

# Complex Formation

complex ions (also called *coordination ions*)

## Bronsted Acids and Bases

*acid* => proton donor

*base* => proton acceptor  
(hydroxide ion donor)

## Lewis Acids and Bases

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

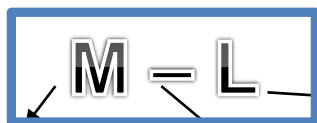
*base* => electron pair donor  
(*ligand*)

*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



Cation

central ion

Ligand, an ion or neutral molecule

ionic bond salt or ion pair

covalent bond complex ion or compound

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



Lewis acid

Lewis base

No. of bonds (coordn no of the metal)

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

*Non labile*  
or inert  
complexes

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

*Labile*  
complexes

- complexes undergo substitution reactions very rapidly
- $\text{Cu}(\text{H}_2\text{O})_4^{2+} + 4 \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+} + 4\text{H}_2\text{O}$

Effect of pH

# Ligands

Ligands generally contain an electronegative atom,

**N, O, X, S**

$\text{NH}_3$  (one unshared pair of e, unidentate L)

$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$   
(ethylen diamine (en))  
bidentate L (2 groups → 2 bonds with the M ion)

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.



- 1:1 reaction  $\rightarrow$  sol. Complex

- $$K = \frac{[ML]}{[M][L]}$$
 stability or formation const

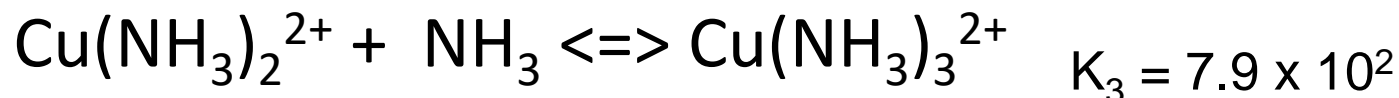
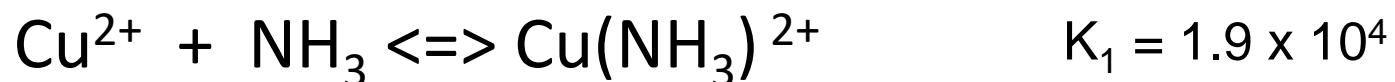
Its reciprocal is instability or dissociation constant.

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

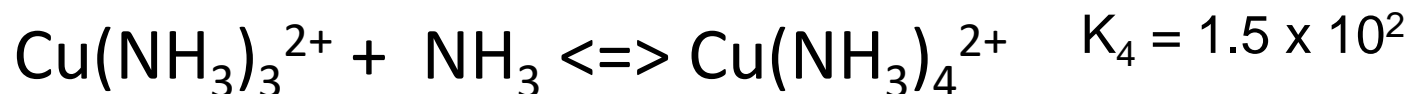
# Stepwise Formation Constant

Consider the reaction of  $\text{NH}_4\text{OH}$  with  $\text{Cu}^{2+}$  ions  
at first, the blue solution turns cloudy with the formation of  
a pale **blue** ppt  $\text{Cu}^{2+} + 2 \text{OH}^- \rightleftharpoons \text{Cu}(\text{OH})_2$

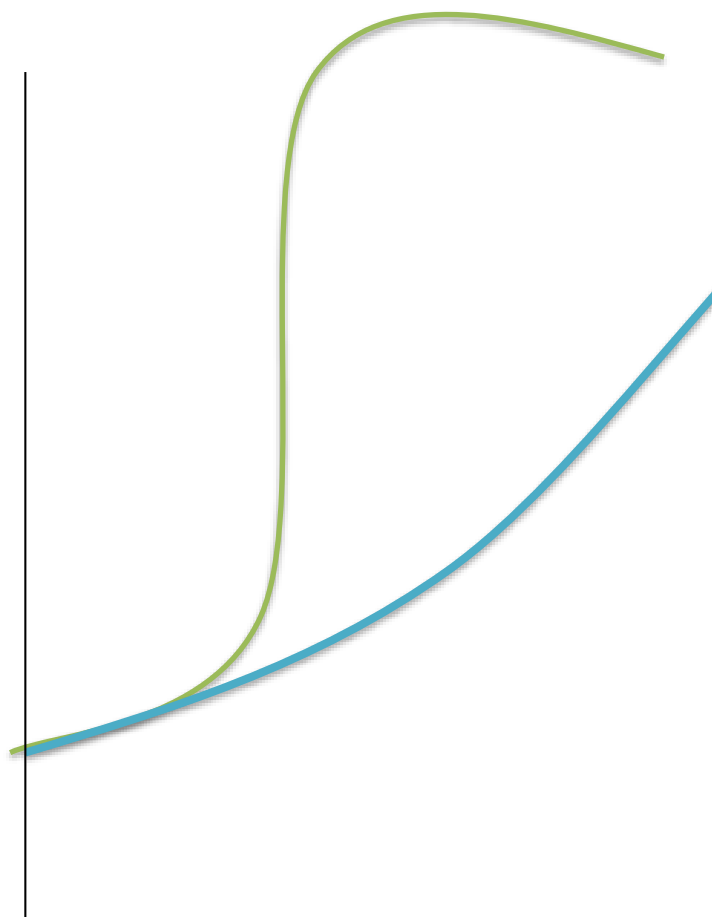
as the concentration of the  $\text{NH}_4\text{OH}$  increases  $\rightarrow \text{NH}_3$   
coordinates with  $\text{Cu}^{2+}$  ion  $\rightarrow$  **blue** colour soln



and finally



pH or pCu



Moles of ammm per mole of  $\text{H}_3\text{O}^+$  or  $\text{Cu}^{2+}$

- **Overall:**

- $\text{Cu}^{2+} + 4 \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$
- $K = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$
- $= K_1 K_2 K_3 K_4 = 8.1 \times 10^{12}$

- Though the value of K is large, this titration is not feasible.
- There is less tendency for  $\text{Cu}(\text{NH}_3)^{2+}$  to
- add a second  $\text{NH}_3$  than for
- free  $\text{Cu}^{2+}$  to bind the first one.
- tendency to add  $\text{NH}_3$
- decreases at each step of the process.

