11.1 Metal-chelate complexes

Metal ← Ligand
(donation of e pair)

Lewis acid → Lewis base

Monodentate: CN-,
Bidentate: en
Multidentate: edta

Titration based on complex formation:
Complexometric titration

11.2 The Chelate effect

Stability increased by multidentate ligands

\[
\text{Cd(H}_2\text{O)}^2+ + 2\text{H}_2\text{N}.\text{NH}_2 \rightleftharpoons \text{Ethylenediamine} \quad \frac{[\text{Cd(NH}_2\text{)}^2]}{[\text{Cd(H}_2\text{O)}^2+][\text{H}_2\text{N}.\text{NH}_2]} = K = 8 \times 10^9
\]

\[
\text{Cd(H}_2\text{O)}^2+ + 4\text{CH}_3.\text{NH}_2 \rightleftharpoons \text{Methylamine} \quad \frac{[\text{Cd(NH}_2\text{)}^2]}{[\text{Cd(H}_2\text{O)}^2+][\text{CH}_3.\text{NH}_2]^4} = K = 4 \times 10^6
\]
11.1. Metal-chelate complexes

11.2. EDTA: widely used as chelator

1) Acid-Base properties

EDTA: $H_6Y^{2+}$

The first four $pK_a$ - carboxyl protons
last two $pK_a$ - ammonium protons

$pk_1 = 0.0$
$pk_2 = 1.5$
$pk_3 = 2.0$
$pk_4 = 2.69$
$pk_5 = 6.13$
$pk_6 = 10.37$

Neutral acid form: tetraprotic: $H_4Y$
protonated form: $Na_2H_2Y\ 2H_2O$
DIFFERENT FORMS OF EDTA IN SOLUTIONS:

- $Y^4^-$
- $HY^3^-$
- $H_2Y^2^-$
- $H_3Y^-$
- $H_4Y$
- $H_5Y^+$
- $H_6Y^{2+}$

$\alpha_{Y^4^-}$: fraction of EDTA in the form of $Y^4^-$

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

$pk_1=0.0$
$p k_2=1.5$
$p k_3=2.0$
$p k_4=2.69$
$p k_5=6.13$
$p k_6=10.37$

**Table 12-1: Values of $\alpha_{Y^4^-}$ for EDTA at 20°C and $\mu = 0.10$ M**

<table>
<thead>
<tr>
<th>pH</th>
<th>$\alpha_{Y^4^-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$1.3 \times 10^{-23}$</td>
</tr>
<tr>
<td>1</td>
<td>$1.4 \times 10^{-18}$</td>
</tr>
<tr>
<td>2</td>
<td>$2.6 \times 10^{-14}$</td>
</tr>
<tr>
<td>3</td>
<td>$2.1 \times 10^{-11}$</td>
</tr>
<tr>
<td>4</td>
<td>$3.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>5</td>
<td>$2.9 \times 10^{-7}$</td>
</tr>
<tr>
<td>6</td>
<td>$1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>7</td>
<td>$3.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>8</td>
<td>$4.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>9</td>
<td>$0.041$</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>$0.98$</td>
</tr>
<tr>
<td>13</td>
<td>$1.00$</td>
</tr>
<tr>
<td>14</td>
<td>$1.00$</td>
</tr>
</tbody>
</table>

EDTA: widely used as a chelator

Figure 12-2: Fractional composition vs. pH for EDTA in different forms.
11.7

2) EDTA complexes

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

only with \( Y^{4-} \)

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

Table 12-2 shows large \( K_f \) for most EDTA complex.

