



# Chapter 17

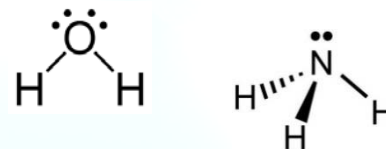
## Complexation and Precipitation Reactions and Titrations

- Complex-formation reactions are widely used in analytical chemistry.
- One of the first uses of these reagents was for titrating cations.
- In addition, many complexes are colored or absorb ultraviolet radiation; the formation of these complexes is often the basis for spectrophotometric determinations.
- Some complexes are sparingly soluble and can be used in gravimetric analysis.
- Complexes are also widely used for extracting cations from one solvent to another and for dissolving insoluble precipitates.
- The most useful complex-forming reagents are organic compounds containing several electron-donor groups that form multiple covalent bonds with metal ions.
- Inorganic complexing agents are also used to control solubility, form colored species, or form precipitates.

## 17A The formation of complexes

- Most metal ions react with electron-pair donors to form coordination compounds or complexes.
- The donor species, **or ligand**, is an ion or a molecule that forms a covalent bond with a cation or a neutral metal atom by donating a pair of electrons that are then shared by the two. A ligand must have at least one pair of unshared electrons available for bond formation.

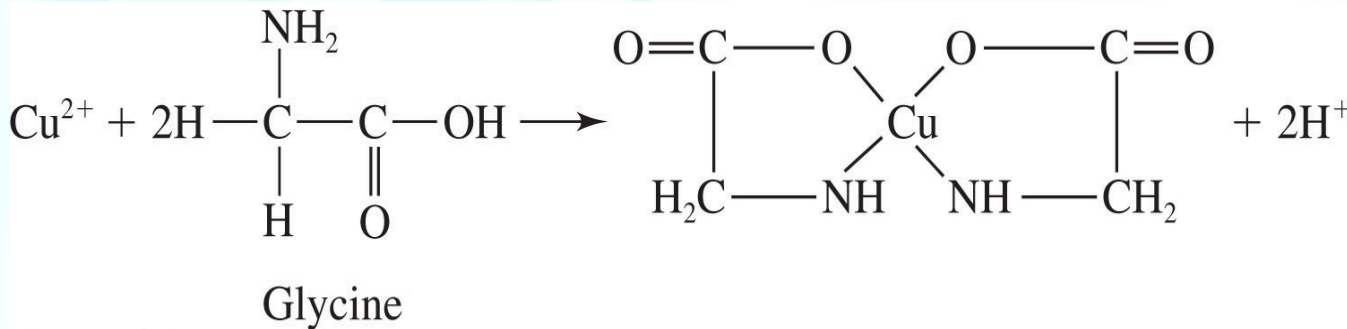
- Water, ammonia, and halide ions are common inorganic ligands.



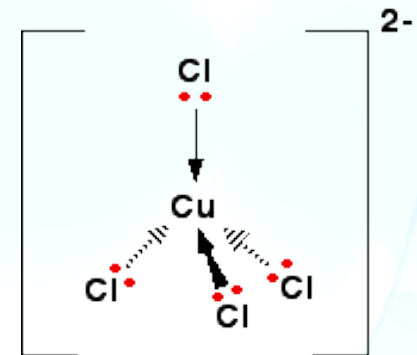
- In fact most metal ions in aqueous solution actually exist as aquo complexes. Copper(II), for example, in aqueous solution is readily complexed by water molecules to form species such as  $\text{Cu}(\text{H}_2\text{O})_4^{+2}$
- We often simplify such complexes in chemical equations by writing the metal ion as if it were uncomplexed  $\text{Cu}^{+2}$ . We should remember, however, that most metal ions are actually aquo complexes in aqueous solution.

- The number of covalent bonds that a cation tends to form with electron donors is its coordination number.
- Typical values for coordination numbers are two, four, and six.
- The species formed as a result of coordination can be electrically positive, neutral, or negative.

