Complexometric titrations

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Lewis acid-base concept

Lewis acid => electron pair acceptor

metal

Lewis base = electron pair donor

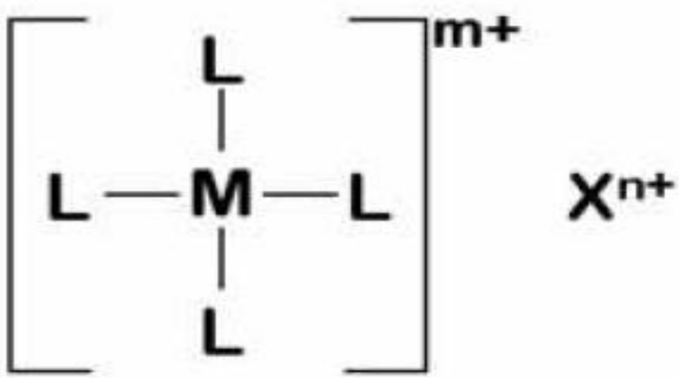
ligand

coordinate covalent bond

ligand donates both electrons of the electron pair bond

Complexes

General structure



- L - ligand
- M - central species
- X - counter ion

$CUSO_4 + 4{:}NH_3 \rightarrow CU(NH_3)_4^{2+}\ SO_4^{2-}$

$M = CU^{2+}$, $L = NH_3$, $X = SO_4^{2-}$

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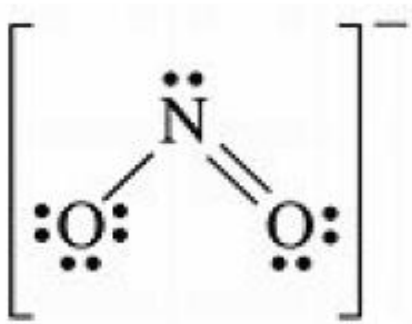
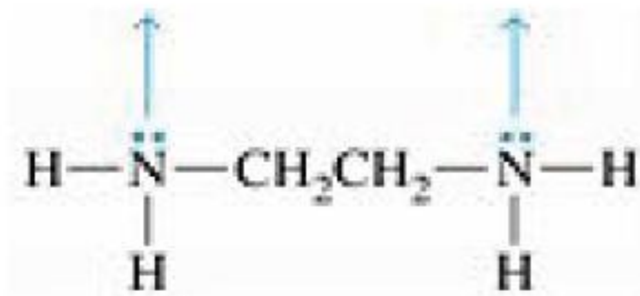
- Formation of soluble complex between metal ion and a complexing agent
- Complex is an anion or a neutral molecule
- Metal ion acts as a Lewis acid (accepts electron pairs)
- ***Complexing agent (ligand)*** acts a Lewis base (donates electron pairs)
- Covalent bond between metal and ligand.

Ligands





the $EDTA^{4-}$ ion

Complexes

Some common ligand groups

halides	Cl^-, Br^-, I^-, F^-	thiocarbonyl	S=CO	hydroxides	OH^-
carbonyls	-CO	mercaptans	-SH	oximes	=N-OH
nitroso	-NO	acids	-COOH	amines	RNH_2

Ligands are typically anionic or polar neutral species when working with aqueous systems.

Ligands have greater or equal two donating electron pairs called chelating agents and the resulting complex called chelate

Complexes

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Ligands can be classified by dentate number - number of bonds/ligand

Monodentate (unidentate)

1 bond/ligand - ammonia NH_3

Bidentate

2 bonds/ligand - ethylene diamine NH2-CH2-CH2-NH2

Multidentate

variable number based on need - EDTA H_4Y

(hexadentate)

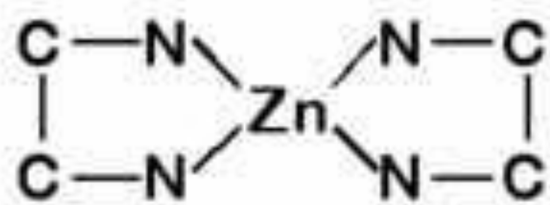
Bidentate ligands

Form two binds / central species.

A good example is ethylene diamine.

$NH_2CH_2CH_2NH_2$ - (en)

The amino groups are far enough apart to permit both to interact.

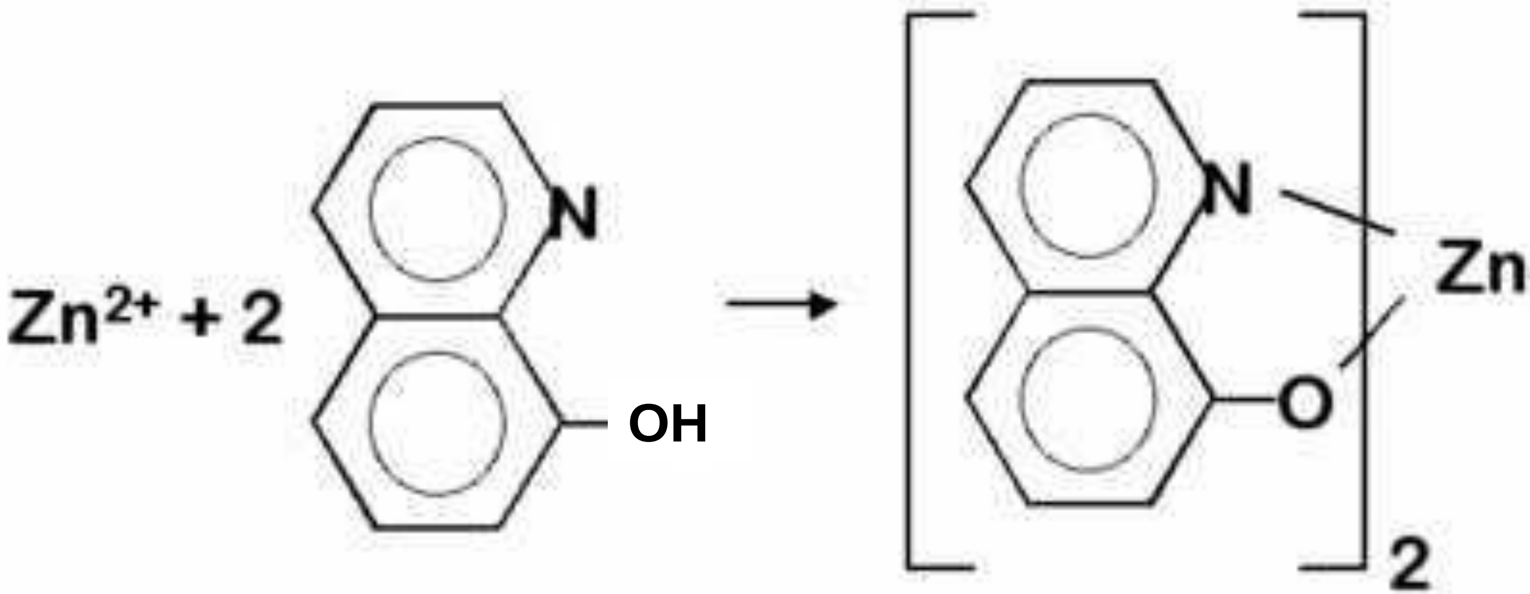
$Zn^{2+} + 2\ en \longrightarrow$ 

en= ethylene diamine =NH2-CH2-CH2-NH2

Bidentate ligands

Other common bidentate ligands.

