Chapter 17

Complexation Reactions and Titrations

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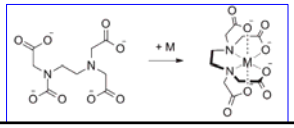
Complexation Titration

- Also knowns as complexometric titration, complexometry, or chelatometry
- One of the classical titrimetric methods developed for the rapid and quantitative chemical analysis of metal ions.
- Based on complex formation between metal ion (cation) and complexing agent (ligand).



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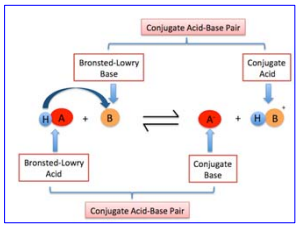
Bronsted-Lowery vs Lewis Acid-Base Concept



- **Lewis base:** electron pair donor (ligand, can be molecules or ions)
- **Coordinate covalent bond:** a bond formed when both electrons of the bond are donated by one atom.

- **Lewis acid:** electron pair acceptor (metal cations, M^{n+})

$$A + B: \rightleftharpoons A \leftarrow B$$

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$Ag^+ + 2(:NH_3) \rightleftharpoons [H_3N:Ag:NH_3]^+$

Electron cofiguration Ag $[Kr]4d^{10}5s^{1}5p^{0}$

Ag^+ $[Kr]4d^{10}5s^{0}5p^{0}$, sp hybrid orbitals

accept 2 pairs of electrons, linear geometry

- **Complex ion:** A charged compound (+ or -) consisting of coordinate covalent bond.
- **Complex (Coordinate compound):** a compound of neutral complex species.

$[Ag(NH_3)_2]^+$ *vs* $[Ag(NH_3)_2](OH)$

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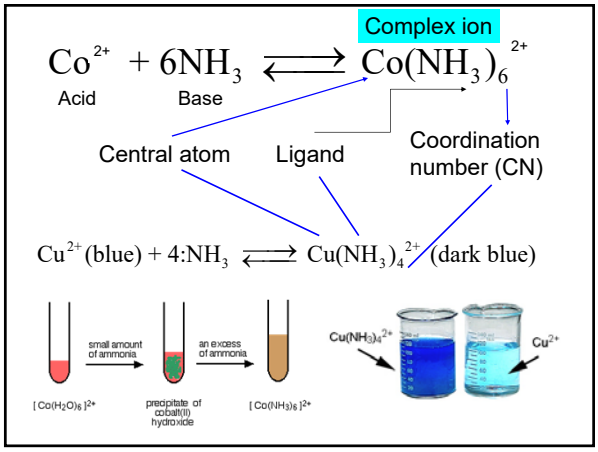

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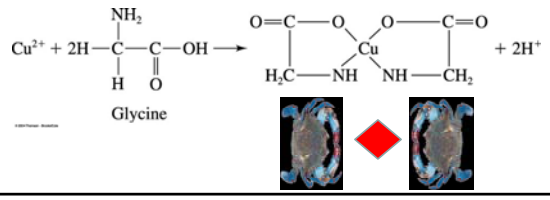
- When a ligand has a single complexing or donor group in its structure, it is said to be *unidentate* (single-toothed),

$:NH_3$, Cl^- $Co(NH_3)_6^{2+}$, $CuCl_4^{2-}$

- when there are two groups, it is *bidentate*,



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- When there are three (four) groups, it is called *tridentate (tetradentate)* ligand, etc.
- When a *bidentate* (or higher number of donor groups present in the ligand) forms a complex with a metal cation, we call the resulting compound a *metal chelate* ("kee'late"-claw).
- As titrants, *multidentate ligands*, particularly those with 4 to 6 donor groups have the advantage that they usually react in a single step process, and their reactions with the metal cation are more complete than their *unidentate* counterparts.

