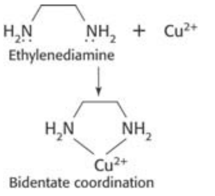
VI. COMPLEXOMETRIC (EDTA) TITRATIONS

(Chapter 11, and L. G. Hargis: Analytical Chemistry: Principles and Techniques (1988) Prentice Hall, Inc.)

Introduction

Most metal ions can accept unshared pairs of electrons from an anion or molecule to form *coordinate covalent bonds*. Usually metals accept 2, 4 or 6 e^- pairs (coordination number)



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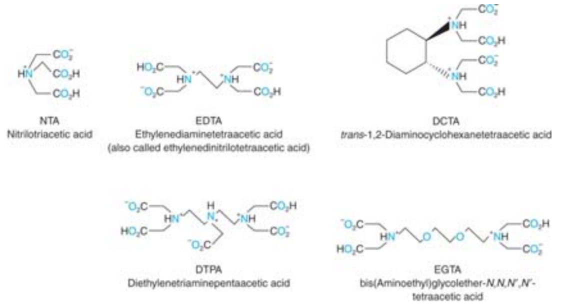
Molecule containing donor atom = ligand

Product resulting from reaction between metal ion and ligand = complex ion or (metal) complex

Ligands with a single donor atom = monodentate (e.g. CN^-, NH_3)
Multidentate ligands have multiple donor atoms and coordinate with a metal ion to form a ring structure = chelate ('claw')

The geometry of the complex can be linear (2 ligands), square planar or tetrahedral (4 ligands), octahedral (6 ligands), or other.



Aminocarboxylic acids as synthetic chelating agents. When a carboxylate O atom binds to a metal ion, it loses its proton

FIGURE 11-4 Structures of analytically useful chelating agents. Nitrilotriacetic acid (NTA) tends to form 2:1 (ligand:metal) complexes with metal ions, whereas the others form 1:1 complexes.

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ATP is a tetradentate ligand that binds to divalent ions (Mg^{2+}, Mn^{2+}, Ni^{2+}) through 4 of the 6 coordination positions (5 & 6: H_2O)

The biologically active form generally is the Mg^{2+} complex

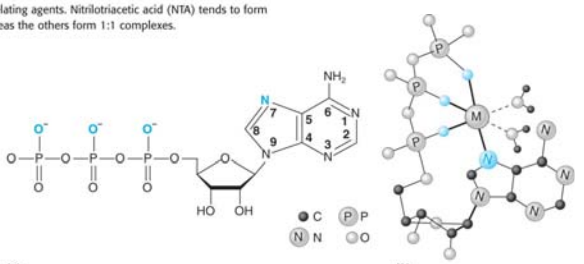
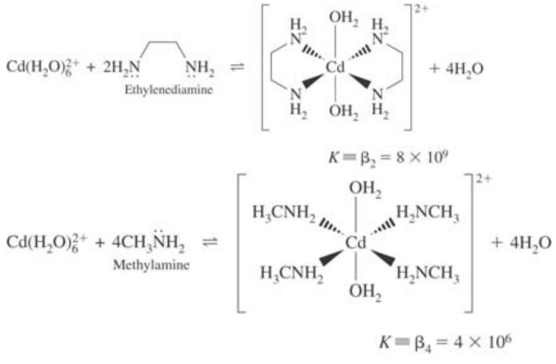


Fig. 11-2, Harris 8th Ed.

Chelate Effect: multidentate ligands form thermodynamically more stable complexes than similar monodentate ligands



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Explanation: $\Delta G = \Delta H - T\Delta S$

ΔH is ~ same for both reactions, but the change in entropy for reactions involving multidentate ligands is more favourable than for monodentate ligands (net gain of species; increases entropy)

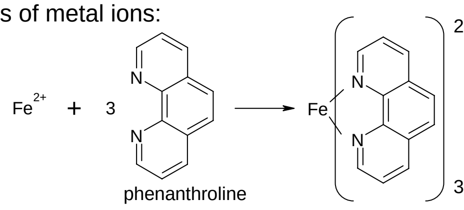
Note: complexation reactions in aqueous solution = ligand exchange reactions (no uncoordinated metal ions in aqueous solution!)

