

Chapter 12

EDTA Titrations

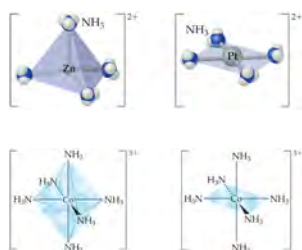
Acids and Bases

- 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

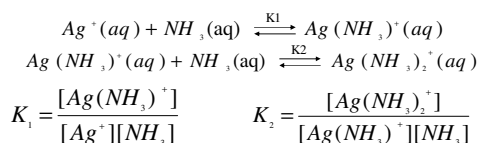
Coordination Number



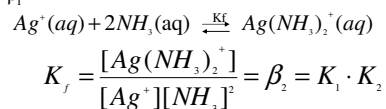
- The atom of the ligand that supplies the nonbonding electrons for the metal-ligand bond is the **donor atom**.
- The number of these atoms is the **coordination number**.

Complex Formation

Formation of coordinate bonds between Lewis Acids/Bases



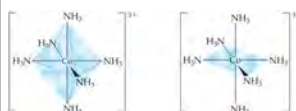
Formation constants (Kf) are the equilibrium constants for complex ion formation. The overall, or cumulative, formation constants are denoted β_i



Geometries

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

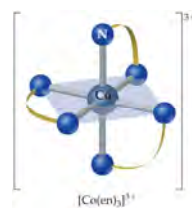
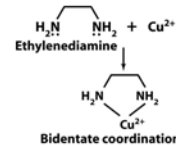
Tetrahedral & Square planar



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

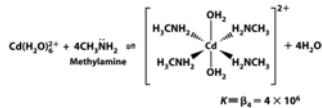
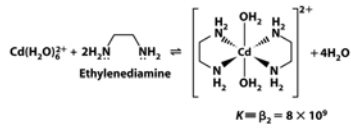
Ligands

- 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, $NH_2CH_2CH_2NH_2$ (i.e., en), each N is a donor atom. → en is **bidentate**.

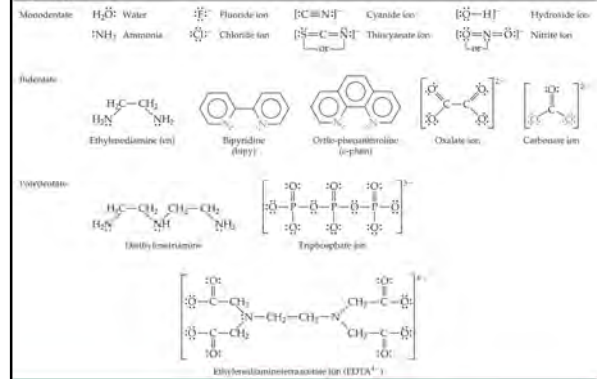


Chelating Effect

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

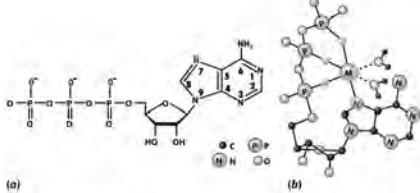
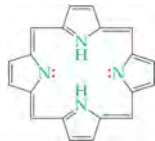


Ligand Type Examples



Chelating Agents

- Porphyrins (tetradentate ligands, in heme and chlorophyll)
- Adenosine triphosphate (ATP)

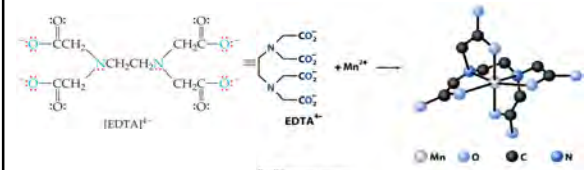


EDTA

Ethylenediaminetetraacetic acid (H_4EDTA or H_4Y)
 Ethylenediaminetetraacetate anion (EDTA^{4-} or Y^{4-})

Ethylenediaminetetraacetate, mercifully abbreviated EDTA, has six donor atoms.

EDTA is a primary standard material.



