

Chapter 12

EDTA Titrations

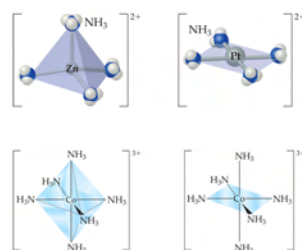
Acids and Bases

- 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

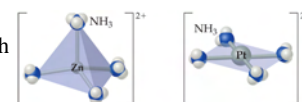
Coordination Number



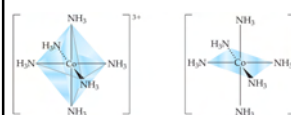
- The atom of the ligand that supplies the nonbonding electrons for the metal-ligand bond is the **donor atom**.
- The number of these atoms is the **coordination number**.

Geometries

There are two common geometries for metals with a coordination number of four:



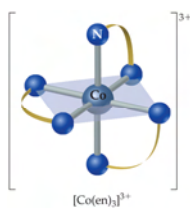
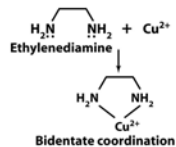
Tetrahedral & Square planar



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

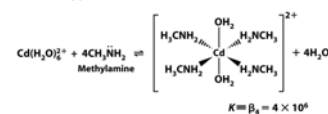
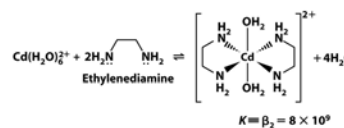
Ligands

- 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. → en is **bidentate**.



Chelating Effect

A multidentate ligand to form more stable metal complexes than those formed by similar monodentate ligand



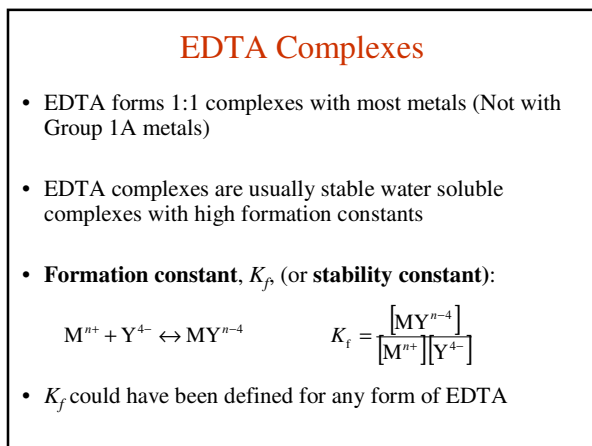
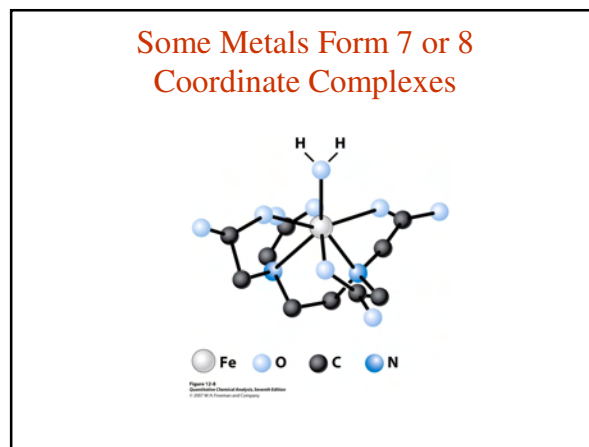
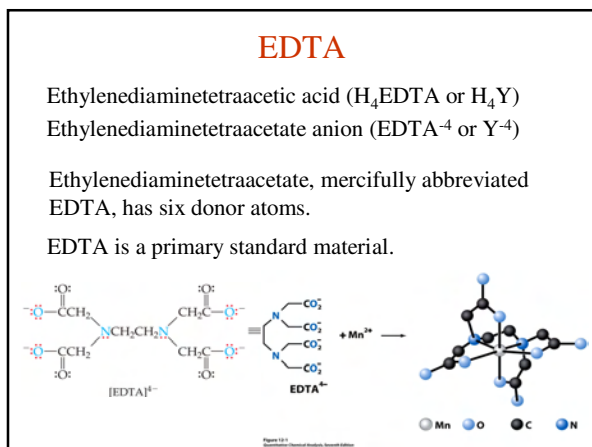
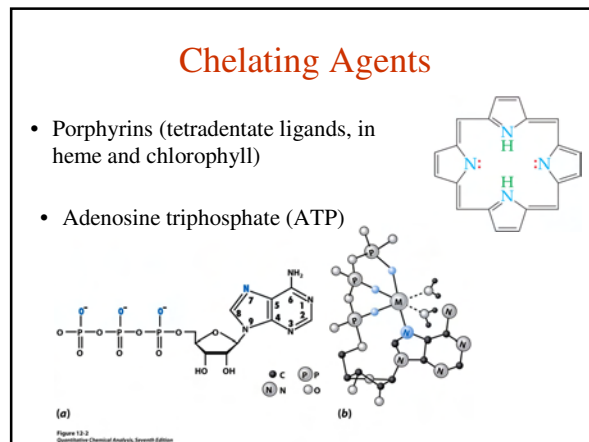
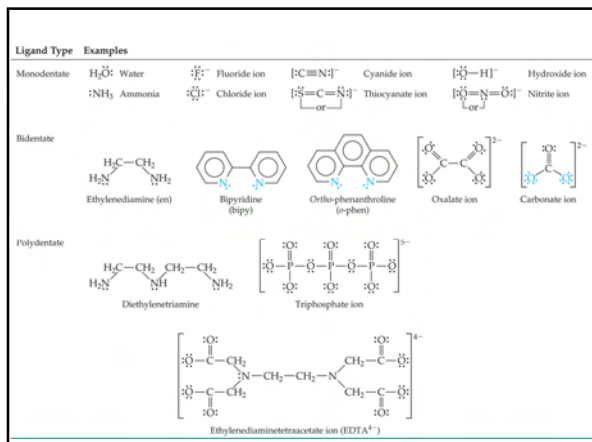