$Cu^{2+} + 4\ NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$ actually should be written as:

$Cu(H_2O)_4^{2+} + 4\ NH_3 \rightleftharpoons Cu(NH_3)_4^{2+} + 4\ H_2O$

Applications of metal complexes:

- As indicators, for titrations (see further) or for direct determination of trace amounts of metal ions:



Ferroin (red)

- Chemical masking: to decrease concentration of a free metal ion to a level where an interfering reaction will not occur
  e.g. in the determination of Ca^{2+} or Mg^{2+} with EDTA, CN^- is added to complex Zn^{2+}, Cd^{2+} and Hg^{2+} which would otherwise also react with EDTA

- Titration of metal ions: complexometric titrations

Does not work well with monodentate ligands. Most metal ions have a coordination number of 4 or 6 and react with that many ligands; e.g. Bi^{3+}

$$Bi^{3+} + Cl^- \rightleftharpoons BiCl^{2+} \qquad K_1 = \frac{[BiCl^{2+}]}{[Bi^{3+}][Cl^-]} = 160$$

$$BiCl^{2+} + Cl^- \rightleftharpoons BiCl_2^+ \qquad K_2 = \frac{[BiCl_2^+]}{[BiCl^{2+}][Cl^-]} = 20$$

$$BiCl_2^+ + Cl^- \rightleftharpoons BiCl_3 \qquad K_3 = \frac{[BiCl_3]}{[BiCl_2^+][Cl^-]} = 200$$

$$BiCl_3 + Cl^- \rightleftharpoons BiCl_4^- \qquad K_4 = \frac{[BiCl_4^-]}{[BiCl_3][Cl^-]} = 10$$

$$K_{overall} = K_1K_2K_3K_4 = 6.4 \times 10^6$$

For a titration, we want a single reaction that essentially goes to completion at the EP. For most monodentate ligands, the individual K's are small and similar in magnitude; at any given time during the titration, there will be a mixture of complexes present → no sharp end point

Multidentate ligands are useful for titrations: react in a single step and have large K's (under the right conditions). Ethylenediaminetetraacetic acid (EDTA) is most widely used ligand

Complexing agents find wide applicability in many aspects of our lives; for instance, EDTA is used:

- as a food additive (e.g. 'Versene'): to complex cofactors of naturally present enzymes, and bacterial/fungal enzymes; to complex metal ions that can catalyze oxidation of flavours and colours
  Added to mayonnaise, canned beans, soft drinks, beer etc.
- in detergents: to chelate Fe^{3+} (replacement of polyphosphate)
- for treatment of heavy metal toxicity (e.g. Pb^{2+}, Cd^{2+})) = chelation therapy; and emergency treatment of hypercalcemia

EDTA:

Forms strong 1:1 complexes with most metal ions (binding through 4 O and 2 N atoms)

Usually, the 6-coordinate species is formed; for large metal ions, ring-strain can be relieved, which opens up 1 to 3 extra coordination positions (e.g. a total of 9 for Pu^{4+}). These are occupied by H_2O molecules.

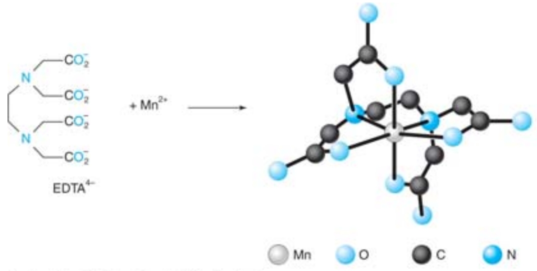


FIGURE 11-1 EDTA forms strong 1:1 complexes with most metal ions, binding through four oxygen and two nitrogen atoms. The six-coordinate geometry of Mn^{2+}-EDTA found in the compound KMnEDTA · $2H_2O$ was deduced from X-ray crystallography. [From J. Stein, J. P. Fackler, Jr., G. J. McClune, J. A. Fee, and L. T. Chan, "Reactions of Mn-EDTA and MnCyDTA Complexes with O_2^-: X-Ray Structure of KMnEDTA · $2H_2O$," *Inorg. Chem.* **1979**, *18*, 3511.]