8 - hydroxyquinoline



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Bidentate ligands

Other common bidentate ligands.

Dimethylglyoxime - DMG $Ni^{2+} + 2\ DMG \rightarrow Ni\ (DMG)_2$

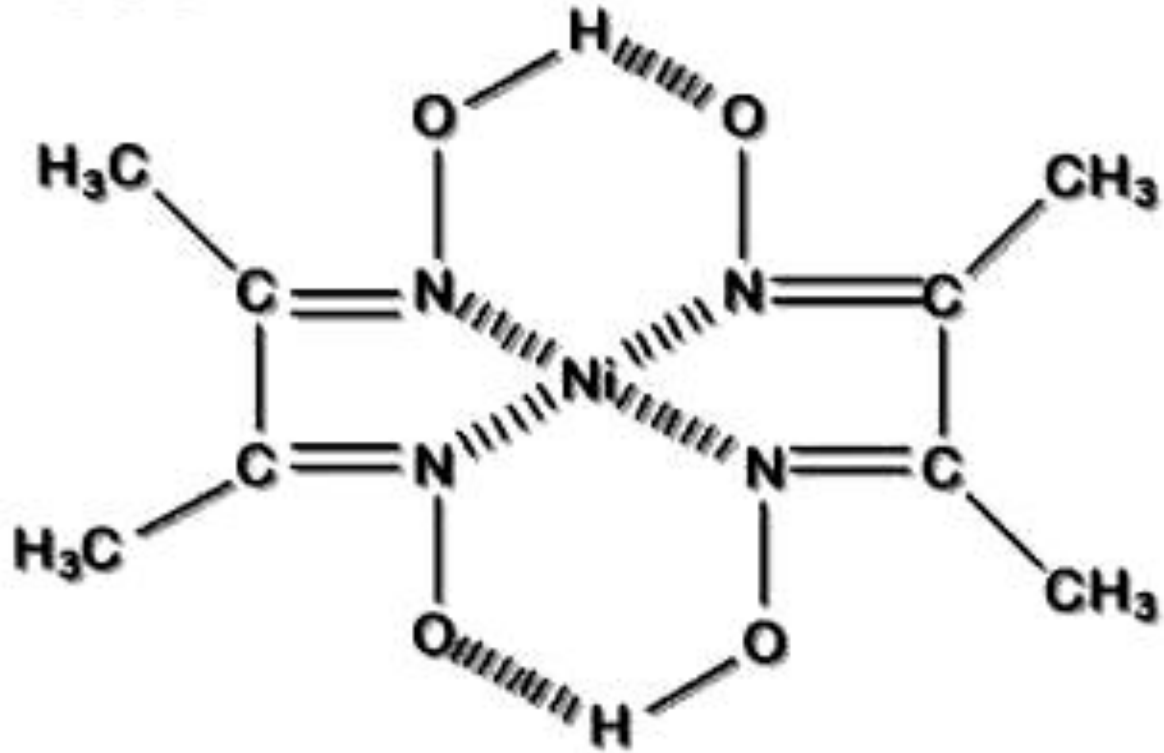

Table1: Typical inorganic complex formation titrations

titrant	Analyte	Remarks
$Hg(No_3)_2$	Br^-, Cl^-,SCN^-,CN^-	neutral mercury complex; $HgBr_2$,$HgCl_2$,$Hg(SCN)_2$, Hg(CN)2,various indicators used
Ag^+	CN^-	$Ag(CN)_2^-$; indicator is I^- ; titrate to first turbidity of AgI
Ni^{2+}	CN^-	$Ni(CN)_4^{2-}$; indicator is I^- ; titrate to first turbidity of AgI
CN^-	CU^{2+}, Hg^{2+}, Ni^{2+}	$Cu(CN)_4^{2-}$,$Hg(CN)_2$,$Ni(CN)_4^{2-}$ various indicators are used

Complexometric titrations

- Monodentate ligands rarely used as titrants
  - Sharp end point generally difficult to achieve
  - Stepwise formation constants are frequently close together, not very large, single stoichiometric complex cannot be observed)
- Most generally useful titrating agents
  - Aminocarboxylic acids – nitrogen and carboxylate groups as ligands
  - 1:1 metal-complex formed