Table 12-2 Formation constants for metal-EDTA complexes

Ion	$\log K_f$	Ion	$\log K_f$	Ion	$\log K_f$
Li^+	2.95	V^{3+}	25.9 ^a	Ti^{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	Pb^{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 ^a	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 $\text{M}^{n+} + \text{Y}^{4-} \rightleftharpoons \text{MY}^{n-4}$. Values in table apply at 25°C and ionic strength 0.1 M unless otherwise indicated.

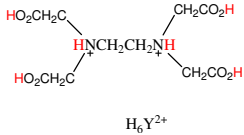
a. 20°C, ionic strength = 0.1 M. b. 20°C, ionic strength = 1 M.

SOURCE: A. E. Martell, R. M. Smith, and R. J. Motekaitis, NIST Critically Selected Stability Constants of Metal Complexes, NIST Standard Reference Database 46, Gaithersburg, MD, 2003.

Table 12-2 Quantitative Chemical Analysis, Seventh Edition © 2003 W. H. Freeman and Company

pH affects EDTA titration

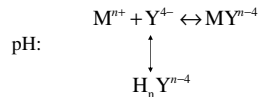
Acid-Base Properties of EDTA:



EDTA is a hexaprotic system (H_6Y^{2+}) with 4 carboxylic acids and 2 ammoniums

$$pK_1 = 0.0 \quad pK_2 = 1.5 \quad pK_3 = 2.0 \quad pK_4 = 2.66$$

$$pK_5 = 6.16 \quad pK_6 = 10.24$$



Fraction of EDTA in the form Y^{4-}

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

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

$$\alpha_{Y^{4-}} = \frac{K_1 K_2 K_3 K_4 K_5}{[H^+]^6 + [H^+]^5 K_1 + [H^+]^4 K_1 K_2 + [H^+]^3 K_1 K_2 K_3 + [H^+]^2 K_1 K_2 K_3 K_4 + [H^+] K_1 K_2 K_3 K_4 K_5 + K_1 K_2 K_3 K_4 K_5}$$