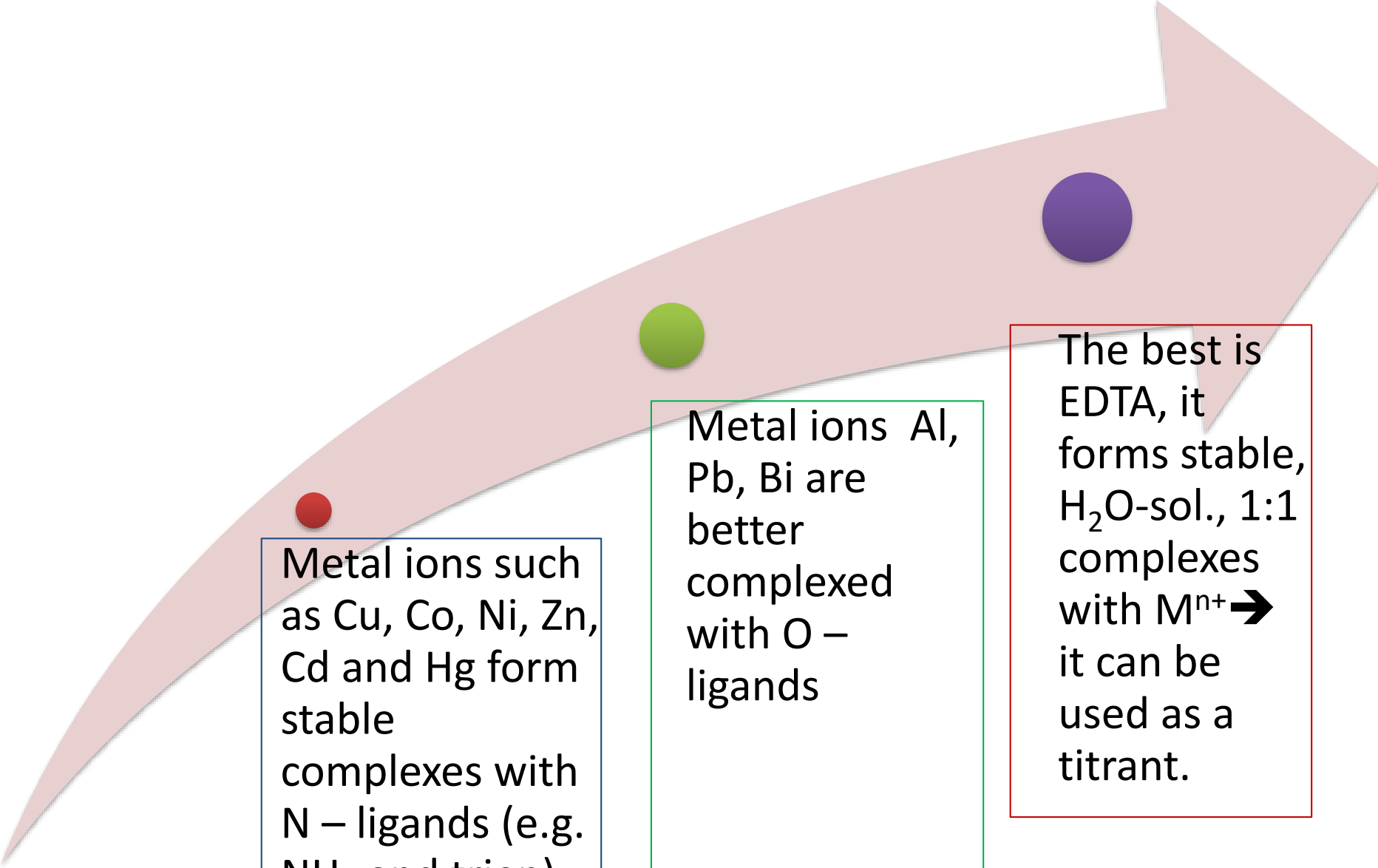


- $K \sim 10^8$
- The reaction is complete at the equivalence point for a feasible titration
- That is why we prefer chelating agents than simple ligands.

## 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 M and 2 atoms on the L

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

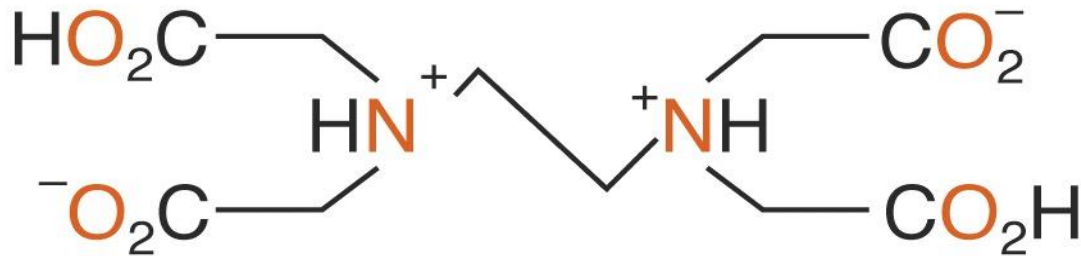


Metal ions such as Cu, Co, Ni, Zn, Cd and Hg form stable complexes with N – ligands (e.g.  $\text{NH}_3$  and trien)

Metal ions Al, Pb, Bi are better complexed with O – ligands

The best is EDTA, it forms stable,  $\text{H}_2\text{O}$ -sol., 1:1 complexes with  $\text{M}^{n+}$  → it can be used as a titrant.

# EDTA



## EDTA

Ethylenediaminetetraacetic acid

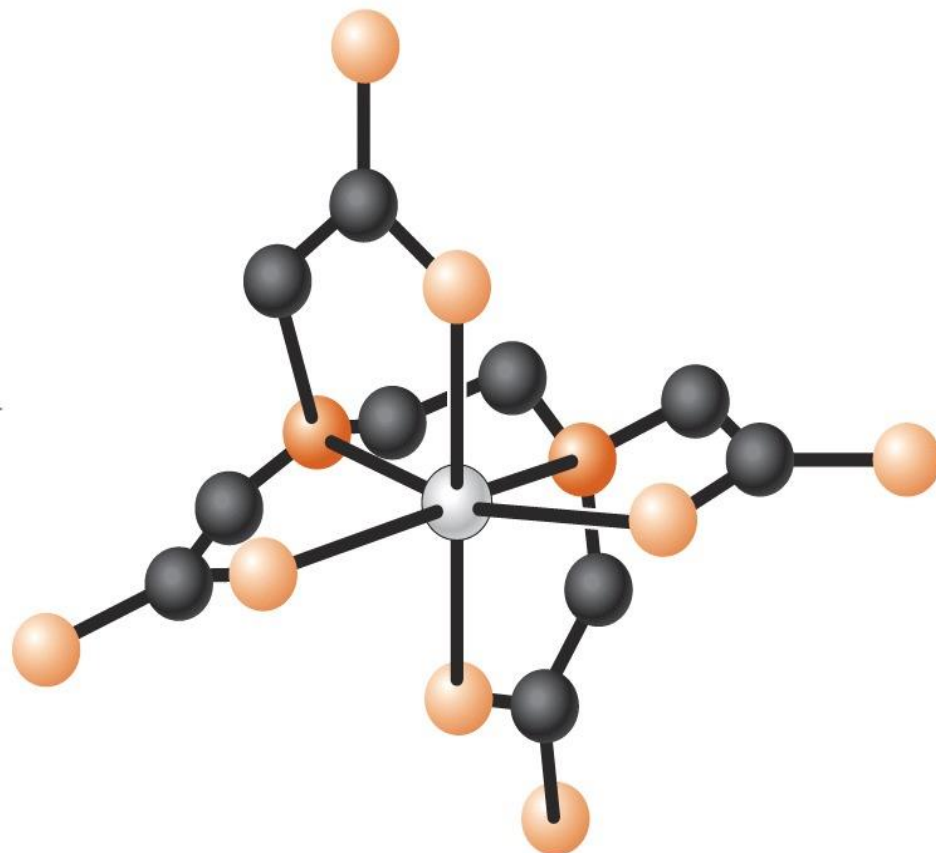
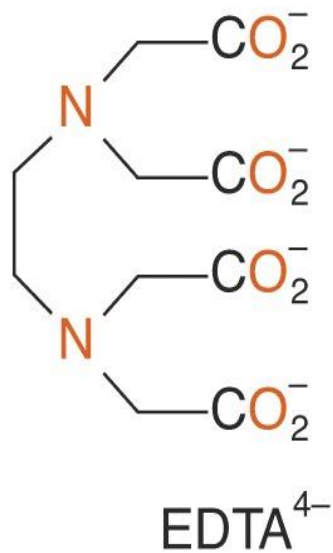
(also called ethylenedinitrilotetraacetic acid)

