

Complex Formation

complex ions (also called *coordination ions*)

Bronsted Acids and Bases

acid => proton donor

base => hydroxide ion donor

Lewis Acids and Bases

acid => electron pair acceptor(**metal**)

base => electron pair donor (**ligand**)

Complex Formation

Lewis Acids and Bases

acid => electron pair acceptor(**metal**)

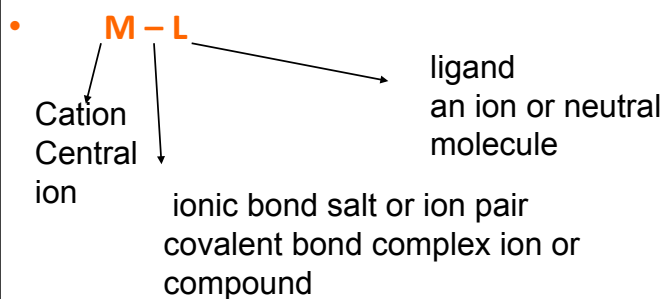
base => electron pair donor (**ligand**)

adduct => product of a Lewis Acid-Base reaction

coordinate covalent bond => both electrons of shared pair contributed by same atom (also called **dative bond**)

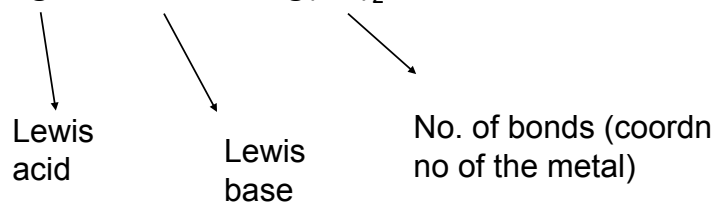
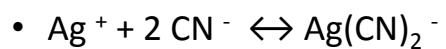
Complexometric Titration

- Concept



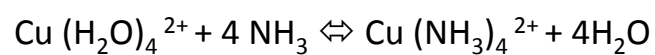
Complexometric Titration

- Involves the formation of a soluble but slightly dissociated complex or complex ion.



$M-L$ bond is often *covalent*, but in some cases the interaction may be one of *coulombic attraction*.

Some complexes undergo substitution reactions very rapidly, and the complex is said to be *labile*.



Effect of pH

- *Non labile* or inert complexes undergo substitution reactions very slowly.
- Co^{2+} complexes are labile, while almost all complexes formed by Co^{3+} , Cr^{3+} are inert.

Ligands

- Ligands generally contain an electronegative atom, **N, O, X, S**
- NH_3 (one unshared pair of electrons, unidentate ligand)
- $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (ethylen diamine) bidentate ligand (has two groups capable of forming 2 bonds with the central atom)
- Cu-en complex

- Interaction of a M^{n+} with two or more functional groups in the same ligand →
- formation of heterocyclic rings and
- compounds are called
- chelates or chelate compounds

- Analytical applications based on the use of chelating agents have been growing

Stability of complexes

- We will focus on the complexation of M^{n+} with chelating agents.
- $M + L \leftrightarrow ML$
- 1:1 reaction \rightarrow sol. Complex
- $K = \frac{[ML]}{[M][L]}$ stability or formation const

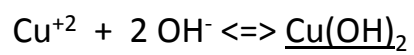
Its reciprocal is instability or dissociation constant.

- $K \sim 10^8$
- The reaction is complete at the equivalence point for a feasible titration

Stepwise Formation Constant

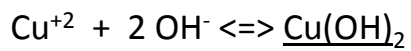
Consider the addition of NH_4OH to a solution of Cu^{+2} ions

at first, the blue solution turns cloudy with the formation of a pale blue precipitate

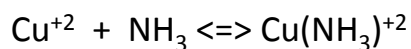


Stepwise Formation Constant

Consider the addition of NH_4OH to a solution of Cu^{2+} ions

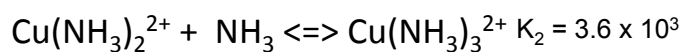
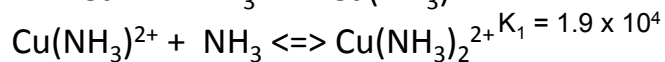
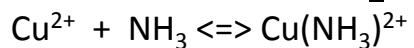
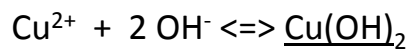


as the concentration of the NH_4OH increases, the NH_3 (main species in NH_4OH) begins to coordinate to the Cu^{2+} ion

