17 Complexation Reaction and Titrations

17A The Formation of Complexes

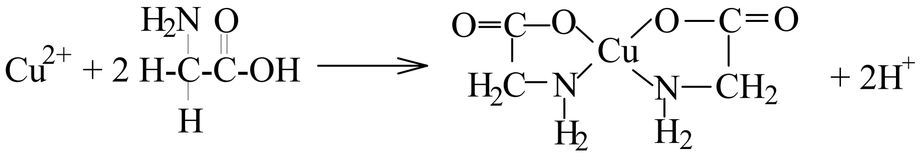
Ligand: an ion or a molecule that forms a covalent bond with a cation or a neutral metal atom by donating a pair of electrons that are then share by the two.

→ water, ammonia and halide ions are common inorganic ligand.

Coordination number: the no. of covalent bonds it tends to form with electron donor species. → 2, 4 and 6

Chelate: a cyclic complex formed when a cation is bonded by two or more donor groups contained in a single ligand.

$Cu(NH_3)_4^{2+}$; $Cu(NH_2CH_2COO)_2$; $CuCl_4^{2-}$



Dentate: means having toothlike

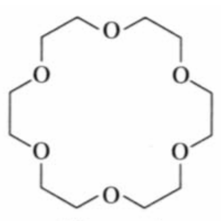
unidentate (a single donor group), bi, tri, tetra, penta, hexa-dentate

Tetradentate & hexadentate ligands are more satisfactory as titrants than ligands with a lesser no. of donor groups for two reasons:

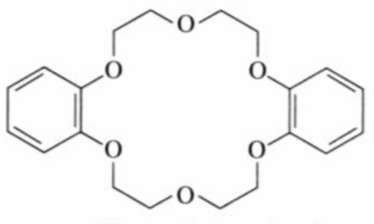
a. react more completely & sharper end points

b. tend to form 1:1 complexes

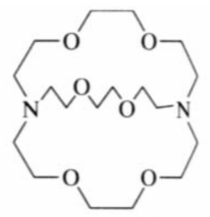
macrocycle: Metal ion-cyclic organic compound



18-crown-6



dibenzo-18-crown-6



cryptand 2,2,2

17A-1 Complexations Equilibria

$M + L \Leftrightarrow ML$ M: metal ion

$ML + L \Leftrightarrow ML_2$ L: ligand

$\vdots \qquad \vdots$

$ML_{n-1} + L \Leftrightarrow ML_n$

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

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

$M + 3L \Leftrightarrow ML_3 \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3} = K_1K_2K_3$

$\vdots$

$M + nL \Leftrightarrow ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n} = K_1K_2K_3\cdots K_n$

$$\alpha_M = \frac{1}{1+\beta_1[L]+\beta_2[L]^2+\beta_3[L]^3+\cdots+\beta_n[L]^n}$$

$$\alpha_{ML} = \frac{\beta_1[L]}{1+\beta_1[L]+\beta_2[L]^2+\beta_3[L]^3+\cdots+\beta_n[L]^n}$$

$$\alpha_{ML2} = \frac{\beta_2[L]^2}{1+\beta_1[L]+\beta_2[L]^2+\beta_3[L]^3+\cdots+\beta_n[L]^n}$$

$$\alpha_{ML_n} = \frac{\beta_n[L]^n}{1+\beta_1[L]+\beta_2[L]^2+\beta_3[L]^3+\cdots+\beta_n[L]^n}$$

17A-2 The Formation of Insoluble species

$M_xA_y(s) \Leftrightarrow xM^{y+}(aq) + yA^{x-}(aq) \qquad K_{sp} = [M^{y+}]^x[A^{x-}]^y$

17A-3 Ligands That Can Protonate

Complexation with protonating ligands

For a diprotic acid: oxalic acid → Ox^{2-}, HOx^-, H_2Ox

$C_T = [H_2Ox] + [HOx^-] + [Ox^{2-}]$

$$\alpha_0 = \frac{[H_2Ox]}{C_T} = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_1 = \frac{[HOx^-]}{C_T} = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_2 = \frac{[Ox^{2-}]}{C_T} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \quad ; \quad [Ox^{2-}] = C_T\alpha_2$$

in very basic solution: $\alpha_2 \approx 1$, → $[Ox^{2-}] \approx C_T$

Conditional formation constants

pH effect on conditional formation constants

Formation constant (K_1) for the reaction of Fe^{3+} with oxalate:

$$K_1 = \frac{[(\mathrm{FeOx})^+]}{[\mathrm{Fe}^{3+}][\mathrm{Ox}^{2-}]} = \frac{[(\mathrm{FeOx})^+]}{[\mathrm{Fe}^{3+}]\alpha_2 c_\mathrm{T}}$$