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Note: the exact coordination number is not important for titrations

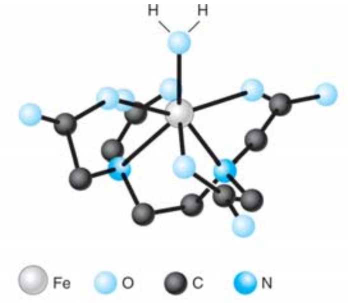

FIGURE 11-8 Seven-coordinate geometry of $Fe(EDTA)(H_2O)^-$. Other metal ions that form seven-coordinate EDTA complexes include Fe^{2+}, Mg^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ru^{3+}, Cr^{3+}, Co^{3+}, V^{3+}, Ti^{3+}, In^{3+}, Sn^{4+}, Os^{4+}, and Ti^{4+}. Some of these same ions also form six-coordinate EDTA complexes. Eight-coordinate complexes are formed by Ca^{2+}, Er^{3+}, Yb^{3+}, and Zr^{4+}. [From T. Mizuta, J. Wang, and K. Miyoshi, "A 7-Coordinate Structure of Fe(III)-EDTA," *Bull. Chem. Soc. Japan* **1993**, *66*, 2547.]

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EDTA is a hexaprotic system: H_6Y^{2+}; neutral acid is tetraprotic: H_4Y
(usual reagent: $Na_2H_2Y{\bullet}2H_2O$ – dissolves better than H_4Y)

$pK_1 = 0.0$
$pK_2 = 1.5$
$pK_3 = 2.00$
$pK_4 = 2.69$
$pK_5 = 6.13$
$pK_6 = 10.37$

pK_1-pK_4: COOH groups
pK_5-pK_6: NH groups

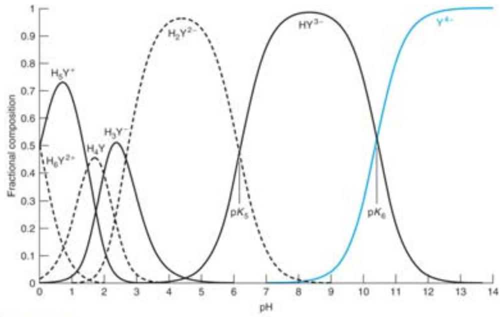

FIGURE 11-7 Fractional composition diagram for EDTA.

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Below pH 10.4, most of the EDTA is *not* in the Y^{4-} form

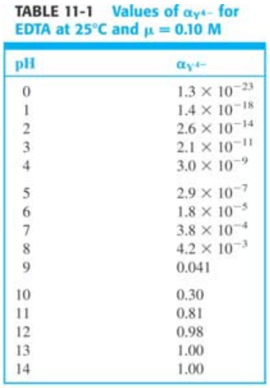

TABLE 11-1 Values of $\alpha_{Y^{4-}}$ for EDTA at 25°C and $\mu = 0.10$ M

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

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

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

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[EDTA] refers to total concentration of all *uncomplexed* EDTA species (*free* EDTA)

$$\alpha_{Y^{4-}} = \frac{K_1K_2K_3K_4K_5K_6}{D}$$

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(Conditional) Formation Constants (or Stability Constants):

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

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K_f defined in terms of Y^{4-}– but other species react to lesser extent with M^{n+} as well. Notice that K_f depends on $[Y^{4-}]$, therefore depends on $[H^+]$