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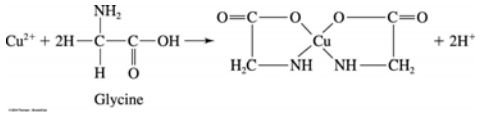
Chelate Effect

- The ability of multidentate ligands to form more stable metal complexes than those formed by similar monodentate ligands
- Often results from the formation of 5-membered "ring" with metal and two atoms on the ligand



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Complexation Equilibria

$$Cu^{2+} + NH_3 \overset{K_1}{\rightleftharpoons} Cu(NH_3)^{2+}$$

$$Cu(NH_3)^{2+} + NH_3 \overset{K_2}{\rightleftharpoons} Cu(NH_3)_2^{2+}$$

$$Cu(NH_3)_2^{2+} + NH_3 \overset{K_3}{\rightleftharpoons} Cu(NH_3)_3^{2+}$$

$$Cu(NH_3)_3^{2+} + NH_3 \overset{K_4}{\rightleftharpoons} Cu(NH_3)_4^{2+}$$

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

$$K_f = K_1 K_2 K_3 K_4 = \beta_4$$

K_f (β_4) –formation constant

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• Complexation reactions occur in a stepwise fasion

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

$$ML + L \rightleftarrows ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftarrows ML_3 \qquad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

...

$$ML_{n-1} + L \rightleftarrows ML_n \qquad K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

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Formation Constants (β_i)

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

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

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

...

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

β_i : cumulated or collective formation constant with i L.

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Alpha (α) Values
Fraction of the Total Metal Concentration

$$\alpha_M = \frac{[M]}{c_M} \qquad \alpha_{ML} = \frac{[ML]}{c_M}$$

$$\alpha_{ML_2} = \frac{[ML_2]}{c_M} \qquad \alpha_{ML_n} = \frac{[ML_n]}{c_M}$$

$$c_M = [M] + [ML] + [ML_2] + ... + [ML_n]$$

$$= [M] + \beta_1[M][L] + \beta_2[M][L]^2 + ... + \beta_n[M][L]^n$$

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

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

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

$$\alpha_{ML_2} = \frac{\beta_2[L]^2}{1+\beta_1[L]+\beta_2[L]^2+\ldots+\beta_n[L]^n}$$

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

$\alpha_i = f(\beta_i,[L])$ [*vs.* $\alpha_i = f(K_a,[H^+])$]

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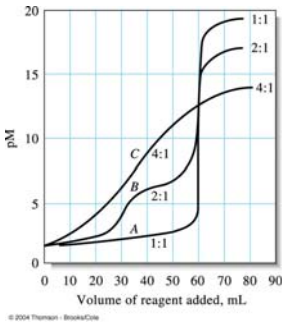
Titration Curves of ML_n



(A) Tetradentate ligand, 1:1
(B) Bidentate ligand 2:1
(C) Unidentate ligand, 4:1

Tetradentate or hexadentate ligands are more satisfactory as titrants than ligands with a lesser number of donor groups because their reactions with cations are more complete and they tend to form 1:1 complexes.

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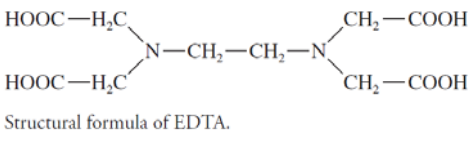
Ethylenediaminetetraacetic Acid (EDTA)



Structural formula of EDTA.

Most widely used complexometric titrant, Hexadentate ligand (4 –COOH+2 amino groups)

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EDTA

- It forms 1:1 complexes with most metals. (Not with Group 1A metals – Na, K, Li)
- Forms stable water soluble complexes.
- High formation constants.
- A primary standard material – a highly purified compound that serves as a reference material.

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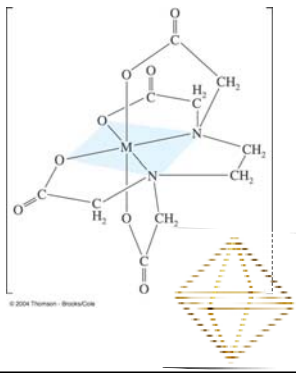
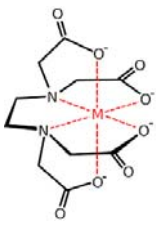
Octahedron Structure of EDTA-M





5 –
five membered rings

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

TABLE 17-4
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}	16.31	V^{3+}	7.9×10^{25}	25.9
Ni^{2+}	4.2×10^{18}	18.62	Th^{4+}	1.6×10^{23}	23.2

*Constants are valid at 20°C and ionic strength of 0.1.
Source: G. Schwarzenbach, Complexometric Titrations, London: Chapman and Hall, 1957, p. 8.