Fractional Composition Diagram for EDTA

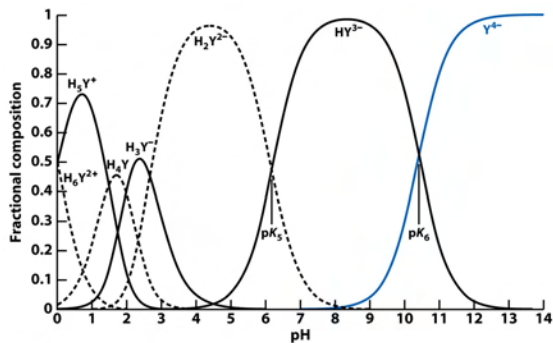


Figure 12-7
Quantitative Chemical Analysis, Seventh Edition
© 2003 W. H. Freeman and Company

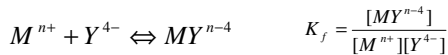
pH Dependence of $\alpha_{Y^{4-}}$

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

Table 12-1
Quantitative Chemical Analysis, Seventh Edition
© 2003 W. H. Freeman and Company

Conditional Formation Constant



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

Conditional formation constant:

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

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)



$$\text{at pH} = 10.00, K_f' = \alpha_{Y^{4-}} K_f = (0.36)(10^{10.65}) = 1.3 \times 10^{10}$$

$$\text{at pH} = 6.00, K_f' = \alpha_{Y^{4-}} K_f = (1.8 \times 10^{-5})(10^{10.65}) = 8.0 \times 10^5$$

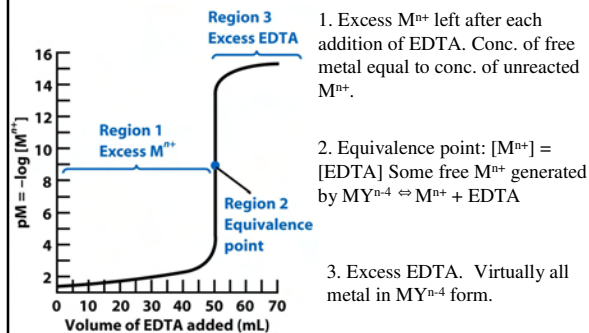


Conc _i	0	0	0.1
Conc _f	x	x	0.1 - x

$$K_f' = \frac{[CaY^{2-}]}{[Ca^{2+}][EDTA]} = \frac{0.1 - x}{x^2} \quad x = [Ca^{2+}] = 2.7 \times 10^{-6} \text{ M at pH} = 10$$

$$= 3.5 \times 10^{-4} \text{ M at pH} = 6$$

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.



$$K'_f = \alpha_{Y^{4-}} K_f = 0.30 * 10^{10.65} = 1.3 \times 10^{10}$$

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
5mL \rightarrow before the equivalence point

$$[Ca^{2+}] = \left(\frac{25.0 - 5.0}{25.0} \right) (0.040) \left(\frac{50.0}{5.00 + 50.0} \right) = 0.0291 \text{ M}$$

Fraction Remaining

$$pCa^{2+} = -\log(0.0291) = 1.54$$

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-}

$$[CaY^{2-}] = (0.040) \left(\frac{50.0}{25.00 + 50.0} \right) = 0.0267 \text{ M}$$

$$Ca^{2+} + EDTA \leftrightarrow CaY^{2-}$$

Conc _i	0	0	0.0267	$K'_f = \frac{[CaY^{2-}]}{[Ca^{2+}][EDTA]} = \frac{0.0267 - x}{x^2} = 1.8 \times 10^{10}$
Conc _f	x	x	0.0267 - x	

$$x = 1.2 \times 10^{-6} \text{ M}$$

$$pCa^{2+} = -\log(1.2 \times 10^{-6}) = 5.91$$

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.

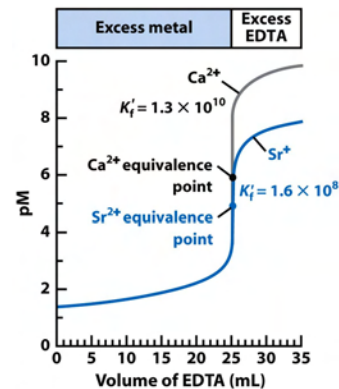
At equivalence point, Vol. of EDTA = 25.0 mL
26.00 mL \rightarrow 1.0 mL excess EDTA, after the equivalence point