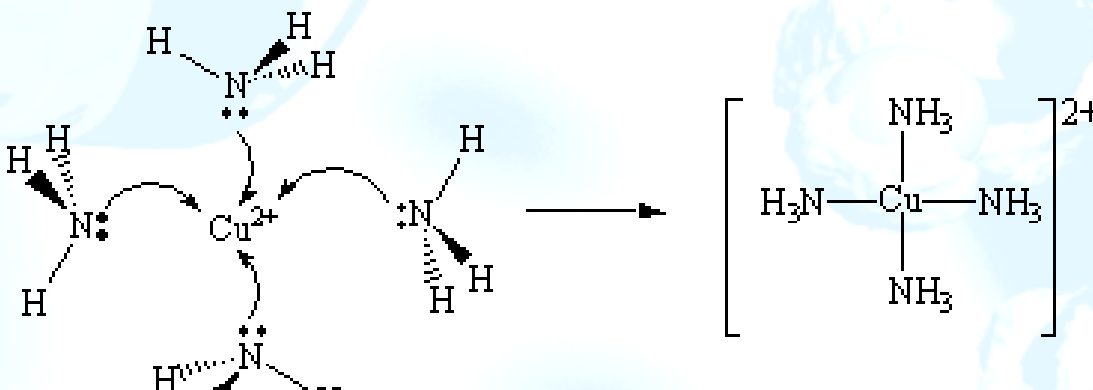
Ex., copper(II), which has a coordination number of four, forms a cationic ammine complex,  $\text{Cu}(\text{NH}_3)_4^{+2}$ ; a neutral complex with glycine,  $\text{Cu}(\text{NH}_2\text{CH}_2\text{COO})_2$ ; and an anionic complex with chloride ion,  $\text{CuCl}_4^{-2}$ .



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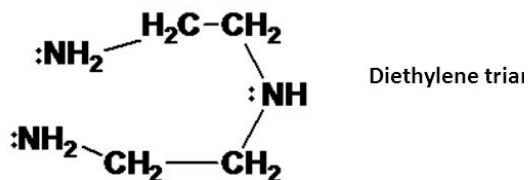
**[CuCl<sub>4</sub>]<sup>2-</sup>**



- Titrations based on complex formation, sometimes called complexometric titrations.
- The truly remarkable growth in their analytical application, based on a particular class of coordination compounds called **chelates**, began in the **1940s**.
- **Chelate is pronounced *kee'late* and is** derived from the Greek word for claw.
- **A chelate is produced when a metal ion coordinates** with two or more donor groups of a single ligand to form a five- or six-membered heterocyclic ring. The copper complex of glycine, mentioned in the previous paragraph, is an example. In this complex, copper bonds to both the oxygen of the carboxyl group and the nitrogen of the amine group
- A ligand that has a single donor group, such as ammonia, is called **unidentate** (single-toothed), whereas one such as glycine, which has two groups available for covalent bonding, is called **bidentate**. **Tridentate, tetradentate, pentadentate, and hexadentate** chelating agents are also known.

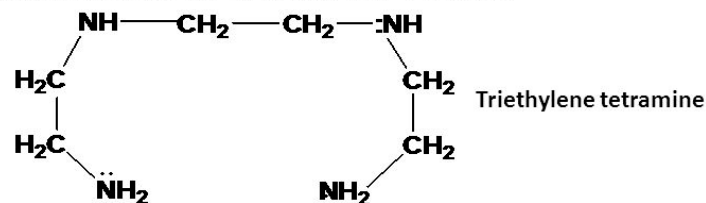
- **Tridentate Ligand:**

The Ligand attached to metal at 3 sites

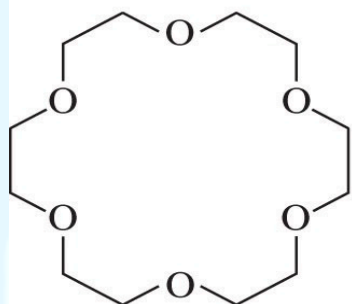


- **Tetradentate Ligand:**

The Ligand attached to metal at 4 sites

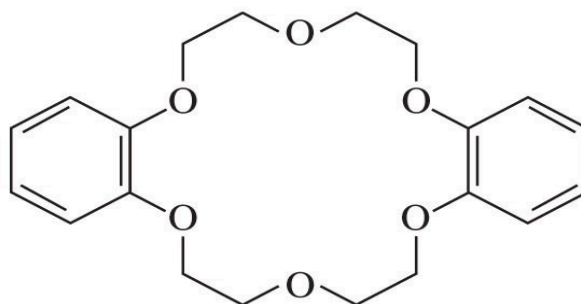


- Another important type of complex is formed between metal ions and cyclic organic compounds, known as macrocycles.
- These molecules contain nine or more atoms in the cycle and include at least three heteroatoms, usually oxygen, nitrogen or sulfur. Crown ethers, such as 18-crown-6 and dibenzo-18-crown-6 are examples of organic macrocycles.