### Table 12-2 Formation constants for metal-EDTA complexes

<table>
<thead>
<tr>
<th>Ion</th>
<th>( \log K_f )</th>
<th>Ion</th>
<th>( \log K_f )</th>
<th>Ion</th>
<th>( \log K_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>2.95</td>
<td>V⁺³</td>
<td>25.9</td>
<td>Ti⁺³</td>
<td>35.3</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.86</td>
<td>Cr⁺³</td>
<td>23.4</td>
<td>Bi⁺³</td>
<td>27.8</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.8</td>
<td>Mn⁺²</td>
<td>25.2</td>
<td>Ce⁺³</td>
<td>15.93</td>
</tr>
<tr>
<td>Be⁺²</td>
<td>9.7</td>
<td>Fe⁺³</td>
<td>25.1</td>
<td>Pr⁺³</td>
<td>16.30</td>
</tr>
<tr>
<td>Mg⁺²</td>
<td>8.79</td>
<td>Co⁺³</td>
<td>41.4</td>
<td>Nd⁺³</td>
<td>16.51</td>
</tr>
<tr>
<td>Ca⁺²</td>
<td>10.65</td>
<td>Zr⁺⁴</td>
<td>29.3</td>
<td>Pm⁺³</td>
<td>16.9</td>
</tr>
<tr>
<td>Sr⁺²</td>
<td>8.72</td>
<td>Hf⁺⁴</td>
<td>29.5</td>
<td>Sm⁺³</td>
<td>17.06</td>
</tr>
<tr>
<td>Ba⁺³</td>
<td>7.88</td>
<td>VO⁺⁴</td>
<td>18.7</td>
<td>Eu⁺³</td>
<td>17.25</td>
</tr>
<tr>
<td>Ra⁺⁴</td>
<td>7.4</td>
<td>VO₂⁺</td>
<td>15.5</td>
<td>Gd⁺³</td>
<td>17.35</td>
</tr>
<tr>
<td>Sc⁺³</td>
<td>23.1</td>
<td>Ti⁺⁵</td>
<td>7.20</td>
<td>Tb⁺³</td>
<td>17.87</td>
</tr>
<tr>
<td>Y⁺⁷</td>
<td>18.08</td>
<td>Ti⁺⁶</td>
<td>6.41</td>
<td>Dy⁺⁷</td>
<td>18.30</td>
</tr>
<tr>
<td>La⁺⁵</td>
<td>15.36</td>
<td>Pd⁺⁴</td>
<td>25.6</td>
<td>Ho⁺⁵</td>
<td>18.56</td>
</tr>
<tr>
<td>V⁺⁷</td>
<td>12.7</td>
<td>Zn⁺⁴</td>
<td>16.5</td>
<td>Er⁺⁵</td>
<td>18.89</td>
</tr>
<tr>
<td>Cr⁺³</td>
<td>13.6</td>
<td>Cd⁺⁴</td>
<td>16.5</td>
<td>Tm⁺⁵</td>
<td>19.32</td>
</tr>
<tr>
<td>Mn⁺³</td>
<td>13.89</td>
<td>Hg⁺²</td>
<td>21.5</td>
<td>Yb⁺⁵</td>
<td>19.49</td>
</tr>
<tr>
<td>Fe⁺²</td>
<td>14.30</td>
<td>Sn⁺²</td>
<td>18.3</td>
<td>Lu⁺⁵</td>
<td>19.74</td>
</tr>
<tr>
<td>Co⁺²</td>
<td>16.45</td>
<td>Pb⁺²</td>
<td>18.0</td>
<td>Th⁺⁵</td>
<td>23.2</td>
</tr>
<tr>
<td>Ni⁺²</td>
<td>18.4</td>
<td>Al⁺³</td>
<td>16.4</td>
<td>U⁺⁵</td>
<td>25.7</td>
</tr>
<tr>
<td>Cu⁺²</td>
<td>18.78</td>
<td>Ga⁺³</td>
<td>21.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti⁺³</td>
<td>21.3</td>
<td>In⁺³</td>
<td>24.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NOTE: The stability constant is the equilibrium constant for the reaction \( M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4} \). Values in table apply at 25°C and ionic strength 0.1 M unless otherwise indicated.

a. 20°C, ionic strength = 0.1 M.  
   b. 20°C, ionic strength = 1 M.


Table 12-2  
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11.8

3) Conditional formation const.

Below pH 10.4, most EDTA exist non \( Y^{4-} \) need to know exact amount of \( Y^{4-} \)

\[ [Y^{4-}] = \alpha Y^{4-} [EDTA], \quad [EDTA] = \text{total conc.} \]

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

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

: conditional formation const.(effective const.)

We need to know \( \alpha Y^{4-} \) at each pH condition.
Ex) The formation constant in Table 12-2 for FeY\(^{-}\) is 
\(10^{25.1} = 1.3 \times 10^{25}\). Calculate the concentration of free Fe\(^{3+}\) in 
solutions of 0.10 M FeY\(^{-}\) at pH 8.00 and at pH 2.00.

At pH 8.0 \([\text{Fe}^{3+}] = 1.35 \times 10^{-12}\)M
At pH 2.0 \([\text{Fe}^{3+}] = 5.44 \times 10^{-7}\)M

At low pH,
Metal-EDTA complex
= less stable.

For a titration,
consider how pH affects
the titration of
Ca\(^{2+}\) with EDTA
11.3. EDTA titration curves

the concentration of free metal ion during titration with EDTA?
similar to the titration of strong acid (~metal) by a strong base (~EDTA)

Reg. 1: Before equivalence point,
M\(^{n+}\) : excess, unreacted
MY\(^{n-4}\) : dissociation - negligible

Reg. 2: At the equivalence point
MY\(^{n-4}\) : dissolves some free M\(^{n+}\),
(MY\(^{n-4}\) ⇌ M\(^{n+}\) + EDTA)

Reg. 3: After equivalence point.