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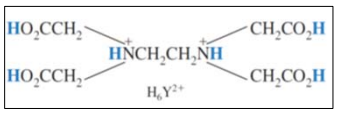
Acid-Base Properties (H_6Y^{2+})



$pK_1 = 0.0$ (CO_2H)	$pK_4 = 2.69$ (CO_2H)
$pK_2 = 1.5$ (CO_2H)	$pK_5 = 6.13$ (NH^+)
$pK_3 = 2.00$ (CO_2H)	$pK_6 = 10.37$ (NH^+)

pK applies at 25°C and $\mu = 0.1$ M, except pK_1 applies at $\mu = 1$ M

The first four values apply to carboxyl protons, and the last two are for the ammonium protons. The neutral acid is tetraprotic, with the formula H_4Y. A commonly used reagent is the disodium salt, $Na_2H_2Y \bullet 2H_2O$.

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EDTA (H_4Y) Disassociation

$$H_6Y^{2+} \underset{}{\overset{K_1}{\rightleftharpoons}} H_5Y^{+} \overset{K_2}{\rightleftharpoons}$$

$$H_4Y \overset{K_3}{\rightleftharpoons} H_3Y^{-} \overset{K_4}{\rightleftharpoons} H_2Y^{2-} \overset{K_5}{\rightleftharpoons} HY^{3-} \overset{K_6}{\rightleftharpoons} Y^{4-}$$

$$\alpha_0 \qquad \alpha_1 \qquad \alpha_2 \qquad \alpha_3 \qquad \alpha_4 (\text{or } \alpha_{Y^{4-}})$$

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

$$\alpha_4 = \frac{[Y^{4-}]}{c_T} = \frac{[Y^{4-}]}{[EDTA]} = \frac{[Y^{4-}]}{[H_6Y^{2+}]+[H_5Y^{+}]+[H_4Y]+[H_3Y^{-}]+[H_2Y^{2-}]+[HY^{3-}]+[Y^{4-}]}$$

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

Conditional formation constant:

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

$$K'_{MY} \le K_{MY} \text{ as } \alpha_4 \le 1.0$$

K'_{MY} is pH dependent!

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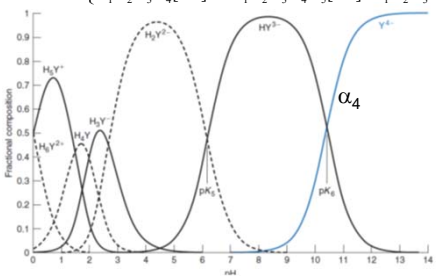
$$\alpha_4 = \frac{[Y^{4-}]}{c_T} = \frac{[Y^{4-}]}{[H_6Y^{2+}]+[H_5Y^{+}]+[H_4Y]+[H_3Y^{-}]+[H_2Y^{2-}]+[HY^{3-}]+[Y^{4-}]}$$

$$= K_1K_2K_3K_4K_5K_6 \Big/ \left\{ \begin{array}{l} [H^+]^6 + K_1[H^+]^5 + K_1K_2[H^+]^4 + K_1K_2K_3[H^+]^3 + \\ K_1K_2K_3K_4[H^+]^2 + K_1K_2K_3K_4K_5[H^+] + K_1K_2K_3K_4K_5K_6 \end{array} \right\}$$



Composition of EDTA solution as a function of pH.

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Excel Computing of Y^{4-} as a function of pH

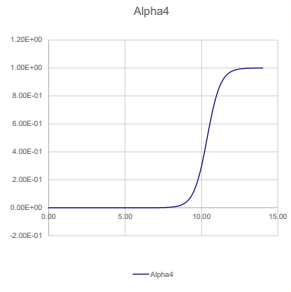

Table 12-1 Values of $\alpha_{Y^{4-}}$ for EDTA at 20°C and $\mu = 0.10$ M

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

Distribution of unprotonated form of Y^{4-} as a function of pH

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Example 17-4 Use speadsheet to construct the titration curve of pCa versus volume of EDTA for 50.0 mL of 0.00500 M Ca^{2+} being titrated with 0.0100 M EDTA in a solution buffered to a constant pH of 10.0

(1) pH = 10.0, α_4 = 0.35,
K_{CaY} = 5.0 e10, $K'_{CaY} = \alpha_4 K_{CaY}$ = 1.75e10