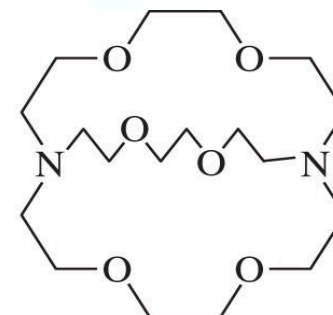


18-crown-6

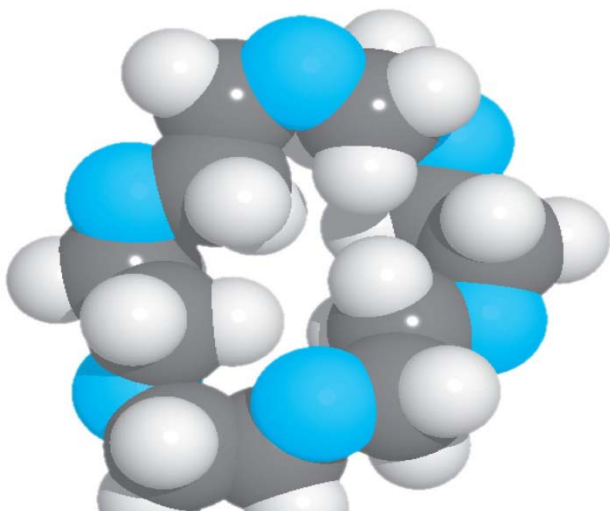
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dibenzo-18-crown-6



cryptand 2,2,2



- Molecular model of 18-crown-6.
- This crown ether can form strong complexes with alkali metal ions. The formation constants of the Na<sup>+</sup>, K<sup>+</sup>, and Rb<sup>+</sup> complexes with 18-crown-6 are in the 10<sup>5</sup> to 10<sup>6</sup> range.

# 17A1- Complexation equilibria

- Complexation reactions involve a metal-ion M reacting with a ligand L to form a complex ML.



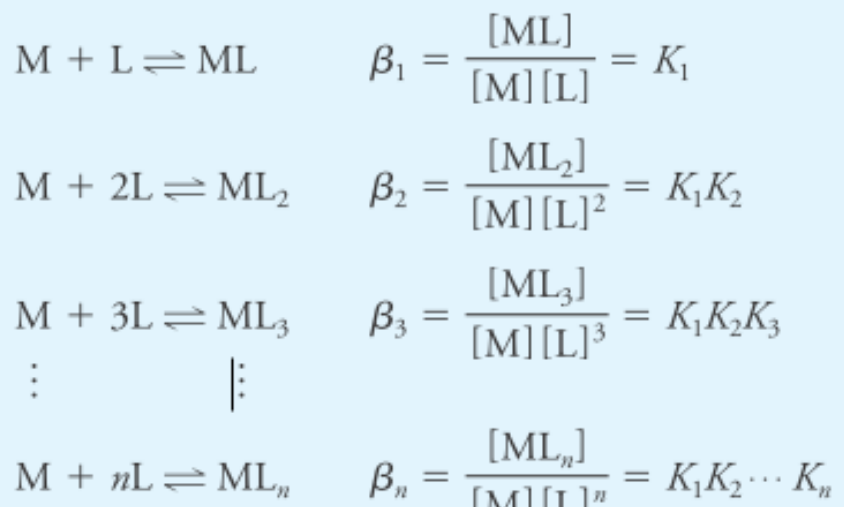
- Complexation reactions occur in a stepwise fashion and additional reactions:



- Unidentate ligands invariably add in a series of steps as shown above.
- With multidentate ligands, the maximum coordination number of the cation may be satisfied with only one or a few added ligands. e.g. Cu(II), with a maximum C.N of 4, can form complexes with ammonia that have the formulas  $Cu(NH_3)^{2+}$ ,  $Cu(NH_3)_2^{2+}$ ,  $Cu(NH_3)_3^{2+}$ , and  $Cu(NH_3)_4^{2+}$
- With the bidentate ligand glycine (gly), the only complexes that form are  $Cu(gly)^{2+}$  and  $Cu(gly)_2^{2+}$

- These have overall formation constants designated by the symbol  $\beta_n$

- Except for the first step, the overall formation constants are products of the Stepwise formation constants for the individual steps leading to the product.





