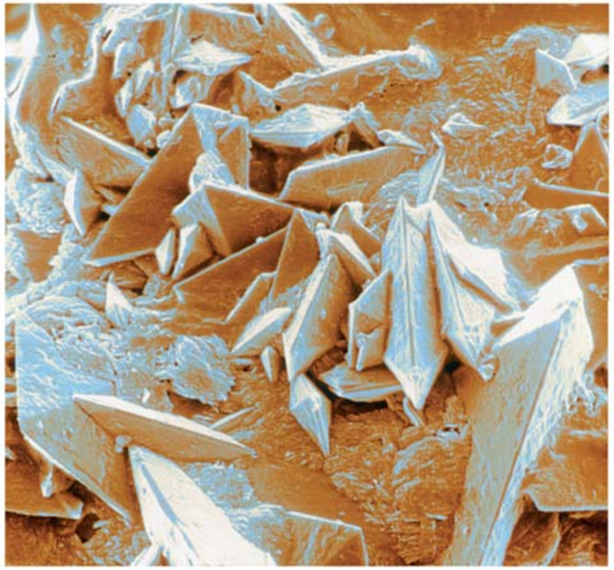
大 学 化 学 (双语)
College Chemistry

College of Chemistry and Materials Science



Chapter 7
Complexation Equilibria and Titrations

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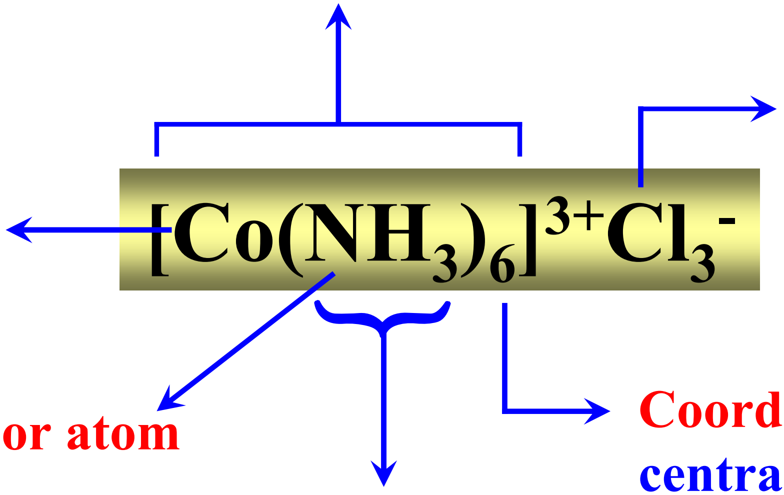
Contents

7.1 Basic Concepts



Coordination sphere (inner), **usually the atoms within square brackets in a formula, includes the central metal ion plus the attached ligands.**

Outer

Central metal ion or atom

$[Co(NH_3)_6]^{3+}Cl_3^-$

Donor atom

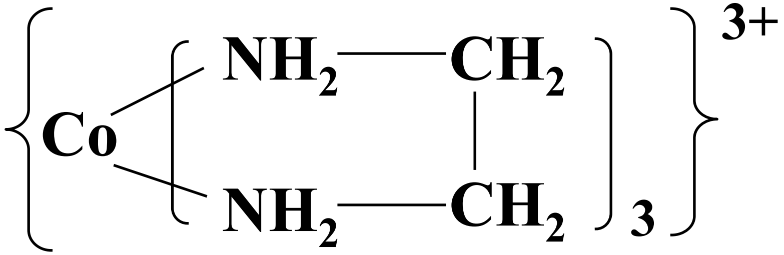
Ligand

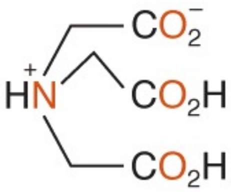
Coordination number of the central metal ion is the number of donor atoms bonded to it.

- **Most metal ions can accept unshared pairs of electrons from an anion or molecule to form *coordinate covalent bonds.* The molecule or ion containing the donor atom is called a *ligand* or *coordination agent* and the product resulting from a reaction between a metal ion and a ligand is referred to as a *coordination compound* or *complex ion.***

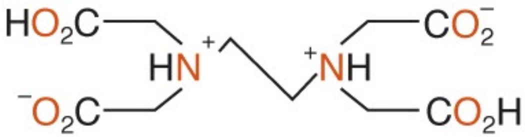
Metal Chelate

- **When a ligand attaches itself to a central metal ion by bonds from two or more donor atoms, it is referred to as a *polydentate ligand*, or a *chelating ligand*. The resulting complex is a *metal chelate* with a ring structure.**

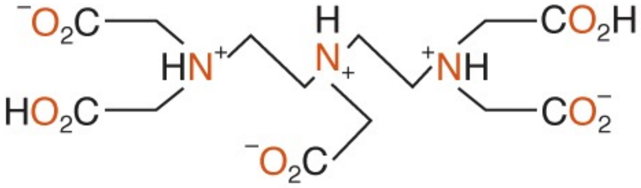




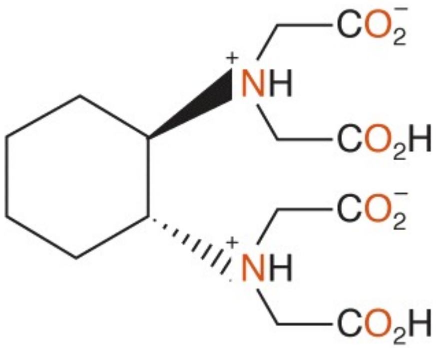
NTA
Nitrilotriacetic acid



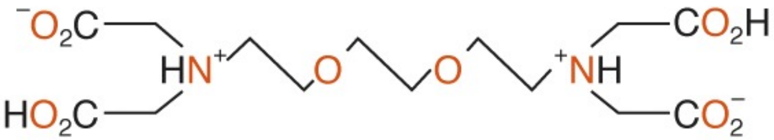
EDTA
Ethylenediaminetetraacetic acid
(also called ethylenedinitrilotetraacetic acid)



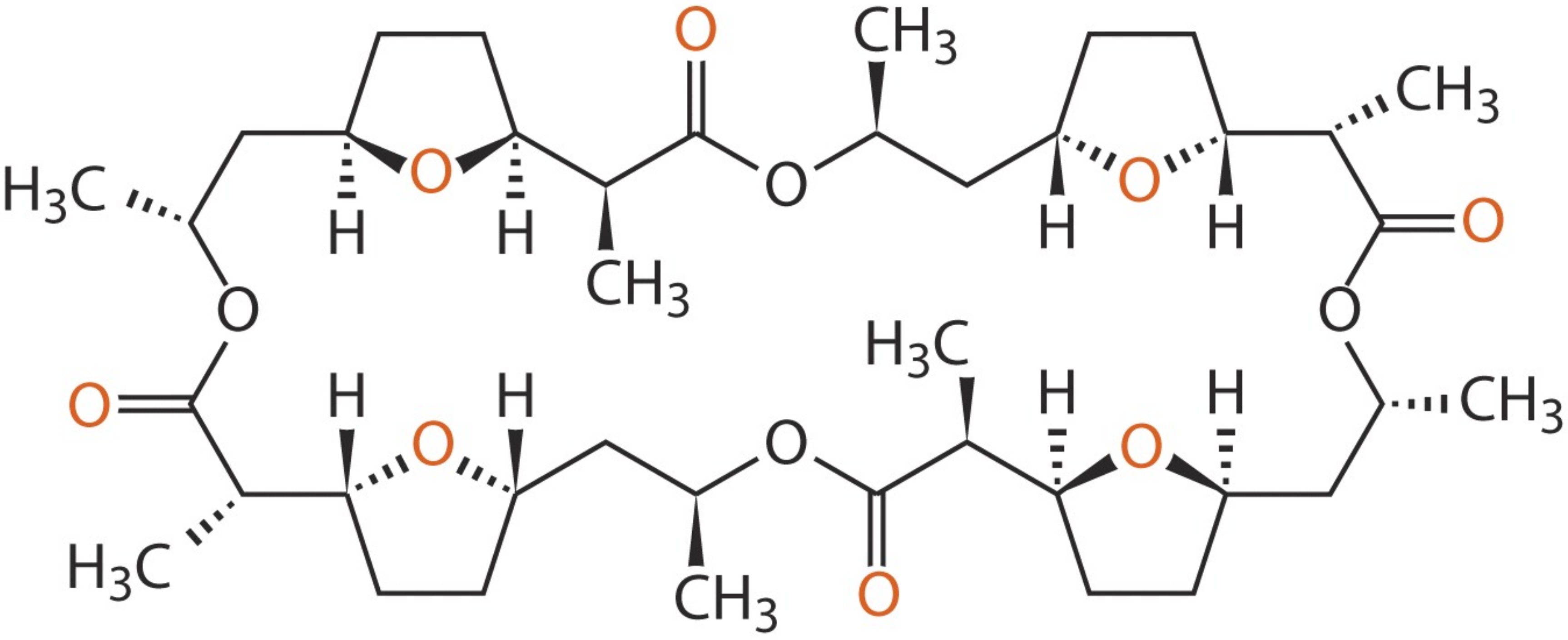
DTPA
Diethylenetriaminepentaacetic acid



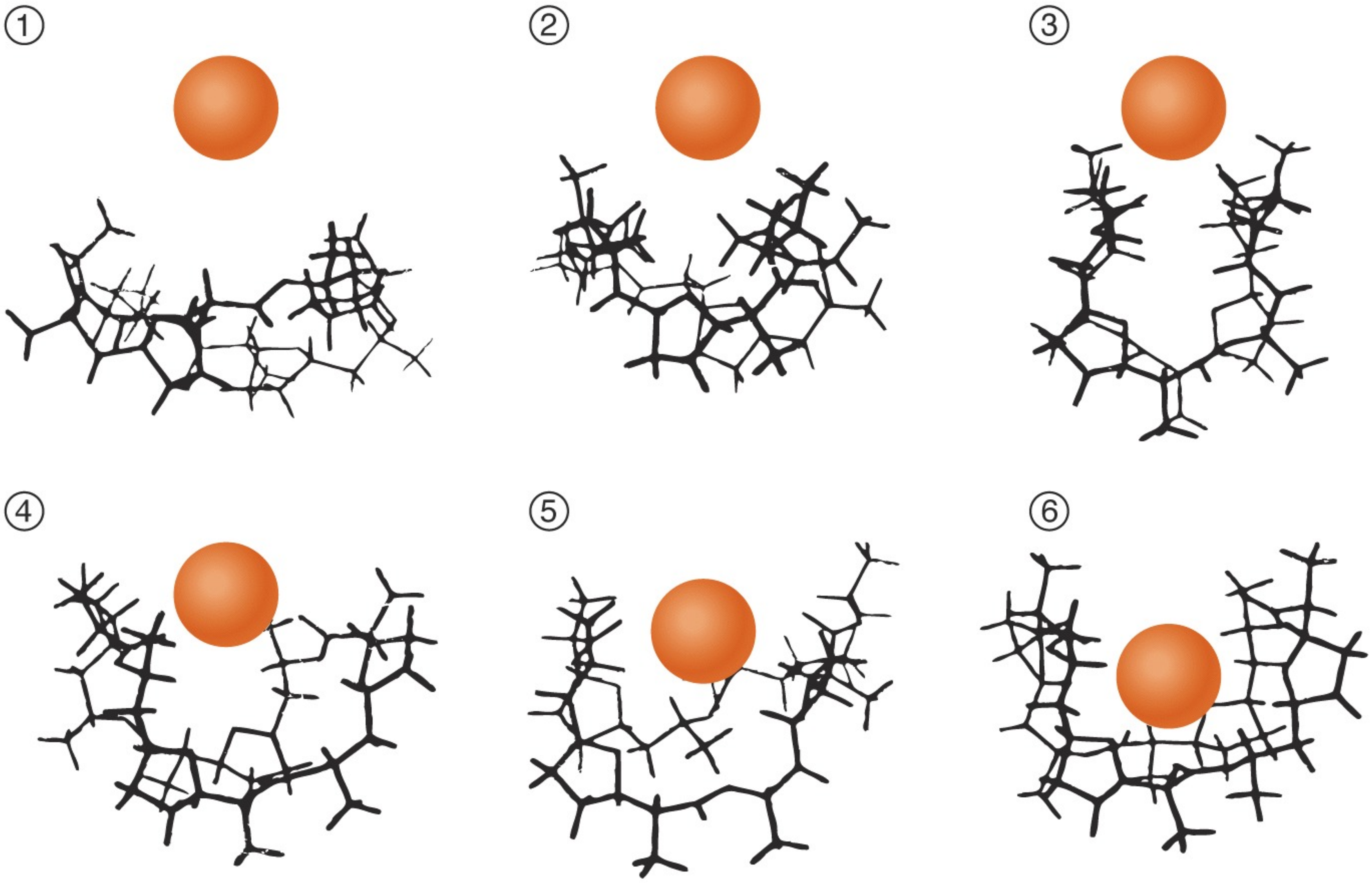
DCTA
trans-1,2-Diaminocyclohexanetetraacetic acid



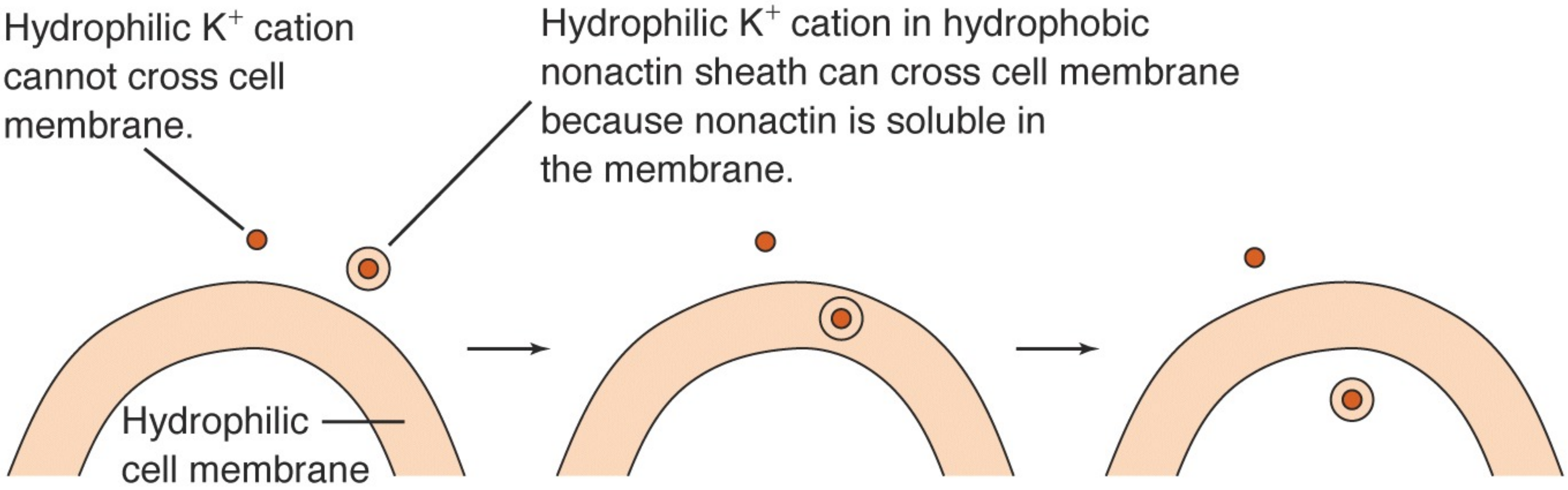
EGTA
bis-(Aminoethyl)glycolether-*N*,*N*,*N*′,*N*′-tetraacetic acid



Structure of nonactin (无活菌素), with ligand stoms in color



Nonactin(活菌素) molecule envelops of K^+ ion.



Ionophore carries K^+ across a cell membrane.