(2) Equivalence point:
v_{EDTA} = 50x0.00500/0.0100 = 25.0 mL

(3) Initial pCa: $[Ca^{2+}]$ = 0.00500 M, pCa = 2.30

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(4) Pre-equivalence point:
Ca (excess) + Y ⇔ CaY (disassociation negligible)

$[Ca] = [50.00x0.00500-v_{EDTA}x0.0100]/(50.00+v_{EDTA})$

v_{EDTA} (mL)	[Ca]	pCa
5.00	3.64e-3	2.44
10.00	2.46e-3	2.61
20.00	7.14e-4	3.15
24.00	1.35e-4	3.87

(5) At equivalence point: CaY ⇔ Ca + Y, [Ca] = [Y]
$[CaY]/[Ca]^2 = K'_{MY}$, $[Ca] = \{[CaY]/K'_{MY}\}^{(1/2)}$
$[Ca] = \{[50.00x0.00500/(50.00+25.00)]/1.75e10\}^{0.5}$
=4.36e-7M , pCa = 6.36

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(6) Post-equivalence point:

Ca	+	Y	⇔	CaY
x		excess		~equivalence concentration

$(50.00x0.00500)/(50.00+v_{EDTA})/\{[Ca][(0.0100xv_{EDTA}-50.00x0.00500)/(50.00+v_{EDTA})]\}=K'_{MY}$

$[Ca]=0.25/\{[0.0100xv_{EDTA}-0.25]xK'_{MY}\}=1.43e-11/(0.0100xv_{EDTA}-0.25)$

V_{EDTA}(mL)	[Ca]	pCa
26.00	1.42e-9	8.85
30.00	2.86-10	9.54
40.00	9.53e-11	10.02
50.00	5.71e-11	10.24

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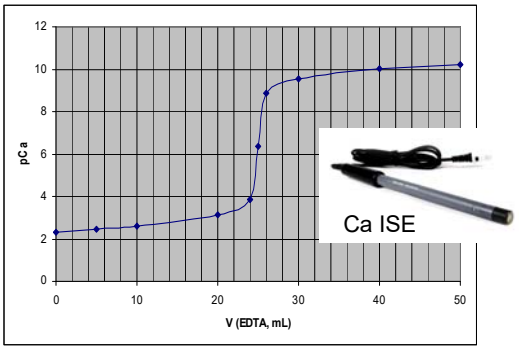

Ca-EDTA Titration Curve at pH 10

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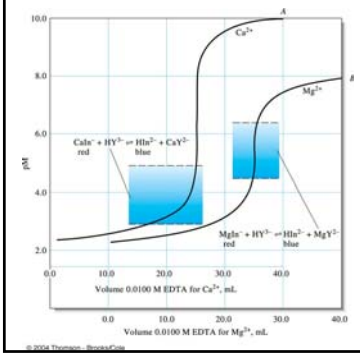
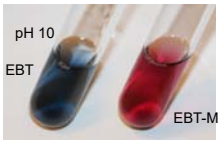
EDTA Titration Curves for Ca (K'2.75e10) and Mg (K'1.72e8) at pH 10



Larger the K'_{MY}
Larger the pM change

Eriochrome Black T



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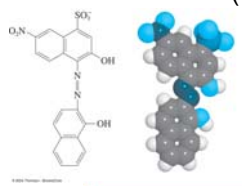
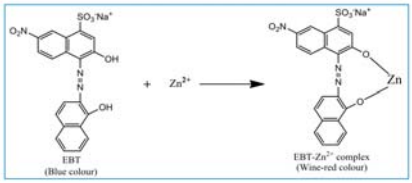
Typical Metal Ion Indicator--Eriochrome Black T (EBT)



A Weak Acid and azo dye



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Indicators for EDTA Titrations

Compounds changing colour when binding to metal ion.
K_f for Metal-In < K_f for Metal-EDTA.