- => H<sub>4</sub>EDTA => H<sub>4</sub>Y

Since the EDTA contains 6 basic sites – 4 COOH, 2 N – 6 acid species can exist

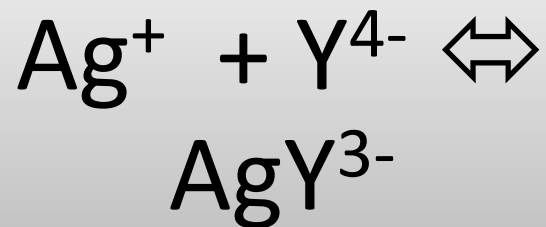


# MnEDTA<sup>2-</sup>

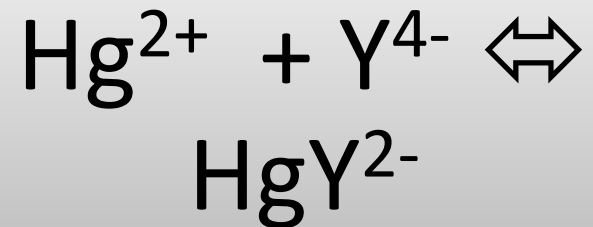




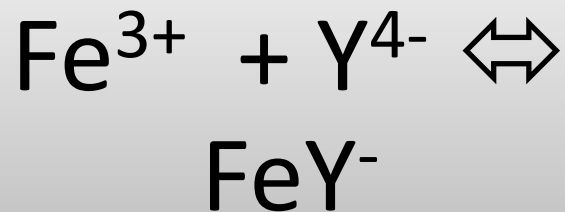
1+ cation



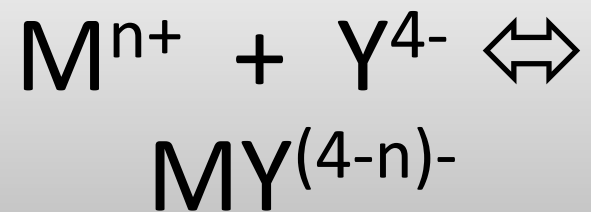
2+ cation



3+ cation



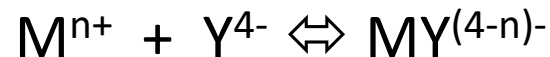
n+ ion



# Equilibria involved in EDTA titrations

- EDTA contains 6 basic sites – 4 COOH, 2 N –  $\rightarrow$  6 acid species can exist

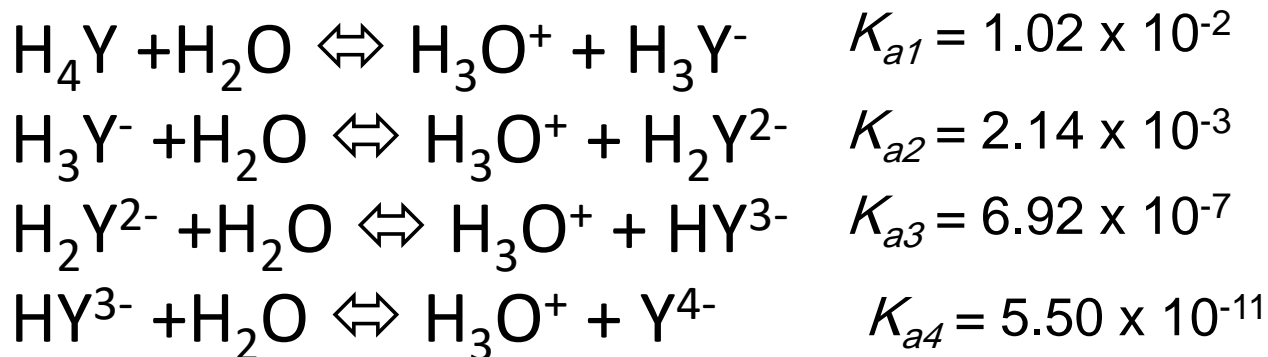
- $H_6Y^{2+}$ ,  $H_5Y^+$ ,  $H_4Y$ ,  $H_3Y^-$ ,  $H_2Y^{2-}$ ,  $HY^{3-}$ .



- The absolute stability or formation const

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

## The pH effect :



- 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  $\text{Y}^{4-}$ ,  $c_y$  total concentration of the uncomplexed EDTA

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

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

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

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

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



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

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

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

$K_{eff}$ , **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  $K_{eff}, \alpha_4$  in tables of constants.