Conditional, or effective, formation constants

pH-dependent, apply *at a single pH only*.

$$K_1^{'} = \alpha_2 K_1 = \frac{[(\mathrm{FeOx})^+]}{[\mathrm{Fe}^{3+}]c_\mathrm{T}}$$

17B Titrations with Inorganic Complexing Agents

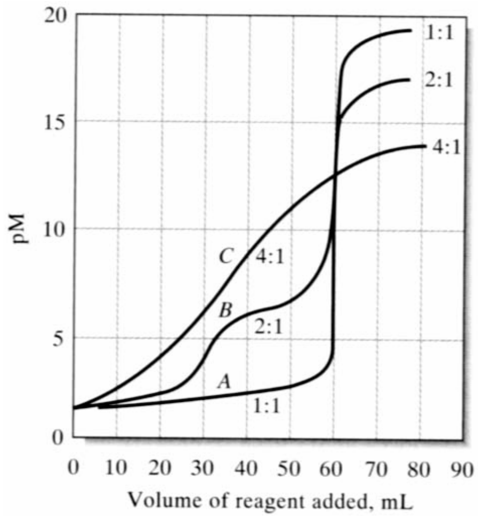


Fig. 17-1 Titration curves for complexometric titrations. Titration of 60.0 mL of a soln that is 0.020 M in M with (curve A) a 0.020-M soln of the tetradentate ligand D to give MD as the product; (curve B) a 0.040-M soln of the bidentate ligand B to give MB_2; and (curve C) a 0.080-M soln of the unidentate ligand A to give MA. The overall formation constant for each product is 10^{20}.

Table 17-1 Typical Inorganic Complex-Formation Titration

Titrant	Analyte	Remarks
$Hg(NO_3)_2$	Br^-, Cl^-, SCN^-, CN^-, thiourea	Products are neutral Hg(II) complexes; various indicators used
$AgNO_3$	CN^-	Product is $Ag(CN)_2^-$; indicator is I^-; titrate to first turbidity of AgI
$NiSO_4$	CN^-	Product is $Ni(CN)_4^{2-}$; indicator is I^-; titrate to first turbidity of AgI
KCN	Cu^{2+}, Hg^{2+}, Ni^{2+}	Products are $Cu(CN)_4^{2-}$, $Hg(CN)_2$, $Ni(CN)_4^{2-}$; various indicator used

17C Organic Complexing Agents

$$n\mathrm{HX(org)} + \mathrm{M}^{n+}\mathrm{(aq)} \Leftrightarrow \mathrm{MX}_n\mathrm{(org)} + n\mathrm{H}^+\mathrm{(aq)}$$

Table 17-2 Organic reagents for extracting metals

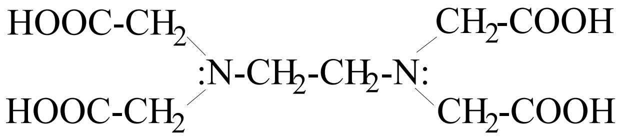
Reagent	Metal Ions extracting Metals	Solvents
8-Hydroxyquinoline	Zn^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, many others	Watetr → Chloroform ($CHCl_3$)
Diphenylthiocarbazone (dithizone)	Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, many others	Watetr → $CHCl_3$ or CCl_4
Acetylacetone	Fe^{3+}, Cu^{2+}, Zn^{2+}, U(VI), many others	Watetr → $CHCl_3$ or CCl_4 C_6H_6
Ammonium pyrrolidine dithiocarbamate	Transition metals	Watetr → Methyl isobutyl ketone
Tenoyltrifluoroacetone	Ca^{2+}, Sr^{2+}, La^{3+}, Pr^{3+}, other rare earths	Watetr → Benzene
Dibenzo-18-crown-6	Alkali metals, some alkaline earths	Watetr → Benzene

17D Aminocarboxylic Acid Titration

in 1945, Schwarzenbach

17D-1 Ethylenediaminetetraacetic acid (EDTA)

(ethylenedinitrilo)tetraacetic acid → hexadentate ligand



$$\begin{matrix} HOOC\text{-}CH_2 & & CH_2\text{-}COOH \\ & :N\text{-}CH_2\text{-}CH_2\text{-}N: & \\ HOOC\text{-}CH_2 & & CH_2\text{-}COOH \end{matrix}$$

(H_4Y)