- For a given species like the free metal M, we can calculate an alpha value, which is the fraction of the total metal concentration in that form.
- Thus,  $\alpha_M$  is the fraction of the total metal present at equilibrium in the free metal form
- $\alpha_{ML}$  is the fraction in the ML form, and so on. The alpha values are given by

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

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

$$\alpha_{ML_2} = \frac{\beta_2[L]^2}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \cdots + \beta_n[L]^n}$$

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



## 17A-2 The Formation of Insoluble Species

- The addition of ligands to a metal ion, however, may result in insoluble species, such as the familiar nickel-dimethylglyoxime precipitate.
- In many cases, the intermediate uncharged complexes in the stepwise formation scheme may be sparingly soluble, whereas the addition of more ligand molecules may result in soluble species. For example, adding  $\text{Cl}^-$  to  $\text{Ag}^+$  results in the insoluble  $\text{AgCl}$  precipitate. Addition of a large excess of  $\text{Cl}^-$  produces soluble species  $\text{AgCl}_2^-$ ,  $\text{AgCl}_3^{-2}$ , and  $\text{AgCl}_4^{-3}$
- For a sparingly soluble salt  $\text{M}_x\text{A}_y$  in a saturated solution,



Hence, for  $\text{BiI}_3$ , the solubility product is written,  $K_{\text{sp}} = [\text{Bi}^{3+}][\text{I}^-]^3$ .

- The formation of soluble complexes can be used to control the concentration of free metal ions in solution and thus control their reactivity. For example, we can prevent a metal ion from precipitating or taking part in another reaction by forming a stable complex, which decreases the free metal-ion concentration.
- The control of solubility by complex formation is also used to achieve the separation of one metal ion from another. If the ligand is capable of protonation, as discussed in the next section, even more control can be accomplished by a combination of complexation and pH adjustment.

## 17A-3 Ligands That Can Protonate

- Complexation equilibria can be complicated by side reactions involving the metal or the ligand.
- Such side reactions make it possible to exert some additional control over the complexes that form. Metals can form complexes with ligands other than the one of interest. If these complexes are strong, we can effectively prevent complexation with the ligand of interest.
- Ligands can also undergo side reactions. One of the most common side reactions is that of a ligand that can protonate, that is, the ligand is a weak acid or the conjugate base of a weak acid.

### *Complexation with Protonating Ligands*

- Consider the case of the formation of soluble complexes between the metal M and the ligand L, where the ligand L is the conjugate base of a polyprotic acid and forms HL, H<sub>2</sub>L, ..., H<sub>n</sub>L.
- (Fe<sup>3+</sup>) and (C<sub>2</sub>O<sub>4</sub><sup>2-</sup> = Ox<sup>2-</sup>) , form complexes with formulas [Fe(ox)]<sup>+1</sup>, [Fe(ox)<sub>2</sub>]<sup>-</sup>, and Fe(ox)<sub>3</sub><sup>3-</sup>.
- In basic solution, where most of the oxalate is present as Ox<sup>2-</sup> before complexation with Fe<sup>3+</sup>, the ferric/oxalate complexes are very stable.

Adding acid, however, protonates the oxalate ion, which in turn causes dissociation of the ferric complexes. Oxalate can protonate to form HOx<sup>-</sup> and H<sub>2</sub>Ox.

➤ For a diprotic acid, like oxalic acid, the fraction of the total oxalate-containing species in any given form,  $\text{Ox}^{2-}$ ,  $\text{HOx}^-$ , and  $\text{H}_2\text{Ox}$ , is given by an alpha value.

➤ Since

$$c_T = [\text{H}_2\text{Ox}] + [\text{HOx}^-] + [\text{Ox}^{2-}]$$

we can write the alpha values,  $\alpha_0$ ,  $\alpha_1$ , and  $\alpha_2$ , as

$$\alpha_0 = \frac{[\text{H}_2\text{Ox}]}{c_T} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

$$\alpha_1 = \frac{[\text{HOx}^-]}{c_T} = \frac{K_{a1}[\text{H}^+]}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

$$\alpha_2 = \frac{[\text{Ox}^{2-}]}{c_T} = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

Equation 17-17

Since we are interested in the free oxalate concentration,  $[\text{Ox}^{2-}] = c_T\alpha_2$

Note that, as the solution gets more acidic, the first two terms in the denominator of Equation 17-17 dominate, and  $\alpha_2$  and the free oxalate concentration decrease. When the solution is very basic, the last term dominates,  $\alpha_2$  becomes nearly unity, and  $[\text{Ox}^{2-}] \approx c_T$ , indicating that nearly all the oxalate is in the  $\text{Ox}^{2-}$  form in basic solution.