K_f often large (> 10^{15})

Mostly 6-coordinate species (octahedral complexes), but larger metal ions can accommodate more ligands

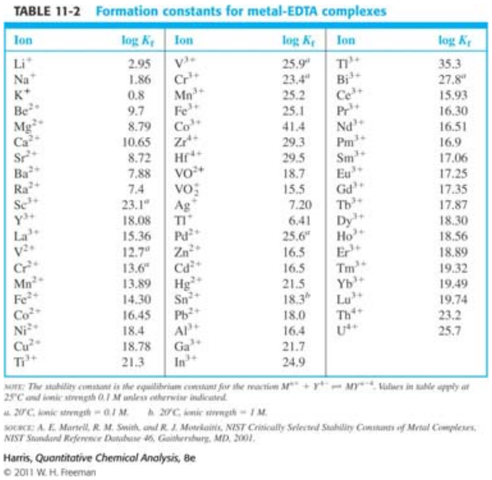

TABLE 11-2 Formation constants for metal-EDTA complexes

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.

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, 2001.

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For EDTA to form a complex with a metal ion, the protons of the carboxyl groups have to be removed. In strongly basic solution, this is because of reaction with OH^-, and most metals react quantitatively with EDTA at pH > 10. In more acidic solutions, the metal ion must be able to displace these protons, and the ability to do so varies from metal to metal. By varying the pH, the reactivity of EDTA towards metal ions can be regulated.

$[Y_4^-] = [EDTA]\,\alpha_{Y_4^-}$

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}]\,[EDTA]\,\alpha_{Y_4^-}}$$

At a fixed pH, $\alpha_{Y_4^-}$ is a constant that can be combined with K_f

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

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Conditional Formation Constant

Allows us to look at EDTA complex formation as if all the uncomplexed EDTA is in one form:
$M^{n+} + EDTA \rightleftharpoons MY^{n-4}$

EXAMPLE: Calculate the concentrations of free Ca^{2+} in a solution of 0.10 M CaY^{2-} at pH 10.00 and 6.00 ($K_f = 10^{10.65}$)

At pH 10: $K'_f = (0.30)\,(10^{10.65}) = 1.34 \times 10^{10}$

At pH 6: $K'_f = (1.8 \times 10^{-5})\,(10^{10.65}) = 8.0 \times 10^{5}$

$\alpha_{Y_4^-}$ values from Table 11-1

$$\underset{x}{Ca^{2+}} + \underset{x}{EDTA} \rightleftharpoons \underset{0.10 - x}{CaY^{2-}}$$

$$\frac{[CaY^{2-}]}{[Ca^{2+}]\,[EDTA]} = \frac{0.10 - x}{x^2} \begin{array}{l} = 1.34 \times 10^{10} \text{ at pH 10} \rightarrow x = 2.7 \times 10^{-6}\text{ M} \\ = 8.0 \times 10^{5} \text{ at pH 6} \rightarrow x = 3.5 \times 10^{-4}\text{ M} \end{array}$$

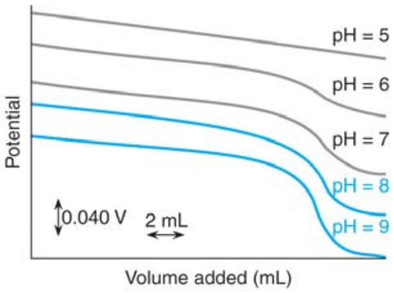

Fig. 11-10, Harris 8th Ed.

For a titration, K has to be large enough in order for the reaction to go to 'completion' (e.g. 99.9%). Below pH 8, titrations of Ca^{2+} with EDTA do not give a sharp end point - K'_f is too small for 'complete' reaction.

For other metal ions with higher K_f, the cut off pH value will be lower.