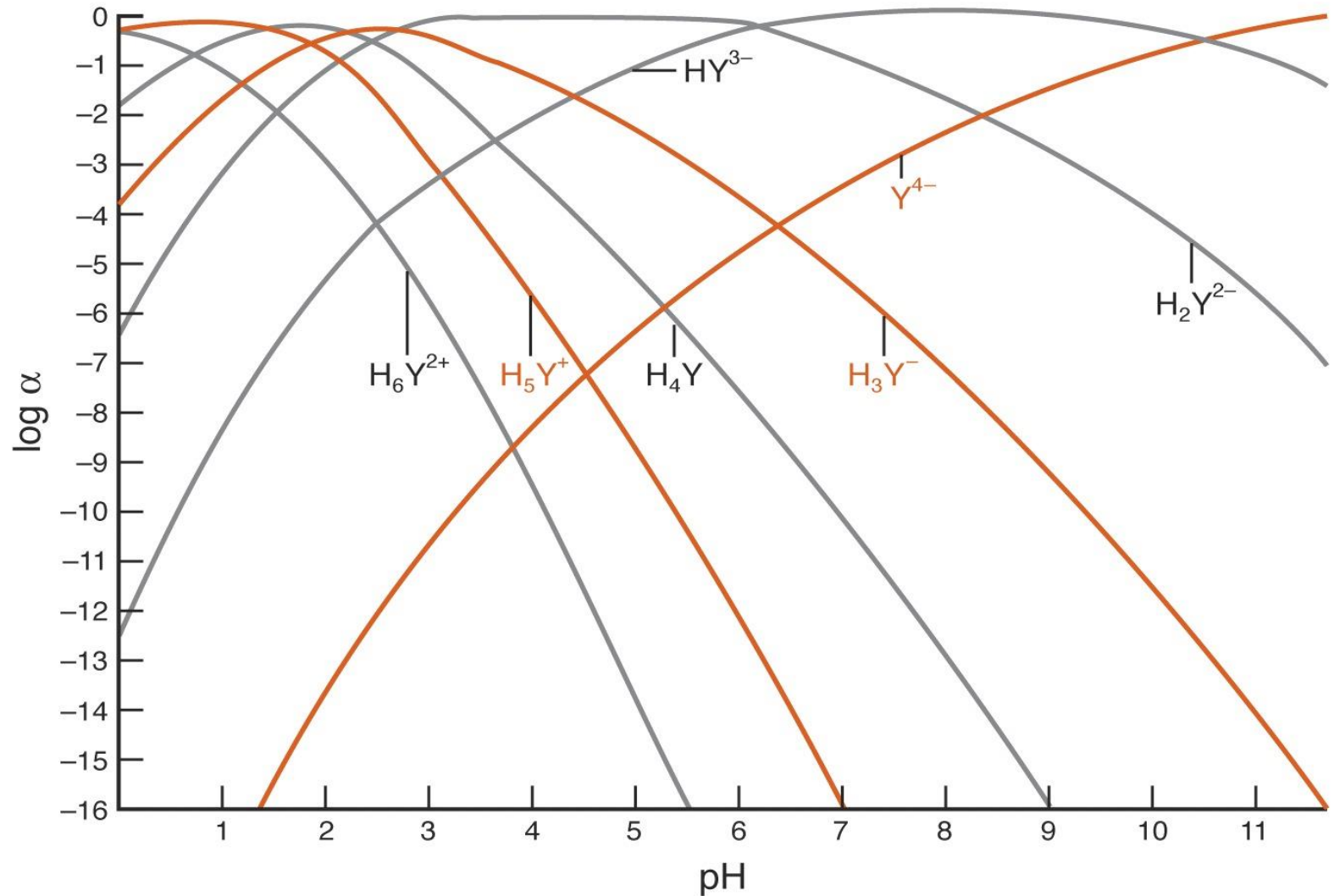
- as the pH goes down,  $\alpha_4$  becomes smaller and  $K_{eff}$  becomes smaller.
- At pH > 12 (EDTA is completely dissociated)
- $\alpha_4 \sim 1$ ,  $K_{eff} \sim K_{abs}$

- 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.

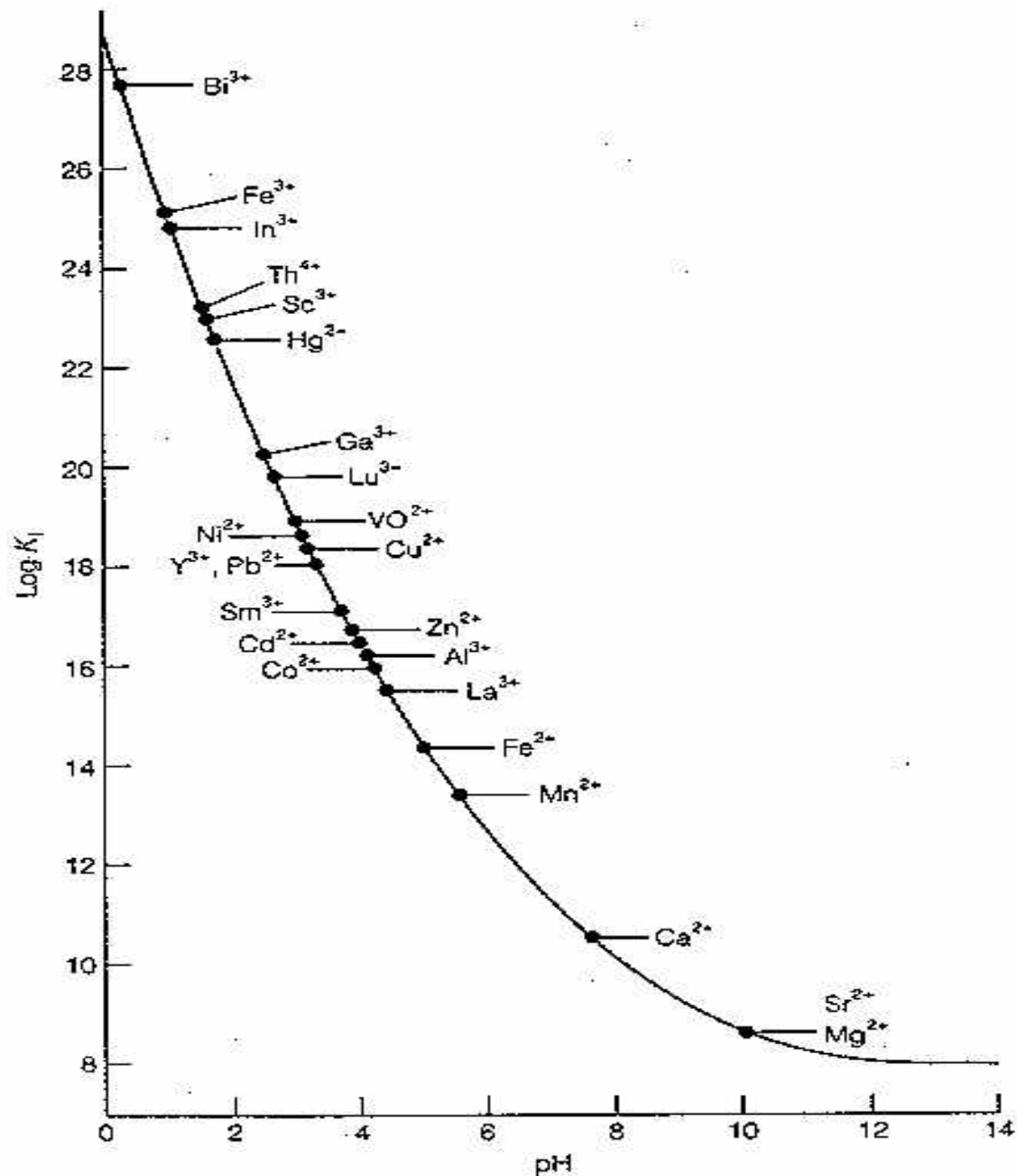
**Table 13-1** Values of  $\alpha_{Y^{4-}}$  for EDTA at 20°C and  $\mu = 0.10$  M

pH	$\alpha_{Y^{4-}}$
0	$1.3 \times 10^{-23}$
1	$1.9 \times 10^{-18}$
2	$3.3 \times 10^{-14}$
3	$2.6 \times 10^{-11}$
4	$3.8 \times 10^{-9}$
5	$3.7 \times 10^{-7}$
6	$2.3 \times 10^{-5}$
7	$5.0 \times 10^{-4}$
8	$5.6 \times 10^{-3}$
9	$5.4 \times 10^{-2}$
10	0.36
11	0.85
12	0.98
13	1.00
14	1.00