## Conditional Formation Constants

- To take into account the effect of pH on the free ligand concentration in a complexation reaction, it is useful to introduce a conditional formation constant, or effective formation constant.
- Such constants are pH-dependent equilibrium constants that apply at a single pH only.

- For the reaction of  $\text{Fe}^{3+}$  with oxalate, for example, we can write the formation constant  $K_1$  for the first complex as

$$K_1 = \frac{[\text{Fe(ox)}^+]}{[\text{Fe}^{3+}][\text{ox}^{2-}]} = \frac{[\text{Fe(ox)}^+]}{[\text{Fe}^{3+}]\alpha_2 c_T}$$

- At a particular pH value,  $\alpha_2$  is constant, and we can combine  $K_1$  and  $\alpha_2$  to yield a new conditional constant  $K_1'$ :

$$K_1' = \alpha_2 K_1 = \frac{[\text{Fe(ox)}^+]}{[\text{Fe}^{3+}]c_T}$$

- The use of conditional constants greatly simplifies calculations because  $c_T$  is often known or is easily computed, but the free ligand concentration is not as easily determined.
- The overall formation constants,  $\beta$  values, for the higher complexes,  $[\text{Fe(ox)}_2]^-$  and  $[\text{Fe(ox)}_3]^{3-}$ , can also be written as conditional constants.

## 17B Titrations with Inorganic Complexing Agents

- Complexation reactions have many uses in analytical chemistry. One of the earliest uses, which is still widespread, is in *complexometric titrations*.
- In these titrations, a metal ion reacts with a suitable ligand to form a complex, and the equivalence point is determined by an indicator or an appropriate instrumental method.
- The formation of soluble inorganic complexes is not widely used for titrations, but the formation of precipitates, particularly with silver nitrate as the titrant, is the basis for many important determinations,

**TABLE 17-1**

### Typical Inorganic Complex-Forming Titrations

<b>Titrant</b>	<b>Analyte</b>	<b>Remarks</b>
Hg(NO <sub>3</sub> ) <sub>2</sub>	Br <sup>-</sup> , Cl <sup>-</sup> , SCN <sup>-</sup> , CN <sup>-</sup> , thiourea	Products are neutral Hg(II) complexes; various indicators used
AgNO <sub>3</sub>	CN <sup>-</sup>	Product is Ag(CN) <sub>2</sub> <sup>-</sup> ; indicator is I <sup>-</sup> ; titrate to first turbidity of AgI
NiSO <sub>4</sub>	CN <sup>-</sup>	Product is Ni(CN) <sub>4</sub> <sup>2-</sup> ; indicator is AgI; titrate to first turbidity of AgI
KCN	Cu <sup>2+</sup> , Hg <sup>2+</sup> , Ni <sup>2+</sup>	Products are Cu(CN) <sub>4</sub> <sup>2-</sup> , Hg(CN) <sub>2</sub> , and Ni(CN) <sub>4</sub> <sup>2-</sup> ; various indicators used

## 17B-1 Complexation Titrations

-Complexometric titration curves are usually a plot of  $pM = -\log [M]$  as a function of the volume of titrant added.

- Usually the ligand is the titrant, and the metal ion is the analyte.