Types of Coordination Compounds

Coordination Compounds

- **Central Atom**
  - **Mononuclear Complex**
  - **Polynuclear Complex**
- **Ligand**
  - **Unidentate Ligand Complex**
  - **Polydentate Ligand Complex**

The Names of Compounds

1. **Binary Compounds contain two different elements. The name of a binary compound consists of the name of the more electropositive element followed by the name of the more electronegative element with its ending replaced by the suffix –*ide*.**

Examples:

NaCl, sodium chloride	**Na_2O, sodium oxide**
KBr, potassium bromide	**CdS, cadmium sulfide**
CaI_2, calcium iodide	**Mg_3N_2, magnesium nitride**
AgF, silver fluoride	**Ca_3P_2, calcium phosphide**
HCl, hydrogen chloride	**Al_4C_3, aluminum carbide**
LiH, lithium hydride	**Mg_2Si, magnesium silicide**

A few polyatomic ions have special names and are treated as if they were single atoms in naming their compound.

NaOH, sodium hydroxide
HCN, hydrogen cyanide
NH_4Cl, ammonium chloride

If a binary hydrogen compound is an acid when it is dissolved in water, the prefix hydro- is used instead of the word hydrogen and the suffix –*ic* replaces the suffix –*ide* when we are referring to the aqueous solution.

HCl(*g*), hydrogen chloride	**HCl(*aq*), hydrochloric acid**
HBr(*g*), hydrogen bromide	**HBr(*aq*), hydrobromic acid**
H_2S(*g*), hydrogen sulfide	**H_2S(*aq*), hydrosulfuric acid**
HCN(*g*), hydrogen cyanide	**HCN(*aq*), hydrocyanic acid**

If a nonmetallic element with variable oxidation number can unite with another nonmetallic element to form more than one compound, the compounds can be distinguished by the Greek prefixes *mono-* (meaning one), *di-*(two), *tri-* (three), *tetra-* (four), *penta-* (five), *hexa-* (six), *hapta-* (seven), and *octa-* (eight). The prefixes precede the name of the constituent to which they refer.

CO, carbon monoxide	PbO, lead monoxide
CO_2, carbon dioxide	PbO_2, lead dioxide
NO_2, nitrogen dioxide	SO_2, sulfur dioxide
N_2O_4, dinitrogen tetraoxide	SO_3, sulfur trioxide
N_2O_5, dinitrogen pentaoxide	BCl_3, boron trichloride

A second method of naming different binary compounds that contain the same elements uses Rome numerals placed in parentheses after the name of the more electropositive element to indicate its oxidation number. This method of naming binary compounds is usually applied to those in which the electropositive element is a metal, but is occasionally applied to other compounds as well.

$FeCl_2$, iron(II) chloride	**SO_2, sulfur(IV) oxide**
$FeCl_3$, iron(III) chloride	**SO_3, sulfur(VI) oxide**
Hg_2O, mercury(I) oxide	**NO, nitrogen(II) oxide**
HgO, mercury(II) oxide	**NO_2, nitrogen(IV) oxide**

2. **Ternary compounds** contain three different elements. For oxyacids:

$HClO_4$, perchloric acid	H_2SO_4, sulfuric acid
$HClO_3$, chloric acid	H_3PO_4, phosphoric acid
$HClO_2$, chlorous acid	H_3PO_3, phosphorous acid
$HClO$, hypochlorous acid	H_3PO_2, hypophosphorous acid

For metal salts of oxyacids:

Oxidation Number	Acids	Salts
+7	$HClO_4$, perchloric acid	$NaClO_4$, sodium perchlorate
+5	$HClO_3$, chloric acid	$NaClO_3$, sodium chlorate
+3	$HClO_2$, chlorous acid	$NaClO_2$, sodium chlorite
+1	$HClO$, hypochlorous acid	$NaClO$, sodium hypochlorite

Rules for Naming Complexes

1. **If a complex is ionic, name the cation first and the anion second, in accord with usual nomenclature.**
2. **Name the ligands first, followed by the central metal.**

3. **Name the ligands alphabetically, (An older system names negative ligands alphabetically, then neutral ligands alphabetically, and finally positive ligands alphabetically.) Negative ligands (anions) have names formed by adding *–o* to the stem name of the group, for example,**

F^-	***fluoro***	NO_3^-	***nitrato***	CN^-	***cyano***
Cl^-	***chloro***	OH^-	***hydroxo***	O^{2-}	***oxo***
Br^-	***bromo***	NH_2^-	***amido***	NO_2^-	***nitro***
I^-	***iodo***	$C_2O_4^-$	***oxalato***		
CO_3^{2-}	***carbonato***	ONO^-	***nitrito***		

For most neutral ligands the name of the molecule is used. The four common exceptions are *aqua* (H_2O), *ammine* (NH_3), *carbonyl* (CO), and *nitrosyl* (NO).

4. **If more than one ligand of a given type is present, the number is indicated by the prefixes *di-* (for two), *tri-* (for three), *tetra-* (for four), *penta-* (for five), and *hexa-* (for six). Sometimes the prefixes *bis*- (for two), *tris*- (for three), and *tetrakis*- (for four) are used when the name of the ligand contains numbers, begins with a vowel, is for a polydentate ligand, or includes *di*-, *tri*-, or *tetra*-.**

5. **When the complex is either a cation or a neutral molecule, the name of the central metal atom is spelled exactly as the name of element and is followed by Roman numeral in parentheses to indicate its oxidation number. When the complex is an anion, the suffix *–ate* is added to the stem for the name of the metal (or sometimes to the stem for the Latin name of the metal), followed by the Roman numeral designation of its oxidation number.**

Examples in which the complex is a cation:

$[Co(NH_3)_6]Cl_3$	**Hexaamminecobalt(III) chloride**
$[Pt((NH_3)_4Cl_2]^{2+}$	**Tetraamminedichloroplatinum(IV) ion**
$[Ag(NH_3)_2]^+$	**Diamminesilver(I) ion**
$[Cr(H_2O)_4Cl_2]Cl$	**Tetraaquadicholrochromium(III) cholride**
$[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	**Tris(ethylenediamine)cobalt(III) sulfate**

Examples in which the complex is neutral:

$[Pt(NH_3)_2Cl_4]$	**Diamminetetrachloroplatinum(IV)**
$[Co(NH_3)_3(NO_2)_3]$	**Triamminetrinitrocobalt(III)**
$[Ni(H_2NCH_2CH_2NH_2)_2Cl_2]$	**Dichlorobis(ethylenediamine)nickel(II)**

Examples in which the complex is an anion:

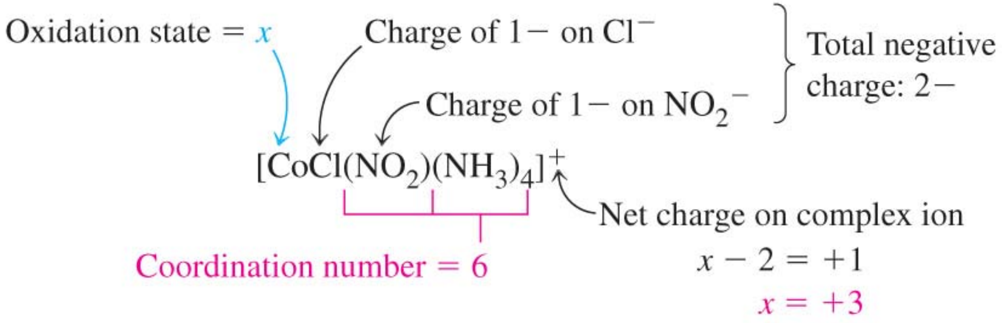
$K_3[Co(NO_2)_6]$	**Potassium hexanitrocobaltate(III)**
$[PtCl_6]^{2-}$	**Hexachloroplatinate(IV)**
$Na_2[SnCl_6]$	**Sodium hexachlorostannate (IV)**

EXAMPLE 24-1

Relating the Formula of a Complex to the Coordination Number and Oxidation State of the Central Metal. What are the coordination number and oxidation state of Co in the complex ion $[CoCl(NO_2)(NH_3)_4]^+$?

Solution

The complex ion has as ligands *one* Cl^- ion, *one* NO_2^- ion, and *four* NH_3 molecules. The coordination number is 6. Of these six ligands, *two* carry a charge of 1− each (the Cl^- and NO_2^- ions) and four are *neutral* (the NH_3 molecules). The total contribution of the anions to the net charge on the complex ion is 2−. Because the net charge on the complex ion is 1+, the oxidation state of the central cobalt ion is +3. Diagrammatically, we can write



Oxidation state = x

Charge of 1− on Cl^-

Charge of 1− on NO_2^-

Total negative charge: 2−

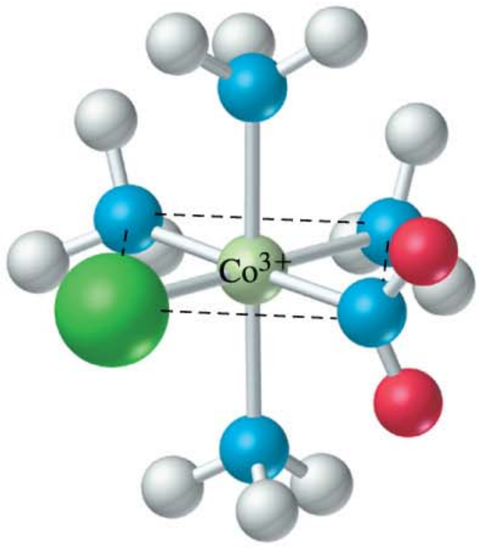
$[CoCl(NO_2)(NH_3)_4]^+$

Net charge on complex ion

Coordination number = 6

$x - 2 = +1$

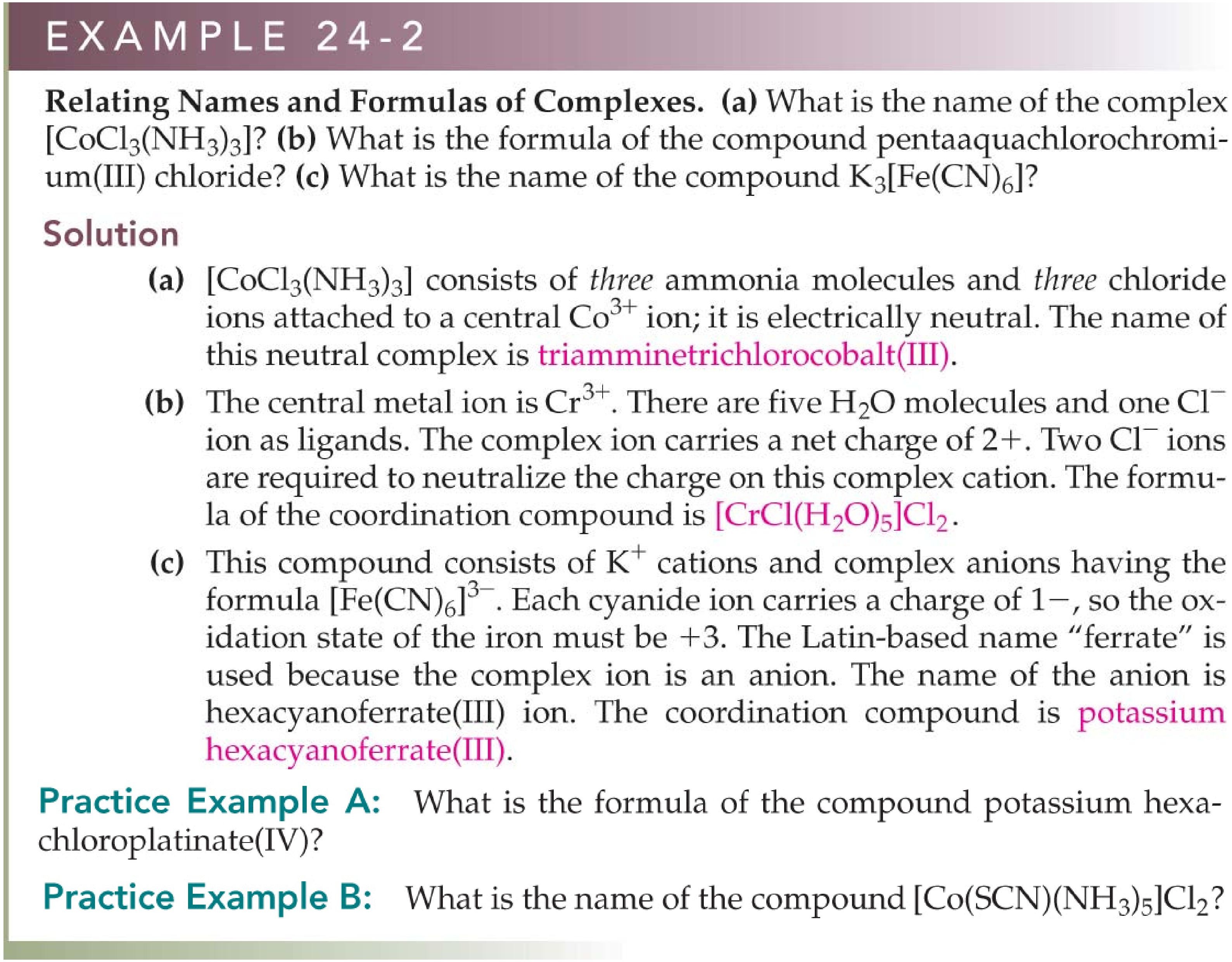
$x = +3$



▲ The complex ion $[CoCl(NO_2)(NH_3)_4]^+$

Practice Example A: What are the coordination number and oxidation state of nickel in the ion $[Ni(CN)_4I]^{3-}$?

Practice Example B: Write the formula of a complex with cyanide ion ligands, an iron ion with an oxidation state of +3, and a coordination number of 6.



EXAMPLE 24-2

Relating Names and Formulas of Complexes. **(a)** What is the name of the complex $[CoCl_3(NH_3)_3]$? **(b)** What is the formula of the compound pentaaquachlorochromium(III) chloride? **(c)** What is the name of the compound $K_3[Fe(CN)_6]$?

Solution

(a) $[CoCl_3(NH_3)_3]$ consists of *three* ammonia molecules and *three* chloride ions attached to a central Co^{3+} ion; it is electrically neutral. The name of this neutral complex is triamminetrichlorocobalt(III).

(b) The central metal ion is Cr^{3+}. There are five H_2O molecules and one Cl^- ion as ligands. The complex ion carries a net charge of 2+. Two Cl^- ions are required to neutralize the charge on this complex cation. The formula of the coordination compound is $[CrCl(H_2O)_5]Cl_2$.

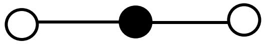
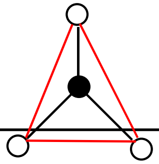
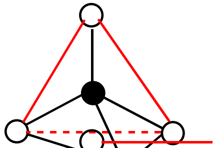
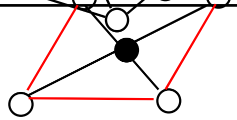
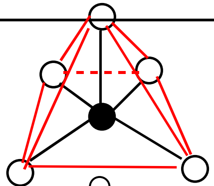
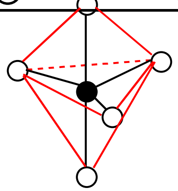
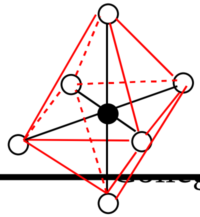
(c) This compound consists of K^+ cations and complex anions having the formula $[Fe(CN)_6]^{3-}$. Each cyanide ion carries a charge of 1−, so the oxidation state of the iron must be +3. The Latin-based name "ferrate" is used because the complex ion is an anion. The name of the anion is hexacyanoferrate(III) ion. The coordination compound is potassium hexacyanoferrate(III).

Practice Example A: What is the formula of the compound potassium hexachloroplatinate(IV)?

Practice Example B: What is the name of the compound $[Co(SCN)(NH_3)_5]Cl_2$?