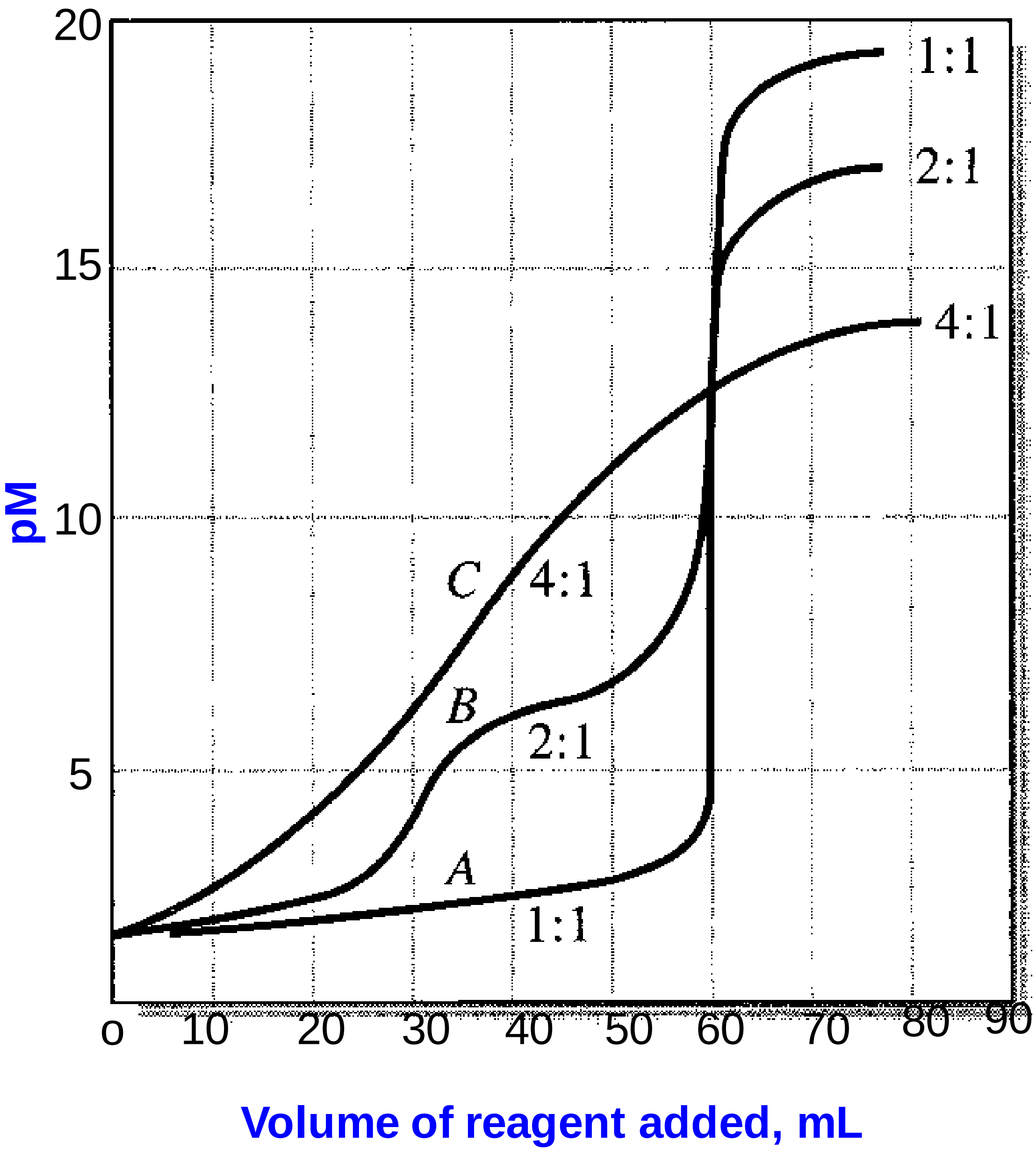

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Figure 1: Titration curves for complexometric titrations. Titration of 60.0 mL of a solution that is 0.020 M in metal M with (A) a 0.020 M solution of the tetradentate ligand D to give MD as the product; (B) a 0.040 M solution of the bidentate ligand B to give MB_2; and (C) a 0.080 M solution of the unidentate ligand A to give MA4' The overall formation constant for each product is 10^{20}.

EDTA

- H_4Y has v.low solubility in water
- Disodium salt, $Na_2H_2Y.2H_2O$ is used to prepare EDTA standard solutions; dissociates to give predominantly H_2Y^{2-}
- pH EDTA will influence distribution of H_4Y, H_3Y^-, H_2Y^{2-}, Y^{4-} .

EDTA, H_4Y

$$H_4Y \rightleftharpoons H^+ + H_3Y^- \qquad K_{a1} = 1.0 \times 10^{-2}$$

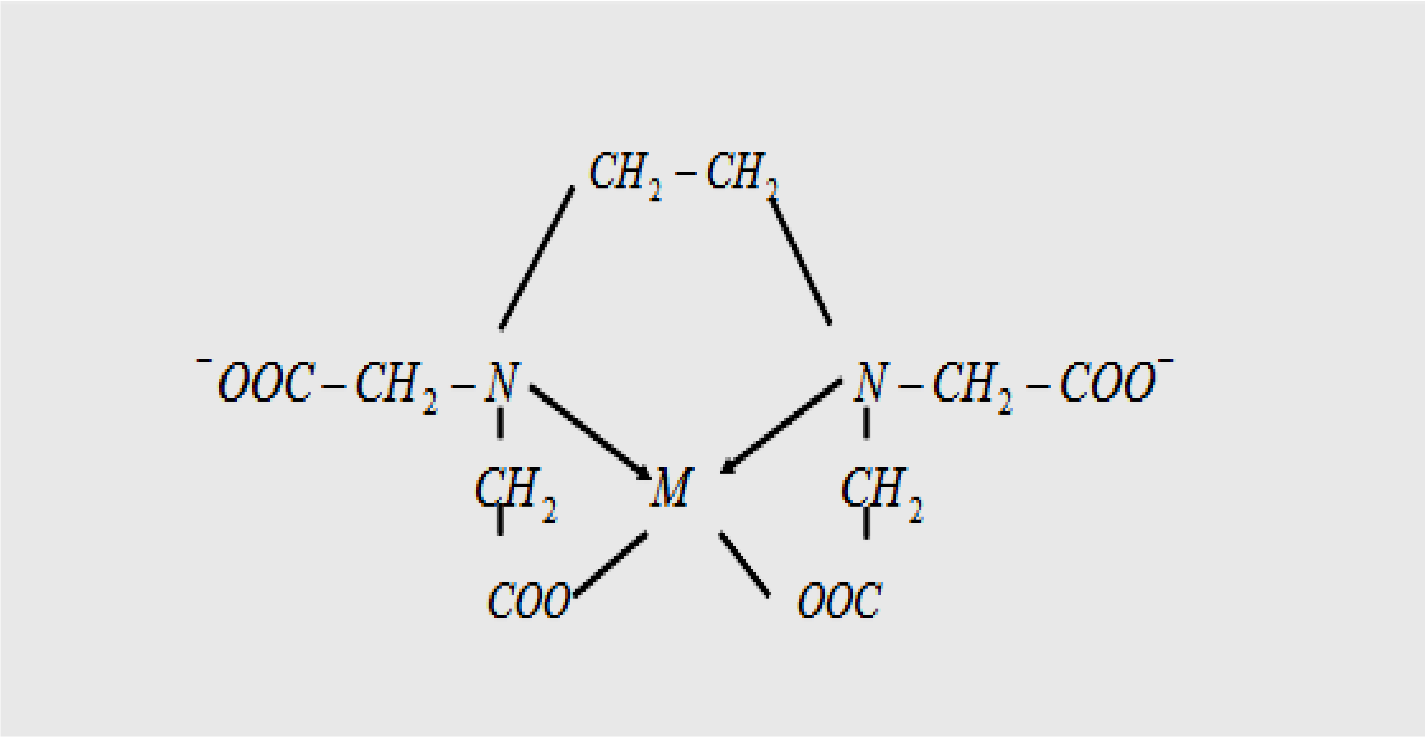
$$H_3Y^- \rightleftharpoons H^+ + H_2Y^{2-} \qquad K_{a2} = 2.2 \times 10^{-3}$$

$$H_2Y^{2-} \rightleftharpoons H^+ + HY^{3-} \qquad K_{a3} = 6.9 \times 10^{-7}$$

$$HY^{3-} \rightleftharpoons H^+ + Y^{4-} \qquad K_{a4} = 5.5 \times 10^{-11}$$

Figure: structure of an EDTA chelate with divalent cation

$$M^{2+} + H_2Y^{2-} \leftrightarrow MY^{2-} + 2H^+$$



Formation constant of metal-EDTA complex

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

$$Ca^{2+} + Y^{4-} \leftrightarrow CaY^{2-}$$

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

EDTA

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Formation constants for some metal - EDTA complexes.

Ion	$\log K_{MY}$	Ion	$\log K_{MY}$	Ion	$\log K_{MY}$
Fe^{3+}	25.1	Pb^{2+}	18.0	La^{3+}	15.4
Th^{4+}	23.2	Cd^{2+}	16.5	Mn^{2+}	14.0
Cr^{3+}	23.0	Zn^{2+}	16.5	Ca^{2+}	10.7
Bi^{3+}	22.8	Co^{2+}	16.3	Mg^{2+}	8.7
Cu^{2+}	18.8	Al^{3+}	16.1	Sr^{2+}	8.6
Ni^{2+}	18.6	Ce^{3+}	16.0	Ba^{2+}	7.8
				Ag^{+}	7.3

EDTA

Effect of pH

The strength and stability of EDTA complexes is pH dependent.

$$M^{2+} + H_2Y^{2-} \rightarrow MY^{2-} + 2H^{+}$$

Since it is the Y^{4-} for which complexes with the metal, anything that alters its availability will affect our titration

- pH is the major concern.