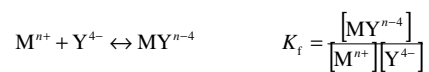
Some Metals Form 7 or 8 Coordinate Complexes



EDTA Complexes

- EDTA forms 1:1 complexes with most metals (Not with Group 1A metals)
- EDTA complexes are usually stable water soluble complexes with high formation constants

- **Formation constant, K_f** (or **stability constant**):



- K_f could have been defined for any form of EDTA

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	Tl ¹⁺	35.3
Na ⁺	1.86	Ce ³⁺	23.4 ^a	Bi ³⁺	27.8 ^a
K ⁺	0.8	Mn ³⁺	25.2	Ce ⁴⁺	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
Se 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 ³⁺	15.5	Gd ³⁺	17.35
Sr ²⁺	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
Cv 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		
Tl ¹⁺	21.3	In ³⁺	24.9		

NOTE: The stability constants are the equilibrium constants for the reaction $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$ 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. F. Harvey, R. M. Joshi, and B. J. Messinger, 2017 Critical Scientific Institute Consensus of Metal Complexes, NIST Standard Reference Database 46, Gaithersburg, MD, 20815.
 Table 12-2 Quantitative Chemical Analysis, Seventh Edition © 2012 W. H. Freeman and Company.

pH affects EDTA titration

Acid-Base Properties of EDTA:

H₆Y²⁺

EDTA is a hexaprotic system (H₆Y²⁺) with 4 carboxylic acids and 2 ammoniums

pK₁ = 0.0 pK₂ = 1.5 pK₃ = 2.0 pK₄ = 2.66
 pK₅ = 6.16 pK₆ = 10.24

pH: $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$

↑

H₀Yⁿ⁻⁴

Fraction of EDTA in the form Y⁴⁻

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

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

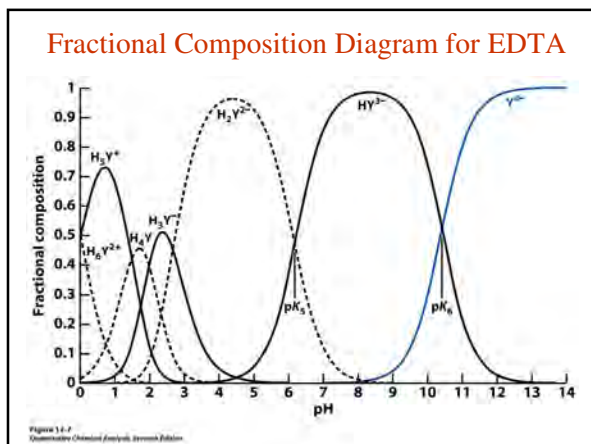
$$\alpha_{Y^{4-}} = \frac{K_1 K_2 K_3 K_4 K_5 K_6}{[H^+]^6 + [H^+]^5 K_1 + [H^+]^4 K_1 K_2 + [H^+]^3 K_1 K_2 K_3 + [H^+]^2 K_1 K_2 K_3 K_4 + [H^+] K_1 K_2 K_3 K_4 K_5 + K_1 K_2 K_3 K_4 K_5 K_6}$$

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 © 2012 W. H. Freeman and Company.



Conditional Formation Constant

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

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

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)



at pH = 10.00, $K_f' = \alpha_{Y^{4-}} K_f = (0.30)(10^{10.65}) = 1.3 \times 10^{10}$

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

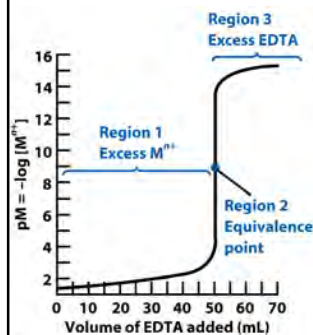


Conc _i	0	0	0.1
Conc _f	x	x	0.1-x

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

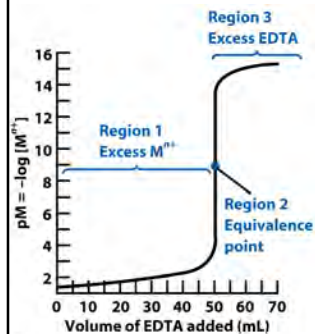
$$= 3.5 \times 10^{-4} \text{ M at pH} = 6$$

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: $[\text{M}^{n+}] = [\text{EDTA}]$ Some free M^{n+} generated by $\text{MY}^{n-4} \leftrightarrow \text{M}^{n+} + \text{EDTA}$
3. Excess EDTA. Virtually all metal in MY^{n-4} form.