Before Titration:
Mg^{2+} + In → MgIn
(colorless) (blue) (red)

During Titration: Before the end point
Mg^{2+} + EDTA → MgEDTA
(free Mg^{2+} ions) (Solution red due to MgIn complex)

At the end point:
MgIn + EDTA → MgEDTA + In
(red) (colorless) (colorless) (Blue)

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EDTA Titration Solution pH must be Controlled for EBT Indicator

Factors Influencing Chemical Specification of Eriochrome Black T (EBT):

1. pH, as EBT is a weak acid, color varies on pH:

H_2In^- (red) $\rightleftharpoons$ HIn^{2-} (blue) K_1 = 5e-7

HIn^{2-} (blue) $\rightleftharpoons$ In^{3-} (orange) K_2 = 2.8e-12

so pH must be controlled ~7-12 [dominated by HIn^{2-} (blue)]

2. $K_{f[M\text{-}In]}$ of M-In complex,

Mg^{2+} + In (blue) $\rightleftharpoons$ MgIn (red) $K_{f[M\text{-}In]}$ =1.0e7

$K_{f[M\text{-}In]}$ must be smaller than $K_{f[M\text{-}Y]}$

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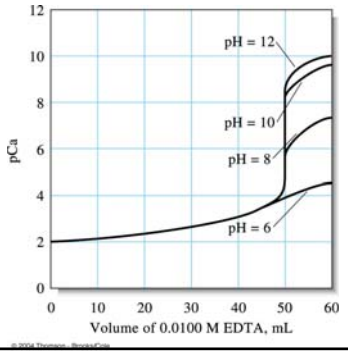
Influence of pH on Titration Curves of Ca-EDTA



The higher pH
The larger pCa change
pH should > 8 for
Ca-EDTA titrations

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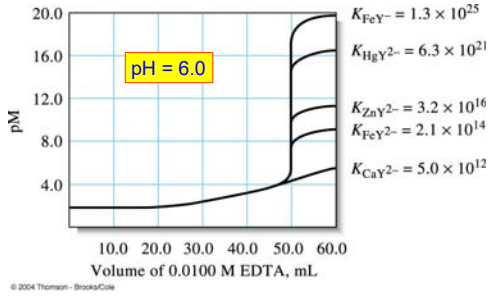
Lower pHs OK for Large K_{MY} Complexes



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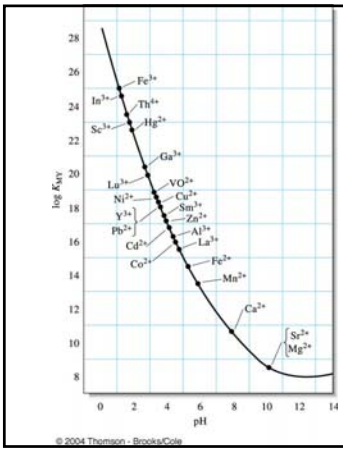

Minimum pH needed for satisfactory titration of various cations with EDTA.

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Effect of Other Complexing Agents on EDTA Titration Curves

- A second complexing agent added to maintain the analyte metal ion in solution (many metal ions form insoluble hydroxides or oxides at slightly high pH).
- To "mask" or remove interfering ions present in the sample matrix.
- The second complexing agent ("masking agent") usually has a higher affinity for the interfering ion than the EDTA to prevent it from reacting with the EDTA.
- Most buffers will complex metal ions because they also contain functional groups (-OH, -COOH, $-NH_2$) which can form coordinate covalent bonds and their effect on the free metal ion concentration must be considered.

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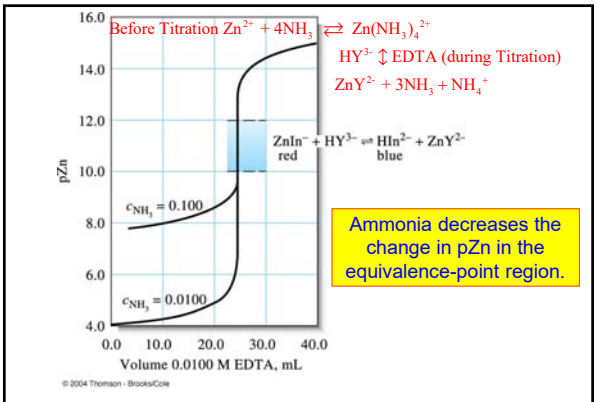

Ammonia decreases the change in pZn in the equivalence-point region.