$$[EDTA] = (0.080) \left(\frac{1.00}{50.0 + 26.00} \right) = 1.05 \times 10^{-3} \text{ M}$$

$$[CaY^{2-}] = (0.040) \left(\frac{50.0}{50.0 + 26.00} \right) = 2.63 \times 10^{-2} \text{ M}$$

$$K'_f = \frac{[CaY^{2-}]}{[Ca^{2+}][EDTA]} = \frac{2.63 \times 10^{-2}}{[Ca^{2+}](1.05 \times 10^{-3})} = 1.8 \times 10^{10} \quad Ca^{2+} = 1.4 \times 10^{-9} \text{ M}$$

$$pCa^{2+} = 8.86$$



pH affects the titration of Ca²⁺ with EDTA

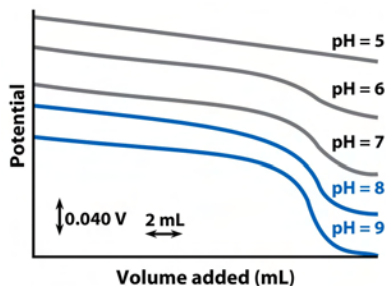


Figure 12-9
Quantitative Chemical Analysis, Seventh Edition
© 2007 W. H. Freeman and Company

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 triethanolamine)

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

$$K_f'' = \alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f$$

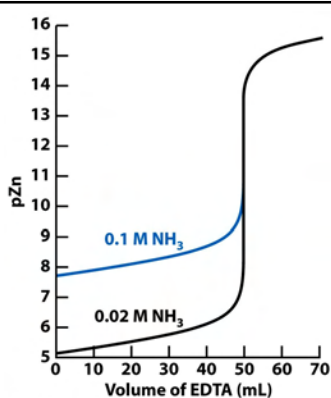


Figure 12-13
Quantitative Chemical Analysis, Seventh Edition
© 2007 W. H. Freeman and Company

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:

$$\text{MgEbT} + \text{EDTA} \leftrightarrow \text{MgEDTA} + \text{EbT}$$

(Red) (Colorless) (Blue)

 - Eriochrome black T is an organic ion
- The indicator *must* bind less strongly than EDTA

Metal Ion Indicators

Table 12-3 Common metal ion indicators

Name	Structure	pK _a	Color of free indicator	Color of metal ion complex
Calmagite		pK _{a1} = 8.1 pK _{a2} = 12.4	H ₂ In ³⁺ red HIn ²⁺ blue In ⁻ orange	Wine red
Eriochrome black T		pK _{a1} = 6.3 pK _{a2} = 11.6	H ₂ In ³⁺ red HIn ²⁺ blue In ⁻ orange	Wine red
Murexide		pK _{a1} = 9.2 pK _{a2} = 10.9	H ₂ In ³⁺ red-violet HIn ²⁺ violet In ⁻ blue	Yellow (with Cu ²⁺ , Ni ²⁺ , Cu ²⁺); red with Ca ²⁺

PREPARATION AND STABILITY:

Calmagite: 0.05 g/100 mL H₂O solution is stable for a year in the dark.

Eriochrome black T: Dissolve 0.1 g of the solid in 7.5 mL of absolute ethanol; solution is stable for months; best used for titrations above pH 6.5.

Murexide: Grind 10 mg of murexide with 5 g of reagent NaCl in a clean mortar; use 0.2–0.4 g of the mixture for each titration.

Xylenol orange: 0.5 g/100 mL H₂O solution is stable indefinitely.

Pyrocatechol violet: 0.1 g/100 mL; solution is stable for several weeks.

Table 12-3 part 1
Quantitative Chemical Analysis, Seventh Edition
© 2007 W. H. Freeman and Company

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.
- Displacement titration:** For metals without a good indicator ion, the analyte can be treated with excess Mg(EDTA)²⁻. The analyte displaces Mg, and then Mg can be titrated with standard EDTA
- Indirect titration:** Anions can be analyzed by precipitation with excess metal ion and then titration of the metal in the dissolved precipitate with EDTA.
- Masking agent:** protects some component of the analyte from reaction with EDTA (render metal ions inactive without actually removing them from solution). **Demasking:** releasing metal ion from a masking agent.