Complexation Equilibria

- Typically Lewis Acid-Base reactions
  Metal + Ligand = Complex   Defined by formation constant, K

- Many metals form more complex coordination compounds, containing several ligands. These may occur in a stepwise fashion

M + L = ML	K_1
ML + L = ML_2	K_2
ML_2 + L = ML_3	K_3
ML_{n-1} + L = ML_n	K_n

- Multiple steps of these reactions can be combined using overall formation constants (β)

M + 3L = ML_3 β =

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Formation Constants for EDTA

Harris, Quantitative Chemical Analysis, 8e
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TABLE 11-2 Formation constants for metal-EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.95	V^{3+}	25.9[a]	Tl^{3+}	35.3
Na^+	1.86	Cr^{3+}	23.4[a]	Bi^{3+}	27.8[a]
K^+	0.8	Mn^{3+}	25.2	Ce^{3+}	15.93
Be^{2+}	9.7	Fe^{3+}	25.1	Pr^{3+}	16.30
Mg^{2+}	8.79	Co^{3+}	41.4	Nd^{3+}	16.51
Ca^{2+}	10.65	Zr^{4+}	29.3	Pm^{3+}	16.9
Sr^{2+}	8.72	Hf^{4+}	29.5	Sm^{3+}	17.06
Ba^{2+}	7.88	VO^{2+}	18.7	Eu^{3+}	17.25
Ra^{2+}	7.4	VO_2^+	15.5	Gd^{3+}	17.35
Sc^{3+}	23.1[a]	Ag^+	7.20	Tb^{3+}	17.87
Y^{3+}	18.08	Tl^+	6.41	Dy^{3+}	18.30
La^{3+}	15.36	Pd^{2+}	25.6[a]	Ho^{3+}	18.56
V^{2+}	12.7[a]	Zn^{2+}	16.5	Er^{3+}	18.89
Cr^{2+}	13.6[a]	Cd^{2+}	16.5	Tm^{3+}	19.32
Mn^{2+}	13.89	Hg^{2+}	21.5	Yb^{3+}	19.49
Fe^{2+}	14.30	Sn^{2+}	18.3[b]	Lu^{3+}	19.74
Co^{2+}	16.45	Pb^{2+}	18.0	Th^{4+}	23.2
Ni^{2+}	18.4	Al^{3+}	16.4	U^{4+}	25.7
Cu^{2+}	18.78	Ga^{3+}	21.7		
Ti^{3+}	21.3	In^{3+}	24.9		

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.

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Complexation Equilibria

- In predicting the completeness of a reaction (complexation, precipitation…), we need to account for all equilibria involving M and L.
  - Often specify conditions for a given system - Conditional Formation Constants (K')

- Conditional Formation Constant for EDTA

  EDTA = ethylendiaminetetraacetic acid, hexaprotic acid!

$H_6Y^{2+} = H^+ + H_5Y^+$	$K_{a1} = 1$
$H_5Y^+ = H^+ + H_4Y$	$K_{a2} = 3.16 \times 10^{-2}$
$H_4Y = H^+ + H_3Y^-$	$K_{a3} = 1.02 \times 10^{-2}$
$H_3Y^- = H^+ + H_2Y^{2-}$	$K_{a4} = 2.14 \times 10^{-3}$
$H_2Y^{2-} = H^+ + HY^{3-}$	$K_{a5} = 6.92 \times 10^{-7}$
$HY^{3-} = H^+ + Y^{4-}$	$K_{a6} = 5.50 \times 10^{-11}$

- Predominant forms depend on pH (Fig 11-7).

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EDTA In Solution

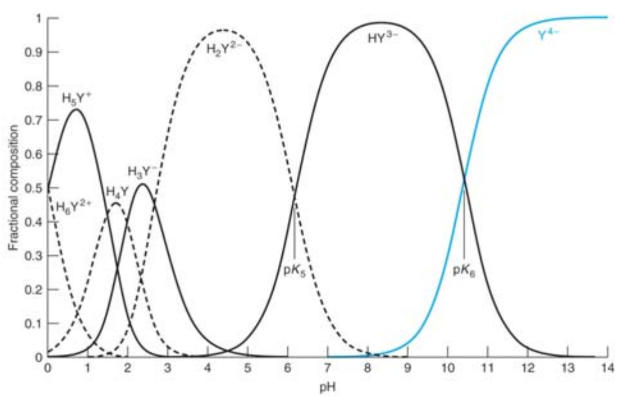

FIGURE 11-7 Fractional composition diagram for EDTA.