Influence of $[NH_3]$ on the Zn-EDTA Titration at pH 9.00

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$M + Y \rightleftharpoons MY$ (EDTA complexing)

$M + nL \rightleftharpoons ML_n$ (second complexing agent)

$K_{MY} = \dfrac{[MY]}{[M][Y]}$ ([M],[Y]--free concentration)

$$K_{MY} = \frac{[MY]}{(\alpha_M c_M)(\alpha_4 c_T)} = \frac{[MY]}{(\alpha_M \alpha_4) c_M c_T}$$

Conditional formation constant:

$$K''_{MY} = \alpha_M \alpha_4 K_{MY} = \frac{[MY]}{c_M c_T}$$

Where $\alpha_M = \dfrac{[M]}{c_M} = \dfrac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n}$

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EDTA Titration Techniques

1. Direct Titration

*Buffer analyte to pH where K_f' for MY is large,
*and M-In color distinct from free In color.
*Auxiliary complexing agent may be used.

2. Back Titration

*Known excess std EDTA added.

*Excess EDTA then titrated with a std sol'n of a second metal ion.

*Note: Std metal ion for back titration must not displace analyte from MY complex.

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2. Back Titration: When to apply it

*Analyte precipitates in the absence of EDTA.
*Analyte reacts too slowly with EDTA.
*Analyte blocks indicator

3. Displacement Titration

*Metal ions with no satisfactory indicator.

*Analyte treated with excess Mg(EDTA)

M + MgY $\rightarrow$ MY + Mg

* K_f' for MY > K_f' for MgY

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4. Indirect Titration

*Anions analyzed: CO_3^{2-}, CrO_4^{2-}, S^{2-}, and SO_4^{2-}.
Precipitate SO_4^{2-} with **excess** Ba^{2+} at pH 1.

*$BaSO_4$(s) washed & boiled with **excess** EDTA at pH 10.

$BaSO_4(s) + EDTA(aq) \rightarrow BaY^{2-}(aq) + SO_4^{2-}(aq)$

Excess EDTA back titrated: $EDTA(aq) + Mg^{2+} \rightarrow MgY^{2-}(aq)$

Alternatively: *Precipitate SO_4^{2-} with **excess** Ba^{2+} at pH 1.

*Filter & wash precipitate.

*Treat excess metal ion in filtrate with EDTA.

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5. Masking

*Masking Agent: Protects some component of analyte from reacting with EDTA.

*F^- masks Hg^{2+}, Fe^{3+}, Ti^{4+}, and Be^{2+}.

*CN^- masks Cd^{2+}, Zn^{2+}, Hg^{2+}, Co^{2+}, Cu^+, Ag^+, Ni^{2+}, Pd^{2+}, Pt^{2+}, Hg^{2+}, Fe^{2+}, and Fe^{3+},

but not Mg^{2+}, Ca^{2+}, Mn^{2+}, Pb^{2+}.

*Triethanolamine: Al^{3+}, Fe^{3+}, and Mn^{2+}.

*2,3-dimercapto-1-propanol: Bi^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, and Pb^{2+}.

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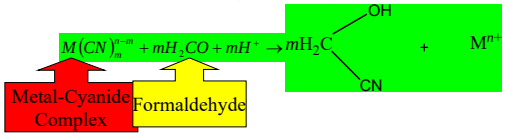
***Demasking**: Releasing masking agent from analyte.



*Oxidation with H_2O_2 releases Cu^{2+} from Cu^+-Thiourea complex.

*Thus, analyte selectivity:

1. pH control
2. Masking
3. Demasking

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Chapter 17 Summary

- Stepwise formation of complexes
- Complexation equilibria
- Calculate alpha values for complexes
- Types of complexometric titrations.
- Species in EDTA solutions
- Structure of EDTA complexes
- Determine conditional formation constants
- Apply EDTA titrations, titration curves, water hardness
- Indicators for EDTA titrations
- Use masking agents for EDTA titrations

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Important Equations

Overall constant

$$M + nL \rightleftharpoons ML_n \quad \beta_n = \frac{[ML_n]}{[M][L]^n} = K_1 K_2 \cdots K_n$$

Alpha values

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

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

Conditional formation constants

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

Zn/EDTA in NH_3 buffer

$$K''_{ZnY} = \alpha_4 \alpha_M K_{ZnY} = \frac{[ZnY^{2-}]}{c_M c_T}$$

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