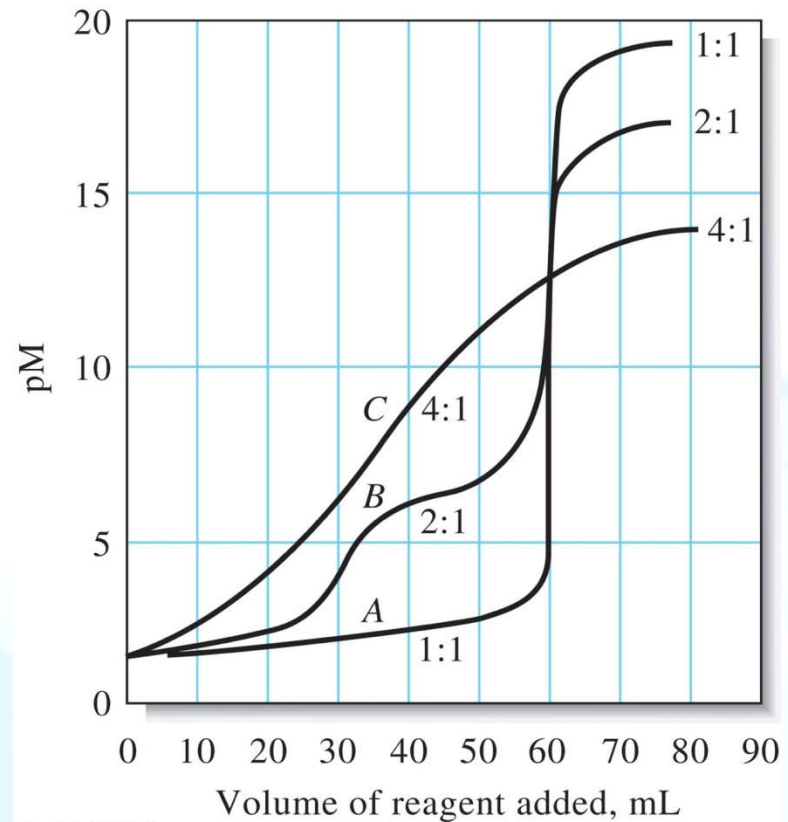
- Many precipitation titrations use the metal ion as the titrant.

- Most simple inorganic ligands are unidentate, which can lead to low complex stability and indistinct titration end points.,

- As titrants, multidentate ligands, particularly those having four or six donor groups, have two advantages over their unidentate counterparts.

-First, they generally react more completely with cations and thus provide sharper end points.

-Second, they ordinarily react with metal ions in a single-step process, whereas complex formation with unidentate ligands usually involves two or more intermediate species



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Figure 17-1 Titration curves for complexometric titrations.

- The most widely used complexometric titration with a unidentate ligand is the titration of cyanide with silver nitrate. This method involves the formation of soluble  $Ag(CN)_2^-$



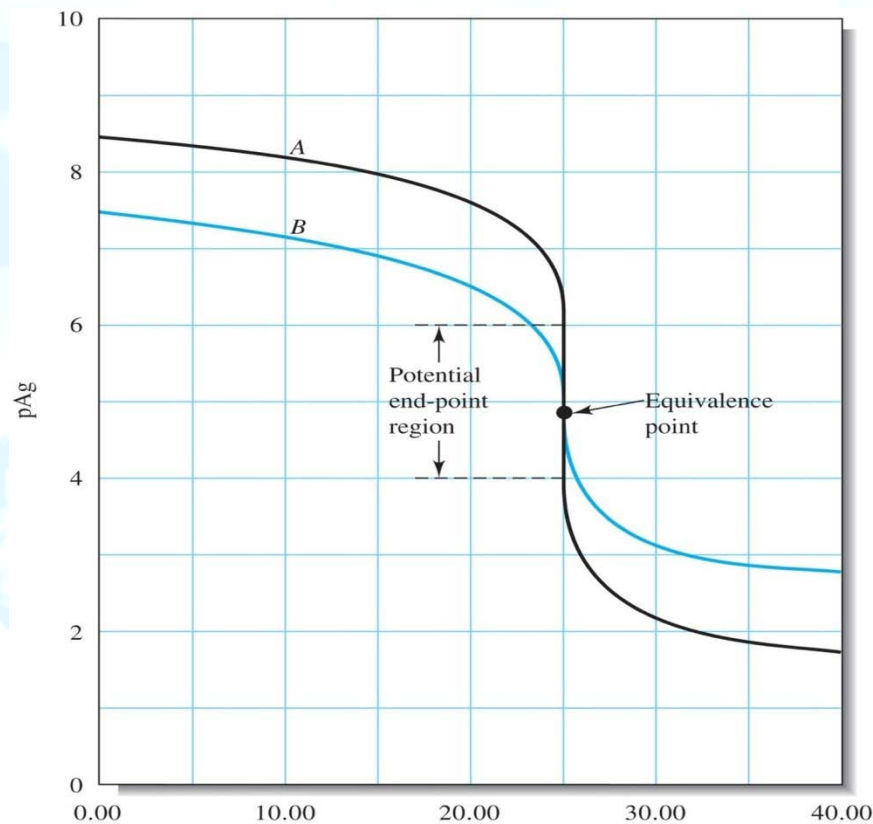
## 17B-2 Precipitation Titrations

Precipitation titrations are based on reactions that yield ionic compounds of limited solubility. Also called as **Precipitation titrimetry**