EDTA is a tetrabasic acid

H_4Y

↓ $K_1 = 1.02 \times 10^{-2}$

H_3Y^-

↓ $K_2 = 2.14 \times 10^{-3}$

H_2Y^{2-}

↓ $K_3 = 6.92 \times 10^{-7}$

HY^{3-}

↓ $K_4 = 5.50 \times 10^{-11}$

Y^{4-}

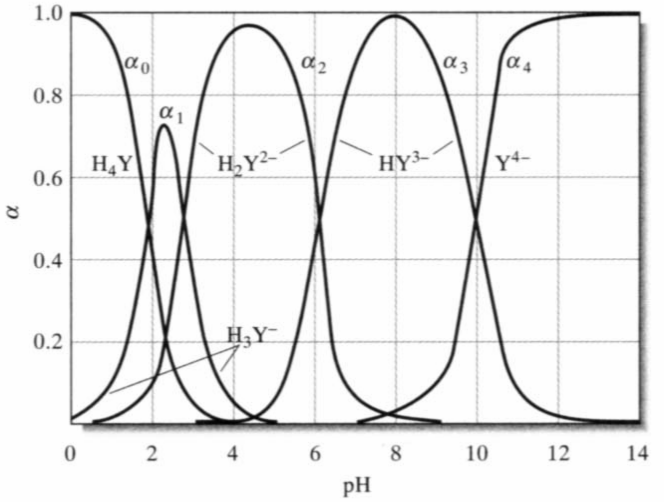
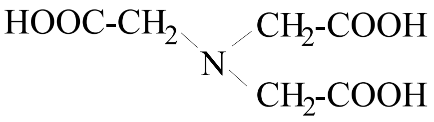


Fig. 17-2 Composition of EDTA solution as a function of pH.

Reagents for EDTA titrations

EDTA, H_4Y and $Na_2H_2Y \cdot 2H_2O$

Nitrilotriacetic acid (NTA)



$\mathrm{HOOC\text{-}CH_2\text{-}N(CH_2\text{-}COOH)_2}$

17D-2 Complexes of EDTA and metal ions

Complexes of EDTA and Metal Ions (**1:1**)

$$Ag^+ + Y^{4-} \Leftrightarrow AgY^{3-}$$

$$Al^{3+} + Y^{4-} \Leftrightarrow AlY^-$$

$$M^{n+} + Y^{4-} \Leftrightarrow MY^{(n-4)+}$$

$$K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}][Y^{4-}]}$$

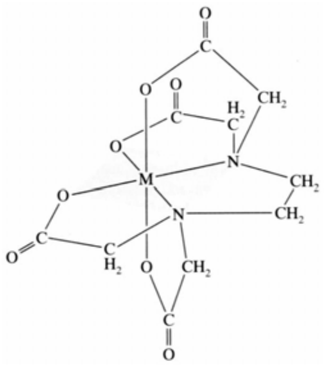


Fig. 17-3 Structure of a metal/EDTA complex. (Hexadentate ligand)

Table 17-3 Formation constants for EDTA complexes

Cation	K_{MY}	$\log K_{MY}$	Cation	K_{MY}	$\log K_{MY}$
Ag^+	2.1×10^7	7.32	Cu^{2+}	6.3×10^{18}	18.80
Mg^{2+}	4.9×10^8	8.69	Zn^{2+}	3.2×10^{16}	16.50
Ca^{2+}	5.0×10^{10}	10.70	Cd^{2+}	2.9×10^{16}	16.46
Sr^{2+}	4.3×10^8	8.63	Hg^{2+}	6.3×10^{21}	21.80
Ba^{2+}	5.8×10^7	7.76	Pb^{2+}	1.1×10^{18}	18.04
Mn^{2+}	6.2×10^{13}	13.79	Al^{3+}	1.3×10^{16}	16.13
Fe^{2+}	2.1×10^{14}	14.33	Fe^{3+}	1.3×10^{25}	25.1
Co^{2+}	2.0×10^{16}	16.21	V^{3+}	7.9×10^{25}	25.9
Ni^{2+}	4.2×10^{18}	18.62	Th^{4+}	1.6×10^{23}	23.2

17D-3 Equilibrium calculations involving EDTA

$$\alpha_4 = \frac{[Y^{4-}]}{c_T}$$

C_T: [*uncomplexed* EDTA]

$$C_T = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^-] + [H_4Y]$$

Conditional Formation Constants

$$M^{n+} + Y^{4-} \Leftrightarrow MY^{(n-4)+} \qquad K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]\alpha_4 c_T}$$

$$K'_{MY} = \alpha_4 K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]c_T}$$

only at the pH for which α_4 is applicable

Computing α_4 Values for EDTA Solutions

$$\alpha_4 = \frac{K_1K_2K_3K_4}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4}$$

$$\alpha_4 = \frac{K_1K_2K_3K_4}{D}$$

$$D = [H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4$$

Table: Values of α_4 for EDTA in Solutions of Various pH

pH	α_4	pH	α_4	pH	α_4	pH	α_4
2.0	3.71×10^{-14}	5.0	3.54×10^{-7}	8.0	5.39×10^{-3}	11.0	0.85
3.0	2.51×10^{-11}	6.0	2.25×10^{-5}	9.0	5.21×10^{-2}	12.0	0.98
4.0	3.61×10^{-9}	7.0	4.8×10^{-4}	10.0	0.35	13.0	1.00

Ex. 17-1 Calculate the molar Y^{4-} conc. in a 0.0200 M EDTA solution that has been buffered to a pH of 10.00.