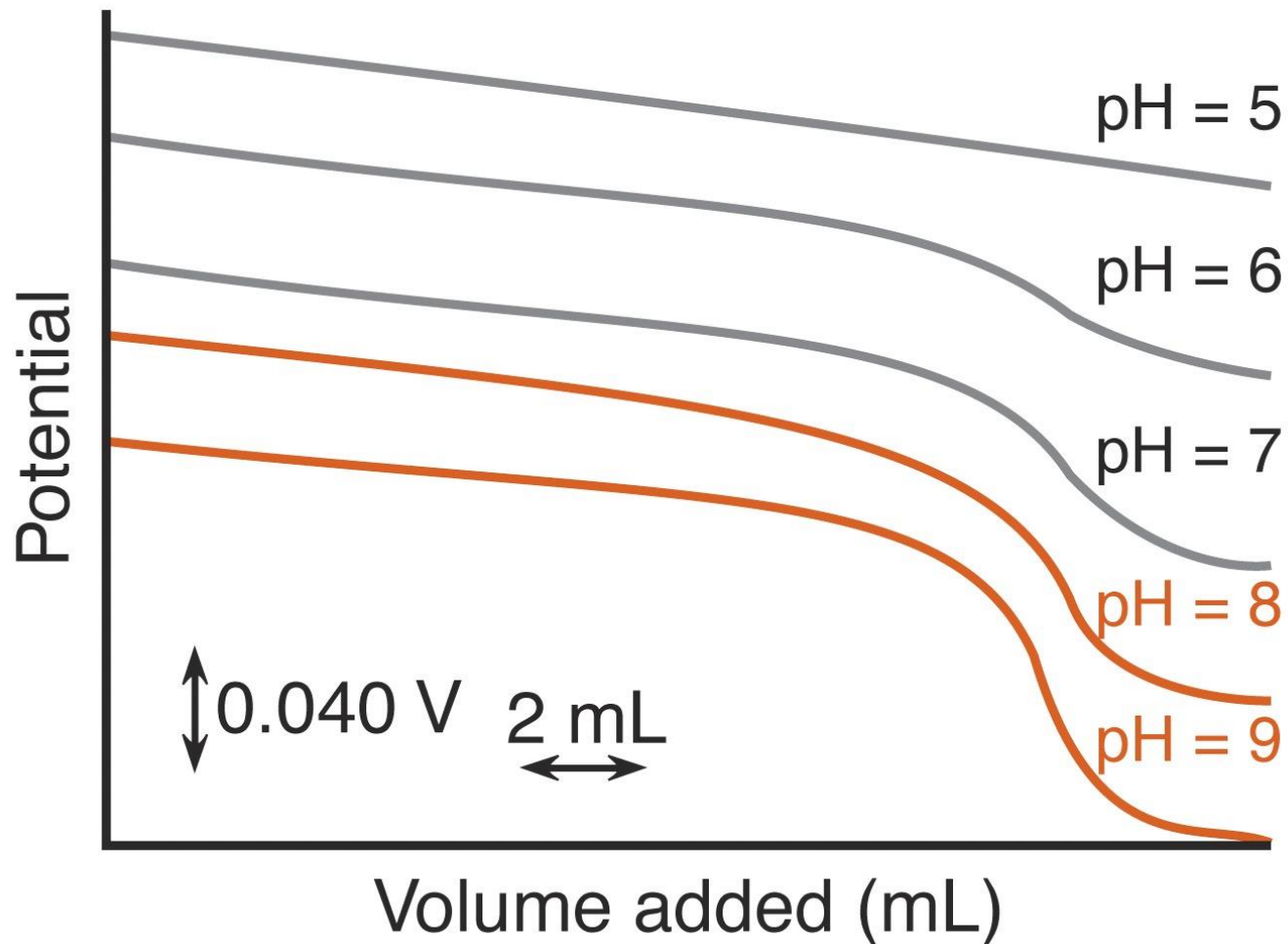
# Fractional Composition Diagram for EDTA



# Minimum pH for Effective EDTA Titrations



# Titration of $\text{Ca}^{+2}$ at various pHs



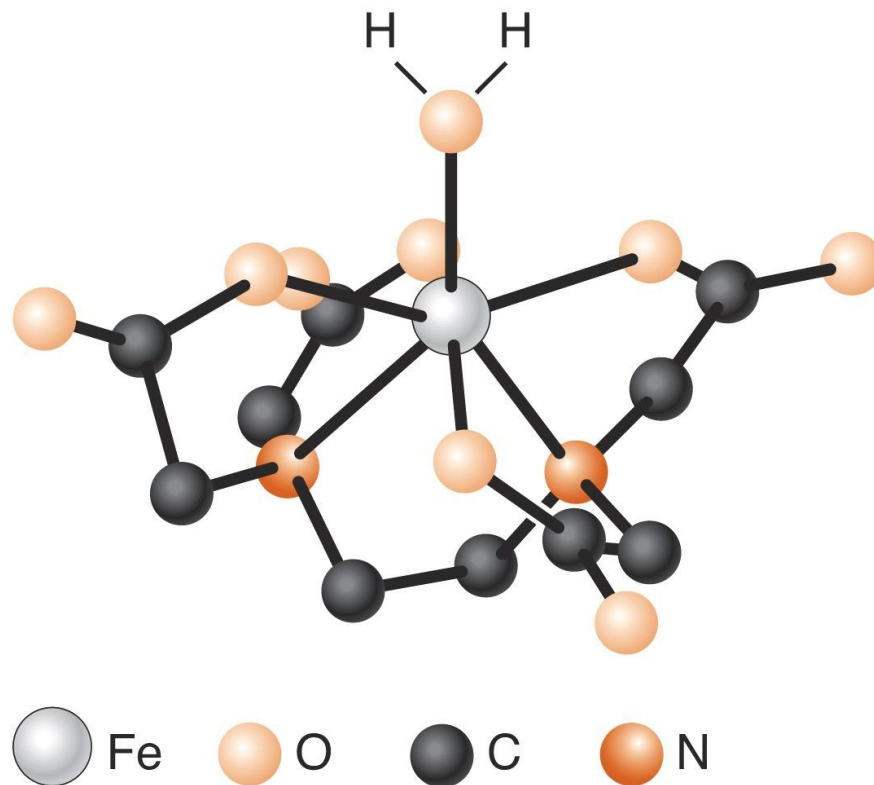
**Table 13-2 Formation constants for metal-EDTA complexes**

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

# 7-Coordinate [Fe<sup>III</sup>EDTA H<sub>2</sub>O]<sup>-1</sup>



- 50.0 mL of a solution which is 0.0100  $M$  in  $\text{Ca}^{2+}$  and buffered at pH 10.0 is titrated with 0.0100  $M$  EDTA solution. Calculate values of  $p\text{Ca}$  at various stages of the titration and plot the titration curve.