7.2 Structures of Complexes

- **Spatial arrangements of atoms include geometries that are linear, trigonal planar, tetrahedral, square planar, square pyramidal, trigonal bipyramidal, and octahedral, among others.**

Geometric Shape	**Diagram of Shape**	**Coordination Number**	**Examples**
Linear		2	$[Ag(NH_3)_2]^+$
Trigonal planar		3	$[HgCl_3]^-$
Tetrahedral		4	$[Zn(CN)_4]^{2-}$
Square planar		4	$[Cu(NH_3)_4]^{2+}$
Square Pyramidal		5	$[VOCl_4]^{2-}$
Trigonal bipyramidal		5	$[Fe(CO)_5]$
Octahedral		6	$[PtCl_6]^{2-}$

Isomerism in Complexes

- These different forms with the same formula are **isomers.**

Structural Isomers

Geometrical isomers, Stereoisomers, (Spatial Isomers)

Optical isomers, (Rotatory Isomers)

Structural Isomers

$[CoSO_4(NH_3)_5]Br$ $[CoBr(NH_3)_5]\,SO_4$

(Red) **(Purple)**

$[Cr(H_2O)_6]Cl_3$ **(Purple)**

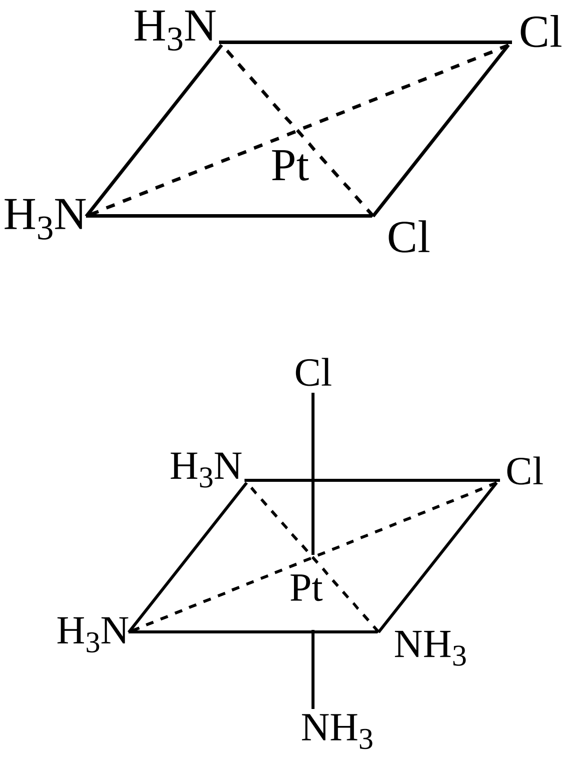
$[CrCl\,(H_2O)_5]Cl_2\cdot H_2O$ **(Bright Green)**

$[CrCl_2(H_2O)_4]Cl\cdot 2H_2O$ **(Dark Green)**

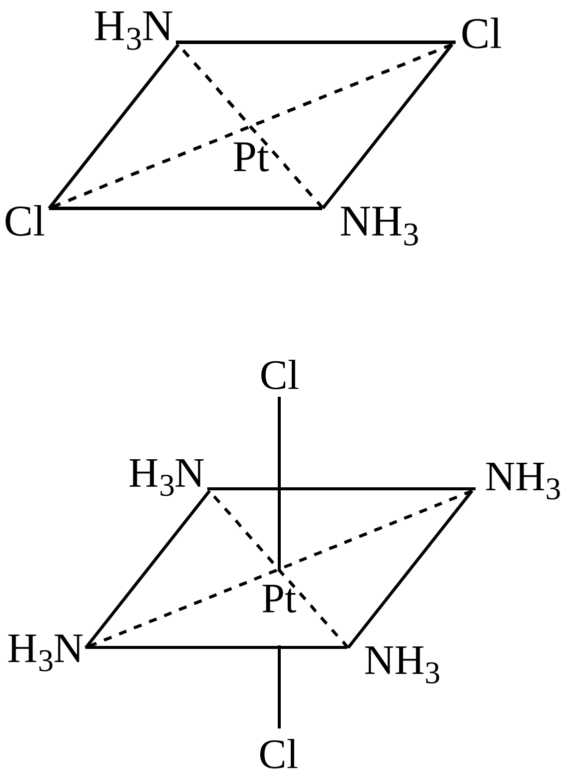
Geometrical isomers, Stereoisomers, (Spatial Isomers)

$PtCl_2(NH_3)_2$

$Pt\ (NH_3)_4Cl_2$

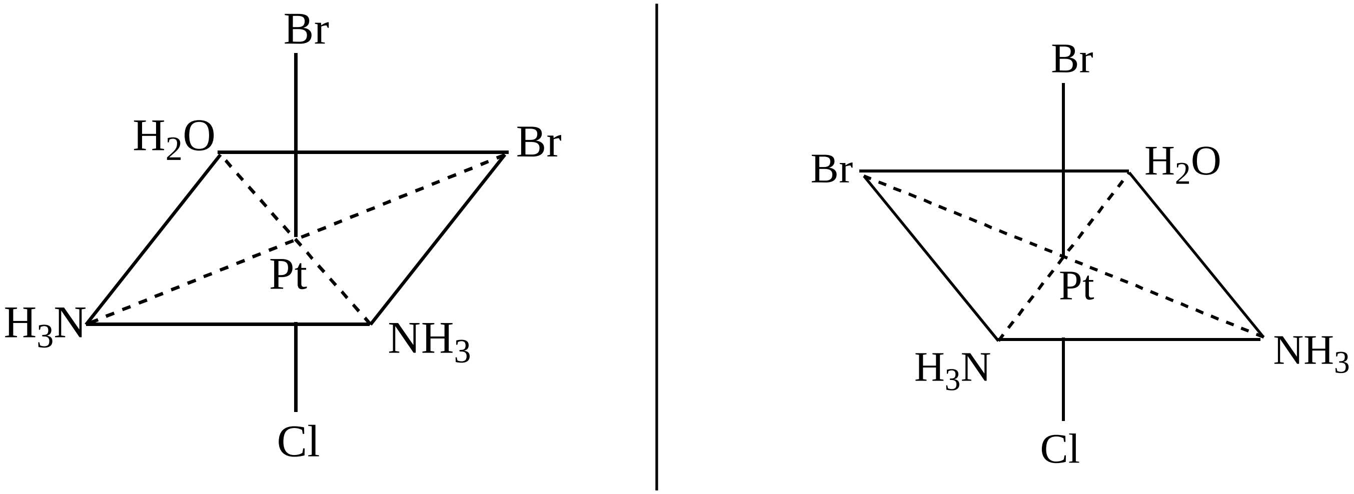


***cis* form**



***trans* form**

Optical isomers, (Rotatory Isomers): Chirality(手性)



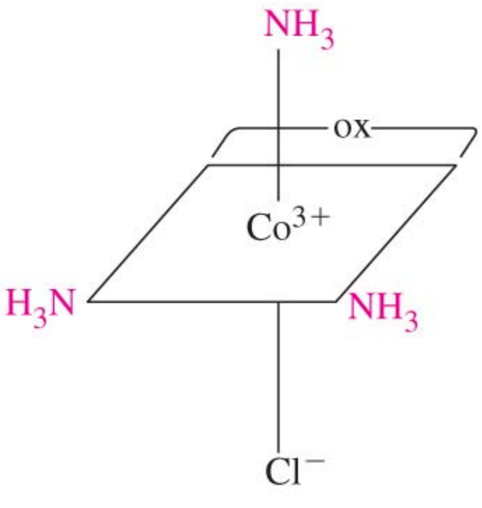
Mirror plane

EXAMPLE 24-3

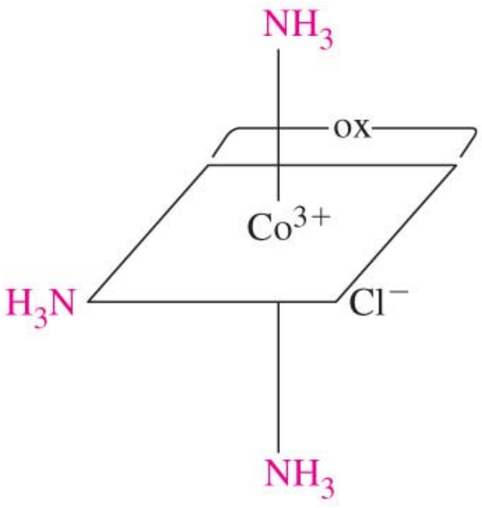
Identifying Geometric Isomers. Sketch structures of all the possible isomers of $[CoCl(ox)(NH_3)_3]$.

Solution

The Co^{3+} ion exhibits a coordination number of 6. The structure is octahedral. Recall that ox (oxalate ion) is a bidentate ligand carrying a double-negative charge (see Table 24.3). Also, as shown in Figure 24-3, a bidentate ligand must be attached in *cis* positions, not *trans*. Once the ox ligand is placed, any position is available to the Cl^-. This leaves two possibilities for the three NH_3 molecules. They can be situated (1) on the same face of the octahedron (*fac* isomer) or (2) around a perimeter of the octahedron (*mer* isomer).



fac isomer



mer isomer

Practice Example A: Sketch the geometric isomers of $[CoCl_2(ox)(NH_3)_2]^-$.

Practice Example B: Sketch the geometric isomers of $[MoCl_2(C_5H_5N)_2(CO)_2]^+$.

7.3 Formation Constant of Complex

For ML_n type complex:

Complexation Equilibria	Stepwise Formation Constant	Cumulative Formation Constant
$M + L \rightarrow ML$	K_1	β_1
$ML + L \rightarrow ML_2$	K_2	$\beta_2 = K_1 K_2$
	…………	
$ML_{n-1} + L \rightarrow ML_n$	K_n	$\beta_n = K_1 K_2 \cdots K_n$

7.3 Species Distribution of Coordination Compound in Solution

Given the total concentration metal ion is *c*(M), that is,

$$\mathbf{c(M) = [M] + [ML] + \cdots + [ML_n]}$$

$$x_0 = \frac{[M]}{c(M)} = \frac{[M]}{[M] + [ML] + \cdots + [ML_n]} = \frac{[M]/[M]}{\frac{[M]}{[M]} + \frac{[ML]}{[M][L]}[L] + \cdots + \frac{[ML]}{[M][L]^n}[L]^n}$$

$$= \frac{1}{1 + \beta_1[L] + \cdots + \beta_n[L]^n}$$

$$x_1 = \frac{[ML]}{c(M)} = \frac{\beta_1[L]}{1 + \beta_1[L] + \cdots + \beta_n[L]^n}$$

……………………

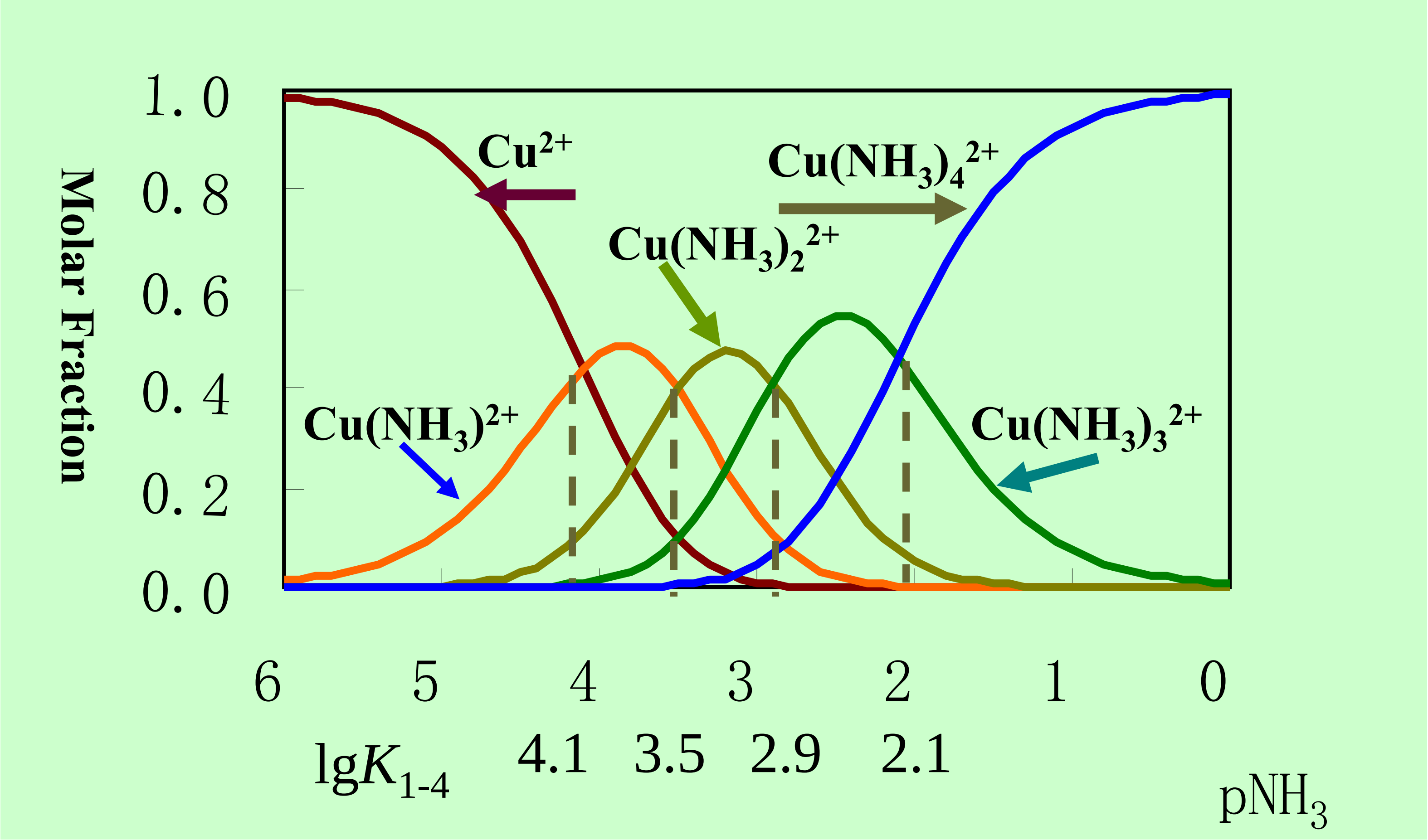
$$x_n = \frac{[ML_n]}{c(M)} = \frac{\beta_n[L]^n}{1 + \beta_1[L] + \cdots + \beta_n[L]^n}$$

Note

- **The molar fraction of the species is just the function of the concentration of ligand, being independent of the overall concentration of metal ions (*c*(M)).**

$$x_0+x_1+\cdots+x_n=1$$

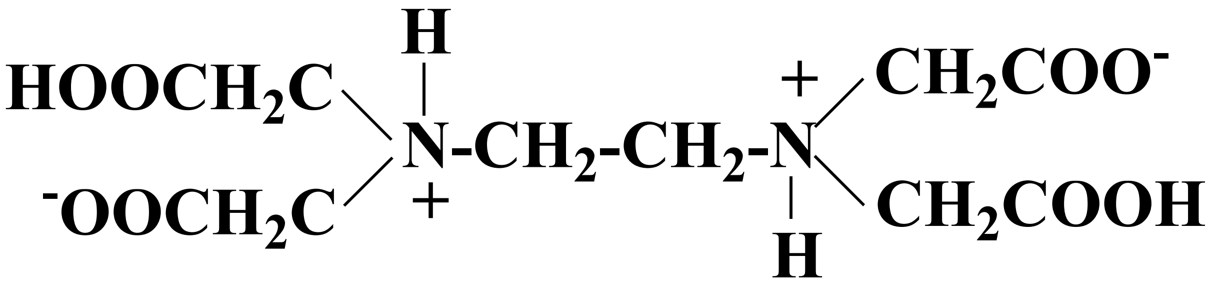
Species Distribution of $[Cu(NH_3)_4]^{2+}$



7.4 EDTA & it’s Complexes

EDTA: (ethylenediaminetetraacetic acid)