At pH 10.00, α_4 is 0.35

$[Y^{4-}] = \alpha_4 C_T = (0.35)(0.0200) = 7.0 \times 10^{-3}$ M

Calculation of the cation concentration in EDTA solutions

Ex. 17-2 Calculate the equilibrium conc. of Ni^{2+} in a solution with an analytical NiY^{2-} conc. of 0.0150 M at pH (a) 3.0 and (b) 8.0.

$Ni^{2+} + Y^{4-} \Leftrightarrow NiY^{2-}$ $\quad K_{NiY} = \frac{[NiY^{2-}]}{[Ni^{2+}][Y^{4-}]} = 4.2 \times 10^{18}$

$[NiY^{2-}] = 0.0150 - [Ni^{2+}]$

If we assume $[Ni^{2+}] << 0.0150$, $[NiY^{2-}] \approx 0.0150$

$[Ni^{2+}] = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^-] + [H_4Y] = C_T$

$$K'_{NiY} = \frac{[NiY^{2-}]}{[Ni^{2+}]c_T} = \frac{[NiY^{2-}]}{[Ni^{2+}]^2} = \alpha_4 K_{NiY}$$

(a) pH 3.0 → $\alpha_4 = 2.5 \times 10^{-11}$, $\frac{0.0150}{[Ni^{2+}]^2} = 2.5 \times 10^{-11} \times 4.2 \times 10^{18} = 1.05 \times 10^8$

$$[Ni^{2+}] = \sqrt{1.43 \times 10^{-10}} = 1.2 \times 10^{-5} \text{M}$$

(b) pH 8.0 → $\alpha_4 = 5.4 \times 10^{-3}$, $K'_{NiY} = 5.4 \times 10^{-3} \times 4.2 \times 10^{18} = 2.27 \times 10^{16}$

$$[Ni^{2+}] = \sqrt{0.0150/(2.27 \times 10^{16})} = 8.1 \times 10^{-10} \text{M}$$

Ex. 17-3 Calculate the conc. of Ni^{2+} in a solution prepared by mixing 50.0 mL of 0.0300 M Ni^{2+} with 50.0 mL of 0.0500 M EDTA. The mixture is buffered to a pH of 3.00.

$C_{NiY^{2-}} = 50.0 \times 0.0300/100 = 0.0150$ M

$$c_{EDTA} = \frac{(50.0\times 0.0500)\text{mmol} - (50.0\times 0.0300)\text{mmol}}{100.0 \text{ mL}} = 0.0100\text{M}$$

assume $[Ni^{2+}] << [NiY^{2-}] \rightarrow [NiY^{2-}] = 0.0150 - [Ni^{2+}] \approx 0.0150$

$C_T = 0.0100$ M $\qquad K'_{NiY} = \frac{0.0150}{[Ni^{2+}]0.0100} = \alpha_4 K_{NiY}$

$$[Ni^{2+}] = \frac{0.0150}{0.0100\times 1.05\times 10^{8}} = 1.4\times 10^{-8} \text{ M}$$

17D-4 EDTA Titration Curves

Ex. 17-4 Derive a curve (pCa as a function of EDTA volume) for the titration of 50.0 mL of 0.00500 M Ca^{2+} with 0.0100 M EDTA in a solution buffered to pH 10.0.

$Ca^{2+} + Y^{4-} \Leftrightarrow CaY^{2-} \qquad K_{CaY} = 5.0 \times 10^{10}$

1. Calculating the conditional constant

$$K'_{CaY} = \frac{[CaY^{2-}]}{[Ca^{2+}]c_T} = \alpha_4 K_{CaY} = 0.35\times 5.0\times 10^{10} = 1.75\times 10^{10}$$

2. Preequivalence-point values for pCa (added 5.0 mL EDTA)

$$[Ca^{2+}] = \frac{50.0\times 0.00500 - 5.00\times 0.0100}{(50+5.00)} + c_T \cong 3.64\times 10^{-3} \text{ M}$$

pCa = -log 3.64 × 10^{-3} = 2.44

3. The equivalence-point pCa (added 25.0 mL EDTA)

$$c_{CaY^{2-}} = \frac{50.0\times 0.00500 \text{ mmol}}{(50+25.0) \text{ mL}} = 3.33\times 10^{-3} \text{ M}$$