11.12

1) Titration calculations
Titration of 50.0 mL of 0.0500 M Mg\(^{2+}\) with 0.0500 M EDTA (pH 10.0)
Mg\(^{2+}\) + EDTA → MgY\(^{-2}\)

\[ K_f' = \alpha_{Y^4} K_f = 0.36 \times (6.2 \times 10^8) = 2.23 \times 10^8 \]

Reg. 1) When 5.0 mL of EDTA added,
\[ pMg^{2+} = \]
11.13  EDTA titration curves

Reg. 2) at eq. 50.0 mL of EDTA added, all converted to Mg-EDTA (MgY²⁻)

\[ [\text{MgY}²⁻] = \text{M} \]

conc. of free metal ion ?

\[
\begin{align*}
\text{MgY}²⁻ & \quad \text{Mg}²⁺ \quad + \quad \text{EDTA} \\
\text{initial} & \quad \text{final} \\
K_f' &= \frac{[\text{MgY}²⁻]}{[\text{Mg}²⁺][\text{EDTA}]} \\
x &= [\text{Mg}²⁺] = \\
p\text{Mg} &= \]

11.14  EDTA titration curves

Reg. 3) After 51.0 mL of EDTA (1.0 mL of EDTA-excess) excess [EDTA] = \text{M}

\[ [\text{MgY}²⁻] = \text{M} \quad (\text{adjusted conc.}) \]

\[
K_f' = \frac{[2.48 \times 10^{-2}]}{[\text{Mg}²⁺][4.98 \times 10^{-4}]} = 2.23 \times 10^{8} \\
[\text{Mg}²⁺] = 2.2 \times 10^{-7} \text{ M}, \quad p\text{Mg} = \]
11-3. EDTA titration curves

Figure 11-11
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11-5. Auxiliary Complexing Agents

1) Metal-Ligand Equilibria.
To permit many metals to be titrated in alkaline sol with EDTA, auxiliary complexing agent is used. It binds metal strongly enough to prevent metal hydroxide

\[
\begin{align*}
\alpha_M &= \frac{[M]}{[M_{\text{tot}}]} \\
\beta_1 &= \frac{[ML]}{[M][L]} \\
\beta_2 &= \frac{[ML_2]}{[M][L]^2}
\end{align*}
\]

\[
M_{\text{tot}} = [M] + [ML] + [ML_2]
\]
11.17

\[ M_{\text{tot}} = [M] + [ML] + [ML_2] \]
\[ = [M] + \beta_1 [M][L] + \beta_2 [M][L]^2 \]
\[ = [M] \{1 + \beta_1 [L] + \beta_2 [L]^2\} \]

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

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

11.18

11-6. Metal ion indicator

End-point detection
1) Metal ion indicator Table 11-3
2) Mercury electrode
3) glass electrode
4) ion-selective electrode

Table 11-3 Common metal ion indicators

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>(pK_a)</th>
<th>Color of free indicator</th>
<th>Color of metal ion complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calmagite</td>
<td>(\text{HN}^+)</td>
<td>(8.1) 12.4</td>
<td>(\text{H}^{+}) red</td>
<td>Wine red</td>
</tr>
<tr>
<td></td>
<td>(\text{In}^3+) blue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{In}^+) orange</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eriochrome black T</td>
<td>(\text{O}S\text{H}^+)</td>
<td>(6.3) 11.6</td>
<td>(\text{H}^{+}) red</td>
<td>Wine red</td>
</tr>
<tr>
<td></td>
<td>(\text{In}^3+) blue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{In}^+) orange</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Murexide</td>
<td>(\text{O}N\text{H}^+)</td>
<td>(9.2) 10.9</td>
<td>(\text{H}^{+}) red-violet</td>
<td>Yellow (with (\text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+})); red with (\text{Ca}^{2+})</td>
</tr>
</tbody>
</table>

PREPARATION AND STABILITY:
Calmagite: 0.65 g/100 ml H_2SO_4 solution is stable for a year in the dark.
Eriochrome black T: Dissolve 0.1 g of the solid in 7.5 ml of triethanolamine plus 2.5 ml of absolute ethanol; solution is stable for months; best used for titrations above pH 6.5.
11.7 EDTA titration technique

**Direct Titration**

**Back Titration**

1) known excess of EDTA is added to analyte
2) excess EDTA is titrated with second metal ion.

Ex) \( \text{Ni}^{2+} \) is back titrated using standard \( \text{Zn}^{2+} \) at pH 5.5 with xylenol orange indicator. A solution containing 25.00 mL of \( \text{Ni}^{2+} \) in dilute HCl is treated with 25.00 mL of 0.05283 M \( \text{Na}_2\text{EDTA} \). The solution is neutralized with NaOH, and the pH is adjusted to 5.5 with acetate buffer. The solution turns yellow when a few drops of indicator are added. Titration with 0.02299 M \( \text{Zn}^{2+} \) requires 17.61 mL to reach the red end point. What is the molarity of \( \text{Ni}^{2+} \) in the unknown?

---

**Homework**

6, 9, 16, 31, 34