H_4Y

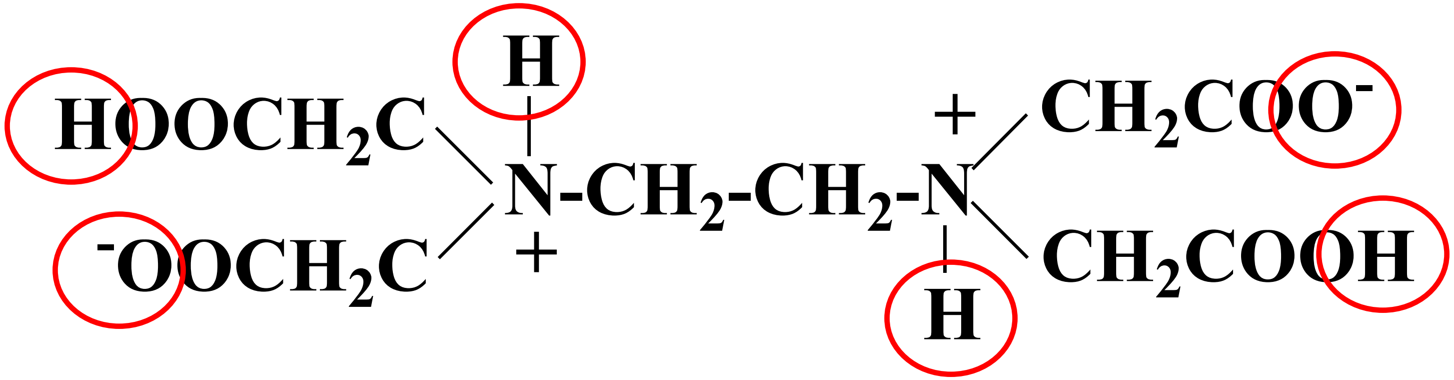


$$HOOCH_2C\diagdown\overset{H}{\underset{+}{N}}-CH_2-CH_2-\overset{+}{\underset{H}{N}}\diagup CH_2COO^- \quad {}^-OOCH_2C\diagup \quad \diagdown CH_2COOH$$

Properties of EDTA → **Tetraprotic acid**

Properties of EDTA → **Hexadentate ligand**

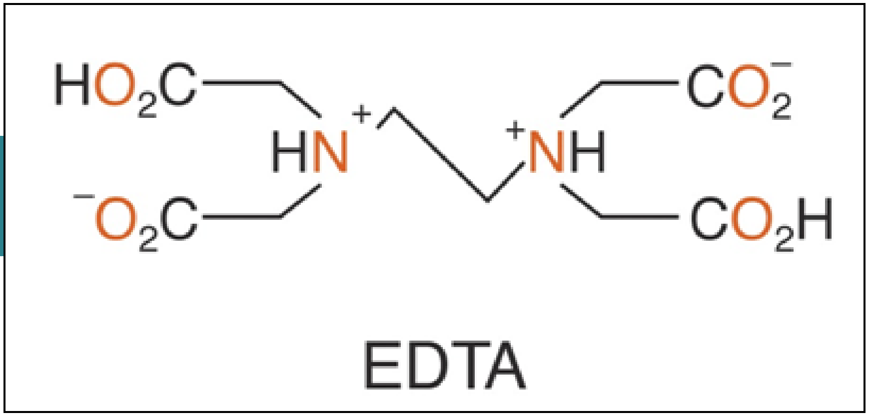
Acidic Property of EDTA

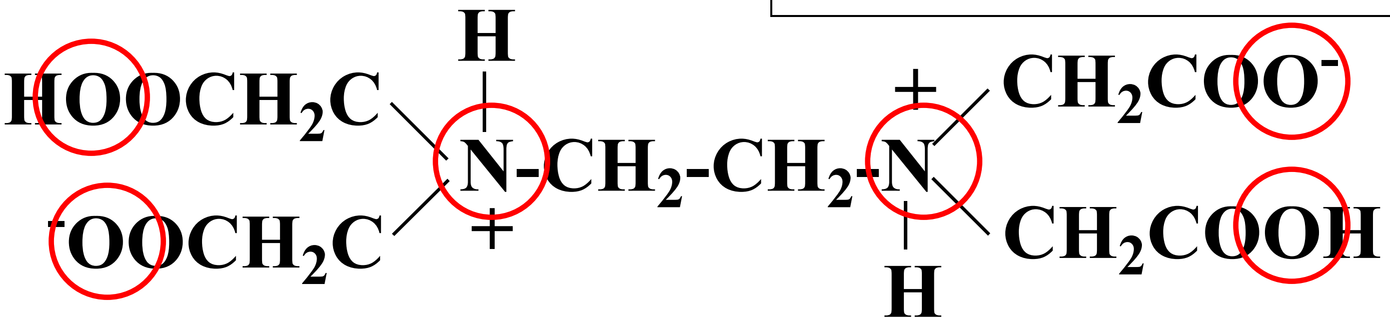


H_6Y^{2+}

H_6Y^{2+}, H_5Y^{+}, H_4Y, H_3Y^{-}, H_2Y^{2-}, HY^{3-}, Y^{4-}

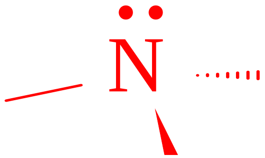
Complex Property of EDTA

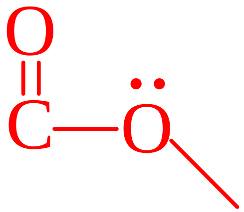




2 nitrogen donor atoms

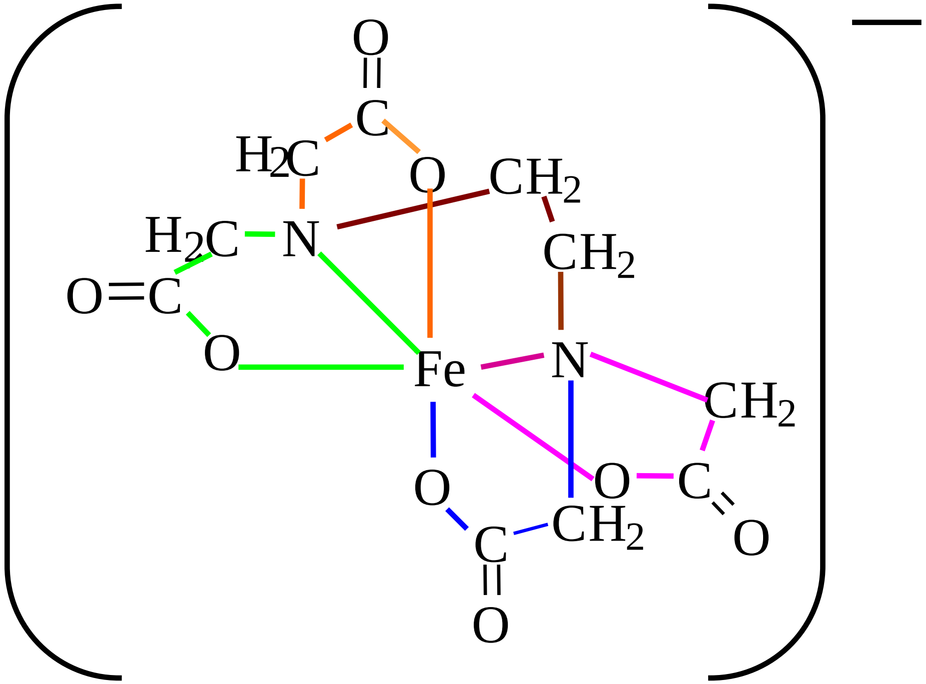
4 oxygen donor atoms

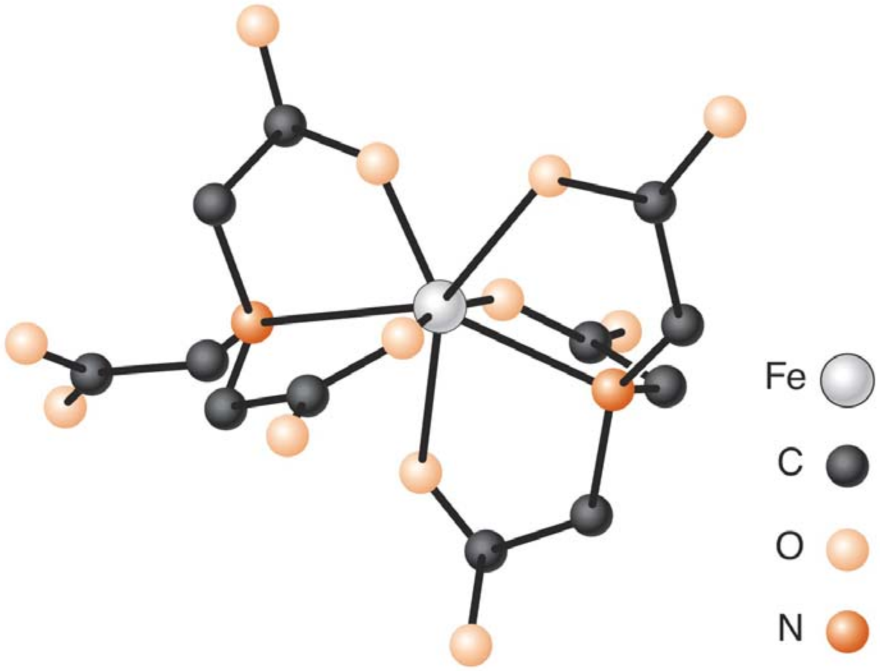


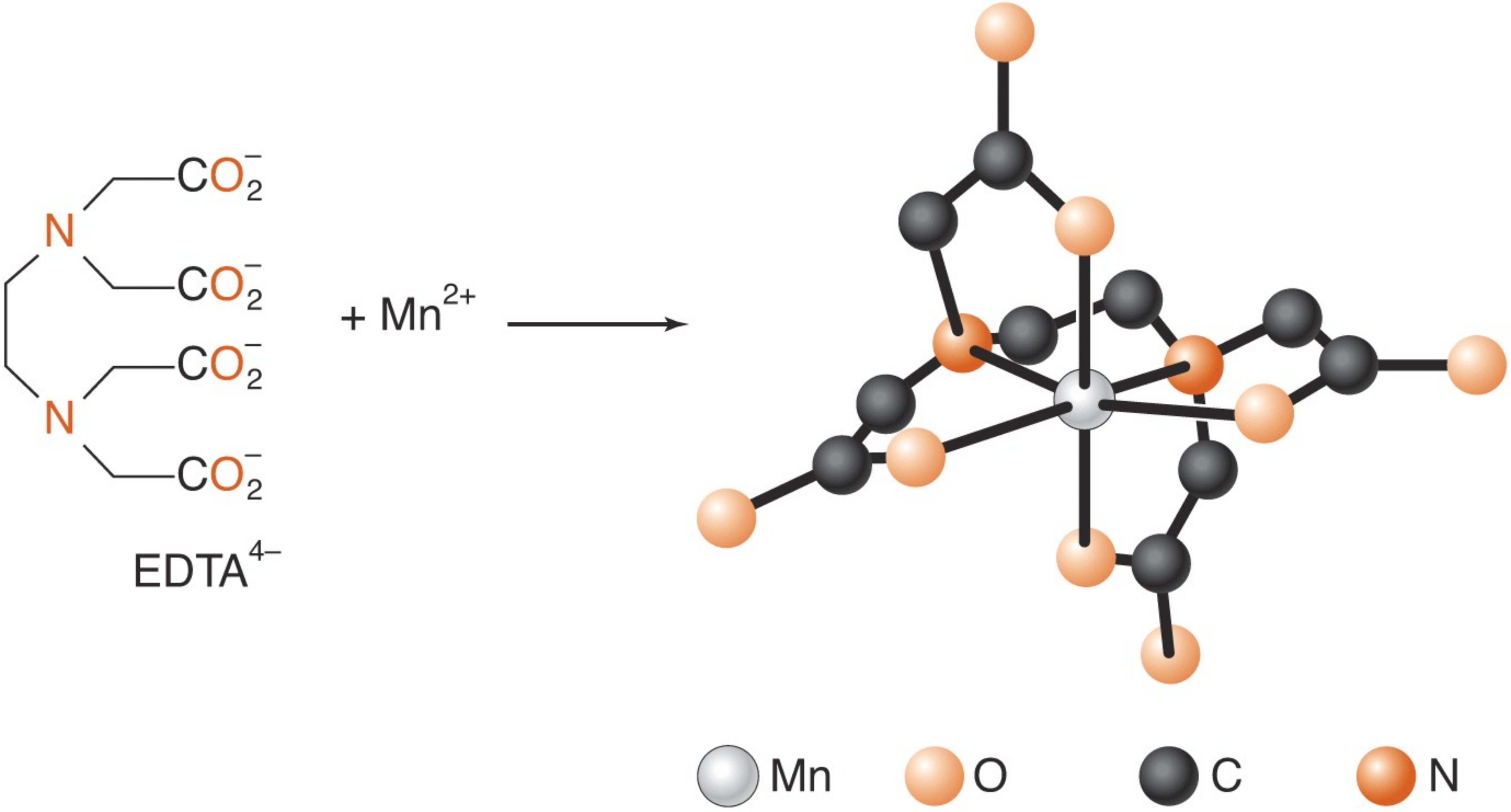


EDTA is a hexadentate ligand.

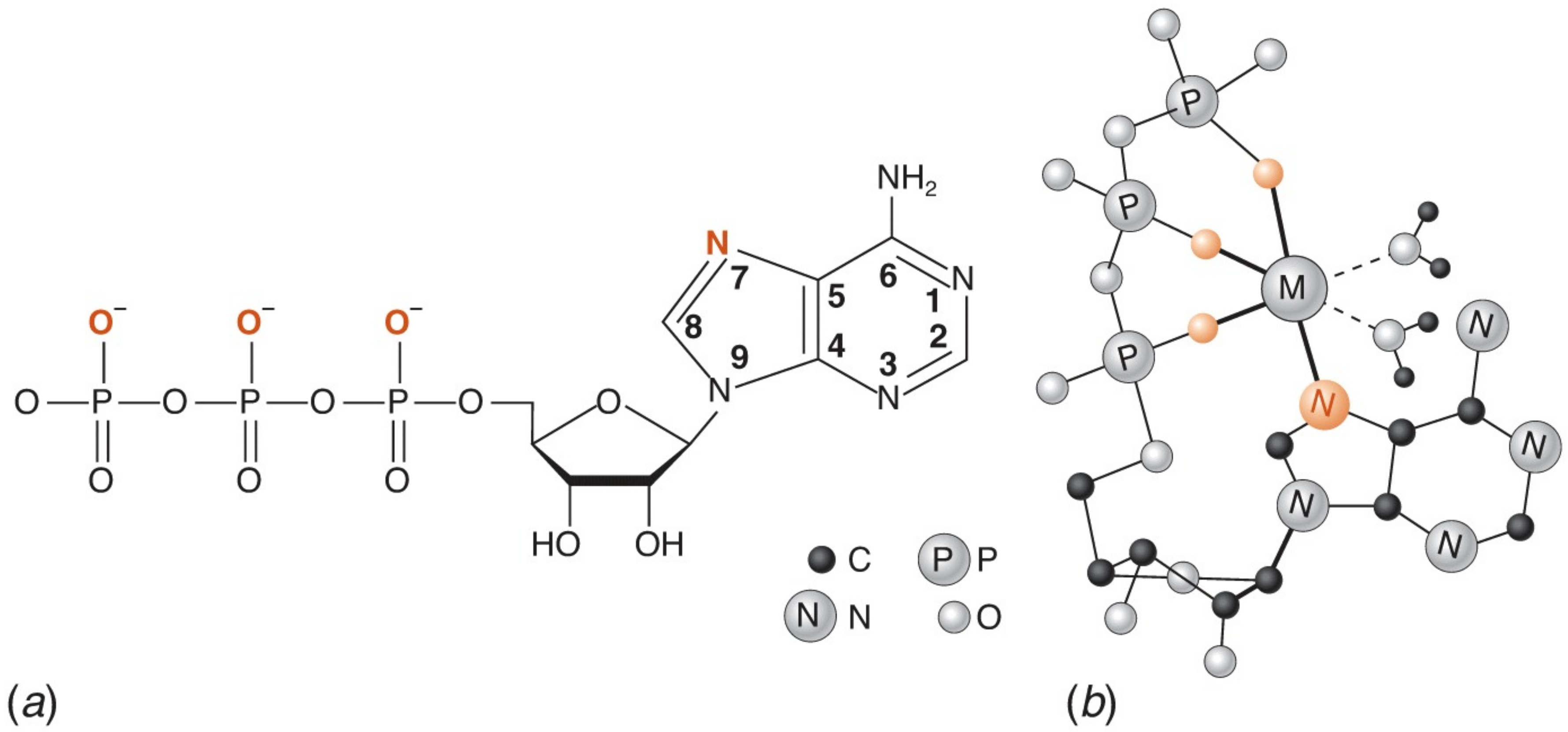
Stereo Structure of Fe-EDTA Complex







EDTA forms strong 1:1 complexes with most metal ions, binding through for oxygen and two nitrogen atoms. The six-coordinate geometry of Mn2+-EDTA was deduced from X-ray crystallography.