$[Ca^{2+}] = C_T$, $\qquad [CaY^{2-}] = 0.00333 - [Ca^{2+}] \approx 0.00333$ M

$$K'_{CaY} = \frac{[CaY^{2-}]}{[Ca^{2+}]c_T} \approx \frac{c_{CaY^{2-}}}{[Ca^{2+}]^2} \text{ ; } [Ca^{2+}] = \sqrt{\frac{c_{CaY^{2-}}}{K'_{CaY}}} = \sqrt{\frac{0.00333}{1.75\times 10^{10}}} = 4.36\times 10^{-7} \text{ M}$$

pCa = -log 4.36 × 10^{-7} = 6.36

4. Postequivalence-point pCa (add 26.0 mL EDTA)

$$c_{CaY^{2-}} = \frac{50.0\times 0.00500 \text{ mmol}}{(50+26.0) \text{ mL}} = 3.29\times 10^{-3} \text{ M}$$

$$c_{EDTA} = \frac{26.0\times 0.0100 - 50.0\times 0.00500}{(50+26.0)} = 1.32\times 10^{-4} \text{ M}$$

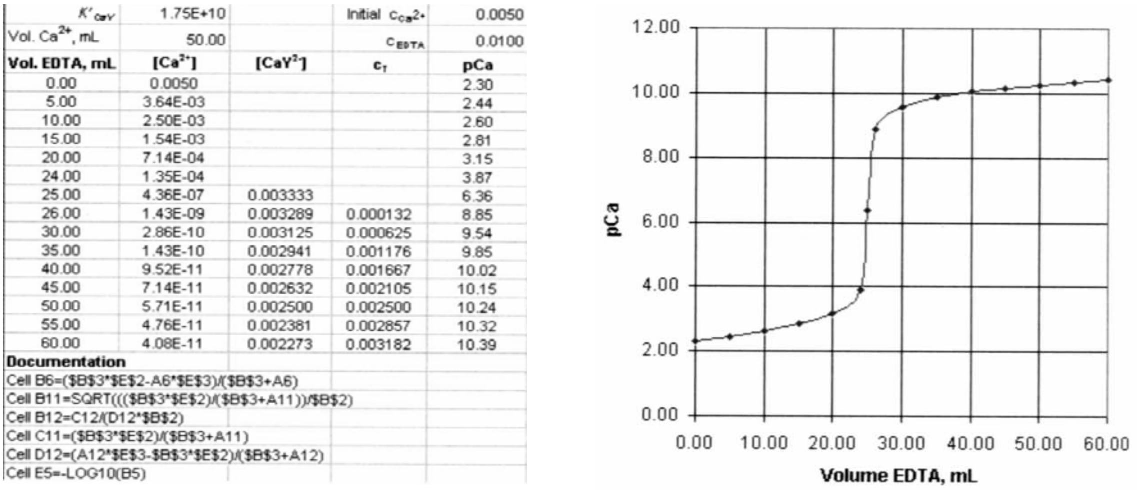
$[CaY^{2-}] = 3.29 \times 10^{-3} - [Ca^{2+}] \approx 3.29 \times 10^{-3}$ M

$c_T = c_{EDTA} + [Ca^{2+}] \approx c_{EDTA} = 1.32 \times 10^{-4}$ M

$$K'_{CaY} = \frac{[CaY^{2-}]}{[Ca^{2+}]c_T} \approx \frac{c_{CaY^{2-}}}{[Ca^{2+}] \times c_{EDTA}}$$

$$[Ca^{2+}] = \frac{c_{CaY^{2-}}}{K'_{CaY} \times c_{EDTA}} = \frac{3.29 \times 10^{-3}}{1.75 \times 10^{10} \times 1.32 \times 10^{-4}} = 1.42 \times 11^{-9}$$

