by similar monodentate ligands
- Thermodynamic explanations for the Chelate effect:
  \[ \Delta G = \Delta H - T \Delta S \]
  \( \Delta S: \) order
The most important chelator - EDTA

- EDTA can form strong complex with almost all metal ions, binding through for oxygen and two nitrogen atoms. The complex is 1:1 six coordinate geometry. (almost all chelate complexes are 1:1, due to the space limitation)
Chemical properties of EDTA

- EDTA is a hexaprotic system \((H_6Y^{2+})\), remains as salt, most common \(Na_2H_4Y\cdotH_2O\)

EDTA
Ethylendiaminetetraacetic acid
(also called ethylenedinitritilotetraacetic acid)

- When EDTA will lost 6 protons, and \(Y^{4-}\) react with metal ions and form complex.

\(\text{pK}_1 = 0.0\)
\(\text{pK}_2 = 1.5\)
\(\text{pK}_3 = 2.0\)
\(\text{pK}_4 = 2.66\)
\(\text{pK}_5 = 6.16\)
\(\text{pK}_6 = 10.24\)
EDTA in solution

- Fraction of EDTA in the form of $Y^{4-}$:
  \[ \alpha_{Y(4-)} = \frac{[Y^{4-}]}{[\text{EDTA}]} \]
  (total concentration of EDTA ions which are not complex with metal ions)

  \[ \alpha_{Y(4-)} = \frac{K_1 K_2 \cdots K_6}{[H^+]^6 + [H^+]^5 K_1 + \cdots [H^+] K_1 K_2 \cdots K_5 + K_1 K_2 \cdots K_6} \]

- $\alpha_{Y(4-)}$ is determined by pH
Equilibrium constant

• For the reaction

\[ M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4} \]

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

\( K_f \) called formation constant or stability constant.

\[ [Y^{4-}] = \alpha_{Y(4-)} [EDTA] \]

\[ K'_{f} = \alpha_{Y(4-)} K_f = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]} \]

\( \alpha_{Y(4-)} \) constant at fix pH

\[ M^{n+} + EDTA \rightleftharpoons MY^{n-4} \]

Conditional formation constant or effective formation constant

EDTA can be treated as if it is in one form
Example  Using the Conditional Formation Constant

The formation constant in Table 13-2 for CaY^{2-} is $10^{10.69} = 4.9 \times 10^{10}$. Calculate the concentrations of free Ca^{2+} in a solution of 0.10 M CaY^{2-} at pH 10.00 and at pH 6.00.

**SOLUTION**  The complex formation reaction is

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

where EDTA on the left side of the equation refers to all forms of unbound EDTA (= Y^{4-}, HY^{3-}, H_2Y^{2-}, H_3Y^{-}, etc.). Using $\alpha_{Y^4-}$ from Table 13-1, we find

At pH 10.00:  \[ K' = (0.36)(4.9 \times 10^{10}) = 1.8 \times 10^{10} \]

At pH 6.00:  \[ K' = (2.3 \times 10^{-5})(4.9 \times 10^{10}) = 1.1 \times 10^6 \]

Because dissociation of CaY^{2-} must produce equal quantities of Ca^{2+} and EDTA, we can write

<table>
<thead>
<tr>
<th></th>
<th>Ca^{2+}</th>
<th>EDTA</th>
<th>CaY^{2-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration (M)</td>
<td>0</td>
<td>0</td>
<td>0.10</td>
</tr>
<tr>
<td>Final concentration (M)</td>
<td>$x$</td>
<td>$x$</td>
<td>$0.10 - x$</td>
</tr>
</tbody>
</table>

\[
\frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{EDTA}]} = \frac{0.10 - x}{x^2} = K' = 1.8 \times 10^{10} \text{ at pH 10.00} \]

\[= 1.1 \times 10^6 \text{ at pH 6.00} \]

Solving for $x$ (= [Ca^{2+}]), we find [Ca^{2+}] = $2.4 \times 10^{-6}$ M at pH 10.00 and $3.0 \times 10^{-4}$ M at pH 6.00. Using the conditional formation constant at a fixed pH, we treat the dissociated EDTA as if it were a single species.
pH effect

- From the example, we can see that the metal-EDTA complex becomes less stable at lower pH. It is due to the fact that the less pH, the lower [Y₄⁻].