- $K_{abs} \text{CaY}^{2-}$  is  $5.0 \times 10^{10}$ ,  $\alpha_4$  at pH 10.0 is 0.35 →
- $K_{eff} = 5.0 \times 10^{10} \times 0.35 = 1.8 \times 10^{10}$



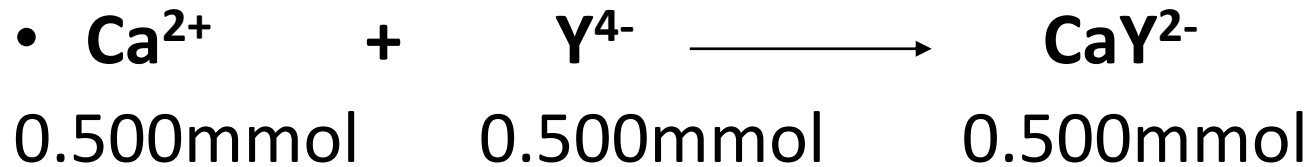
## (1) Start of titration

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

## (2) After addn of 10.0 mL of titrant

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

### (3) Equivalence point



- $[\text{Ca}^{2+}] = c_y,$

- $[\text{CaY}^{2-}] \sim 0.500\text{mmol}/100\text{mL}$

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

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

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

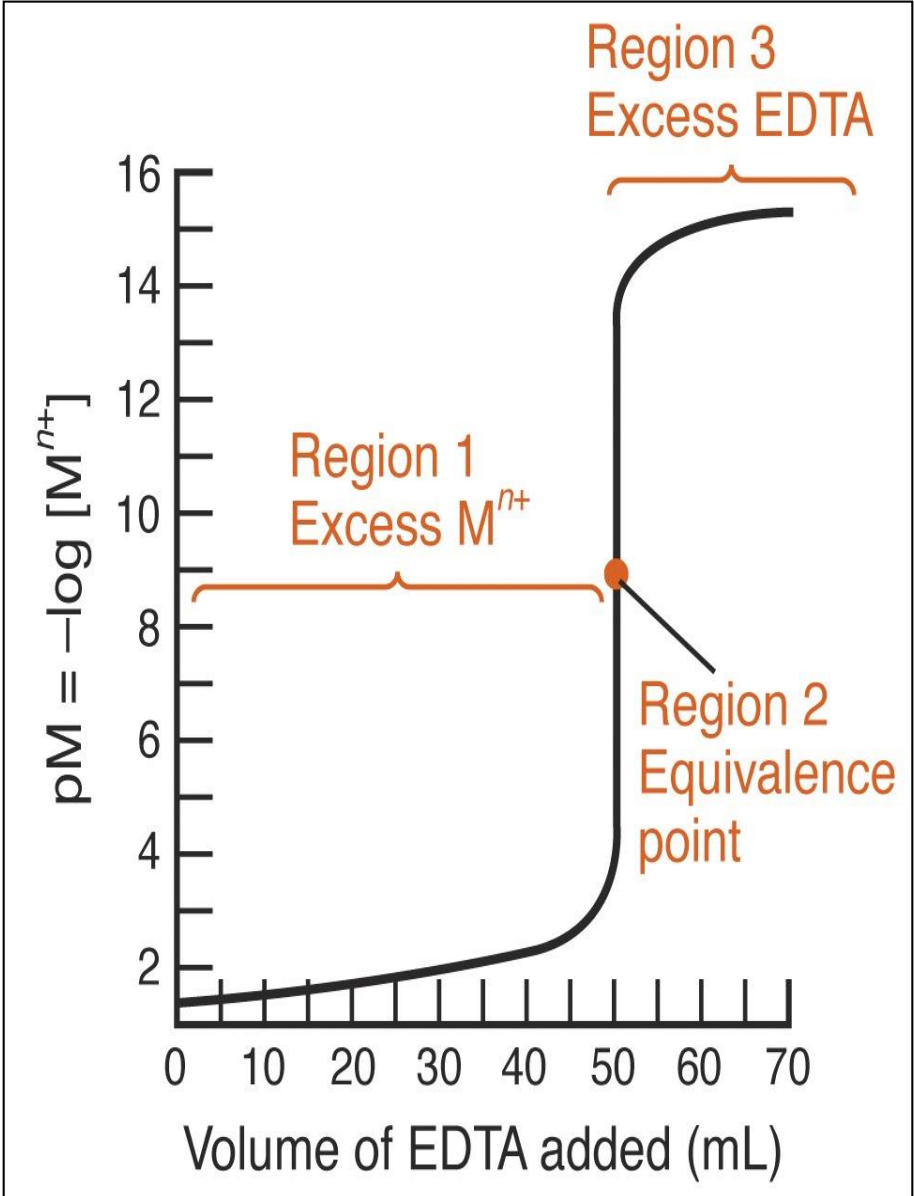
#### (4) After addn of 60.0 mL of titrant

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

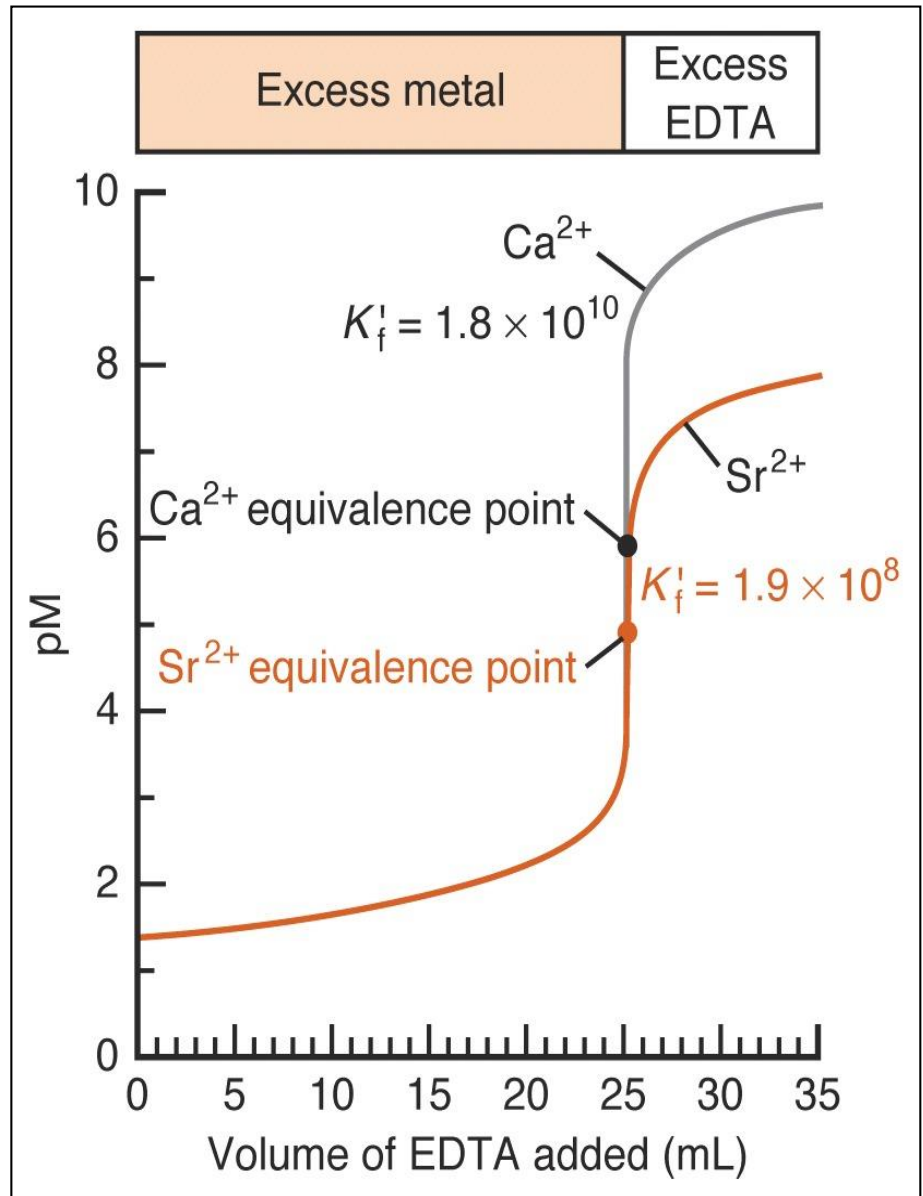
$$\frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}] c_y} = K_{eff}$$