$$\mathbf{pCa = -log\ 1.42 \times 10^{-9} = 8.85}$$



K'_{CaY}	1.75E+10		Initial $c_{Ca^{2+}}$	0.0050
Vol. Ca^{2+}, mL	50.00		c_{EDTA}	0.0100
Vol. EDTA, mL	**$[Ca^{2+}]$**	**$[CaY^{2-}]$**	**c_T**	**pCa**
0.00	0.0050			2.30
5.00	3.64E-03			2.44
10.00	2.50E-03			2.60
15.00	1.54E-03			2.81
20.00	7.14E-04			3.15
24.00	1.35E-04			3.87
25.00	4.36E-07	0.003333		6.36
26.00	1.43E-09	0.003289	0.000132	8.85
30.00	2.86E-10	0.003125	0.000625	9.54
35.00	1.43E-10	0.002941	0.001176	9.85
40.00	9.52E-11	0.002778	0.001667	10.02
45.00	7.14E-11	0.002632	0.002105	10.15
50.00	5.71E-11	0.002500	0.002500	10.24
55.00	4.76E-11	0.002381	0.002857	10.32
60.00	4.08E-11	0.002273	0.003182	10.39
Documentation				
Cell B6=(B3*E2-A6*E3)/(B3+A6)				
Cell B11=SQRT(((B3*E2)/(B3+A11))/B2)				
Cell B12=C12/(D12*B2)				
Cell C11=(B3*E2)/(B3+A11)				
Cell D12=(A12*E3-B3*E2)/(B3+A12)				
Cell E5=-LOG10(B5)				

Fig. 17-5 Spreadsheet for the titration of 50.00 mL of 0.00500 M Ca^{2+} with 0.0100 M EDTA in a solution buffered at pH 10.0.

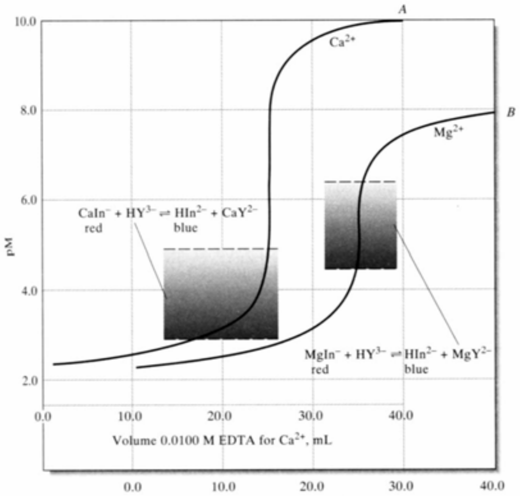


Fig. 17-6 EDTA titration curves for 50.00 mL of 0.00500 M Ca^{2+} ($K'_{CaY}=1.75\times10^{10}$) and Mg^{2+} ($K'_{MgY}=1.72\times10^{8}$) at pH 10.0.

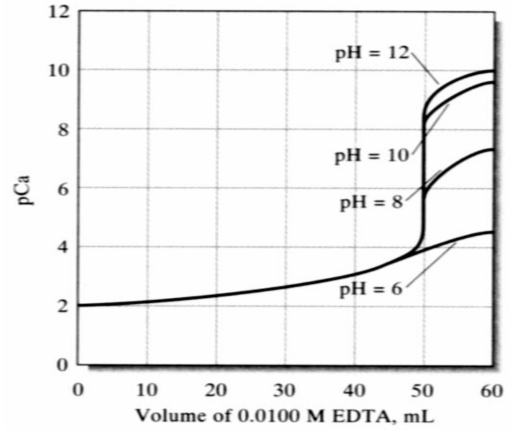


Fig. 17-7 Influence of pH on the titration of 0.0100 M Ca^{2+} with 0.0100 M EDTA.

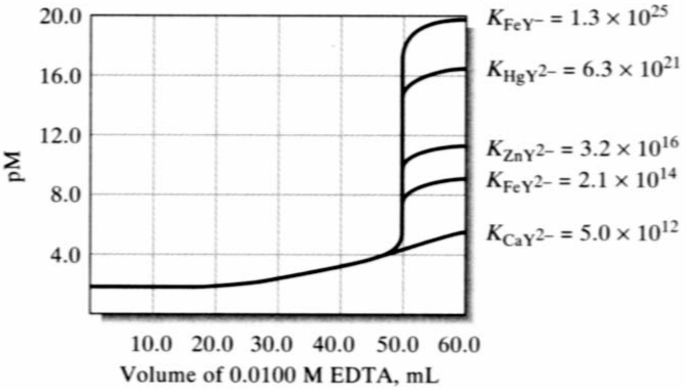
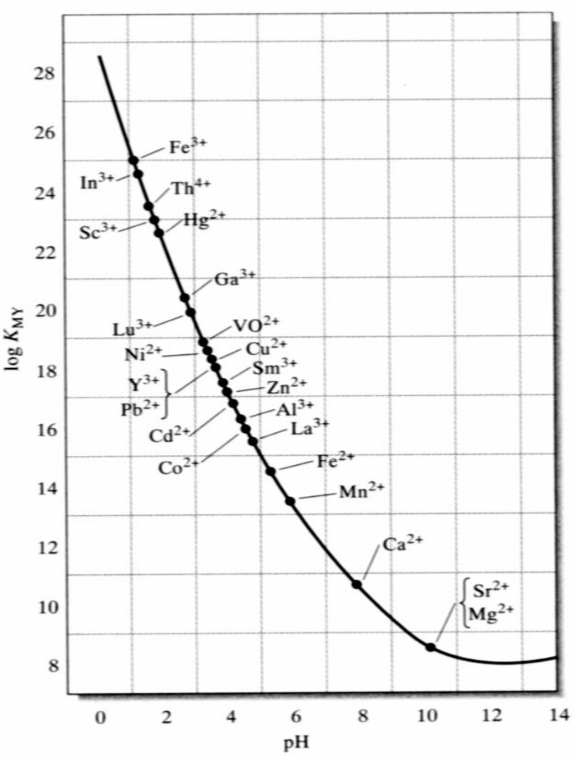