EDTA Titrations:

$M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$ $\quad K'_f = K_f \bullet \alpha_{Y_4^-}$

Try to determine $[M^{n+}]$ at each point during titration; plot pM *vs.* V_{EDTA}

EXAMPLE: titration of 50.0 mL of 0.0400 M Ca^{2+} (buffered to pH 10) with 0.0800 M EDTA

$K'_f = 1.34 \times 10^{10}$ $\quad V_{EP} = 25.0$ mL

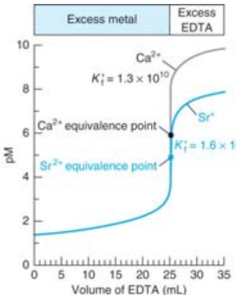

FIGURE 11-12 Theoretical titration curves for the reaction of 50.0 mL of 0.040 0 M metal ion with 0.080 0 M EDTA at pH 10.00.

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- *Before EP*: e.g. 5.0 mL EDTA added:

$$[Ca^{2+}] = \frac{25.0 - 5.0}{25.0} \; (0.0400) \; \frac{50.0}{50.0 + 5.0} = 0.0291 \text{ M or } pCa^{2+} = 1.54$$

- *At EP*: exactly enough EDTA added to react with all Ca^{2+}:

$$[CaY^{2-}] = 0.0400 \; \frac{50.0}{50.0 + 25.0} = 0.0267 \text{ M}$$

A small amount of Ca^{2+} is generated by dissociation of CaY^{2-}:

$$\underset{0.0267 - x}{CaY^{2-}} \rightleftharpoons \underset{x}{Ca^{2+}} + \underset{x}{EDTA}$$

$$K'_f = \frac{[CaY^{2-}]}{[Ca^{2+}]\,[EDTA]} = 1.34 \times 10^{10} = \frac{0.0267 - x}{x^2} \rightarrow x = 1.4 \times 10^{-6} \text{ M}$$

or $pCa^{2+} = 5.85$

- *After EP*: excess EDTA:

e.g. 26.0 mL EDTA solution added:

$$[EDTA] = 0.0800 \; \frac{26.0 - 25.0}{50.0 + 26.0} = 1.05 \times 10^{-3} \text{ M}$$

$$[CaY^{2-}] = 0.0400 \; \frac{50.0}{50.0 + 26.0} = 0.0263 \text{ M} \quad \left(= 0.0267 \; \frac{75.0}{75.0 + 1.0} \right)$$

$$K'_f = \frac{[CaY^{2-}]}{[Ca^{2+}]\,[EDTA]} = 1.34 \times 10^{10} \rightarrow Ca^{2+} = 1.9 \times 10^{-9} \text{ M}$$

or $pCa^{2+} = 8.73$

Auxiliary Complexing Agents:

EDTA titrations are best performed at high pH, where $[Y^{4-}]$ is high.

Problem: precipitation of metals as metal hydroxides / oxides!

Solution: use auxiliary complexing agent (e.g. ammonia, triethanolamine, tartaric acid) that binds metals strong enough to prevent hydroxides from being formed, but weakly enough that metals are released when EDTA is added.

Metal M forming two complexes with auxiliary complexing ligand L:

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

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

β= *overall* or *cumulative* formation constant
$\beta_n = K_1K_2 \ldots K_n$

$$\alpha_M = \frac{[M]}{C_M}$$

Fraction of M that is not complexed; C_M = total conc. of M (= [M] + [ML] + [ML$_2$])

Mass balance for M: $C_M = [M] + [ML] + [ML_2]$
$= [M] + \beta_1 [M]\,[L] + \beta_2 [M]\,[L]^2$
$= [M]\,(1 + \beta_1[L] + \beta_2[L]^2)$

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

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EXAMPLE: ammonia complexes of Zn: $Zn(NH_3)^{2+}$, $Zn(NH_3)_2^{2+}$, $Zn(NH_3)_3^{2+}$, $Zn(NH_3)_4^{2+}$ ($\beta_1 = 10^{2.18}$; $\beta_2 = 10^{4.43}$; $\beta_3 = 10^{6.74}$; $\beta_4 = 10^{8.70}$)