(a) Structure of adenosine triphosphate (ATP), with ligand atoms shown in color. (b) Possible structure of a metal-ATP complex; the metal, M, has four bonds to ATP and two bonds to H_2O ligands.

Characteristic of EDTA Complex

1. **EDTA almost can react with all of the metal ions to form coordination compounds;**
2. **The formed coordination compounds are very stable, $\lg K > 15$;**
3. **1:1 complexes with virtually all multivalent metal ions；**
4. **The speed of reaction is fast with excellent solubility.**

7.5 Protonation Constant of EDTA

Protonation Equi.	**Protonation Constant**	**Cumulative protonation constant**
$Y + H \longrightarrow HY$	$K_1 = 10^{10.34}$	$\beta_1^H = 10^{10.34}$
$HY + H \longrightarrow H_2Y$	$K_2 = 10^{6.24}$	$\beta_2^H = 10^{16.58}$
$H_2Y + H \longrightarrow H_3Y$	$K_3 = 10^{2.75}$	$\beta_3^H = 10^{19.33}$
$H_3Y + H \longrightarrow H_4Y$	$K_4 = 10^{2.07}$	$\beta_4^H = 10^{21.40}$
$H_4Y + H \longrightarrow H_5Y$	$K_5 = 10^{1.6}$	$\beta_5^H = 10^{23.0}$
$H_5Y + H \longrightarrow H_6Y$	$K_6 = 10^{0.9}$	$\beta_6^H = 10^{23.9}$

Species Distribution of EDTA

$$x_0 = \frac{[\mathrm{Y}]}{c(\mathrm{EDTA})} = \frac{[\mathrm{Y}]}{[\mathrm{Y}]+[\mathrm{HY}]+\cdots+[\mathrm{H_6Y}]}$$

$$= \frac{[\mathrm{Y}]/[\mathrm{Y}]}{\frac{[\mathrm{Y}]}{[\mathrm{Y}]}+\frac{[\mathrm{HY}]}{[\mathrm{Y}][\mathrm{H}]}[\mathrm{H}]+\cdots+\frac{[\mathrm{H_6Y}]}{[\mathrm{Y}][\mathrm{H}]^6}[\mathrm{H}]^6} = \frac{1}{1+\beta_1^{\mathrm{H}}[\mathrm{H}]+\cdots+\beta_6^{\mathrm{H}}[\mathrm{H}]^6}$$

$$x_1 = \frac{[\mathrm{HY}]}{c(\mathrm{EDTA})} = \frac{\beta_1^{\mathrm{H}}[\mathrm{H}]}{1+\beta_1^{\mathrm{H}}[\mathrm{H}]+\cdots+\beta_6^{\mathrm{H}}[\mathrm{H}]^6}$$

....

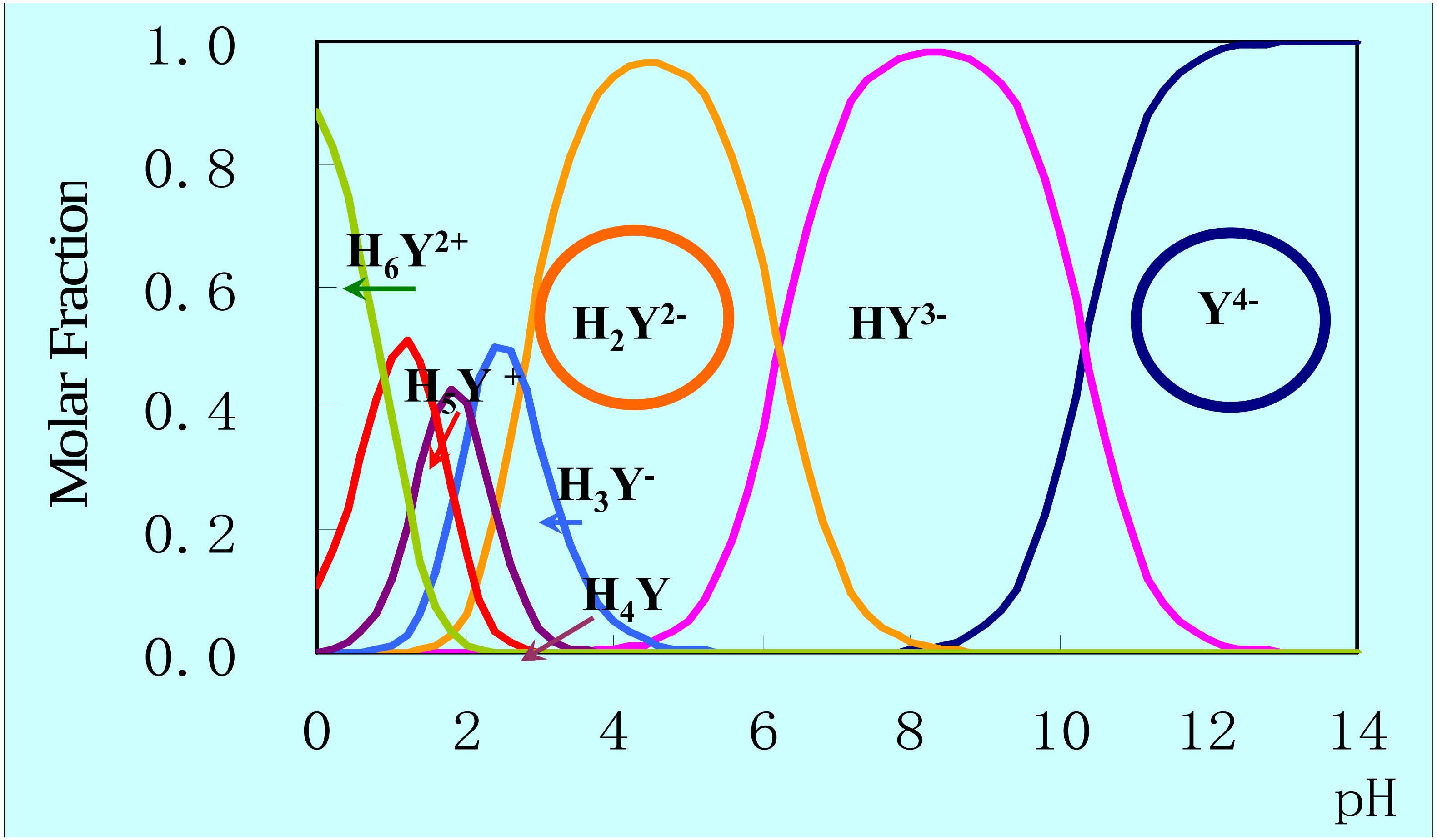
$$x_6 = \frac{[\mathrm{H_6Y}]}{c(\mathrm{EDTA})} = \frac{\beta_6^{\mathrm{H}}[\mathrm{H}]^6}{1+\beta_1^{\mathrm{H}}[\mathrm{H}]+\cdots+\beta_6^{\mathrm{H}}[\mathrm{H}]^6}$$

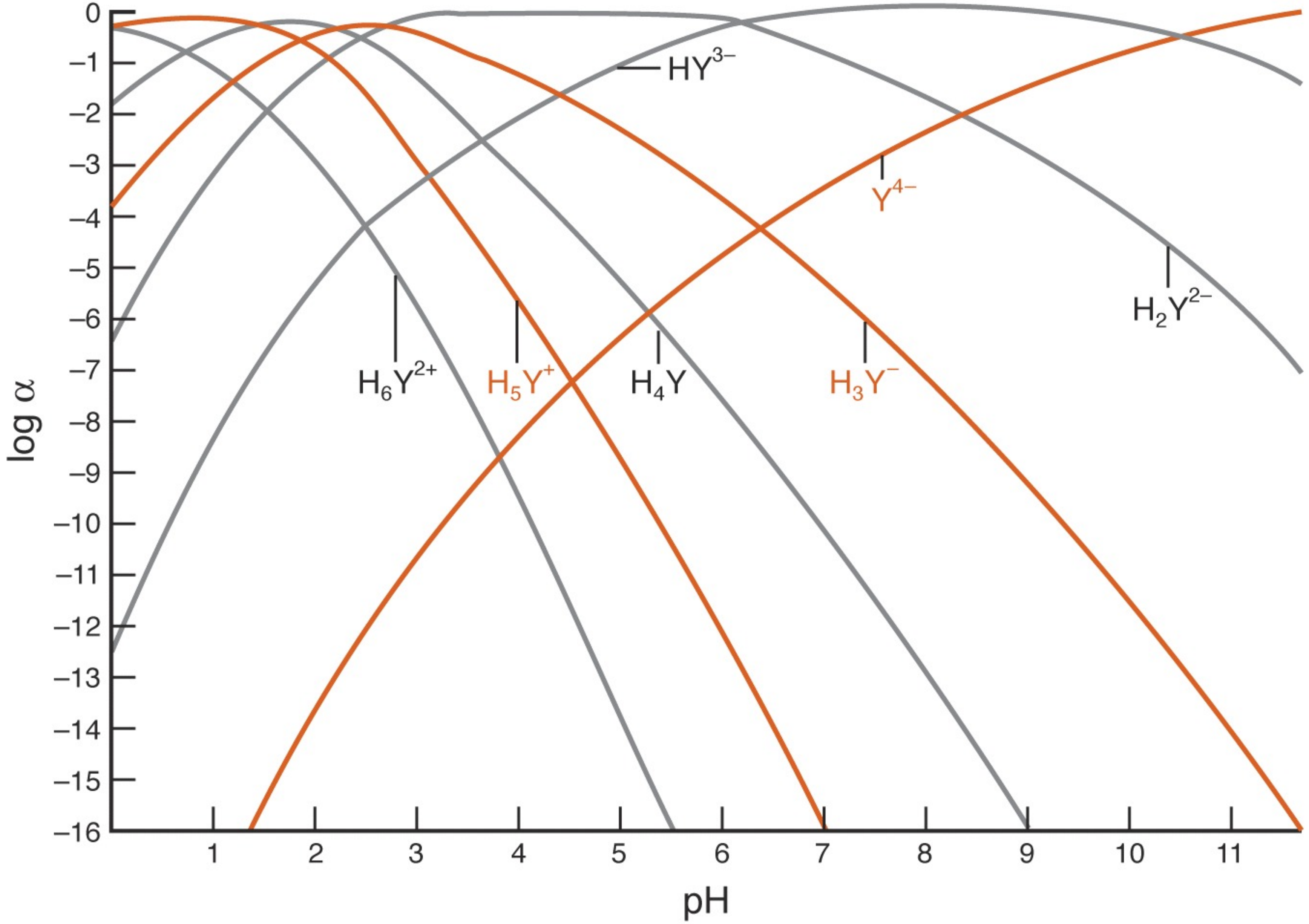
$$\boxed{x_0+x_1+\cdots+x_6=1}$$

Note:

- **The molar fraction of the species is just the function of the concentration of hydronium ion, being independent of the overall concentration of EDTA (*c*(EDTA)).**

$$x_0+x_1+\cdots+x_6=1$$


Molar Fraction
1.0
0.8
0.6
0.4
0.2
0.0
H_6Y^{2+}
H_5Y^+
H_4Y
H_3Y^-
H_2Y^{2-}
HY^{3-}
Y^{4-}
0
2
4
6
8
10
12
14
pH


0
−1
−2
−3
−4
−5
−6
−7
−8
−9
−10
−11
−12
−13
−14
−15
−16
log α
1
2
3
4
5
6
7
8
9
10
11
pH
HY^{3-}
Y^{4-}
H_2Y^{2-}
H_6Y^{2+}
H_5Y^{+}
H_4Y
H_3Y^{-}

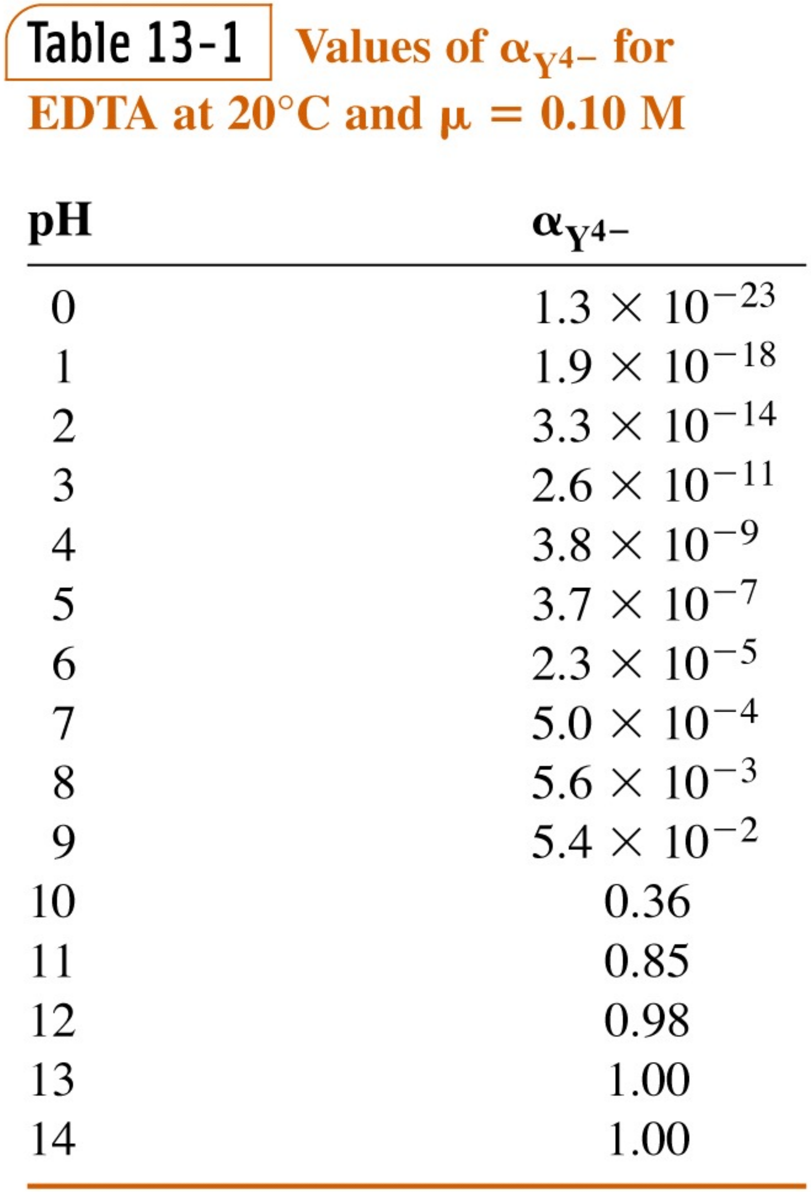


Table 13-1 Values of $\alpha_{Y^{4-}}$ for EDTA at 20°C and $\mu = 0.10$ M

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

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[EDTA]} \text{(相当于} \chi_{Y^{4-}} \text{)}$$

$$= \frac{[Y^{4-}]}{[Y^{4-}]+[HY^{3-}]+[H_2Y^{2-}]+\cdots+[H_6Y^{2+}]}$$

(相当于$\chi_{Y^{4-}}$,即Y^{4-}的摩尔分数)