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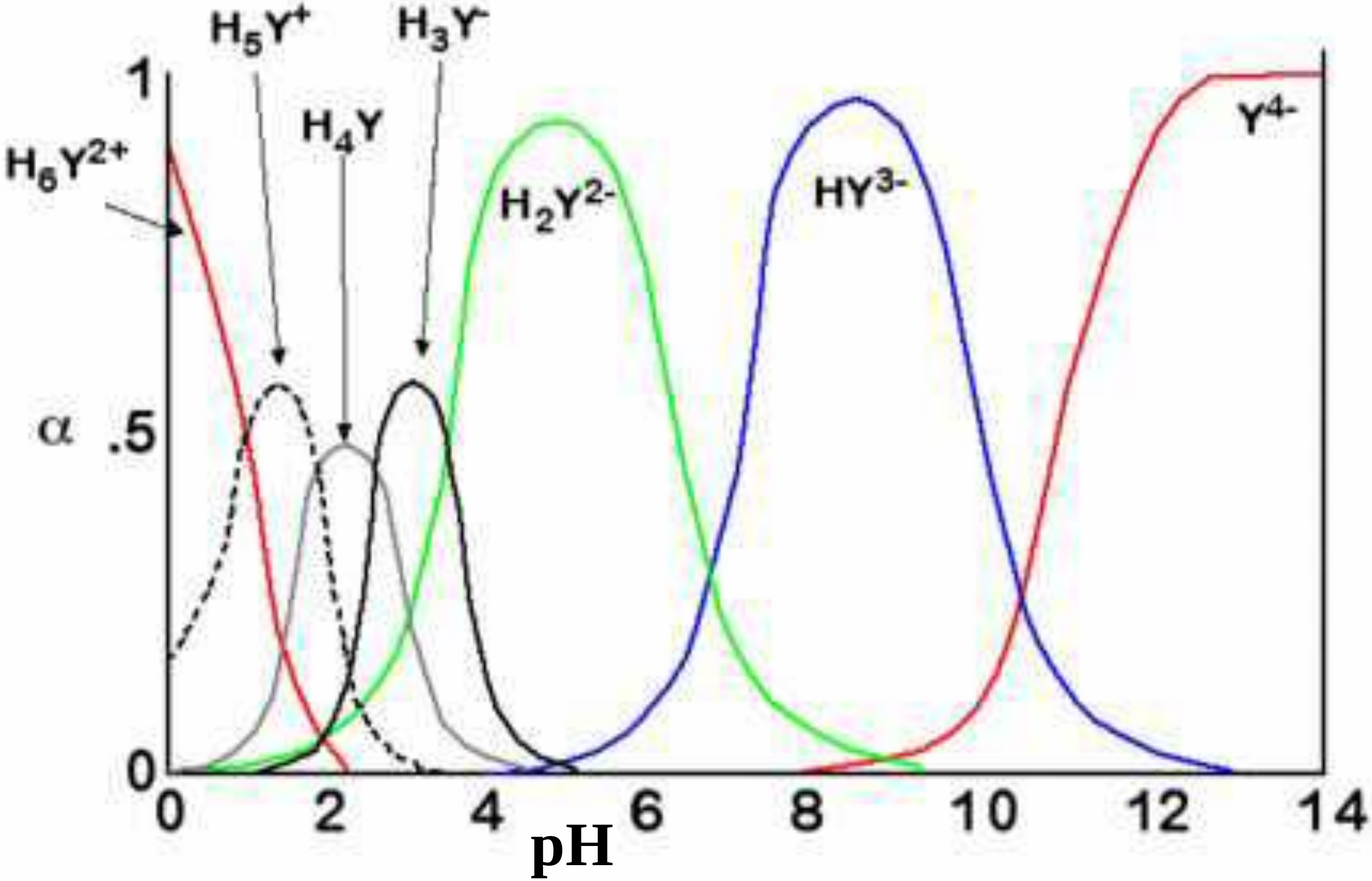
EDTA