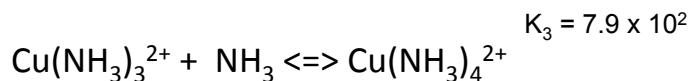


Stepwise Formation Constant

Consider the addition of NH_4OH to a solution of Cu^{2+} ions

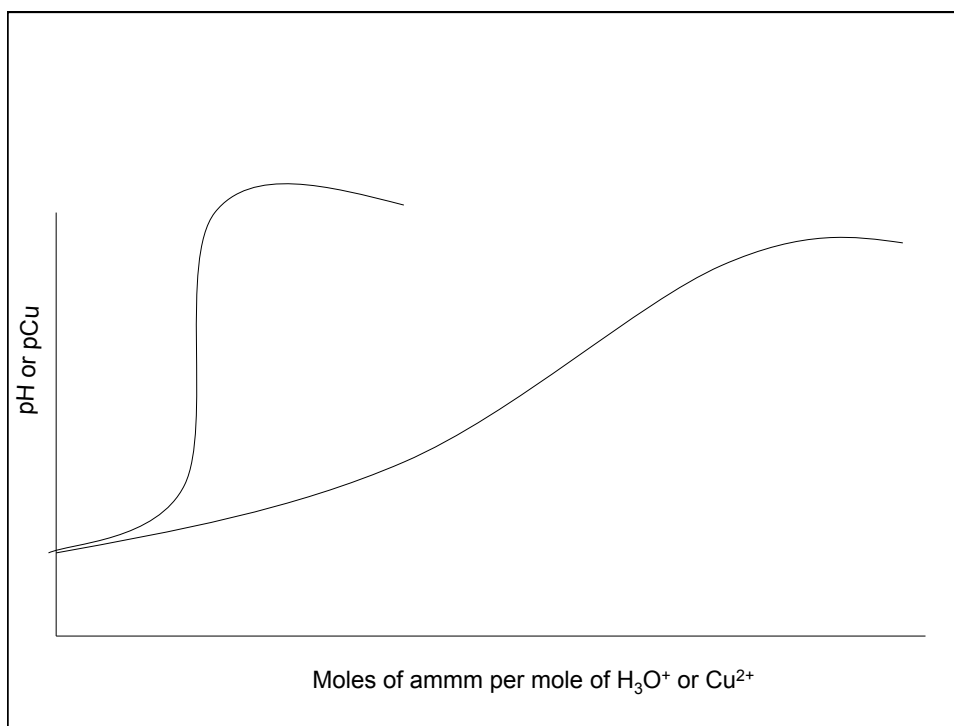


and finally



- $\text{Cu}^{2+} + 4 \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$
- $K = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$
- $= K_1 K_2 K_3 K_4 = 8.1 \times 10^{12}$
- Though the value of K is large, this titration is not feasible.

- There is less tendency for $\text{Cu}(\text{NH}_3)_2^{2+}$ to add a second ammonia than for free Cu^{2+} to bind the first one.
- Actually the tendency to add ammonia molecules decreases at each step of the process.



- $K \sim 10^8$
- The reaction is complete at the equivalence point for a feasible titration
- That is why we prefer chelating agents than simple ligands.

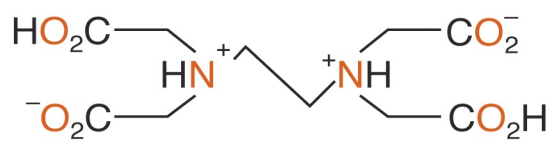
Chelate Effect

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

- Are all kinds of ligands suitable for all the metal cations?

- Metal ions such as Cu, Co, Ni, Zn, Cd and Hg form stable complexes with N – ligands (e.g. ammonia and trien p 200)
- Metal ions Al, Pb, Bi are better complexed with O – ligands
- The best is EDTA, it forms stable, water-sol., 1:1 complexes with M^{n+} → it can be used as a titrant.