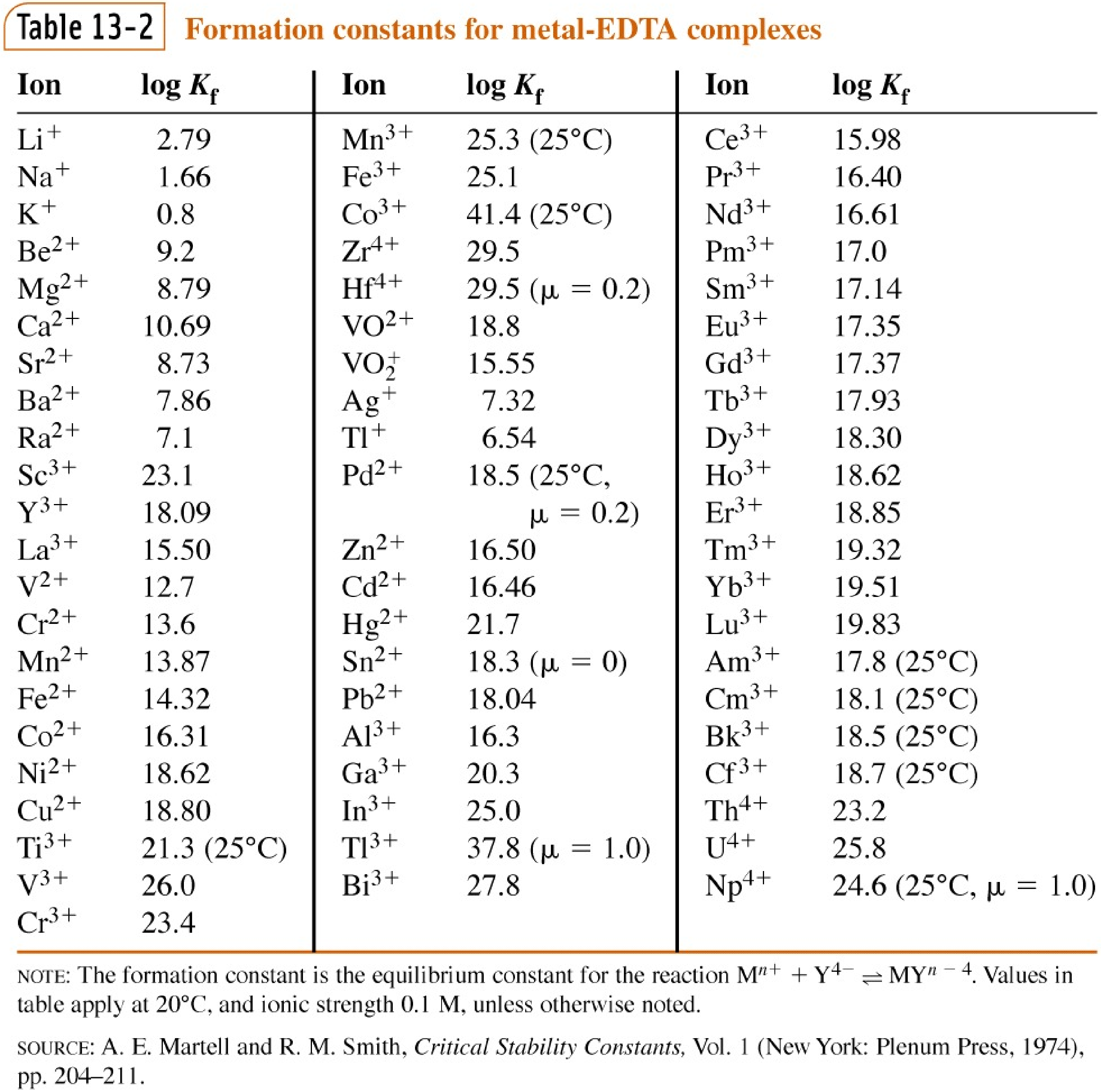


Table 13-2 Formation constants for metal-EDTA complexes

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			Er^{3+}	18.85
La^{3+}	15.50	Zn^{2+}	16.50	Tm^{3+}	19.32
V^{2+}	12.7	Cd^{2+}	16.46	Yb^{3+}	19.51
Cr^{2+}	13.6	Hg^{2+}	21.7	Lu^{3+}	19.83
Mn^{2+}	13.87	Sn^{2+}	18.3 ($\mu = 0$)	Am^{3+}	17.8 (25°C)
Fe^{2+}	14.32	Pb^{2+}	18.04	Cm^{3+}	18.1 (25°C)
Co^{2+}	16.31	Al^{3+}	16.3	Bk^{3+}	18.5 (25°C)
Ni^{2+}	18.62	Ga^{3+}	20.3	Cf^{3+}	18.7 (25°C)
Cu^{2+}	18.80	In^{3+}	25.0	Th^{4+}	23.2
Ti^{3+}	21.3 (25°C)	Tl^{3+}	37.8 ($\mu = 1.0$)	U^{4+}	25.8
V^{3+}	26.0	Bi^{3+}	27.8	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.

7.6 K(MY), α & K'(MY) of Coordination Compounds

1. **Formation Constant: K(MY)**

$$K(\mathrm{ML}) = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]}$$

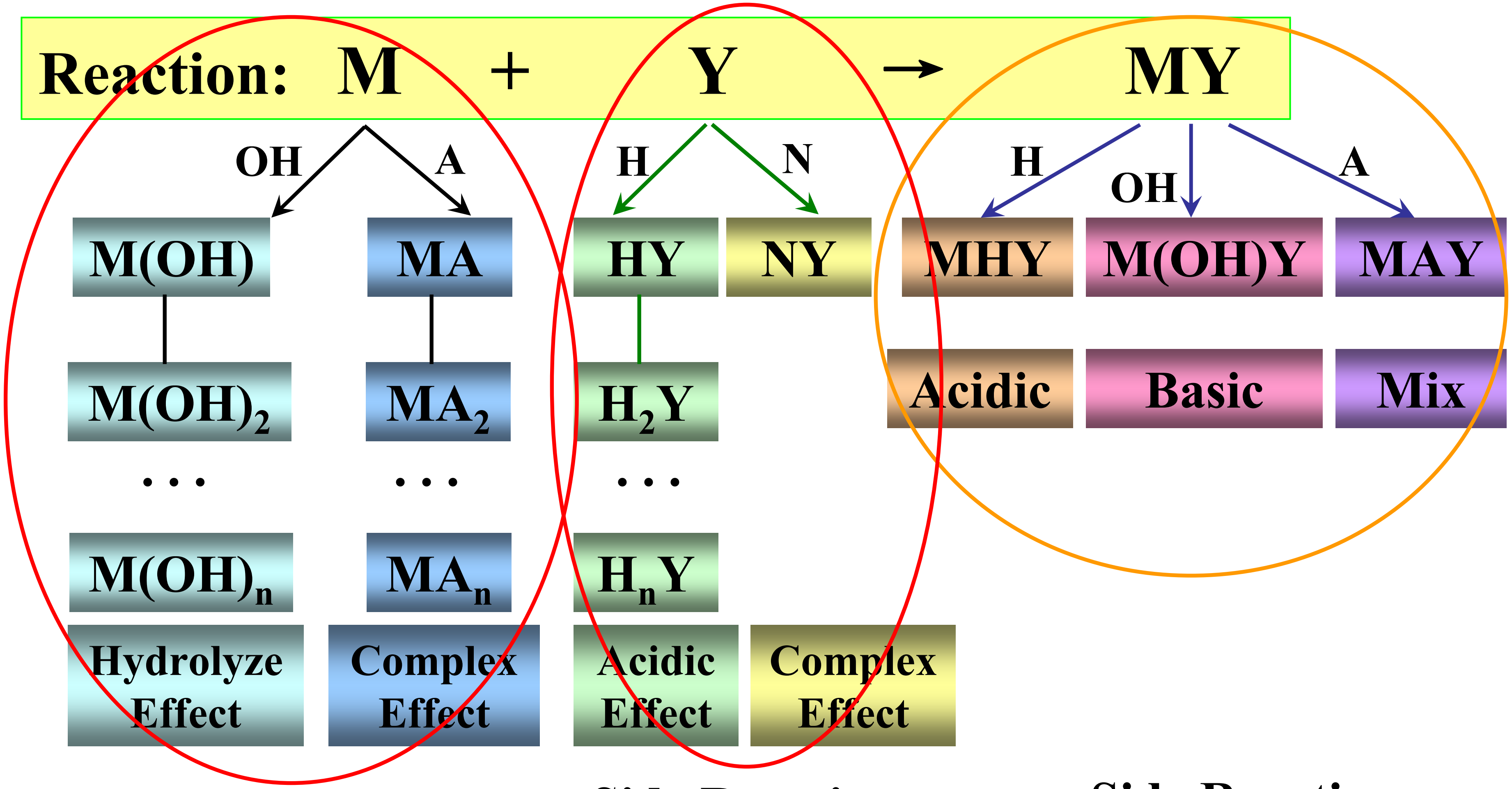
$$\mathrm{M} + \mathrm{L} = \mathrm{ML}$$

Given the ligand is EDTA:

$$\mathrm{M} + \mathrm{Y} = \mathrm{MY}$$

$$K(\mathrm{MY}) = \frac{[\mathrm{MY}]}{[\mathrm{M}][\mathrm{Y}]}$$

Side Reaction of Complex Reaction



Reaction: M + Y → MY

OH

A

M(OH)

$M(OH)_2$

…

$M(OH)_n$

MA

MA_2

…

MA_n

Hydrolyze Effect

Complex Effect

H

N

HY

H_2Y

…

H_nY

NY

Acidic Effect

Complex Effect

H

OH

A

MHY

M(OH)Y

MAY

Acidic

Basic

Mix

Side Reaction of M

Side Reaction of Y

Side Reaction of MY

2. Conditional Formation Constant: K'(MY)

$$K'(\mathrm{MY}) \equiv \frac{[(\mathrm{MY})']}{[\mathrm{M}'][\mathrm{Y}']}$$

[(MY)’]: The overall concentration of the formed coordination compound.

[M’]: The overall concentration of metal ion except that react with Y.

[Y’]: The overall concentration of ligand except that react with M.

3. Side Reaction Coefficient, α

$$\alpha(\mathrm{Y}) \equiv \frac{[\mathrm{Y}']}{[\mathrm{Y}]}$$

$$\alpha(\mathrm{M}) \equiv \frac{[\mathrm{M}']}{[\mathrm{M}]}$$

$$\alpha(\mathrm{MY}) \equiv \frac{[(\mathrm{MY})']}{[\mathrm{MY}]}$$

4. How to Calculate α & K'(MY)

(1) Acid effect coefficient of Y (α(Y)) and conditional formation constant

$$\alpha\{\mathrm{Y(H)}\} = \frac{[\mathrm{Y'}]}{[\mathrm{Y}]} = \frac{[\mathrm{Y}]+[\mathrm{HY}]+[\mathrm{H_2Y}]+\cdots+[\mathrm{H_6Y}]}{[\mathrm{Y}]}$$

$$= 1 + \frac{[\mathrm{HY}]}{[\mathrm{Y}][\mathrm{H}]}[\mathrm{H}] + \frac{[\mathrm{H_2Y}]}{[\mathrm{Y}][\mathrm{H}]^2}[\mathrm{H}]^2 + \cdots + \frac{[\mathrm{H_6Y}]}{[\mathrm{Y}][\mathrm{H}]^6}[\mathrm{H}]^6$$

$$= 1 + \beta_1^{\mathrm{H}}[\mathrm{H}] + \beta_2^{\mathrm{H}}[\mathrm{H}]^2 + \cdots + \beta_6^{\mathrm{H}}[\mathrm{H}]^6$$

表 7.2 EDTA 的各级稳定常数和累积稳定常数

质子化平衡	逐级稳定常数	累积稳定常数 （或累积质子化常数）
$Y + H = HY$	$K_1 = 10^{10.34}$	$\beta_1^H = 10^{10.34}$
$HY + H = H_2Y$	$K_2 = 10^{6.24}$	$\beta_2^H = 10^{16.58}$
$H_2Y + H = H_3Y$	$K_3 = 10^{2.75}$	$\beta_3^H = 10^{19.33}$
$H_3Y + H = H_4Y$	$K_4 = 10^{2.07}$	$\beta_4^H = 10^{21.40}$
$H_4Y + H = H_5Y$	$K_5 = 10^{1.6}$	$\beta_5^H = 10^{23.0}$
$H_5Y + H = H_6Y$	$K_6 = 10^{0.9}$	$\beta_6^H = 10^{23.9}$

表 7.5 不同 pH 下 EDTA 的 lgα{Y(H)}

pH	lgα{Y(H)}	pH	lgα{Y(H)}	pH	lgα{Y(H)}
0.0	23.64	2.8	11.09	8.0	2.27
0.4	21.32	3.0	10.60	8.4	1.87
0.8	19.08	3.4	9.70	8.8	1.48
1.0	18.01	3.8	8.85	9.0	1.28
1.4	16.02	4.0	8.44	9.5	0.83
1.8	14.27	4.4	7.64	10.0	0.45
2.0	13.51	4.8	6.84	11.0	0.07
2.4	12.19	5.0	6.45	12.0	0.00

- **Just take into account the acid effect:**

$$K'(\mathrm{MY}) = \frac{[\mathrm{MY}]}{[\mathrm{M}][\mathrm{Y}']} = \frac{[\mathrm{MY}]}{[\mathrm{M}][\mathrm{Y}]\alpha(\mathrm{Y})}$$

$$= \frac{K(\mathrm{MY})}{\alpha(\mathrm{Y})}$$

Or: $\lg K'(\mathrm{MY}) = \lg K(\mathrm{MY}) - \lg \alpha(\mathrm{Y})$

Criterion for Successful Titration

Given the end point error is ±0.1%, then

$$[(MY)']=0.999c(M)$$

$$[M']=[Y']=0.001c(M)$$

$$K'(MY) \geq \frac{0.999c(M)}{\{0.001c(M)\}^2} = \frac{10^6}{c(M)}$$

$$\therefore \quad \lg c(M)K'(MY) \geqslant 6$$

Requirements of Acidity for Successful Titration

The highest acidity (the lowest pH value) :

$\because$ $\lg K'(\mathrm{MY}) = \lg K(\mathrm{MY}) - \lg \alpha\{\mathrm{Y(H)}\}$

$\lg c(\mathrm{M}) K'(\mathrm{MY}) \geqslant 6$

$\therefore$ $\lg \alpha\{\mathrm{Y(H)}\} \leqslant \lg K(\mathrm{MY}) + \lg c(\mathrm{M}) - 6 \longrightarrow \mathrm{pH}$

The lowest acidity (the highest pH value) :

1. **Confirm the concentration of the OH^- when the metal ions begin to hydrolyze.**
2. **Calculate the pOH, then the pH**

(2) Side reaction coefficient of M (α(M)) and conditional formation constant

Complex effect Coefficient:

$$\alpha\{\mathrm{M(A)}\} = \frac{[\mathrm{M'}]}{[\mathrm{M}]} = 1 + \beta_1[\mathrm{A}] + \beta_2[\mathrm{A}]^2 + \cdots + \beta_n[\mathrm{A}]^n$$

Hydrolyze effect Coefficient:

$$\alpha\{\mathrm{M(OH)}\} = 1 + \beta_1[\mathrm{OH}] + \beta_2[\mathrm{OH}]^2 + \cdots + \beta_n[\mathrm{OH}]^n$$

Overall side reaction coefficient of M:

$$\alpha\{\mathrm{M(A,OH)}\} = \alpha\{\mathrm{M(A)}\} + \alpha\{\mathrm{M(OH)}\} - 1$$