Fraction of free Zn^{2+} in the presence of 0.10 M NH_3? (ignore: $NH_3 \rightleftharpoons NH_4^+$)

$$\alpha_{Zn^{2+}} = \frac{1}{1 + 10^{2.18}(0.10) + 10^{4.43}(0.10)^2 + 10^{6.74}(0.10)^3 + 10^{8.70}(0.10)^4}$$

$$= 1.8 \times 10^{-5}$$

EDTA titrations in the presence of auxiliary complexing agents:

EXAMPLE: Titration of 50.0 mL of 1.00×10^{-3} M Zn^{2+} with 1.00×10^{-3} M EDTA at pH 10.00 in the presence of 0.10 M NH_3 (V_{EP} = 50.0 mL)

With $\alpha_{Zn^{2+}} = 1.8 \times 10^{-5}$ (see above) and $\alpha_{Y^{4-}} = 0.30$ (slide 8), we find a new conditional formation constant:

$$K_f'' = \alpha_{Zn^{2+}}\,\alpha_{Y^{4-}}\,K_f = (1.8 \times 10^{-5})\,(0.30)\,(10^{16.5}) = 1.7 \times 10^{11}$$

→ Takes into account that only some of the zinc is in the Zn^{2+} form, and only some of the EDTA is in the Y^{4-} form

- *Before EP* (e.g. 20.0 mL added):

$$C_{Zn^{2+}} = \frac{50.0 - 20.0}{50.0}(1.00 \times 10^{-3})\frac{50.0}{50.0 + 20.0} = 4.3 \times 10^{-4}\ M$$

$\hookrightarrow$ Zn^{2+} not bound to EDTA; most of this is bound to NH_3

$$[Zn^{2+}] = \alpha_{Zn_{2+}} C_{Zn^{2+}} = (1.8 \times 10^{-5})(4.3 \times 10^{-4}) = 7.7 \times 10^{-9}$$

or $pZn^{2+} = 8.11$

Note that $[Zn^{2+}][OH^-]^2 = (10^{-8.11})(10^{-4})^2 = 10^{-16.11} < K_{sp}$ of $Zn(OH)_2$ $(10^{-15.5})$

- *At EP* (50.0 mL added):

$$[ZnY^{2-}] = 1.00 \times 10^{-3}\ \frac{50.0}{50.0 + 50.0} = 5.00 \times 10^{-4}\ M$$

A small amount of Zn^{2+} is generated by dissociation of ZnY^{2-}:

$$\underset{(5.00 \times 10^{-4} - x)}{ZnY^{2-}} \rightleftharpoons \underset{x}{Zn^{2+}} + \underset{x}{EDTA}$$

$$K''_f = \frac{[ZnY^{2-}]}{C_{Zn^{2+}}[EDTA]} = 1.7 \times 10^{11} = \frac{(5.00 \times 10^{-4}) - x}{x^2} \rightarrow x = C_{Zn^{2+}} = 5.4 \times 10^{-8}\ M$$

$$[Zn^{2+}] = \alpha_{Zn_{2+}} C_{Zn^{2+}} = (1.8 \times 10^{-5})(5.4 \times 10^{-8}) = 9.7 \times 10^{-13}\ M$$

or $pZn^{2+} = 12.01$

- *After EP* (e.g. 60.0 mL EDTA added): no need to bother about NH_3, since both $[ZnY^{2-}]$ and [EDTA] are known:

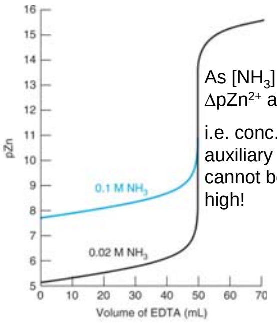
$$[ZnY^{2-}] = 1.00 \times 10^{-3}\ \frac{50.0}{50.0 + 60.0} = 4.5 \times 10^{-4}\ M$$

$$[EDTA] = 1.00 \times 10^{-3}\ \frac{60.0 - 50.0}{50.0 + 60.0} = 9.1 \times 10^{-5}\ M$$

$$K'_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][EDTA]} = \alpha_{Y_{4^-}} K_f = (0.30)(10^{16.5})$$

$$= \frac{4.5 \times 10^{-4}}{[Zn^{2+}]\ 9.1 \times 10^{-5}} \rightarrow [Zn^{2+}] = 5.2 \times 10^{-16}\ M$$

$pZn^{2+} = 15.28$



As $[NH_3]$ ↑, ΔpZn^{2+} at EP ↓

i.e. conc. of auxiliary ligand cannot be too high!

FIGURE 11-14 Titration curves for the reaction of 50.0 mL of 1.00×10^{-3} M Zn^{2+} with 1.00×10^{-3} M EDTA at pH 10.00 in the presence of two different concentrations of NH_3.
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Metal Ion Indicators:

Exhibit colour change when metal ion is bound – *must bind metal less strongly than EDTA*

e.g. MgIn + EDTA $\rightleftharpoons$ MgEDTA + In (at pH 10)

Red Blue

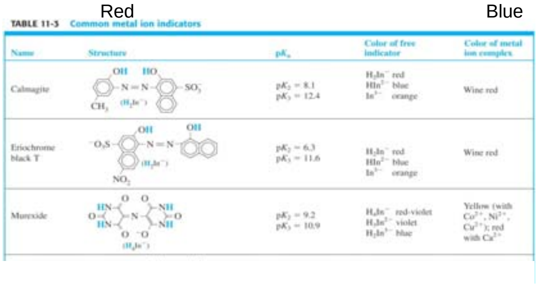

TABLE 11-3 Common metal ion indicators

Name	Structure	pK_a	Color of free indicator	Color of metal ion complex
Calmagite	(H_2In^-)	$pK_2 = 8.1$ $pK_3 = 12.4$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Eriochrome black T	(H_2In^-)	$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Murexide	(H_4In^-)	$pK_2 = 9.2$ $pK_3 = 10.9$	H_4In^- red-violet H_3In^{2-} violet H_2In^{3-} blue	Yellow (with Co^{2+}, Ni^{2+}, Cu^{2+}); red with Ca^{2+}

Analyte (Mg^{2+}) binds strongly to In at beginning of titration; EDTA added during titration reacts with free Mg^{2+}. When all free Mg^{2+} is used up, the EDTA displaces the small amount of In from MgIn, giving the colour change.

Most metal indicators are also acid-base indicators; the colour of the free indicator depends on the pH. Not all transitions will be easy to see (spectrophotometer can be useful, but is less convenient)

Hg electrodes and ion-selective electrodes are also used in EDTA titrations.

Standardization of EDTA solutions:

Although available as a primary standard, EDTA is often standardized against a Ca^{2+} solution (from primary standard $CaCO_3$).

Eriochrome black T or Calmagite are commonly used as indicator, but they form only a weak complex with Ca^{2+}:

$$\underset{}{Ca^{2+}} + \underset{\text{blue}}{HIn^{2-}} \rightleftharpoons \underset{\text{red}}{CaIn^-} + H^+$$

In early stages of the titration, the equilibrium lies to the right because there is a large excess of Ca^{2+}. As the titration proceeds, the equilibrium shifts to the left, causing a gradual colour change before the EP.

To circumvent this problem, a small amount of Mg^{2+} (binds the indicator more strongly) is added to the EDTA solution; the titration now becomes:

$$Ca^{2+} + MgY^{2-} \rightleftharpoons CaY^{2-} + Mg^{2+} \qquad K_f\,(CaY^{2-}) > K_f\,(MgY^{2-})$$

$$Mg^{2+} + CaIn^- \rightleftharpoons MgIn^- + Ca^{2+} \qquad K_f\,(CaIn^-) < K_f\,(MgIn^-)$$

$MgIn^-$ (red) will remain essentially undissociated until the EP is reached.