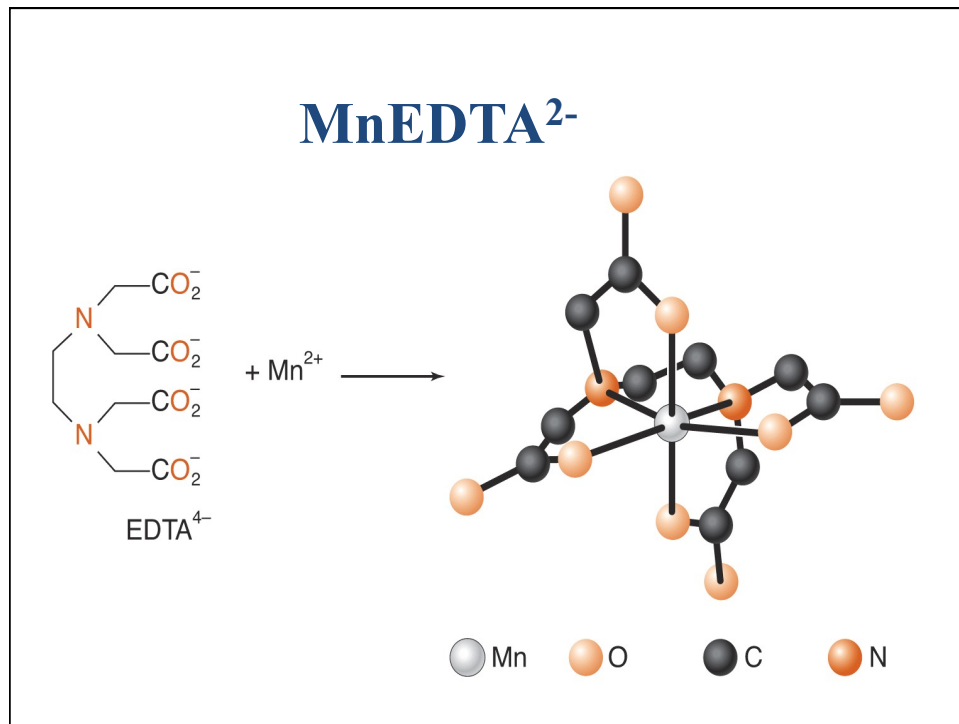
EDTA



EDTA

Ethylenediaminetetraacetic acid
(also called ethylenedinitrilotetraacetic acid)

- => H_4EDTA => H_4Y

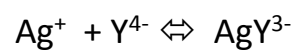


EDTA

ethylenediaminetetraacetate anion

=> EDTA⁴⁻ => Y⁴⁻

+1 cation

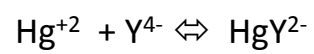


EDTA

ethylenediaminetetraacetate anion



+2 cation

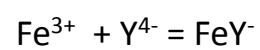


EDTA

ethylenediaminetetraacetate anion



+3 cation

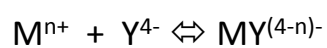


EDTA

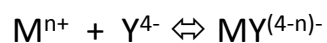
ethylenediaminetetraacetate anion

=> EDTA^{4-} => Y^{4-}

+n ion



Equilibria involved in EDTA titrations



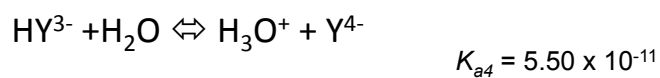
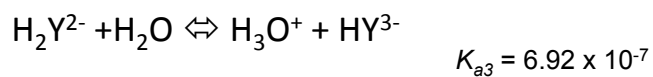
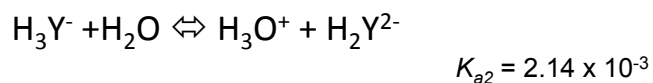
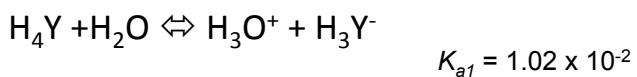
- The absolute stability or formation const

- $$K_{abs} = \frac{[\text{MY}^{(4-n)-}]}{[\text{M}^{n+}][\text{Y}^{4-}]}$$
 stability or formation const

- Since the EDTA contains 6 basic sites – 4 COOH, 2 N – 6 acid species can exist
- H_6Y^{2+} , H_5Y^+ , H_4Y , H_3Y^- , H_2Y^{2-} , HY^{3-} .