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[H_6Y^{2+}] + [H_5Y^+] + [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]}$$

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

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pH Dependence of EDTA Formation Constant

- Typically focus on fully deprotonated form (Y^{4-}):

$M^{n+} + Y^{4-} = MY^{n-4}$

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

This is just like M^{n+} + EDTA = MY^{n-4}, or looking at all forms of EDTA

- We can calculate K'_f at any pH
- We'd like to work where K'_f is large, where is this?

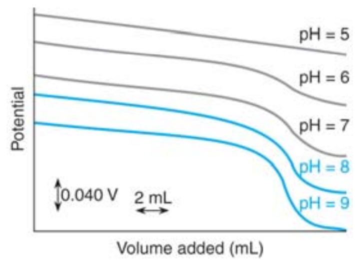

TABLE 11-1 Values of $\alpha_{Y^{4-}}$ for EDTA at 25°C and μ = 0.10 M

pH	$\alpha_{Y^{4-}}$
0	1.3×10^{-23}
1	1.4×10^{-18}
2	2.6×10^{-14}
3	2.1×10^{-11}
4	3.0×10^{-9}
5	2.9×10^{-7}
6	1.8×10^{-5}
7	3.8×10^{-4}
8	4.2×10^{-3}
9	0.041
10	0.30
11	0.81
12	0.98
13	1.00
14	1.00

Harris, *Quantitative Chemical Analysis*, 8e

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If it were only that easy!

What do we need to be concerned with when working with metal ions and high pH?

$$M^{n+} + nOH^- = M(OH)_n\ (s)$$

How do we avoid this? Two options:

1. Work at low pH.

2. Add something to prevent hydroxide formation. Characteristics?
   - Must bind more strongly than OH^-
   - Must bind less strongly than EDTA
   - Will keep M^{n+} in solution until it can be complexed by EDTA
     - Most commonly used auxiliary complexing agent is ammonia, serves two purposes:

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How Do We Handle Complexing Agents?

- Many metals form more than one complex with ammonia (and other complexing agents)

$$M + L = ML \qquad \beta_1 = K_1 = \frac{[ML]}{[M][L]}$$

$$M + 2L = ML_2 \qquad \beta_2 = K_1K_2 = \frac{[ML_2]}{[M][L]^2}$$

- Since EDTA only binds with free M^{n+}, need to know fraction of M present in the solution

$$\alpha_{M^{n+}} = \frac{[M]}{C_M} = \frac{[M]}{[M]+[ML]+[ML_2]}$$

- Use β equilibria to simplify:

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

- Now we arrive at a new conditional formation constant for a given pH and $[NH_3]$ (or [L]): $K_f'' = \alpha_{M^{n+}}\alpha_{Y^{4-}}K_f$

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EDTA Titration Curves

Much like strong acid/base titration

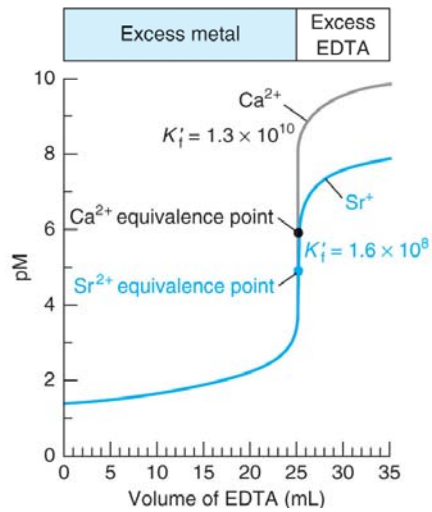
(Figure 12-10)

Before adding titrant:

Before equivalence point:

At equivalence point:

After equivalence point:



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EDTA Titration Considerations

Requirements for indicators for complexometric titrations:

1. Must bind metal ion of interest
2. Must have different properties (color) in the bound and unbound state
3. Must bind less strongly than the complexing agent (EDTA)

EDTA titration techniques: READ this section carefully.

- Direct titration
- Back titration
- Displacement Titration
- Indirect Titration

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