Fig. 17-8 Titration curves for 50.0 mL of 0.0100 M of various cations at pH 6.0.

Fig. 17-9 Min. pH needed for satisfactory titration of various cations with EDTA.



17D-5 The effect of other complexing agents on EDTA titration curves

Auxiliary complexing agents must be used in EDTA titrations to prevent precipitation of the analyte as a hydrous oxide. Such reagents cause end points to be **less sharp**.

ex: Zn ion in NH_3 solution (buffer soln)

in basic : $Zn^{2+} + 2OH^- \Leftrightarrow Zn(OH)_2(s)$

$Zn(NH_3)_3^{2+} + HY^{3-} \Leftrightarrow ZnY^{2-} + 3NH_3 + NH_4^+$

$Zn(NH_3)_3^{2+}$, $Zn(NH_3)_2^{2+}$, and $Zn(NH_3)^{2+}$

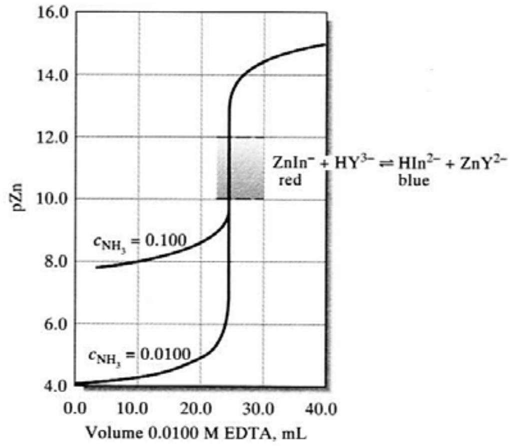
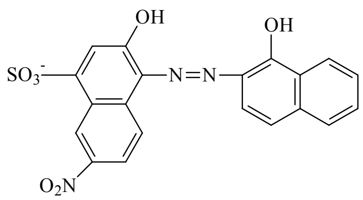


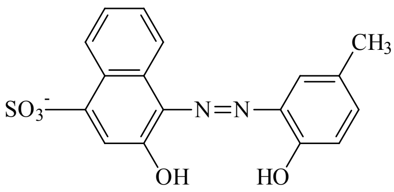
Fig. 17-10 Influence of ammonia conc. on the end point for the titration of 50.0 mL of 0.00500 M Zn^{2+}. Solutions are buffered to pH 9.00.

17D-6 Indicator for EDTA titration

Reilley & Barnard: nearly 200 organic compounds

***Eriochrome Black T (EBT)** ***Calmagite**





$H_2O + H_2In^- \Leftrightarrow HIn^{2-} + H_3O^+ \quad K_1 = 5 \times 10^{-7}$

red blue

$H_2O + HIn^{2-} \Leftrightarrow In^{3-} + H_3O^+ \quad K_2 = 2.8 \times 10^{-12}$

blue orange

$MIn^- + HY^{3-} \Leftrightarrow HIn^{2-} + MY^{2-}$

red **blue**

pH	color	predominant form
1 - 6.9	purple-red	H_2EBT^-
6.9 - 11.5	blue	$HEBT^{2-}$
11.5 - 14	orange	EBT^{3-}

Ex. 17-5 Determine the transition range for Eriochrome Black T in titrations of Mg^{2+} and Ca^{2+} at pH 10.0 given that (a) the K_2 for the indicator is

$$HIn^{2-} + H_2O \Leftrightarrow In^{3-} + H_3O^+ \quad K_2 = \frac{[H_3O^+][In^{3-}]}{[HIn^{2-}]} = 2.8\times10^{-12}$$

(b) K_f for $MgIn^-$: $Mg^{2+} + In^{3-} \Leftrightarrow MgIn^-$ $\quad K_f = \frac{[MgIn^-]}{[Mg^{2+}][In^{3-}]} = 1.0\times10^{7}$