EDTA equilibria

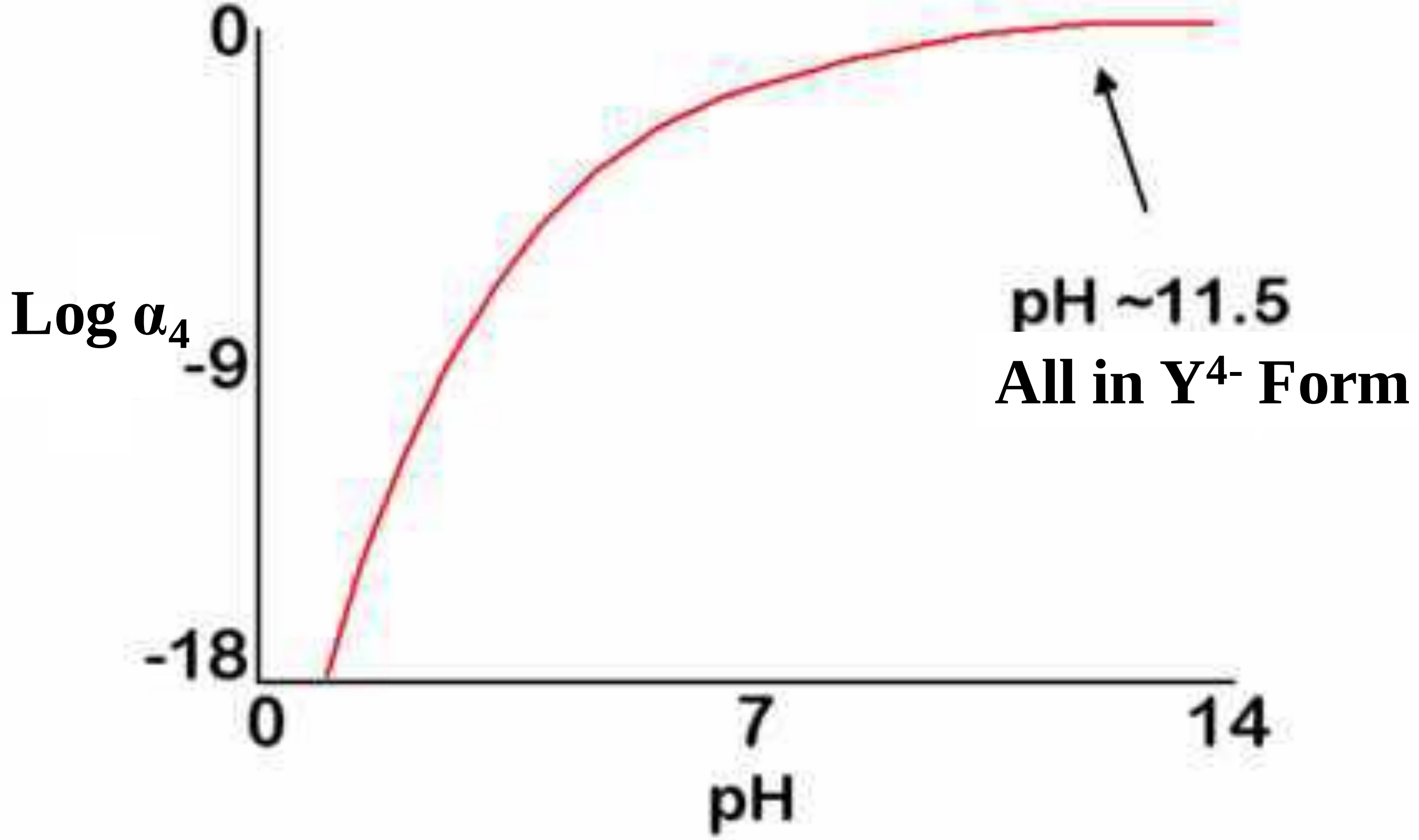


Table: α_4 values for EDTA in solutions at different pH values

pH	α_4	pH	α_4
2	3.7×10^{-14}	8	5.4×10^{-3}
3	2.5×10^{-11}	9	5.2×10^{-2}
4	3.6×10^{-9}	10	3.5×10^{-1}
5	3.5×10^{-7}	11	8.5×10^{-1}
6	2.2×10^{-5}	12	9.8×10^{-1}
7	4.8×10-^{4}		

Conditional formation constant:

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

$$\alpha_4 = [Y^{4-}]/C_t$$

$$K_{MY} = [MY^{(n-4)+}]/[M^{n+}][Y_4-]$$

$$K_{MY} = [MY^{(n-4)+}]/[M^{n+}] \times \alpha_4 C_t$$

$$K_{MY} \times \alpha_4 \times C_t \times [M^{n+}] = [MY^{(n-4)+}]$$

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

Can be calculated at any known pH

$K'_{MY} = \alpha_4 K_{MY}$ = **conditional formation constant** $\geq 10^6$ for **successful determination**

Small values of K'_{MY} required more basic solutions this mean **larger α_4 values**

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Example 1: Calculate K'_{NiY} at pH 3 and 8, given K_{NiY}= $4.2*10^{18}$, $\alpha_4 = 2.5 * 10^{-11}$ and $5.4 * 10^{-3}$ at pH 3 and 8 respectively.

$K'NiY = \alpha_4 K_{NiY}$

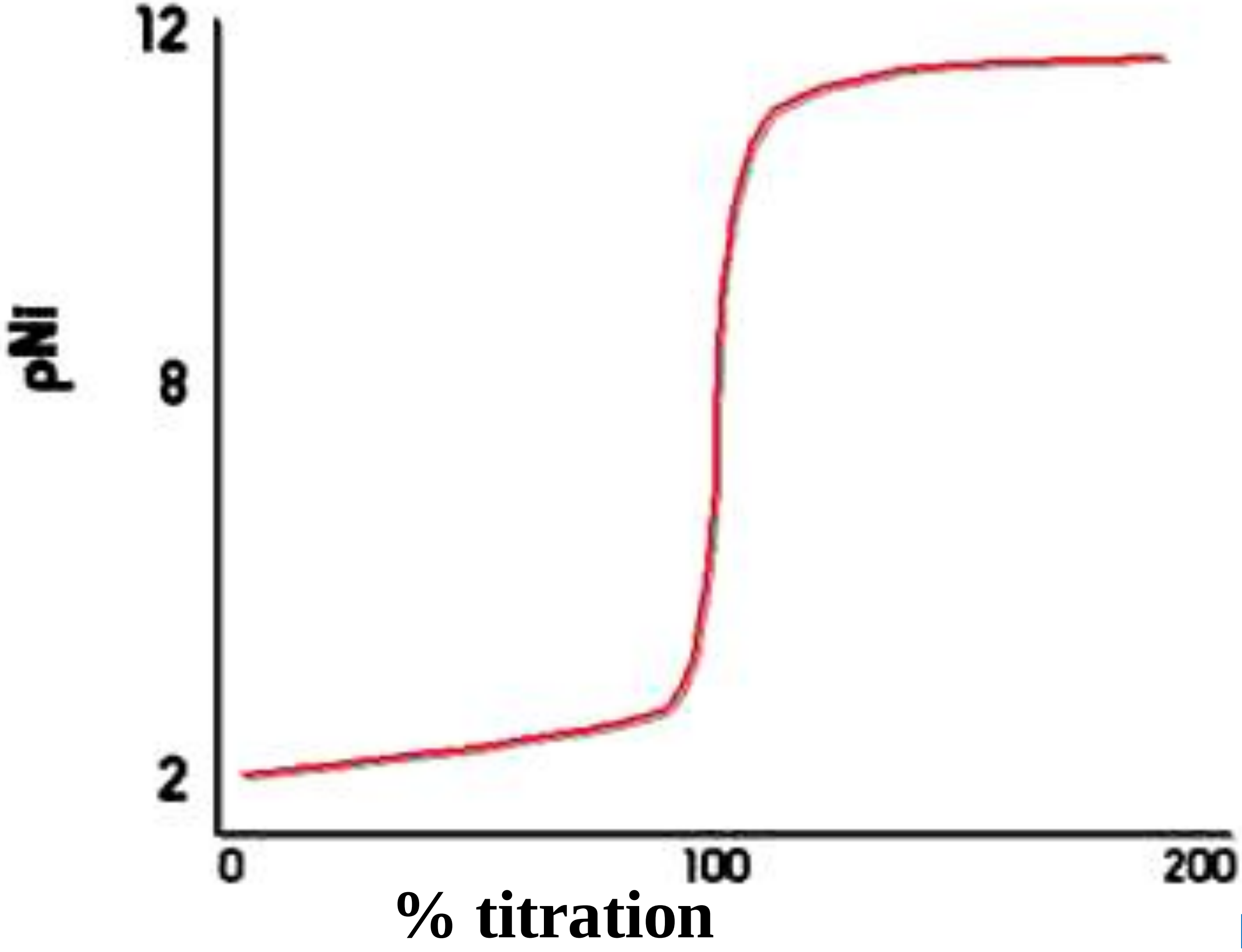
1.At pH $_3$ $K'_{NiY} = 2.5 * 10^{-11} * 4.2*10^{18} = 1.05*10^{8}$

2.At pH $_8$ $K'_{NiY} = 5.4*10^{-3}*4.2*10^{18} = 2.23*10^{16}$

Example 2: Calculate the molar Y^{4-} concentration in 0.02 M EDTA soln.at pH 10.where α_4 =0.35