Equilibria involved in EDTA titrations

The pH effect (p202, 203)



- What is the predominant species at pH 12?
- Y^{4-}
- At lower pH values protonated species
- At pH = 4 H_2Y^{2-}
- $$Cu^{2+} + H_2Y^{2-} \rightleftharpoons CuY^{2-} + 2H^+$$

- How can you estimate the value of pH for a complexometric titration?

EDTA

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

The fraction of EDTA in the Y^{4-} , c_y total concentration of the uncomplexed EDTA

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

Where $c_y = [\text{Y}^{4-}] + [\text{HY}^{3-}] + [\text{H}_2\text{Y}^{2-}] + [\text{H}_3\text{Y}^-] + [\text{H}_4\text{Y}]$

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

$$\alpha_4 = \frac{K_{a1} K_{a2} K_{a3} K_{a4}}{K_{a1} K_{a2} K_{a3} K_{a4} + [\text{H}_3\text{O}^+] K_{a1} K_{a2} K_{a3} + [\text{H}_3\text{O}^+]^2 K_{a1} K_{a2} + [\text{H}_3\text{O}^+]^3 K_{a1} + [\text{H}_3\text{O}^+]^4}$$

$$[\text{Y}^{4-}] = \alpha_4 c_y$$

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

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

$$K_{abs} \alpha_4 = \frac{[MY^{-(4-n)}]}{[M^{n+}] c_y} = K_{eff}$$

K_{eff} , *effective or conditional stability constant*, it is pH dependant

- K_{eff} is more important than K_{abs}
- It shows the actual tendency to form the metal complex at the pH value in question
- It can be estimated from values of K_{eff} , α_4 in tables of constants.

It may be noted that, as the pH goes down, α_4 becomes smaller and K_{eff} becomes smaller.

At pH > 12 (EDTA is completely dissociated)
 $\alpha_4 \sim 1$, $K_{eff} \sim K_{abs}$

Table 13-1 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	1.9×10^{-18}
2	3.3×10^{-14}
3	2.6×10^{-11}
4	3.8×10^{-9}
5	3.7×10^{-7}
6	2.3×10^{-5}
7	5.0×10^{-4}
8	5.6×10^{-3}
9	5.4×10^{-2}
10	0.36
11	0.85
12	0.98
13	1.00
14	1.00

- In EDTA titrations, M^{n+} solutions are buffered \rightarrow pH is const.
- At high pH values many M^{n+} tend to hydrolyse and even \rightarrow hydroxides
- M^{n+} concentration is kept as low as
- 0.010 - 0.0010 M to decrease the chance of precipitation.