- **Simultaneously taking into account the acid effect and side reaction of metal ions:**

$$K'(\mathrm{MY}) = \frac{[(\mathrm{MY})]}{[\mathrm{M'}][\mathrm{Y'}]} = \frac{K(\mathrm{MY})}{\alpha(\mathrm{M})\alpha(\mathrm{Y})}$$

- **Simultaneously taking into account the acid effect of ligand (Y), side reaction of metal ions (M) and coordination compound (MY):**

$$K'(\mathrm{MY}) = \frac{[(\mathrm{MY})']}{[\mathrm{M'}][\mathrm{Y'}]} = K(\mathrm{MY})\frac{\alpha(\mathrm{MY})}{\alpha(\mathrm{Y})\alpha(\mathrm{M})}$$

7.7 Metallochromic Indicator

- **These indicators are weak complexing agents that exhibit different colors in their complexed and uncomplexed forms.**

$$\mathbf{M + In \rightleftharpoons MIn} \qquad K(\mathrm{MIn}) = \frac{[\mathrm{MIn}]}{[\mathrm{M}][\mathrm{In}]}$$

$$\mathbf{MIn \quad + \quad Y \; = \; MY \quad + \quad In}$$

(color A) **(colorless)** **(color B)**

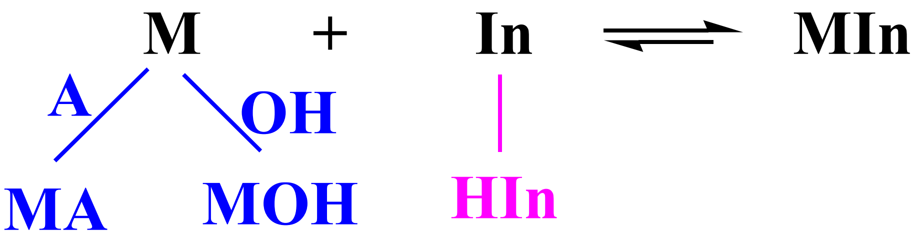
Requirements of Metallochromic Indicator

1. **At given pH extent, In and MIn exhibit distinct color change.**
2. **The metal-titrant complex must be more stable than the metal-indicator complex.**

$$K'(\mathrm{MIn}) > 10^4$$

$$\frac{K'(\mathrm{MY})}{K'(\mathrm{MIn})} > 10^2$$

Theoretical Color Change Point of Indicator



$$M + In \rightleftharpoons MIn$$

$$K'(\mathrm{MIn}) = \frac{[\mathrm{MIn}]}{[\mathrm{M}'][\mathrm{In}']} = K(\mathrm{MIn})\frac{1}{\alpha(\mathrm{M})\alpha\{\mathrm{In(H)}\}}$$

At theoretical color change point: [MIn] = [In’]

$$\mathrm{pM}'_t = \log K'(\mathrm{MIn})$$

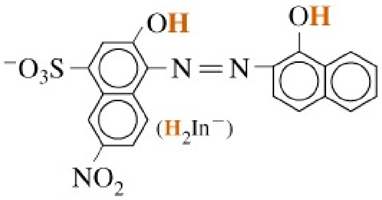
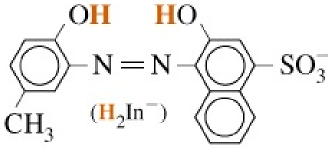
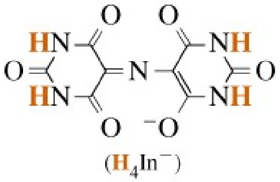
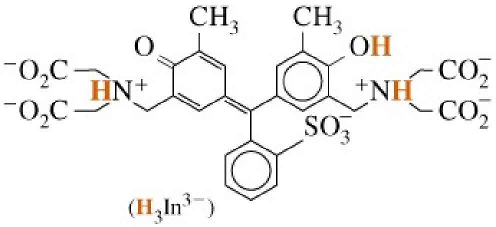
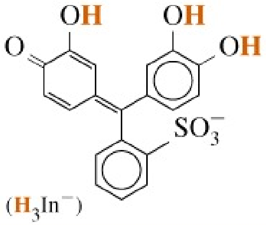
$$= \log K(\mathrm{MIn}) - \log\alpha(\mathrm{M}) - \log\alpha\{\mathrm{In(H)}\}$$

Note:

Compare $pM' = \log K'(MIn)$ with $pH = pK(HIn)$

- **For given indicator at constant temperature, $K(HIn)$ is a constant.**
- **The theoretical color change point of metallochromic indicator is not a definite datum because $K'(MIn)$ changes with titration condition.**

Table 13-3 **Common metal ion indicators**

	Name	**Structure**	**pK_a**	**Color of free indicator**	**Color of metal ion complex**
铬黑T	Eriochrome black T	 (H_2In^-)	$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
钙镁试剂	Calmagite	 (H_2In^-)	$pK_2 = 8.1$ $pK_3 = 12.4$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
红紫酸铵	Murexide	 (H_4In^-)	$pK_2 = 9.2$ $pK_3 = 10.9$	H_4In^- red-violet H_3In^{2-} violet H_2In^{3-} blue	Yellow (with Co^{2+}, Ni^{2+}, Cu^{2+}); red with Ca^{2+}
二甲酚橙	Xylenol orange	 (H_3In^{3-})	$pK_2 = 2.32$ $pK_3 = 2.85$ $pK_4 = 6.70$ $pK_5 = 10.47$	H_5In^- yellow H_4In^{2-} yellow H_3In^{3-} yellow H_2In^{4-} violet HIn^{5-} violet In^{6-} violet	Red
邻苯二酚紫	Pyrocatechol violet	 (H_3In^-)	$pK_1 = 0.2$ $pK_2 = 7.8$ $pK_3 = 9.8$ $pK_4 = 11.7$	H_4In red H_3In^- yellow H_2In^{2-} violet HIn^{3-} red-purple	Blue

PREPARATION AND STABILITY:

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.

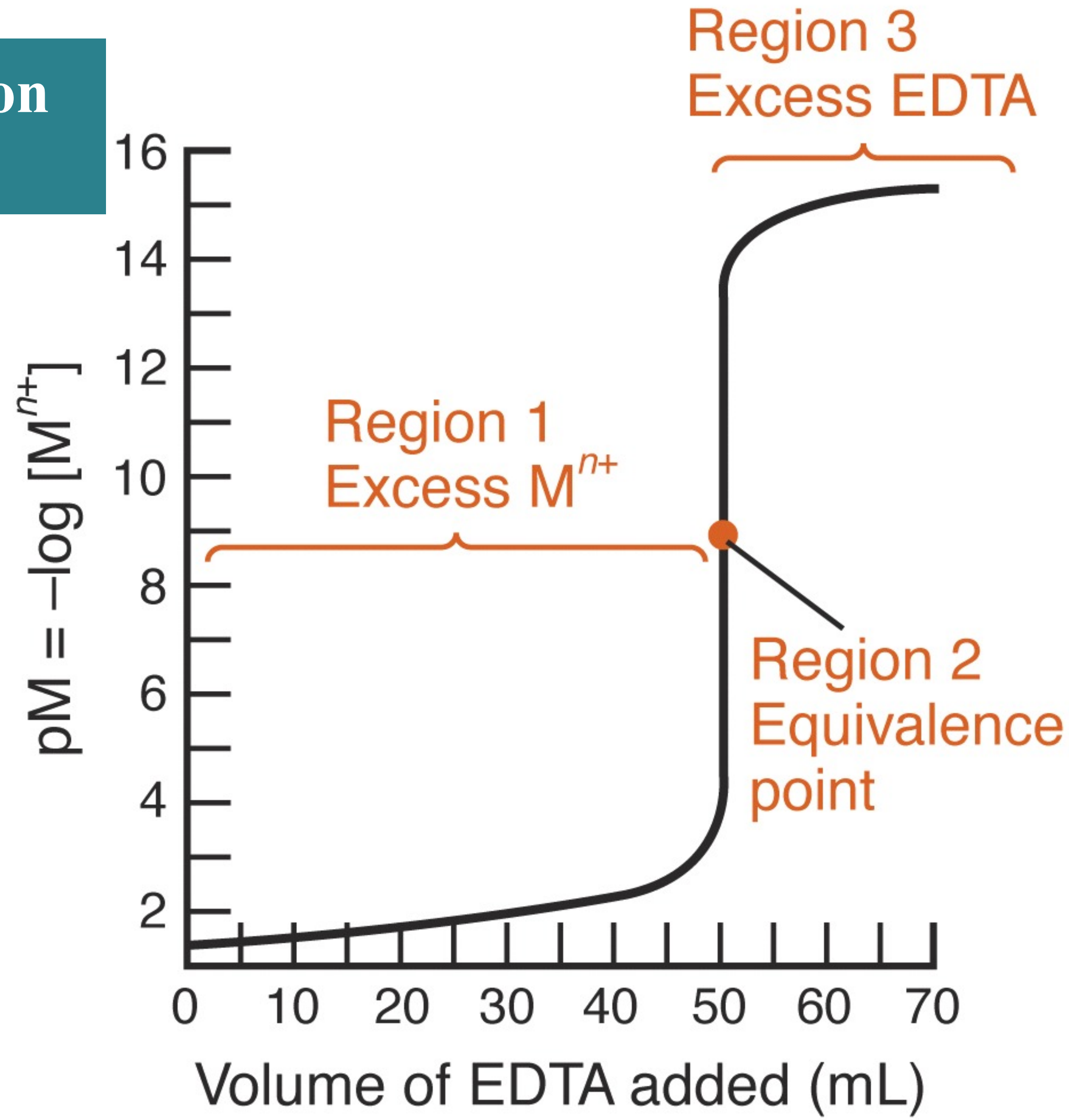
Calmagite: 0.05 g/100 mL H_2O; solution is stable for a year in the dark.

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 H_2O; solution is stable indefinitely.

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

7.8 Complexation Titration Curves



Three regions in an EDTA titration illustrated for reaction of 50.0 mL of 0.0500 M^{n+} with 0.0500 M EDTA, assuming $K'_f = 1.15 \times 10^{16}$.

Region	Major constituent	[M’]
Before titration	M	$c(\mathrm{M})$
Before the equivalence point	$\mathrm{MY} + \mathrm{M}'$	$\dfrac{\text{amount M' remaining (mol)}}{\text{volume (L)}}$ $[\mathrm{M}']=c(\mathrm{M})-[\mathrm{MY}]$
At the equivalence point	MY	$\sqrt{\dfrac{c_{\mathrm{stoi}}(\mathrm{M})}{K'(\mathrm{MY})}}$
After the equivalence point	$\mathrm{MY} + \mathrm{Y}'$	$K'(MY) = \dfrac{[MY]}{[M'][Y']}$ $\dfrac{[\mathrm{MY}]}{[\mathrm{Y}']}\cdot\dfrac{1}{K'(\mathrm{MY})}$

At the equivalence point

- **At SP (stoichiometric point), [M’]=[Y’].**
- **If complexes are stable enough, then**

$[MY]_{sp}=c_{sp}(M)-[M']_{sp}\approx c_{sp}(M)$

- **Substitute into conditional constant, then we get**

$$K'(MY)=\frac{[MY]}{[M'][Y']} \Rightarrow [M']_{sp}=\sqrt{\frac{c_{sp}[M]}{K'(MY)}}$$

$$(pM')_{sp}=\frac{1}{2}(\lg K'(MY)+pc_{sp}(M))$$

- ***$c_{sp}(M)$* denotes analytical concentration of the metal ion at SP and is half of the initial concentration of metal ions, if the same concentration level of EDTA is used in the titration.**

Example. Titration Calculations

- Calculate the shape of the titration curve for the reaction of 50.0 mL of 0.0400 M Ca^{2+} (buffered to pH 10.00) with 0.0800 M EDTA.
- $Ca^{2+} + EDTA = CaY^{2-}$

$$K'_f = \alpha_{Y^{4-}} K_f = (0.36)(4.9 \times 10^{10}) = 1.8 \times 10^{10}$$

- The equivalence volume is 25.0 mL. Because K_f’ is large, it is reasonable to say that the reaction goes to completion with each addition of titrant. We want to make a graph in which pCa^{2+}(=-log[Ca^{2+}]) is plotted versus milliliters of added EDTA.

Region 1 Before the Equivalence Point

- Consider the addition of 5.0 mL of EDTA.

$$[Ca^{2+}] = (\frac{25.0 - 5.0}{25.0})(0.0400)(\frac{50.0}{55.0}) = 0.0291M$$

$$pCa^{2+} = -\log[Ca^{2+}] = 1.54$$

- In a similar manner, we could calculate pCa^{2+} for any volume of EDTA less than 25.0 ML

Region 2 At the Equivalence Point

- Virtually all the metal is in the form CaY^{2-}. Assuming negligible dissociation, the concentration of CaY^{2-} is equal to the original concentration of Ca^{2+}, with a correction for dilution.

$$[CaY^{2-}] = (0.0400)(\frac{50.0}{75.0}) = 0.0267M$$

	Ca^{2+} +	EDTA =	CaY^{2-}
Initial Concentration (M)	--	--	0.0267
Final Concentration (M)	x	x	0.0267-x

$$\frac{[CaY^{2-}]}{[Ca^{2+}][EDTA]} = K_f^{'} = 1.8\times 10^{10}$$

$$\frac{0.0267 - x}{x^2} = 1.8\times 10^{10} \Rightarrow x = 1.2\times 10^{-6}M$$

$$pCa^{2+} = -\log x = 5.91$$

Region 3 After the Equivalence Point

- Virtually all the metal is in the form CaY^{2-}, and there is excess, unreacted EDTA. The concentration of CaY^{2-} and excess EDTA are easily calculated. For Example, at 26.0 mL, there is 1.0 mL excess EDTA

$$[EDTA] = (0.0800(\frac{1.0}{76.0}) = 1.05 \times 10^{-3} M$$

$$[CaY^{2-}] = (0.0400M)(\frac{50.0}{76.0}) = 2.63 \times 10^{-2} M$$

$$\frac{[CaY^{2-}]}{[Ca^{2+}][EDTA]} = K_f^{'} = 1.8 \times 10^{10}$$

$$\frac{2.63 \times 10^{-2}}{[Ca^{2+}](1.05 \times 10^{-3})} = 1.8 \times 10^{10} \Rightarrow [Ca^{2+}] = 1.4 \times 10^{-9} M$$

$$pCa^{2+} = -\log x = 8.86$$

The titration Curve

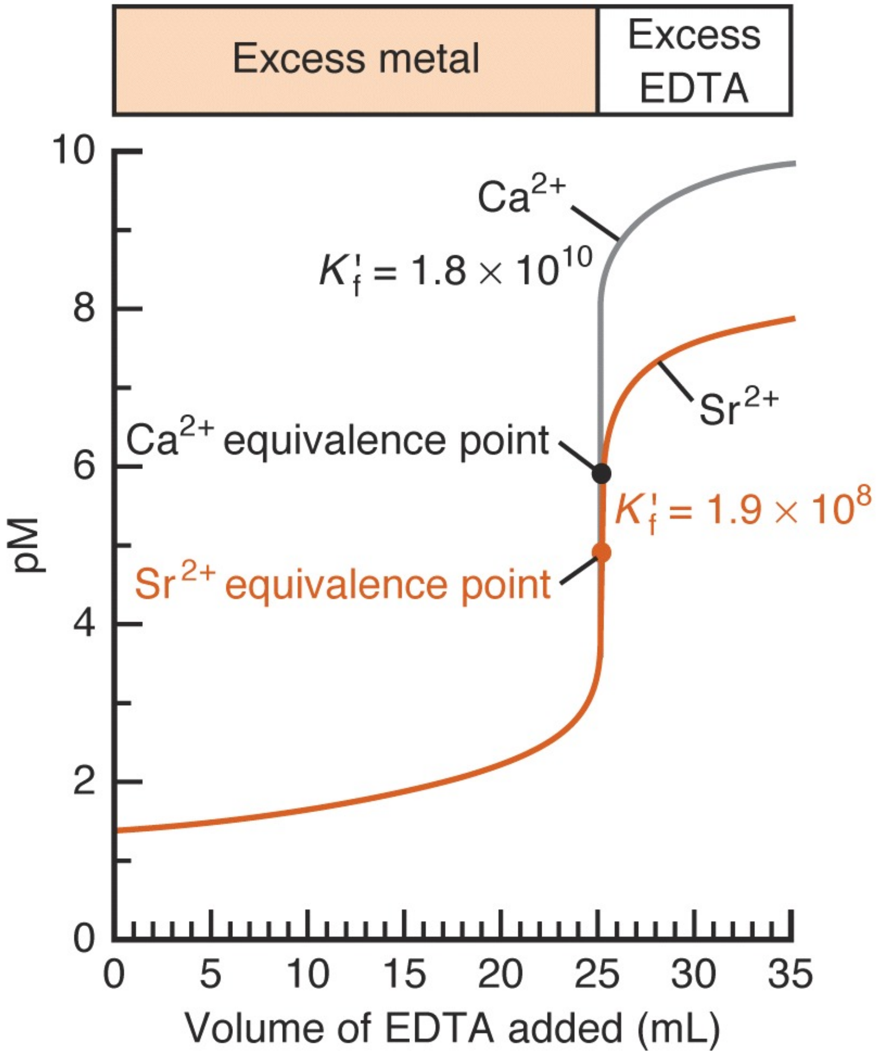


Fig. 13-10 Theoretical titration curves for the reaction of 50.0 mL of 0.0400 M Ca^{2+} with 0.0800 M EDTA at pH 10.00.