$Y^{4-} = \alpha_4 Ct = 0.35 * 0.02 = 7 * 10^{-3}$ M

EDTA titrations

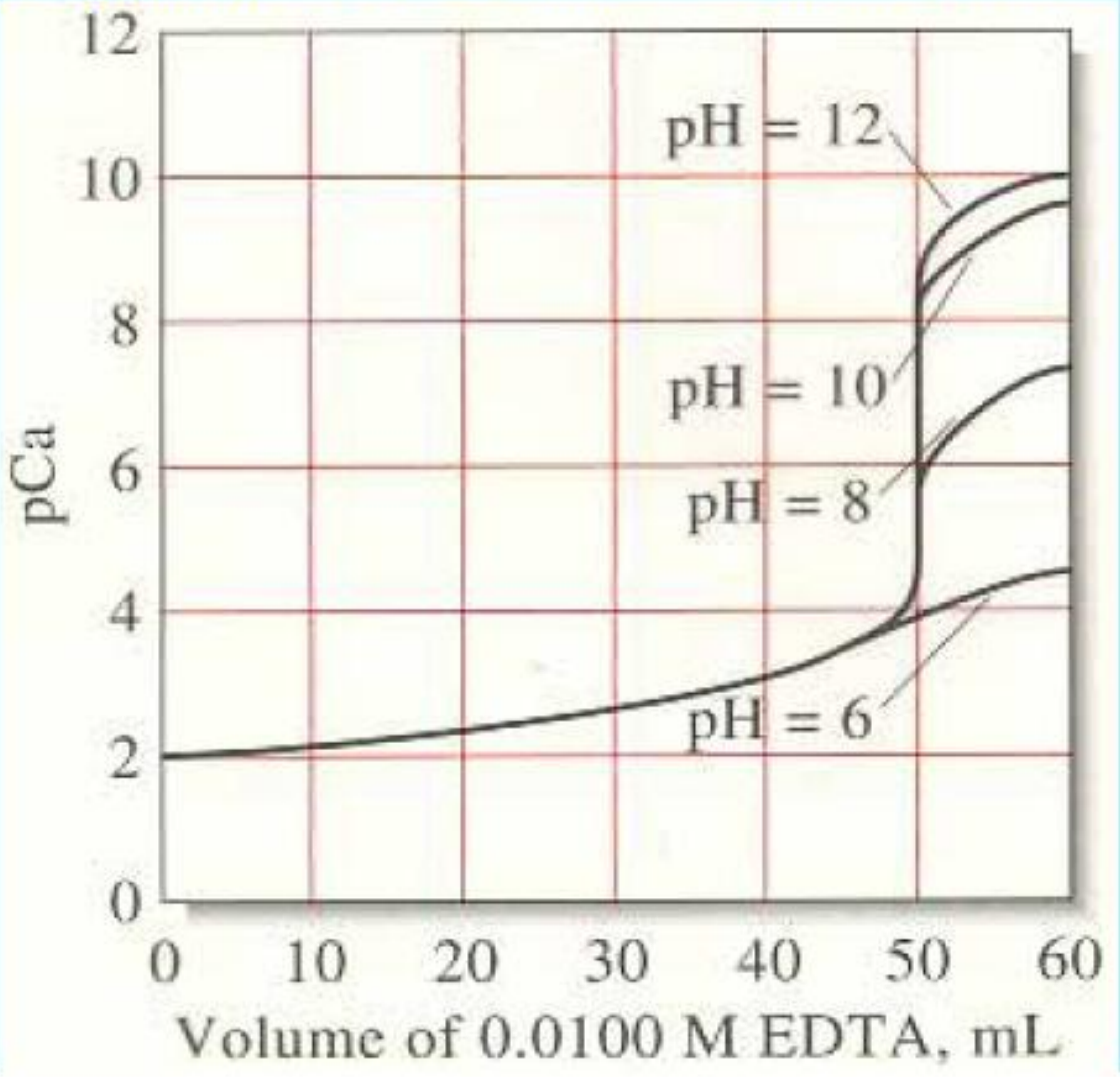


Titration curves

- pH changes the equilibrium constant of the MY complex
- less stable complexes can only be titrated in basic solution
- more stable complexes can be titrated in more acid solution, without significant dissociation
- metals that don't form a stable complex at low pH will not interfere wit determination of stable complexes

E) Please note the effect of increasing pH on the relative change of pCa before and after the equivalence point.

Note that the endpoint becomes sharper as pH increases.



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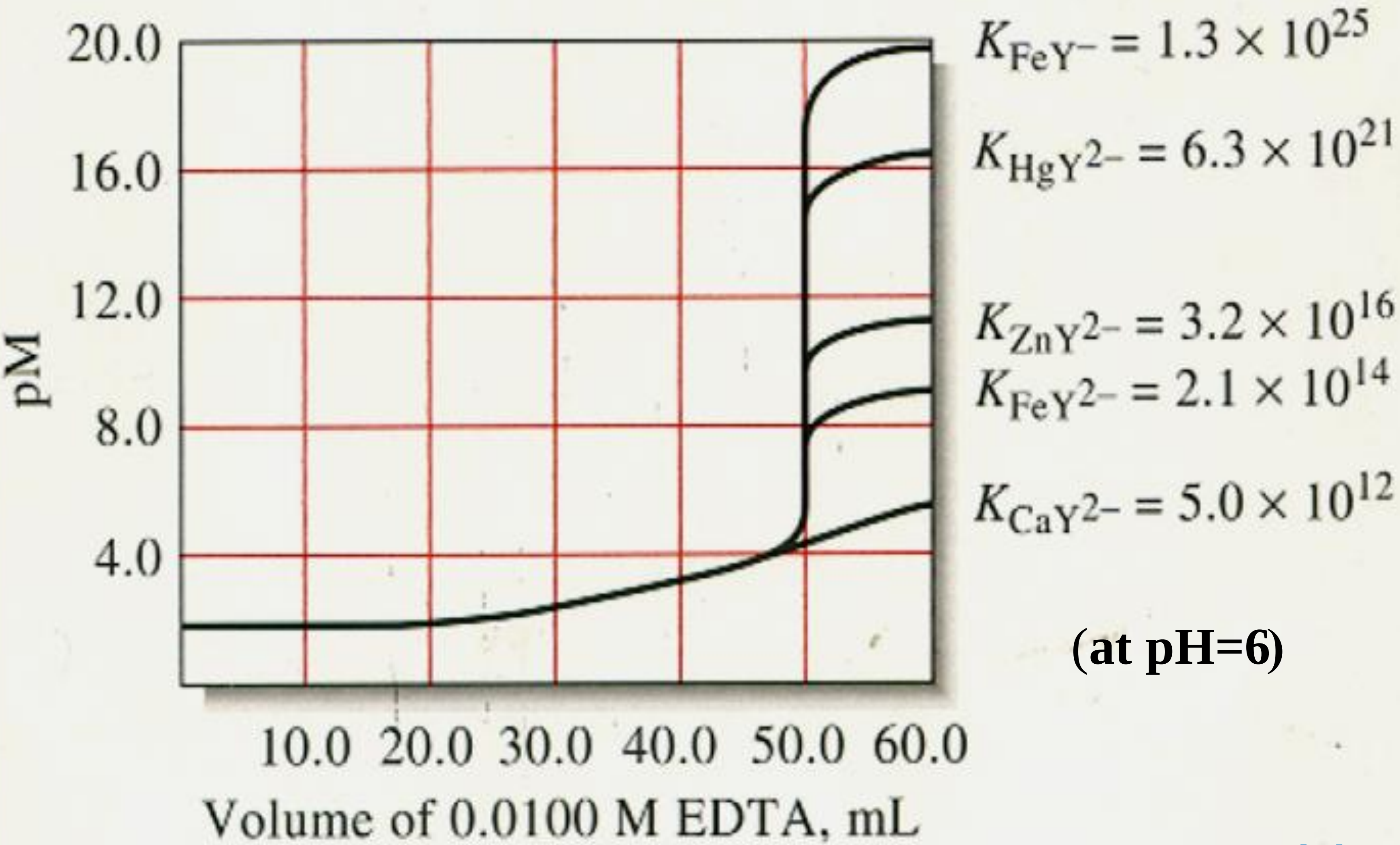
Complex of Metal/EDTA Titration Curves