EDTA Titration Curve



1. Titration reaction: $\text{M}^{n+} + \text{EDTA} \rightleftharpoons \text{MY}^{n-4} \quad K_f' = \alpha_{Y^{4-}} K_f$
2. Reaction completes at each point in the titration if K_f' is large.
3. Plot $\text{pM} (= -\log[\text{M}^{n+}])$ vs. volume of EDTA added

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

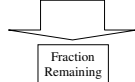
- 5.00 ml, Before the equivalence point
- 25.00 ml, At the equivalence point
- 26.00 ml, After the equivalence point

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 → before the equivalence point

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



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

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-}

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



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

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

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

EDTA Titration Curve

EXAMPLE: Derive a titration curve for the titration of 50.0 mL of 0.040 M Ca^{2+} (buffered at $\text{pH}=10$) 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

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

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

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

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

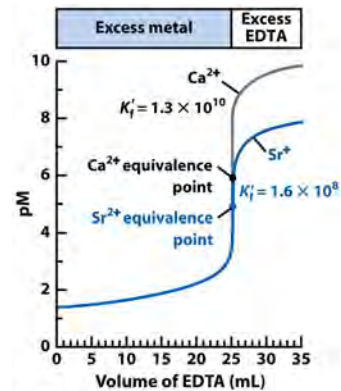


Figure 12-11
Quantitative Chemical Analysis, Seventh Edition
© 2001 W. H. Freeman and Company

pH affects the titration of Ca^{2+} with EDTA

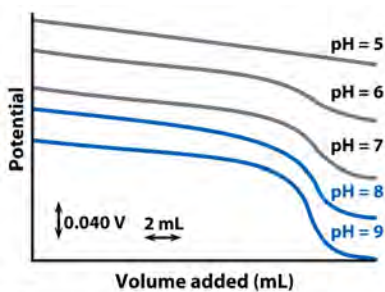


Figure 12-9
Quantitative Chemical Analysis, Seventh Edition
© 2001 W. H. Freeman and Company

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 tris(hydroxymethyl)aminomethane)

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

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

K_f'' is the effective formation constant at a fixed concentration of auxiliary complexing agent.

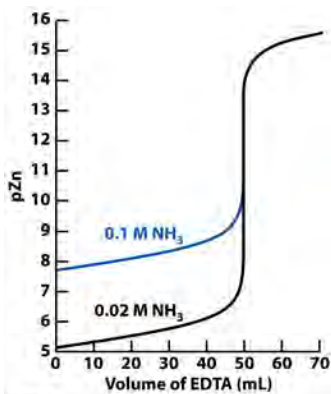


Figure 12-12
Quantitative Chemical Analysis, Seventh Edition
© 2001 W. H. Freeman and Company

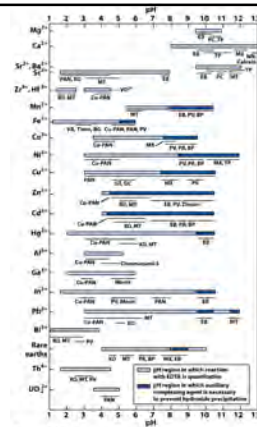


Figure 12-14

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 ₁ = 8.1 pK ₂ = 12.4	H ₂ In ³⁻ red HIn ²⁻ blue In ⁻ orange	Wine red
Eriochrome black T		pK ₁ = 6.3 pK ₂ = 11.6	H ₂ In ³⁻ red HIn ²⁻ blue In ⁻ orange	Wine red
Hexamide		pK ₁ = 9.2 pK ₂ = 10.9	H ₂ In ³⁻ red + violet HIn ²⁻ blue In ⁻ blue	Yellow (with Cu ²⁺ , Ni ²⁺ , Co 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 triethanolamine plus 2.5 mL of absolute ethanol; solution is stable for months; best used for titrations above pH 6.3.

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

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

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

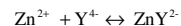
Table 12-3 part 1
Quantitative Chemical Analysis, Seventh Edition
© 2003 W. H. Freeman and Company

EDTA Titration Techniques

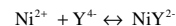
- Direct titration:** analyte is titrated with standard EDTA with solution buffered at a pH where K_f' is large
- Back titration:** known excess of EDTA is added to analyte. Excess EDTA is titrated with 2nd metal ion.

Example: 25.0 mL of an unknown Ni²⁺ solution was treated with 25.00 mL of 0.05283 M Na₂EDTA. The pH of the solution was buffered to 5.5 and then back-titrated with 17.61 mL of 0.02299 M Zn²⁺. What was the unknown Ni²⁺ in M?

$$\text{mol EDTA} = (25.00 \text{ mL})(0.05283 \text{ M}) = 1.32 \text{ mmol EDTA}$$



$$\text{mol Zn}^{2+} = (17.61 \text{ mL})(0.02299 \text{ M}) = 0.4049 \text{ mmol Zn}^{2+}$$



$$\text{mol Ni}^{2+} = 1.321 \text{ mmol EDTA} - 0.4049 \text{ mmol Zn}^{2+} = 0.916 \text{ mmol}$$

$$\text{M Ni}^{2+} = (0.916 \text{ mmol}) / (25.00 \text{ mL}) = 0.0366 \text{ M}$$

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.