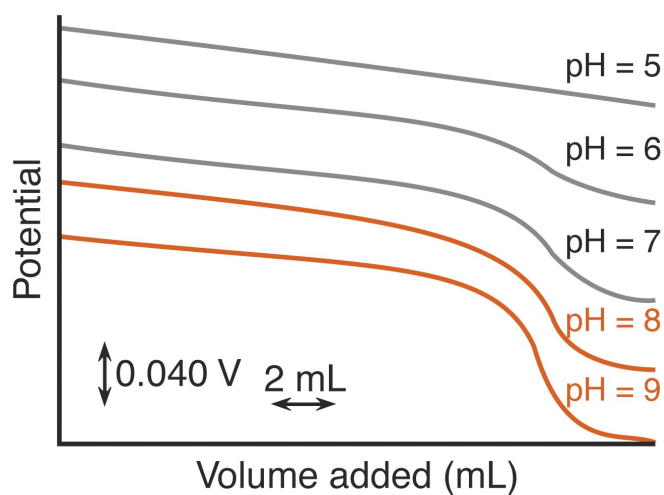
Table 13-2 Formation constants for metal-EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li ⁺	2.79	Mn ³⁺	25.3 (25°C)	Ce ³⁺	15.98
Na ⁺	1.66	Fe ³⁺	25.1	Pr ³⁺	16.40
K ⁺	0.8	Co ³⁺	41.4 (25°C)	Nd ³⁺	16.61
Be ²⁺	9.2	Zr ⁴⁺	29.5	Pm ³⁺	17.0
Mg ²⁺	8.79	Hf ⁴⁺	29.5 ($\mu = 0.2$)	Sm ³⁺	17.14
Ca ²⁺	10.69	VO ²⁺	18.8	Eu ³⁺	17.35
Sr ²⁺	8.73	VO ₂ ⁺	15.55	Gd ³⁺	17.37
Ba ²⁺	7.86	Ag ⁺	7.32	Tb ³⁺	17.93
Ra ²⁺	7.1	Tl ⁺	6.54	Dy ³⁺	18.30
Sc ³⁺	23.1	Pd ²⁺	18.5 (25°C, $\mu = 0.2$)	Ho ³⁺	18.62
Y ³⁺	18.09	Zn ²⁺	16.50	Er ³⁺	18.85
La ³⁺	15.50	Cd ²⁺	16.46	Tm ³⁺	19.32
V ²⁺	12.7	Hg ²⁺	21.7	Yb ³⁺	19.51
Cr ²⁺	13.6	Sn ²⁺	18.3 ($\mu = 0$)	Lu ³⁺	19.83
Mn ²⁺	13.87	Pb ²⁺	18.04	Am ³⁺	17.8 (25°C)
Fe ²⁺	14.32	Al ³⁺	16.3	Cm ³⁺	18.1 (25°C)
Co ²⁺	16.31	Ga ³⁺	20.3	Bk ³⁺	18.5 (25°C)
Ni ²⁺	18.62	In ³⁺	25.0	Cf ³⁺	18.7 (25°C)
Cu ²⁺	18.80	Tl ³⁺	37.8 ($\mu = 1.0$)	Th ⁴⁺	23.2
Tl ³⁺	21.3 (25°C)	Bi ³⁺	27.8	U ⁴⁺	25.8
V ³⁺	26.0			Np ⁴⁺	24.6 (25°C, $\mu = 1.0$)
Cr ³⁺	23.4				

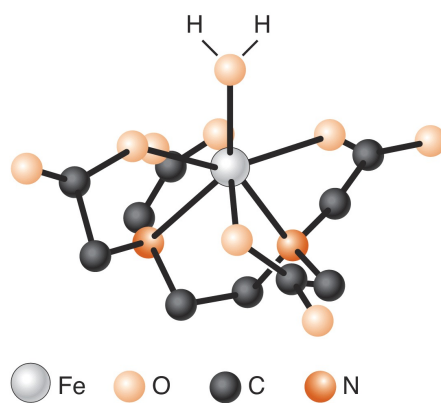
NOTE: The formation constant is the equilibrium constant for the reaction $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$. Values in table apply at 20°C, and ionic strength 0.1 M, unless otherwise noted.

SOURCE: A. E. Martell and R. M. Smith, *Critical Stability Constants*, Vol. 1 (New York: Plenum Press, 1974), pp. 204-211.