(at pH=6)

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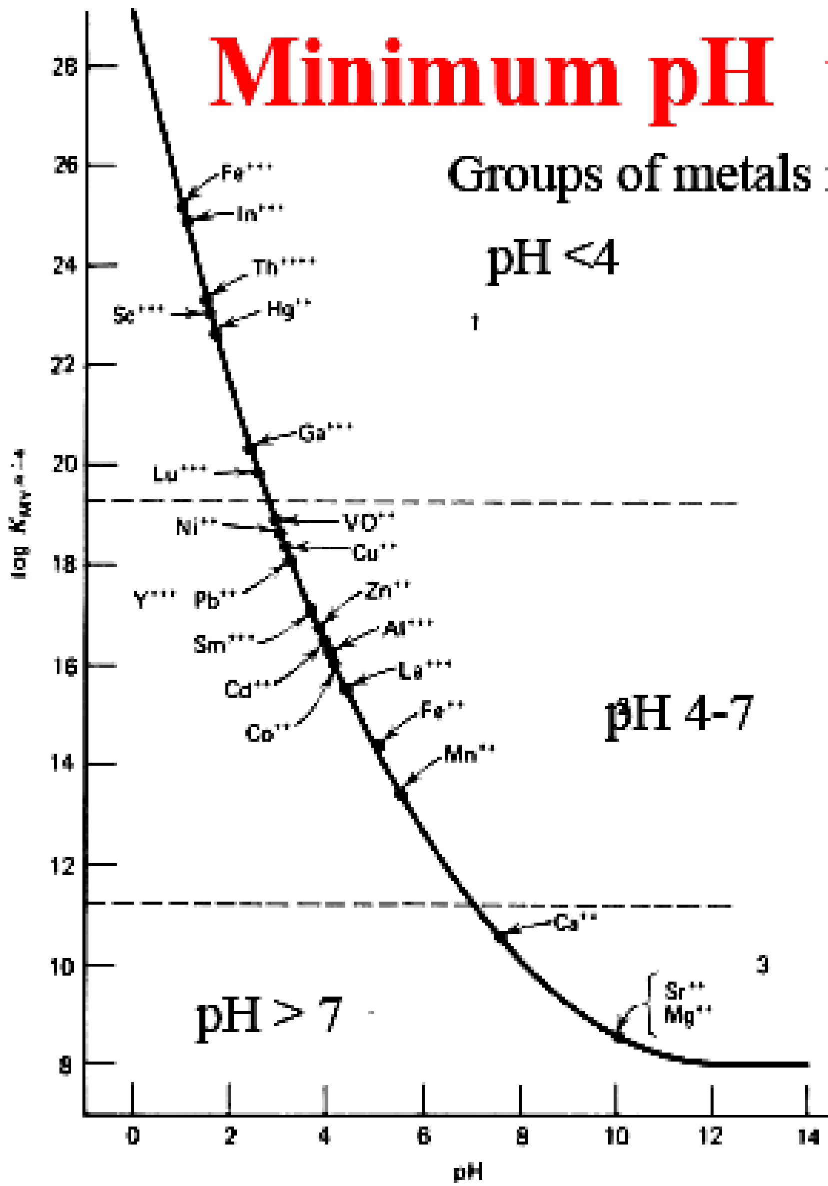
Minimum pH to titrate metals



- points are pH at which K' is 10^6 for each metal
- judged as minimum K' needed for sharp endpoint
- at high pH all metals will titrate
- at most acidic only first group titrate

Auxiliary complexing agents

Many EDTA titrations are complicated by the tendency on the part of the cation being titrated to form a hydroxide at the pH needed for a satisfactory end point. here ,an auxiliary complexing agent is needed to keep the cation in solution. for example , ammonia forms ammine complexes with zinc(II) and prevents the formation of sparingly soluble zinc hydroxide .the larger concentration of NH3 as auxiliary complexing reagent has the effect of decreasing the change in pZn in the equivalent point region.So,it is desirable to keep the concn of any auxiliary complexing reagent at the minimum needed to prevent hydroxide formation

$$Zn^{2+} + OH^{-} \rightarrow Zn(OH)_2\downarrow$$

$$Zn(NH_3)_4^{2+} + HY^{3-} \rightarrow ZnY^{2-} + 3NH_3 + NH_4^{+}$$

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Masking Agents

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- auxillary ligand that forms stable complex with potential interference
  - at pH=10, CN^- masks
    $M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}$

$$M(CN)_x^{y+}$$

- masking agent complex has greater stability constant than EDTA complex

Masking Agents

masking agent	pH	ions masked	ions titrated
cyanide	10	Cu, Co, Ni, Zn, Cd, Hg, Pt, Pd	alkaline earths, rare earths, Pb, Mn lanthanide series as scandium
triethanolamine	10	Sn, Al, Fe	Zn, Cd, Pb, Mn, rare earths **(La ,Y, Ac)**
aluminum flouride	10	Al, alkaline earths, rare earths	Zn, Cd, Mn
	6	Al, Ti	Cu
ascorbic acid	2	Cu, Fe, Hg	Bi, Th

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Indicators for EDTA titrations

In general ,these indicators are organic dyes that form chelates with metal ions weaker than EDTA - metals chelates. they are intensely colored as to be discernible to the eye in the range of 10^{-6}-10^{-7} M and used at definite pH range.

Example: *Eriochrome black T*(Erio T) .the predominant equilibrium for the indicator in acidic and mod.alkaline solution is:

H_2ind^- (acidic) ↔ $HInd^{2-}$ (mod.alk.) ↔ **ind^{3-}**(alka.)

Red blue orange

Indicators for EDTA titrations

$$M^{2+} H_2Y^{2-} \leftrightarrow MY^{2-} + 2H^{+}$$

$$M^{+2}\text{(metal ion)} + Hind^{2-} \leftrightarrow Mind^{-} \text{ (red)}$$

$$Mind^{-} + H2Y^{2-} \leftrightarrow Hind^{2-} + MY^{2-}$$

(red) (blue)

Since it is easier to EDTA to react with the uncomplexed metal, that reaction occurs first.