<table>
<thead>
<tr>
<th>pH</th>
<th>α₅⁻⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.3 × 10⁻²³</td>
</tr>
<tr>
<td>1</td>
<td>1.9 × 10⁻¹⁸</td>
</tr>
<tr>
<td>2</td>
<td>3.3 × 10⁻¹⁴</td>
</tr>
<tr>
<td>3</td>
<td>2.6 × 10⁻¹¹</td>
</tr>
<tr>
<td>4</td>
<td>3.8 × 10⁻⁹</td>
</tr>
<tr>
<td>5</td>
<td>3.7 × 10⁻⁷</td>
</tr>
<tr>
<td>6</td>
<td>2.3 × 10⁻⁵</td>
</tr>
<tr>
<td>7</td>
<td>5.0 × 10⁻⁴</td>
</tr>
<tr>
<td>8</td>
<td>5.6 × 10⁻³</td>
</tr>
<tr>
<td>9</td>
<td>5.4 × 10⁻²</td>
</tr>
<tr>
<td>10</td>
<td>0.36</td>
</tr>
<tr>
<td>11</td>
<td>0.85</td>
</tr>
<tr>
<td>12</td>
<td>0.98</td>
</tr>
<tr>
<td>13</td>
<td>1.00</td>
</tr>
<tr>
<td>14</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Auxiliary complexing agents

• In order to ensure accurate titration using EDTA, pH should be higher. However, many metal ions will precipitate as hydroxide, e.g. Fe(OH)$_2$ at high pH, heterogeneous reaction is hard to be completed.

• Hydrolysis is unavoidable, especially for > 2+ metal ions

• Auxiliary complexing agent is a ligand that binds to the metal ions strong enough to prevent the formation of hydroxide by weakly enough to give up the metal to EDTA.
The amount of free metal ion

**Fraction of free metal ion**

- For complexing reaction ($K$ equilibrium constant; $\beta$: cumulative formation constant):
  
  $M + L \rightleftharpoons ML \quad K_1 = \beta_1 = \frac{[ML]}{[M][L]}$
  
  $ML + L \rightleftharpoons ML_2 \quad K_2 = \frac{[ML_2]}{[M][L]}$

  
  $M + 2L \rightleftharpoons ML_2 \quad \beta_2 = \frac{[ML_2]}{[M][L]^2} = K_1 K_2$
  
  $M + nL \rightleftharpoons ML_n \quad \beta_n = K_1 K_2 \ldots K_n$

- Fraction of metal ion $\alpha = \frac{[M]}{C_m}$

  $C_m$ (the total amount of $M$) $= [M] + [ML] + [ML_2]$
  
  $= [M] + \beta_1 [M][L] + \beta_2 [M][L]^2$

  $\alpha = \frac{[M]}{C_m} = \frac{1}{1 + \beta_1 [L] + \beta_2 [L]^2}$

- In general $\alpha_n = \frac{1}{1 + \beta_1 [L] + \beta_2 [L]^2 \ldots \beta_n [L]^n}$

  $= \frac{[M]}{C_m}$
Example of using auxiliary complexing agent

- At high pH, hydrolysis can happen to Zn(2+) and form Zn(OH)\(_n\)-n+2 or Zn(OH)\(_2\) or ZnO
- Using NH\(_3\) as complexing agents to form Zn(NH\(_3\))\(^{2+}\), Zn(NH\(_3\))\(^{2+}\)_\(_2\), Zn(NH\(_3\))\(^{2+}\)_\(_2\)
  \[ \alpha_{Zn(2+)} = \frac{1}{1 + \beta_1[NH_3] + \beta_2[NH_3]^2 + \beta_3[NH_3]^3 + \beta_4 [NH_3]^4} \]
  free Zn(2+): [Zn]=C\(_{zn}\) (total Zn)x \( \alpha_{Zn(2+)} \)
- Using EDTA to titrate the Zn in NH\(_3\):
  Zn\(^{2+}\) + Y\(^{4-}\) ⇌ ZnY\(^{2-}\)
  \( K_f = [ZnY^{2-}]/[Zn^{2+}][Y^{4-}] \) where \( [Zn^{2+}]=C_{zn} \alpha_{Zn(2+)} \); \( [Y^{4-}]= C_{EDTA} \alpha_{Y(4-)} \)

\( K_f'' = \alpha_{zn} \alpha_Y K_f = [ZnY]/C_{zn} C_{EDTA} \)
Consider the titration of 50.0 mL of 1.00 × 10⁻³ M Zn²⁺ with 1.00 × 10⁻³ M EDTA at pH 10.00 in the presence of 0.10 M NH₃. (This is the concentration of NH₃. There is also NH₄⁺ in the solution.) The equivalence point is at 50.0 mL. Find pZn²⁺ after addition of 20.0, 50.0, and 60.0 mL of EDTA.

**Solution**

In Equation 13-17, we found that α_{Zn²⁺} = 1.8 × 10⁻⁵. Table 13-1 tells us that α_{Y⁴⁻} = 0.36. Therefore, the conditional formation constant is

\[ K'_r = \alpha_{Zn²⁺} \alpha_{Y⁴⁻} K_f = (1.8 \times 10^{-5})(0.36)(10^{16.50}) = 2.05 \times 10^{11} \]

(a) Before the equivalence point—20.0 mL: Because the equivalence point is 50.0 mL, the fraction of Zn²⁺ remaining is 30.0/50.0. The dilution factor is 50.0/70.0.