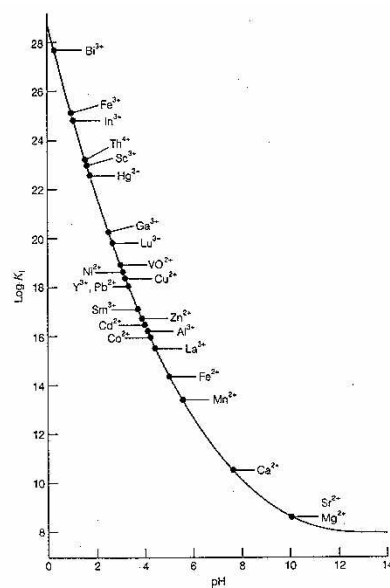
Titration of Ca²⁺ at various pHs



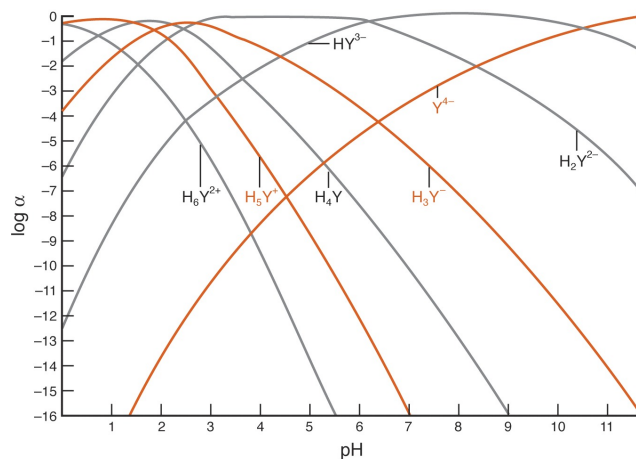
7-Coordinate $[\text{Fe}^{\text{III}}\text{EDTA H}_2\text{O}]^{-1}$



Minimum
pH for
Effective
EDTA
Titrations



Fractional Composition Diagram for EDTA



- 50.0 mL of a solution which is 0.0100 M in Ca^{2+} and buffered at pH 10.0 is titrated with 0.0100 M EDTA solution. Calculate values of pCa at various stages of the titration and plot the titration curve.
- $K_{abs} CaY^{2-}$ is 5.0×10^{10} , α_4 at pH 10.0 is 0.35 $\rightarrow K_{eff} = 5.0 \times 10^{10} \times 0.35$
- $= 1.8 \times 10^{10}$

Start of titration

- $[\text{Ca}^{2+}] = 0.0100 \text{ mmol/mL}$
- $p\text{Ca} = -\log [\text{Ca}^{2+}] = 2.00$

After addn of 10.0 mL of titrant

- Start Ca^{2+}
- $50.0 \text{ mL} \times 0.0100 \text{ mmol/mL}$
- EDTA 10.0 mL , 0.0100 mmol/mL
- 10.0 mL reacted, 40.0 mL remained
- $40.0 \text{ mL} \times 0.0100 \text{ mmol/mL} = 60.0 \text{ } \mu\text{mol}$
- $[\text{Ca}^{2+}] = 0.0067 \text{ M}$
- $p\text{Ca} = 2.17$

Equivalence point

- $\text{Ca}^{2+} + \text{Y}^{4-} \rightleftharpoons \text{CaY}^{2-}$
- 0.500mmol 0.500mmol 0.500mmol
- $[\text{Ca}^{2+}] = c_y$, $[\text{CaY}^{2-}] \sim 0.500\text{mmol}/100\text{mL}$

$$\frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}] c_y} = K_{eff}$$

$$\frac{5.0 \times 10^{-3}}{[\text{Ca}^{2+}]^2} = 1.8 \times 10^{10}$$

$$[\text{Ca}^{2+}] = 5.2 \times 10^{-7} \quad p\text{Ca} = 6.28$$

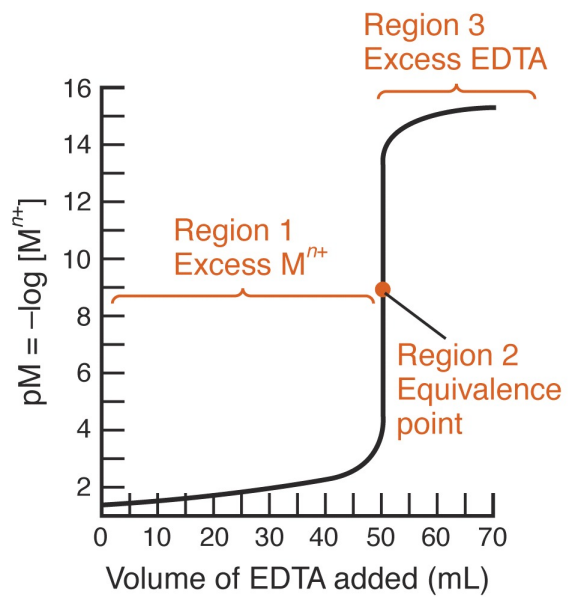
After addn of 60.0 mL of titrant

- 0.100 mmol EDTA, 0.500mmol $[\text{CaY}^{2-}]$
- $c_y = 0.100 \text{ mol}/110\text{mL} = 9.1 \times 10^{-4} \text{ M}$
- $[\text{CaY}^{2-}] = 0.500 \text{ mmol}/110 \text{ mL}$
- $= 4.55 \times 10^{-3} \text{ M}$