Factors affecting the shape of Titration Curves

Given E_t = -0.1% $$[\mathrm{M'}] = c_{\mathrm{M,\,remaining}} = \frac{0.1\% c_{\mathrm{M}}}{2} = c_{\mathrm{M}} \cdot 10^{-3.30}$$

$$\mathrm{pM'} = \mathrm{p}c_{\mathrm{M}} + 3.30$$

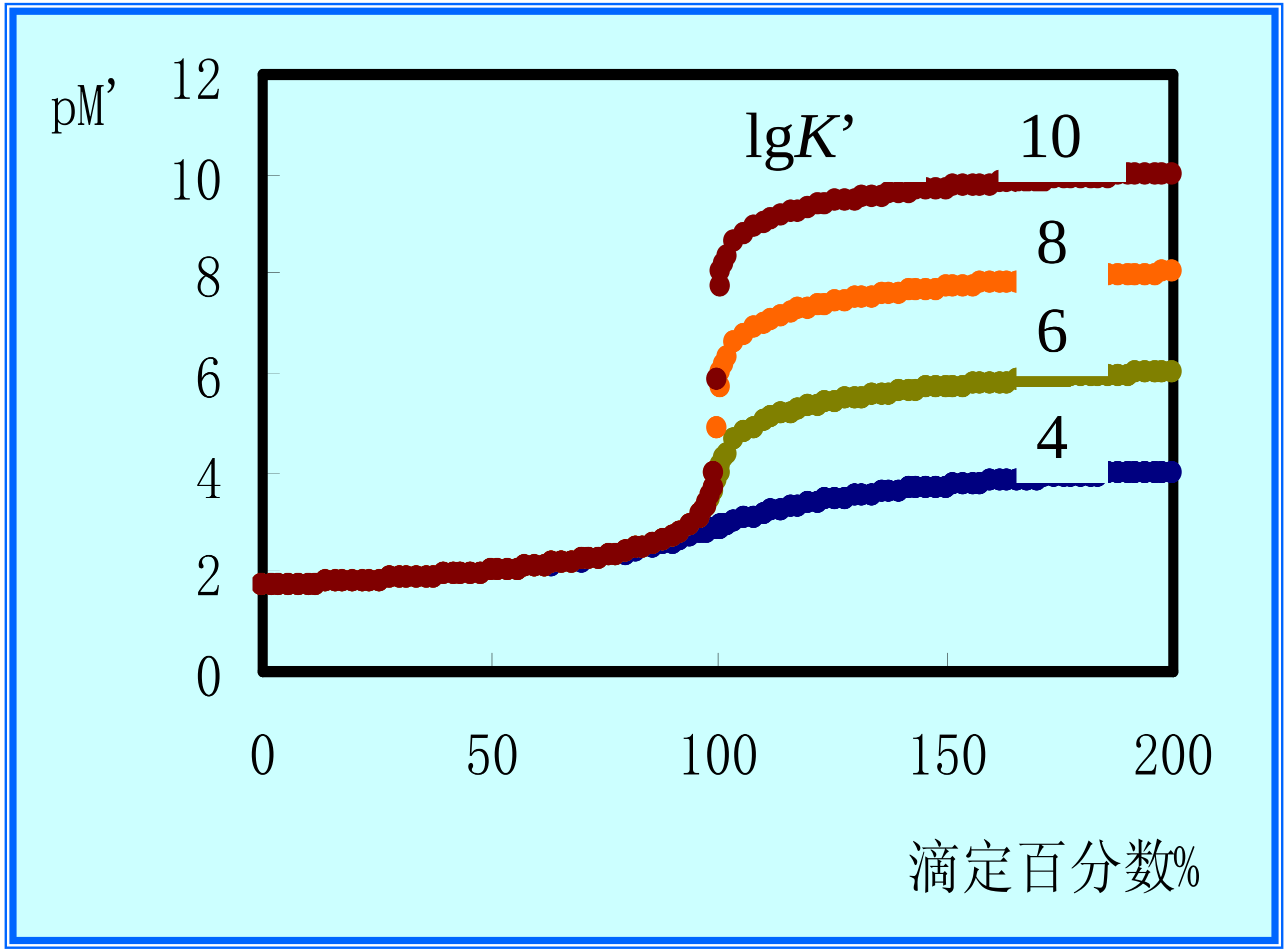
Given E_t = +0.1% $$[\mathrm{M'}] = \frac{[\mathrm{MY}]}{[\mathrm{Y'}]K'(\mathrm{MY})}$$

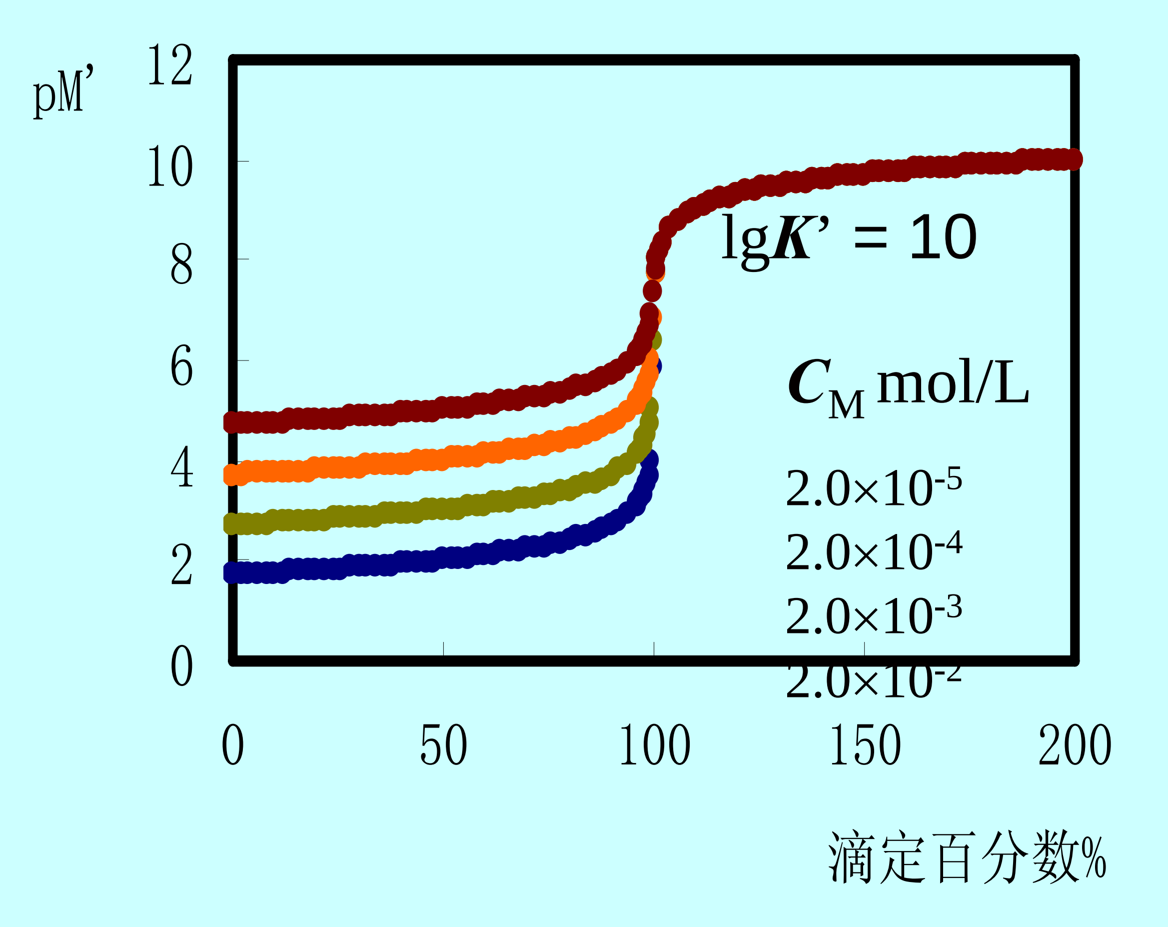
$$\mathrm{pM'} = \lg K'_{\mathrm{MY}} + \lg\frac{[\mathrm{Y'}]}{[\mathrm{MY}]} = \lg K'_{\mathrm{MY}} + \lg\frac{1}{1000} = \lg K'_{\mathrm{MY}} - 3$$

The magnitude of the break $= (\lg K'_{\mathrm{MY}} - 3) - (\mathrm{p}c_{\mathrm{M}} + 3.30)$

$$= \lg K'_{\mathrm{MY}} - \mathrm{p}c_{\mathrm{M}} - 6.30$$

Effect of *K*' on the Sharp of the Break




pM'
12
10
8
6
4
2
0
0
50
100
150
200
滴定百分数%
lgK' = 10
C_M mol/L
2.0×10^-5
2.0×10^-4
2.0×10^-3
2.0×10^-2

7.9 End Point Errors

$$E_t = \frac{[\mathrm{L'}]_{\mathrm{end}} - [\mathrm{M'}]_{\mathrm{end}}}{c_{\mathrm{stoi}}} \times 100\%$$

Given

$$\Delta \mathrm{pM'} = \mathrm{pM'}_{\mathrm{end}} - \mathrm{pM'}_{\mathrm{stoi}}$$

$$\rightarrow [\mathrm{M'}]_{\mathrm{end}} = [\mathrm{M'}]_{\mathrm{stoi}} 10^{-\Delta \mathrm{pM'}}$$

$$\Delta \mathrm{pL'} = \mathrm{pL'}_{\mathrm{end}} - \mathrm{pL'}_{\mathrm{stoi}}$$

$$\rightarrow [\mathrm{L'}]_{\mathrm{end}} = [\mathrm{L'}]_{\mathrm{stoi}} 10^{-\Delta \mathrm{pL'}}$$

At equivalence point: $K'_{\text{stoi}}(\text{ML})=K'_{\text{end}}(\text{ML})$,

$$[\text{ML}]_{\text{stoi}} \approx [\text{ML}]_{\text{end}} = c_{\text{stoi}}(\text{M})$$

$$[\text{M}']_{\text{stoi}} = [\text{L}']_{\text{stoi}} = \sqrt{\frac{c_{\text{stoi}}(\text{M})}{K'(\text{ML})}}$$

$$\because \quad \frac{[\text{ML}]_{\text{stoi}}}{[\text{M}']_{\text{stoi}}[\text{L}']_{\text{stoi}}} = \frac{[\text{ML}]_{\text{end}}}{[\text{M}']_{\text{end}}[\text{L}']_{\text{end}}} \rightarrow \frac{[\text{M}']_{\text{end}}}{[\text{M}']_{\text{stoi}}} = \frac{[\text{L}']_{\text{stoi}}}{[\text{L}']_{\text{end}}}$$

$$\text{pM}'_{\text{end}} - \text{pM}'_{\text{stoi}} = \text{pL}'_{\text{stoi}} - \text{pL}'_{\text{end}} \rightarrow \Delta\text{pM}' = -\Delta\text{pL}'$$

$$E_t = \frac{[L']_{end} - [M']_{end}}{c_{stoi}(M)} \times 100\%$$

$$= \frac{[L']_{stoi} \times 10^{-\Delta pL'} - [M']_{stoi} \times 10^{-\Delta pM'}}{c_{stoi}(M)} \times 100\%$$

$$= \frac{\sqrt{\frac{c_{stoi}}{K'(ML)}}(10^{\Delta pM'} - 10^{-\Delta pM'})}{c_{stoi}(M)} \times 100\%$$

$$= \frac{10^{\Delta pM'} - 10^{-\Delta pM'}}{\sqrt{c_{stoi}(M)K'(ML)}} \times 100\%$$

Ringbom Equation

∵ **At equivalence point:** $\alpha_{\mathrm{end}}(\mathrm{M}) \approx \alpha_{\mathrm{stoi}}(\mathrm{M})$

∴ $\Delta\mathrm{pM} \approx \Delta\mathrm{pM}'$

$$\rightarrow K_{\mathrm{t}} = \frac{10^{\Delta\mathrm{pM}} - 10^{-\Delta\mathrm{pM}}}{\sqrt{c_{计}(\mathrm{M})K'(\mathrm{MY})}} \times 100\%$$

$$\lg K_{\mathrm{t}} = -\frac{1}{2}\lg[c_{\mathrm{stoi}}(\mathrm{M})K'(\mathrm{MY})] + [\lg(10^{\Delta\mathrm{pM}} - 10^{-\Delta\mathrm{pM}}) + 2]$$

7-10 Titration Methods and Applications

1. Direct Titration

- Based on indicators that respond to the analyte itself or an added metal ion.
- Advantages: simple, fast, and less likely to introduce errors.
- First choice for a selected method.
- Ex. The determination of water hardness by complexometric titration is a good example to show application of complexometric titrationl.

2. Back Titration

1. The reaction rate between metal ion and EDTA is slow
2. Metal ions is apt to undergo hydrolysis to form hydroxo complex at the titration pH and an proper auxiliary complexing reagent.
3. The complex of the metal ion with the indicator is more stable than the metal EDTA complex so that the indicator is blocked.

EX. Titration of Al^{3+} using EDTA is such an example.

pH 3.5, added excess EDTA, pH 5~6, use $Zn^{2+} \rightarrow Y$

3. Demasking

1. A simple way to cope with a sample containing more than one metal ions.

Ex. In the determination of Al^{3+} in the presence of Pb^{2+}, Zn^{2+}, and Cd^{2+}.

- Al3+ can be liberated after back titration: when back titration reaches the endpoint, NaF is added to the solution to liberated Al^{3+} from AlF_6.
- $AlY^- + 6F^- + 2H^+ = AlF_6^{3-} + H_2Y^{2-}$
- The liberated EDTA can be titrated by Zn^{2+} standard solution.

4. Indirect titration

1. Metal ions which form EDTA complexes are not stable enough to facilitate titration
2. Non-metal ions which react stoichiometrically with metal ions.

Ag^+的测定

$\lg K(\mathrm{Ag-Y}) = 7.3,$

if $c(Ag^+) = 0.01\ mol\cdot dm^{-3}$,

then lgcK'<6, cannot direct titration

待测的Ag^+离子溶液

⇩

$[Ni(CN)_4]^{2-}$溶液

$$2\,Ag^+(aq) + [Ni(CN)_4]^{2-}(aq) = 2\,[Ag(CN)_2]^-(aq) + Ni^{2+}(aq)$$

↑

用EDTA标准液滴定

NiY^{2-}