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

# Three Regions of EDTA Titration



# Theoretical titration curves



# Masking

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

- With certain  $\text{M}^{n+}$  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,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  are complexed with EDTA
- At pH>12 →  $\text{Mg}(\text{OH})_2$  ppt →  $\text{Ca}^{2+}$  is only complexed

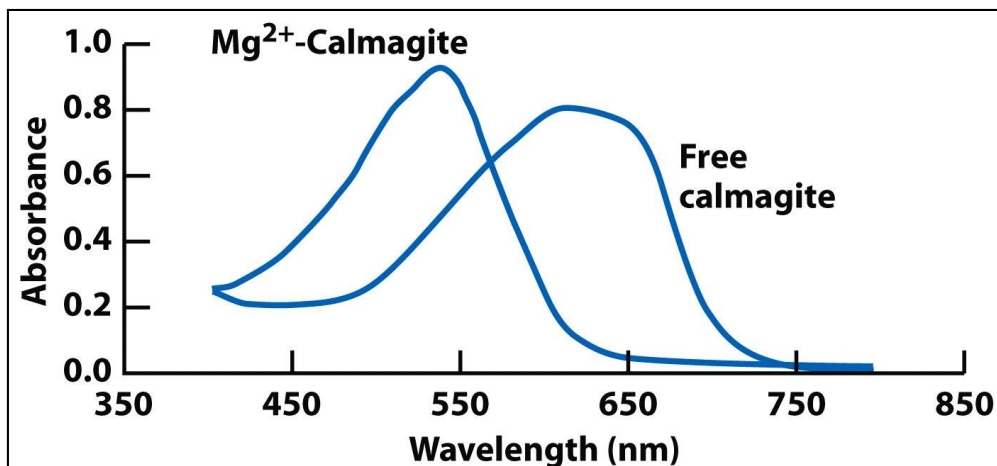
# Metal Ion Indicators

- The most common technique to detect the e. p. in EDTA titrations is to use a metal ion indicator.
- are compounds whose colour changes when they bind to a metal ion.  
*M - In must be less strongly than M - EDTA.*



**In a direct titration,**  
✓  $M^{n+}$  is titrated with standard EDTA.

✓ The  $M^{n+}$  is buffered to a pH at which the  $K_{eff}$  for the M-EDTA complex is large and the color of the  $In_{free}$  is different from that of the  $M-In$  complex.



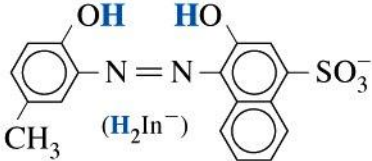
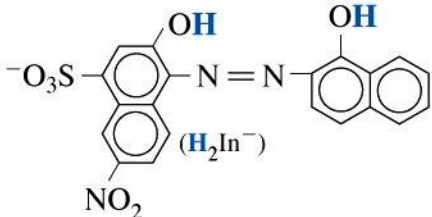
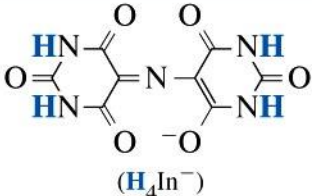
# EDTA indicators

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

- *EBT* is unstable in solution, it must be freshly prepared
- *Calmagite* is stable in aq. Soln  $\text{H}_3\text{In}$
- $\text{H}_2\text{In}^-$  red,  $\text{HIn}^{2-}$  blue,  $\text{In}^{3-}$  reddish orange



**Table 12-3 Common metal ion indicators**

Name	Structure	pK <sub>a</sub>	Color of free indicator	Color of metal ion complex
Calmagite		<p>pK<sub>2</sub> = 8.1 pK<sub>3</sub> = 12.4</p>	<p>H<sub>2</sub>In<sup>-</sup> red HIn<sup>2-</sup> blue In<sup>3-</sup> orange</p>	Wine red
Eriochrome black T		<p>pK<sub>2</sub> = 6.3 pK<sub>3</sub> = 11.6</p>	<p>H<sub>2</sub>In<sup>-</sup> red HIn<sup>2-</sup> blue In<sup>3-</sup> orange</p>	Wine red
Murexide		<p>pK<sub>2</sub> = 9.2 pK<sub>3</sub> = 10.9</p>	<p>H<sub>4</sub>In<sup>-</sup> red-violet H<sub>3</sub>In<sup>2-</sup> violet H<sub>2</sub>In<sup>3-</sup> blue</p>	<p>Yellow (with Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>); red with Ca<sup>2+</sup></p>

**PREPARATION AND STABILITY:**

**Calmagite:** 0.05 g/100 mL H<sub>2</sub>O; solution is stable for a year in the dark.

**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.

**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 H<sub>2</sub>O; solution is stable indefinitely.

**Pyrocatechol violet:** 0.1 g/100 mL; solution is stable for several weeks.

**Table 12-3 part 1**

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**Table 12-3 Common metal ion indicators**

Name	Structure	$pK_a$	Color of free indicator	Color of metal ion complex
Xylenol orange	<p style="text-align: center;">(<math>H_3In^{3-}</math>)</p>	$pK_2 = 2.32$ $pK_3 = 2.85$ $pK_4 = 6.70$ $pK_5 = 10.47$ $pK_6 = 12.23$	$H_5In^-$ yellow $H_4In^{2-}$ yellow $H_3In^{3-}$ yellow $H_2In^{4-}$ violet $HIn^{5-}$ violet $In^{6-}$ violet	Red
Pyrocatechol violet	<p style="text-align: center;">(<math>H_3In^-</math>)</p>	$pK_1 = 0.2$ $pK_2 = 7.8$ $pK_3 = 9.8$ $pK_4 = 11.7$	$H_4In$ red $H_3In^-$ yellow $H_2In^{2-}$ violet $HIn^{3-}$ red-purple	Blue

**PREPARATION AND STABILITY:**

**Calmagite:** 0.05 g/100 mL  $H_2O$ ; solution is stable for a year in the dark.

**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.

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**Xylenol orange:** 0.5 g/100 mL  $H_2O$ ; solution is stable indefinitely.