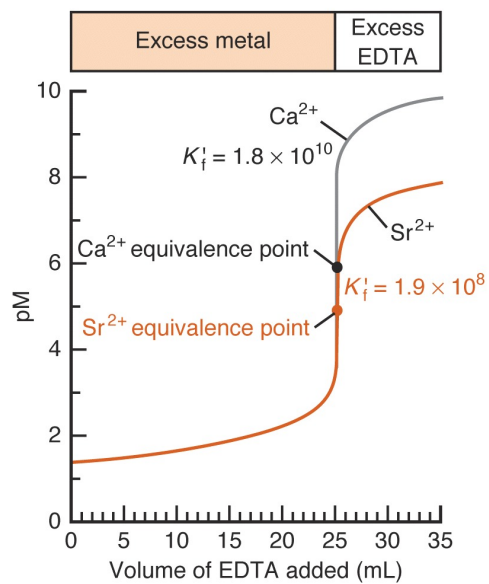
$$\frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}] c_y} = K_{eff}$$

$$[\text{Ca}^{2+}] = 2.8 \times 10^{-10} \text{ M} \rightarrow p\text{Ca} = 9.55$$

Three Regions of EDTA Titration



Theoretical titration curves



Masking

- Ni^{2+} forms stable cyanide complex $[\text{Ni}(\text{CN})_4]^{2-}$
- Pb^{2+} does not .
- Mixture ($\text{Pb}^{2+} + \text{Ni}^{2+}$), in the presence of CN^- ,
- Pb^{2+} can be titrated against EDTA without interference from Ni^{2+}

Masking

- With certain M^{n+} that hydrolyse readily, it may be necessary to add complexing ligands → preventing pptn of $\text{M}(\text{OH})_n$
- Acetate or ammonia

Hydrolysis effect

- Hydrolysis may compete with the complexometric titration.
- Extensive hydrolysis → pptn of hydroxides, which reacts slowly with EDTA
- Pptn can be a sort of masking
- e.g. at pH=10, Ca^{2+} , Mg^{2+} are complexed with EDTA
- At pH>12 → $\text{Mg}(\text{OH})_2$ ppt → Ca^{2+} is only complexed

EDTA indicators

- EBT, loss of H^+ from phenolic OH, O^- and azo gp
- $\text{H}_2\text{In}^- + \text{H}_2\text{O} \rightleftharpoons \text{HIn}^{2-} + \text{H}_3\text{O}^+$
- red blue
- $\text{pK}_a = 6.3$
- In^{3-} yellowish-orange
- At pH 8-10, EDTA titrn, → blue HIn^{2-} which forms 1:1 wine red complexes with many cations e.g. Mg^{2+} , Ca^{2+} , Zn^{2+} and Ni^{2+}

- *EBT* is unstable in solution, it must be freshly prepared
- *Calmagite* is stable in aq. Soln H_3In
- H_2In^- red, HIn^{2-} blue, In^{3-} reddish orange

EDTA Indicators

Table 13-3 Common metal ion indicators

Name	Structure	pK _a	Color of free indicator	Color of metal ion complex
Eriochrome black T		pK ₂ = 6.3 pK ₃ = 11.6	H ₂ In ⁻ red HIn ²⁻ blue In ³⁻ orange	Wine red
Calmagite		pK ₂ = 8.1 pK ₃ = 12.4	H ₂ In ⁻ red HIn ²⁻ blue In ³⁻ orange	Wine red
Murexide		pK ₃ = 9.2 pK ₅ = 10.9	H ₄ In ⁻ red-violet H ₃ In ²⁻ violet H ₂ In ³⁻ blue	Yellow (with Co ²⁺ , Ni ²⁺ , Cu ²⁺); red with Ca ²⁺
Xylenol orange		pK ₂ = 2.32 pK ₃ = 2.85 pK ₄ = 6.70 pK ₅ = 10.47	H ₄ In ⁻ yellow H ₃ In ²⁻ yellow H ₂ In ³⁻ yellow HIn ⁴⁻ violet HIn ⁵⁻ violet In ⁶⁻ violet	Red
Pyrocatechol violet		pK ₁ = 0.2 pK ₂ = 7.8 pK ₃ = 9.8 pK ₄ = 11.7	H ₄ In red H ₃ In ⁻ yellow H ₂ In ²⁻ violet HIn ³⁻ red-purple	Blue

PREPARATION AND STABILITY:

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 6.5.