Therefore, the concentration of Zn²⁺ not bound to EDTA is

\[ C_{Zn²⁺} = \left( \frac{30.0}{50.0} \right) \left( 1.00 \times 10^{-3} \right) \left( \frac{50.0}{70.0} \right) = 4.3 \times 10^{-4} \text{ M} \]

However, nearly all the zinc not bound to EDTA is bound to NH₃. The concentration of free Zn²⁺ is

\[ [Zn²⁺] = \alpha_{Zn²⁺} C_{Zn²⁺} = (1.8 \times 10^{-5})(4.3 \times 10^{-4}) = 7.7 \times 10^{-9} \text{ M} \]

\[ \Rightarrow \quad pZn²⁺ = -\log[Zn²⁺] = 8.11 \]

Let's try a sanity check. The product [Zn²⁺][OH⁻]² is [10⁻⁸.11][10⁻⁴.00]² = 10⁻¹⁶.11, which does not exceed the solubility product of Zn(OH)₂ (K_{sp} = 10⁻¹⁵.52).

(b) At the equivalence point—50.0 mL: At the equivalence point, the dilution factor is 100/100.0, so [ZnY²⁻] = (50.0/100.0)(1.00 × 10⁻³ M) = 5.00 × 10⁻⁴ M. As in section 13-3, we write

\[ C_{Zn²⁺} + \text{EDTA} \rightleftharpoons ZnY²⁻ \]

| Initial concentration (M) | 0 | 0 | 5.00 × 10⁻⁴ |
| Final concentration (M)   | x | x | 5.00 × 10⁻⁴ - x |

\[ K'_r = 2.05 \times 10^{11} = \frac{[ZnY²⁻]}{[C_{Zn²⁺}][\text{EDTA}]} = \frac{5.00 \times 10^{-4} - x}{x^2} \]

\[ \Rightarrow \quad x = C_{Zn²⁺} = 4.9 \times 10^{-8} \text{ M} \]

\[ [Zn²⁺] = \alpha_{Zn²⁺} C_{Zn²⁺} = (1.8 \times 10^{-5})(4.9 \times 10^{-8}) = 8.9 \times 10^{-13} \text{ M} \]

\[ \Rightarrow \quad pZn²⁺ = -\log[Zn²⁺] = 12.05 \]

(c) After the equivalence point—60.0 mL: Almost all zinc is in the form ZnY²⁻. With a dilution factor of 50.0/110.0 for zinc, we find

\[ [ZnY²⁻] = \left( \frac{50.0}{110.0} \right) \left( 1.00 \times 10^{-3} \right) = 4.5 \times 10^{-4} \text{ M} \]

We also know the concentration of excess EDTA, whose dilution factor is 10.0/110.0:

\[ [\text{EDTA}] = \left( \frac{10.0}{110.0} \right) \left( 1.00 \times 10^{-3} \right) = 9.1 \times 10^{-5} \text{ M} \]

Once we know [ZnY²⁻] and [EDTA], we can use the equilibrium constant to find [Zn²⁺]:

\[ \frac{[ZnY²⁻]}{[Zn²⁺][\text{EDTA}]} = \frac{\alpha_{Y⁴⁻} K_f}{[Zn²⁺][\text{EDTA}]} = \frac{(0.36)(10^{16.50})}{4.5 \times 10^{-4}} = 1.1 \times 10^{16} \]

\[ \frac{[Zn²⁺]}{[9.1 \times 10^{-5}]} = 1.1 \times 10^{16} \quad \Rightarrow \quad [Zn²⁺] = 4.3 \times 10^{-16} \text{ M} \]

\[ \Rightarrow \quad pZn²⁺ = 15.36 \]

Note that past the equivalence point the problem did not depend on the presence of NH₃, because we knew the concentrations of both [ZnY²⁻] and [EDTA].
End-point detection

- Metal ion indicators
  - Color change when bind to the detect ion
    \[
    \text{MgIn + EDTA} \rightarrow \text{MgEDTA + In} \\
    \text{red} \quad \text{colorless} \quad \text{colorless} \quad \text{blue}
    \]
  - The binding between indicator and metal has to be weaker than metal-EDTA, so indicator will release the metal to EDTA
- Mercury electrode e.g. Hg drop
- Ion selective electrode
- pH electrode
Properties of Umass Boston
EDTA Titration techniques

• Direct titration
  – Control pH, in buffer solution
  – Auxiliary complexing agent to prevent hydrolysis

• Back titration
  – HOW: adding known excess amount of EDTA, the excess EDTA will be titrated by the second ion solution with known concentration (standard solution)
  – WHY:
    • The ion will precipitate without EDTA
    • The reaction is slow under normal titration condition
    • No good indicator
  – Conditions: the bond between the second ion and EDTA has to be weaker than that of analyte ion with EDTA.
EDTA Titration techniques

• Displacement titration
  – How: adding known amount of EDTA complex solution, the analyt metal ion can replace the metal ion bonded with EDTA.
  \[ \text{Hg}^{2+} + \text{MgY}^{2-} \rightarrow \text{MY}^{n-4} + \text{Mg}^{2+}, \text{Mg is then titrated with EDTA.} \]
  – Why: no good indicator.

• Indirect titration: determine anions

• Masking: to prevent the interfering between ions. Cyanide (CN\(^{-}\)) is the typically used to mask (caution!!). Demasking