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**Table 12-3 part 2**

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# EDTA titration techniques

- Direct titration:
- Back titration:
- Displacement titration:
- Indirect titration:
- Masking agent:

# 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  $\text{M}^{n+}$  which forms complexes with ammonia

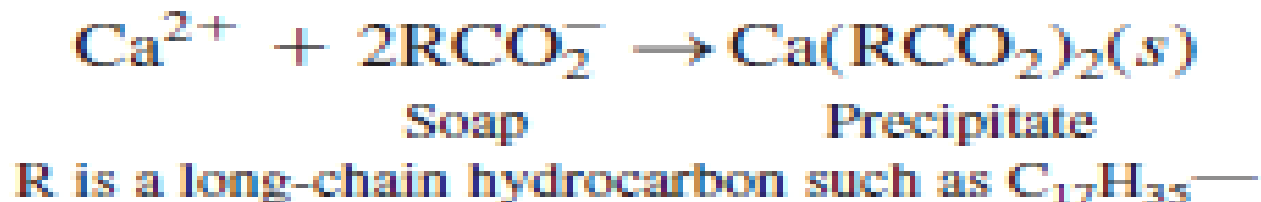
# Determination of total hardness of water

➤  $\text{Ca}^{2+} + \text{Mg}^{2+}$

➤  $\text{Ca}^{2+}$  - In complex is too weak (for a proper colour change) compared to  $\text{Mg}^{2+}$  - In, pH 10.

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

- *Hardness* is the total concentration of alkaline earth (Group 2) ions (mainly  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), in water.
- Hardness is commonly expressed as the equivalent number of milligrams of  $\text{CaCO}_3$  per liter.
- Thus, if  $[\text{Ca}^{2+}]$  &  $[\text{Mg}^{2+}] = 1 \text{ mM}$ , we would say that the hardness is 100 mg  $\text{CaCO}_3$  per liter because  $100 \text{ mg CaCO}_3 = 1 \text{ mmol CaCO}_3$ .
- Water of hardness less than 60 mg  $\text{CaCO}_3$  per liter is considered to be “soft.”
- If the hardness is above 270 mg/L, the water is considered to be “hard.”
- Hard water reacts with soap to form insoluble curds.



- Titration with EDTA at pH 10 in  $\text{NH}_3$  buffer then gives the total concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  .
- $\text{Ca}^{2+}$  can be determined separately if the titration is carried out at pH 13 without ammonia.
- At this pH,  $\text{Mg}(\text{OH})_2$  precipitates and is inaccessible to EDTA.
- Interference by many metal ions can be reduced by the right choice of indicators.

## 2- Back titration

- $M^{n+} + \text{EDTA} \rightarrow$  slow reaction or when a suitable ind is not available.
- $M^{n+} + \text{excess EDTA} \rightarrow$  Vrem titrate against  $\text{Mg}^{2+}$  ind EBT or calmagite
- It can be used for the deternm of  $M^{n+}$  in ppts, e.g.  $\text{Pb}^{2+}$  in lead sulphate and  $\text{Ca}^{2+}$  in  $\text{CaC}_2\text{O}_4$  (oxalate)



### 3- Replacement

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

### 4- Indirect

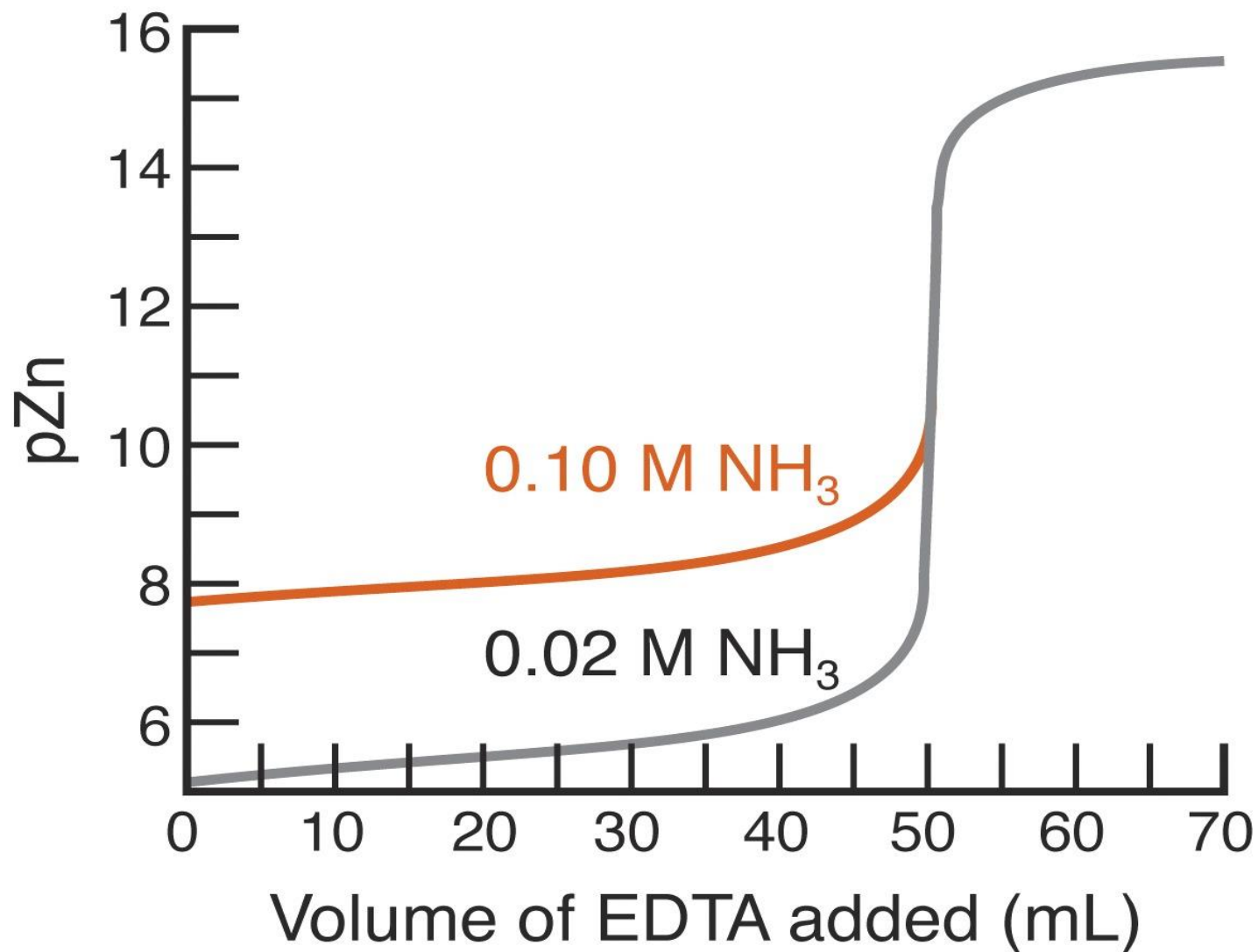
- $\text{SO}_4^{2-} + \text{excess Ba}^{2+} \rightarrow \text{BaSO}_4 + \text{Ba}^{2+}$
- EDTA
- $\text{MgNH}_4\text{PO}_4 \rightleftharpoons \text{Mg}^{2+} + \text{NH}_4\text{PO}_4^{2-}$   
EDTA  $\rightarrow$  detn of  $\text{PO}_4^{3-}$

# 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 pH 3.5 in the presence of alkaline earth cations.
- Interference will occur at pH 10 in an amm buffer

# Titration curves in presence of $\text{NH}_3$



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