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

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.

Application of EDTA titrations

- 1- Direct
- Complexing agents, citrate and tartarate, are added to prevent pptn of hydroxides
- $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer (pH 9-10) is used for M^{n+} which forms complexes with ammonia

Detmn of total hardness of water

- $\text{Ca}^{2+} + \text{Mg}^{2+}$
- Ca^{2+} - In complex is too weak (for a proper colour change) compared to Mg^{2+} - In, pH10.

Determn of total hardness of water

- If the sample does not contain Mg^{2+}
- Add Mg^{2+} to EDTA \rightarrow titrant (pH 10) $MgY^{2-} + Y^{4-}$
- Add to Ca^{2+} soln \rightarrow CaY^{2-} (more stable) + Mg^{2+} (free to react with In \rightarrow red colour)
- At e.p. no Ca^{2+} , additional titrant \rightarrow $MgIn^-$ to MgY^{2-} \rightarrow HIn^{2-} (blue)

2- Back titration

- $M^{n+} + EDTA \rightarrow$ slow reaction or when a suitable ind is not available.
- $M^{n+} +$ excess EDTA \rightarrow Vrem titrate against Mg^{2+} ind EBT or calmagite
- It can be used for the determn of M^{n+} in ppts, e.g. Pb^{2+} in lead sulphate and Ca^{2+} in CaC_2O_4 (oxalate)

3- Replacement

- No suitable ind
- An excess of a Mg^{2+} – EDTA soln is added $\rightarrow M^{2+}$ displaces Mg^{2+} from the relatively weak EDTA complex
- $M^{2+} + MgY^{2-} \rightleftharpoons MY^{2-} + Mg^{2+}$
- (titrate against EDTA)

4- Indirect

- $SO_4^{2-} + \text{excess } Ba^{2+} \rightarrow BaSO_4 + Ba^{2+}$
- EDTA
- $MgNH_4PO_4 \rightleftharpoons Mg^{2+} + NH_4PO_4^{2-}$
- EDTA \rightarrow detn of PO_4^{3-}

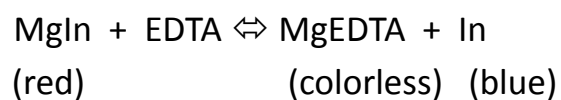
Selectivity in EDTA titrn

- Adjusting pH → degree of selectivity
- Some M^{n+} form stable complexes at lower pH values, while others do not.
- e.g. Fe (III) is complexed with EDTA at pH 2 in the presence of Fe (II)

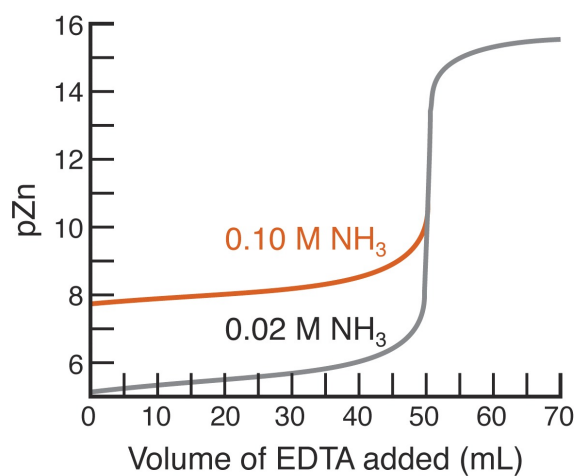
- Ni (II) is complexed at 3.5 in the presence of alkaline earth cations.
- Interference will occur at pH 10 in an amm buffer

Metal Ion Indicators

Erichrome Black T



Titration curves in presence of NH_3



Guide to EDTA titrations, light color, pH range for quantitative analysis, dark area where ammonia must be present