(c) K_f for $CaIn^-$: $Ca^{2+} + In^{3-} \Leftrightarrow CaIn^-$ $\quad K_f = 2.5 \times 10^{5}$

$$\frac{[MgIn^-][H_3O^+]}{[HIn^{2-}][Mg^{2+}]} = 2.8\times10^{-12} \times 1.0\times10^{7} = 2.8\times10^{-5}$$

$$[Mg^{2+}] = \frac{[MgIn^-]}{[HIn^{2-}]}\times\frac{[H_3O^+]}{2.8\times10^{-5}} = \frac{[MgIn^-]}{[HIn^{2-}]}\times\frac{1.0\times10^{-10}}{2.8\times10^{-5}}$$

For a color change; $[MgIn^-]/[HIn^{2-}]$ = from 10/1 to 1/10 (10~0.1)

$[Mg^{2+}] = 3.6 \times 10^{-5}$ M ~ 3.6×10^{-7} M $\Rightarrow$ pMg = 5.4 ± 1.0

$$[Ca^{2+}] = \frac{[CaIn^-]}{[HIn^{2-}]}\times\frac{1.0\times10^{-10}}{2.8\times10^{-12}\times2.5\times10^{5}}$$

$[Ca^{2+}] = 1.4 \times 10^{-3}$ M ~ 1.4×10^{-5} M $\Rightarrow$ pCa = 3.8 ± 1.0

17D-7 Titration Methods Employing EDTA

1. Direct-titration methods: 40 cations

Based on indicators for the analyte: for Mg^{2+}: indicator → EBT or calmagite

Based on indicators for an added metal ion

for Ca^{2+} : indicator → EBT + small amount of $MgCl_2$ or Mg-EDTA

Potentiometric Methods

Spectrophotometric Methods

2. Back-titration methods:

used when no suitable indicator is available, when the reaction between analyte and EDTA is slow, or when the analyte forms ppts at the pH required for its titration.

Titrant : EDTA and standard Mg^{2+} or Zn^{2+} soln

MgEDTA or ZnEDTA complexes must less stable than analyte-EDTA complex.

3. Displacement method :

used when no indicator for an analyte is available

sample + excess Mg^{2+}- or Zn^{2+}-EDTA complex

$$MgY^{2-} + M^{2+} \text{ (analyte cation)} \quad \Leftrightarrow \quad MY^{2-} + \underset{\substack{\uparrow \\ \text{standard EDTA solution}}}{Mg^{2+}}$$

* **Masking agent**: a complexing agent that reacts selectively with a component from interfering in an analysis.

ex: CN^- for Mg^{2+} and Ca^{2+} analysis, in the presence of ions- Cd, Co, Cu, Ni, Zn and Pd ions.

17D-8 The Scope of EDTA Titration

Metal cation exception of the alkali metal ions

17D-9 The Determining of Water Hardness

Water "hardness": the capacity of cations (Ca, Mg and heavy-metal ions) in the water to replace the Na or K ions in soaps and form sparingly soluble products.

Hardness expressed in terms of the conc. of $CaCO_3$ equivalent to the total conc. of all multivalent cations in the sample.

Titrant: EDTA, pH: **10 → NH_3 buffer**

Indicator: Calmagite or EBT + Mg-EDTA, End-point color : **pink-red → blue**

***Calculation of Titration Results**

Conc. of EDTA titrant expressed in

(a). **Molarity (M)**

$$\text{EDTA (M)} = \frac{\text{mmole of EDTA}}{\text{mL}} = \frac{\text{mole of EDTA}}{\text{L}}$$

(b). **Titer** or EDTA for a certain ion or compound

$$\text{EDTA titer} = \frac{\text{mg of species}}{\text{mL EDTA}} = \frac{\text{g of species}}{\text{L EDTA}}$$

Ex. Exactly 0.1001 g of pure $CaCO_3$ (100.1 g/mol) is dissolved in 100.0 mL of water. A 10.0-mL aliquot is titrated with 9.00 mL of EDTA. Calculate the molarity of the EDTA and its titer for $CaCO_3$.

$$\text{M of EDTA} = \frac{100.1\,\text{mg} \times \frac{10}{100} \times \frac{1\,\text{mmol}}{100.1\,\text{mg}}}{9.00\,\text{mL}} = 0.0111\,\text{M}$$

$$\text{EDTA titer} = \frac{100.1\,\text{mg} \times \frac{10}{100}}{9.00\,\text{mL}} = 1.112\,\text{mg/mL}$$

Ex. A 50.00-mL water sample requires 12.00 mL of 0.0100 M EDTA. Calculate the hardness of this sample as ppm $CaCO_3$ (100.1 g/mol).

mg $CaCO_3$ = (12.00 mL)(0.0100 M)(100.1 mg /mmole) = 12.01 mg

ppm $CaCO_3$ = 12.01 mg/0.0500 L = 240.2 ppm