M-Ind is harder for EDTA to react with so we must insure that only a small amount of indicator is used.

Table: some common metal indicators for EDTA titrations

Indicator	color of uncomplexed form of indicator	Color of complexed form of ind.with metal
Eriochrome black t	pH<6.3 red , 6.3<pH<11.6 blue, 11.6<pH orange	red
calmagite	pH < 8.1 red 8.1< pH <12.4 blue 12.4 < pH orange	red
Murexide	pH < 9.2 red 9.2 < pH <10.9 violet 10,9 < pH blue	**Yellow or red,** related to metal ion
Xylenol orange	pH < 6.7 yellow 6.7< pH violet	red
Pyrocatechol violet	pH < 7.8 yellow 7.8 < pH < 9.8 violet 9.8 < pH pink	blue

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Application of EDTA titrations

- EDTA does not have high selectivity
- For samples with mixture of metal ions
  - Require separation of ions by precipitation or extraction

Applications

- Titration of magnesium and calcium in the presence of cadmium, cobalt, copper, nickel, zinc ions – use masking agent such as cyanide ion. Cyanide ions complexes interfering ions – stable complexes are formed.

Types of EDTA Titrations

1. Direct titration

- metal ion, adjust pH, masking agent, indicator in solution
- titrate with EDTA to endpoint

Eg.Ca lactate, Ca gluconate

Titration of zinc(II) with EDTA

- Before equivalence point, red color is due to formation of zinc-indicator complex.
- Addition of EDTA titrant which will complex free zinc ions.
- After free zinc ions has been titrated, EDTA will react with zinc from zinc-indicator complex

$$ZnIn^{-} \quad + \quad HY^{3-} \rightarrow \quad ZnY^{2-} \quad + \quad HIn^{2-}$$

red *blue*

- Color of solution will gradually change from red to blue.
- Equivalence point reached when all $ZnIn^-$ has been changed to ZnY^{2-} and the solution is a pure blue color.

2. Back titration

Used when the reaction with EDTA is slowly and no indicator.

- **known excess of EDTA is added to analyte**
- **excess EDTA titrated with std. soln. of a second metal ion as Zn^{2+} or Mg^{2+}**
- **back titration necessary if analyte**

Cation form precipitate with the analyte anion under the conditions of analysis ;the excess EDTA keeps he cation in solution.

3.Alkalimetric titration

Titration of Hydrogen ion

$$M^{2+} + H2Y^{2-} \rightarrow MY^{2-} + 2H^{+}$$

- $M^{n+} + \underset{excess}{EDTA} \Leftrightarrow M\text{-}EDTA + H^{+}$
- liberated H^{+} can be titrated with NaOH where:
- $H^{+} \equiv M^{n+}$

4. Displacement of metal ion

Sample treated with excess of Mg-EDTA Or Zn-EDTA. sample to determined must form more stable complex with EDTA than do Mg or Zn.

$M^{2+} + MgY2- \rightarrow MY^{2-} + Mg^{2+}$

(Ni^{2+}, Co^{2+}, Ca^{2+},Mn^{2+} , Zn^{2+})

$Ni^{2+} + MgY^{2-} \rightarrow NiY^{2-} + Mg^{2+}$ ($Mg^{2+} \equiv Ni^{2+}$)

$M^{2+} + ZnY^{2-} \rightarrow MY^{2-} + Zn^{2+}$

(Fe^{3+}, Hg^{2+}, pb^{2+})

$Fe^{3+} + ZnY^{2-} \rightarrow FeY^{-} + Zn^{2+}$ ($Zn^{2+} \equiv Fe^{3+}$)

Librated $Zn^{2+}$and Mg^{2+} can be determined with standard EDTA solution.

5. Indirect titration

- anions that precipitate certain metals can be analyzed with EDTA
- sulfate analyzed by precipitation with excess Ba^{+2}

$So4^{2-} \equiv Ba^{2+} \equiv EDTA$

Water hardness

The hardness of water is defined as the combined concentration of **$[Ca^{2+}] + [Mg^{2+}]$** ,typically above 0.6 mM .in order to determine water hardness. the sum of calcium and magnesium concentration is determined by titration with **EDTA** in presence of **ammonia buffer at pH= 10** using **Eriochrome black T** as indicator. the result is expressed in term of mg $CaCO_3$ per liter of water.

$$H_2Y^{2-} + Ca^{2+} \rightarrow CaY^{2-} + 2H^+$$

$$H2Y^{2-} + Mg^{2+} \rightarrow MgY^{2-} + 2H^+$$

$$H_2Y^{2-} + Mg_{ind}^{-}\ (red) \rightarrow MgY^{2-} + H_{ind2-}(blue) + H^+$$

(at eq.point)

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Example2: **Complete the equation: $AgCl + NH_3 \rightarrow$**

$AgCl + 2\ NH_3 \rightarrow Ag(NH_3)_2^{+} + Cl^{-}$

Example3: **Indicate the oxidation state of the central metal ion of the following:**

(a)$CuBr_4^{2-}$ or $[CuBr_4]^{2-}$ (b)$ZnCl_4^{2-}$,(c) $PtCl_4^{2-}$, (d) $Co(en)_3^{2+}$e $Cu(CN)_2^{-}$

(a) +2 (b) +2 (c) +2 (d) +2 (e) +1

Example 5: describe the preparation of 2L of 0.1 M from Na_2H_2Y(FW= 372 g).

1L M Na_2H_2Y ≡ 372 g

1L 0.1 M ≡ 37.2 g

2L 0.1 M ≡ 74.4 g

Dissolve 74.4 g of Na_2H_2Y in water and dilute to exactly 2 L.

Example6: calculate the concentration of $Mg(NO_3)_2$(148 g) in term of (g/L) if 25 ml of $Mg(NO_3)_2$ was titrated with 0.05 M of EDTA ,where the volume of EDTA consumed at equivalent point was 37.5 ml.

$37.5 \times 0.05 = 25 \times M$

$M = 0.075$

$C(g/L) = 0.075 \times 148 = 11.10\ g/L$

Example 8:

An EDTA solution is standardized against high purity $CaCO_3$ by dissolving 0.3982 g of $CaCO_3$ in HCL and adjusting the pH to 10. The solution is then titrated with EDTA requiring 38.26 mL. Find the molarity of EDTA.

Solution :

EDTA reacts with metal ions in a 1:1 ratio. Therefore,

mmol $CaCO_3$ = mmol EDTA

mg/FW = Molarity x V_{mL}

398.2/100.0 = M x 38.26

M_{EDTA} = 0.1041

Hardness of water :Ca^{2+}+ Mg^{+2}

50ml water sample + 10 ml NH3 buffer (pH 10) (5.4 g of NH4Cl +70 ml of 5 N of NH3 soln.)&final vol. 100 ml. add few drops of EBT indicator .color of the solution will be wine red. final color is blue at end point.

Calculations:

Moles of EDTA .=0.05 ×vol. of EDTA(10 ml)=0.05 ×10 ×10^{-3}=0.05 ×10^{-2} moles = moles of $Ca^{2+}$and Mg^{+2}