EDTA Titration Techniques:

- Direct Titration

  Analyte solution is buffered to a pH where K_f' is large, and colour of free indicator is different from metal-indicator complex. If auxiliary complexing agent is added, the stability of the metal-(auxiliary complexing agent) complex must be less than that of the metal-EDTA complex.

- Back Titration

  Is necessary if the analyte precipitates in the absence of EDTA, if it reacts too slowly with EDTA, or if it blocks the indicator (i.e. cannot be displaced by EDTA from the indicator).

  A known excess of EDTA is added to the analyte solution; the excess is titrated with a standard solution of another metal ion, *which must not displace analyte from EDTA (often* Mg^{2+} *is used)!*

  If the analyte precipitates without EDTA, an acidified solution of analyte (metals in general dissolve better at low pH) is treated with excess EDTA, then adjusted to the required higher pH.

EXAMPLE: Analysis of Ni^{2+} with a back titration using standard Zn^{2+} at pH 5.5

To 25.00 mL of the Ni^{2+} solution, 25.00 mL of 0.05283 M Na_2Y_4 is added. After pH adjustment and addition of indicator, 17.71 mL of 0.02299 M Zn^{2+} is required to reach the end point. What is $[Ni^{2+}]$?

(Answer worked in class)

Other EDTA titration techniques include displacement titrations (for metals with no suitable indicator e.g. Hg^{2+}), and indirect titrations of anions that precipitate with certain metal ions (e.g. analysis of SO_4^{2-}, after precipitation with Ba^{2+}, filtration, treatment with excess standard EDTA, and back titration with Mg^{2+}).

Application: determining the 'hardness' of water with EDTA:

Water hardness is a measure of the total concentration of alkaline earth (Group 2) ions, mainly Ca^{2+} and Mg^{2+}.

Usually expressed as the equivalent #mg's of $CaCO_3$/L, e.g. if $[Ca^{2+}] + [Mg^{2}] = 1$ mM, the hardness is 100 mg $CaCO_3$/L (MM $CaCO_3$ = 100).

http://en.wikipedia.org/wiki/Limescale

'Soft' water has a hardness < 60 mg $CaCO_3$/L, and can lead to corrosion of pipes. 'Hard' water has a hardness > 270 mg $CaCO_3$/L, and can lead to deposition of Ca and Mg minerals (limescale in water heaters, pipes etc.). Ca^{2+} also precipitates soap:
$Ca^{2+} + 2\,RCOO^- \rightarrow Ca(OOCR)_2$

Temporary hardness is caused by $Ca(HCO_3)_2$ and can be removed by boiling:

$$CaCO_3\downarrow + CO_2\uparrow + H_2O \rightleftharpoons Ca(HCO_3)_2$$

$CaCO_3$ precipitates and the water left is now softer, but $CaCO_3$ has to be removed or (some of) it will dissolve again.

Permanent hardness is mainly caused by Ca^{2+}/Mg^{2+} sulfates and chlorides – cannot be removed by boiling, but can be removed by ion exchange (replacement of Ca^{2+}/Mg^{2+} by Na^+).

Determination of the hardness of water involves direct titration with EDTA of Ca^{2+} and Mg^{2+} (together) at pH 10 (NH_3 buffer). Fe^{3+} may have to be reduced with ascorbic acid to Fe^{2+} first, and then Fe^{2+} is masked with CN^- (which also masks several other minor metal ions).

If the titration is performed at pH = 12-13 (without NH_3; NaOH or KOH is used instead), $Mg(OH)_2$ precipitates and Ca^{2+} can be determined separately.

Several test kits are available that allow for quick determination of water hardness on site. With test strips, the colour of the strip indicates the hardness, and rough results can be obtained in seconds. Liquid based tests are also used and produce more accurate results.