- The slow rate at which most precipitates form, however, limits the number of precipitating agents that can be used in titrations to a handful.
- Here to the most widely used and important precipitating reagent, silver nitrate, which is used for the determination of the halogens, the halogenlike anions, mercaptans, fatty acids, and several divalent inorganic anions, will be discussed.
- Titrations with silver nitrate are sometimes called **argentometric titrations**.

### *The Shapes of Titration Curves*

- Titration curves for precipitation reactions are calculated in a completely analogous way to the methods described in Section 14B for titrations involving strong acids and strong bases.
- The only difference is that the solubility product of the precipitate is substituted for the ion-product constant for water.
- Most indicators for argentometric titrations respond to changes in the concentrations of silver ions. Because of this response, titration curves for precipitation reactions usually consist of a plot of  $pAg$  versus volume of the silver reagent (usually





## EXAMPLE 17-1

Calculate the silver ion concentration in terms of  $pAg$  during the titration of 50.00 mL of 0.05000 M NaCl with 0.1000 M  $AgNO_3$  after the addition of the following volumes of reagent: (a) in the preequivalence point region at 10.00 mL, (b) at the equivalence point (25.00 mL), (c) after the equivalence point at 26.00 mL. For  $AgCl$ ,  $K_{sp} = 1.82 \times 10^{-10}$ .

### Solution

#### (a) Preequivalence-Point Data

At 10.00 mL,  $[Ag^+]$  is very small and cannot be computed from stoichiometric considerations, but the molar concentration of chloride,  $c_{NaCl}$  can be obtained readily. The equilibrium concentration of chloride is essentially equal to  $c_{NaCl}$ .

$$\begin{aligned} [Cl^-] &\approx c_{NaCl} = \frac{\text{original no. mmol } Cl^- - \text{no. mol } AgNO_3 \text{ added}}{\text{total volume of solution}} \\ &= \frac{(50.00 \times 0.05000 - 10.00 \times 0.1000)}{50.00 + 10.00} = 0.02500 \text{ M} \end{aligned}$$

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.02500} = 7.28 \times 10^{-9} \text{ M}$$

$$pAg = -\log(7.28 \times 10^{-9}) = 8.14$$

Additional points in the preequivalence-point region can be obtained in the same way. Results of calculations of this kind are shown in the second column of [Table 17-2](#).

**TABLE 17-2**Changes in pAg in Titration of Cl<sup>-</sup> with Standard AgNO<sub>3</sub>

Volume of AgNO <sub>3</sub>	pAg	
	50.00 mL of 0.0500 M NaCl with 0.1000 M AgNO <sub>3</sub>	50.00 mL of 0.005 M NaCl with 0.0100 M AgNO <sub>3</sub>
10.00	8.14	7.14
20.00	7.59	6.59
24.00	6.87	5.87
25.00	4.87	4.87
26.00	2.88	3.88
30.00	2.20	3.20
40.00	1.78	2.78

**(b) Equivalence Point pAg**

At the equivalence point,  $[\text{Ag}^+] = [\text{Cl}^-]$ , and  $[\text{Ag}^+][\text{Cl}^-] = K_{\text{sp}} = 1.82 \times 10^{-10} = [\text{Ag}^+]^2$

$$[\text{Ag}^+] = \sqrt{K_{\text{sp}}} = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5}$$

$$\text{pAg} = -\log(1.35 \times 10^{-5}) = 4.87$$

**(c) Postequivalence-Point Region**

At 26.00 mL of AgNO<sub>3</sub>, Ag<sup>+</sup> is in excess so

$$[\text{Ag}^+] = c_{\text{AgNO}_3} = \frac{(26.00 \times 0.1000 - 50.00 \times 0.05000)}{76.00} = 1.32 \times 10^{-3} \text{ M}$$

$$\text{pAg} = -\log(1.32 \times 10^{-3}) = 2.88$$

Additional results in the postequivalence-point region are obtained in the same way and are shown in Table 17-2. The titration curve can also be derived from the charge-balance equation as shown for an acid/base titration in Feature 14-1.

## The Effect of Concentration on Titration Curves

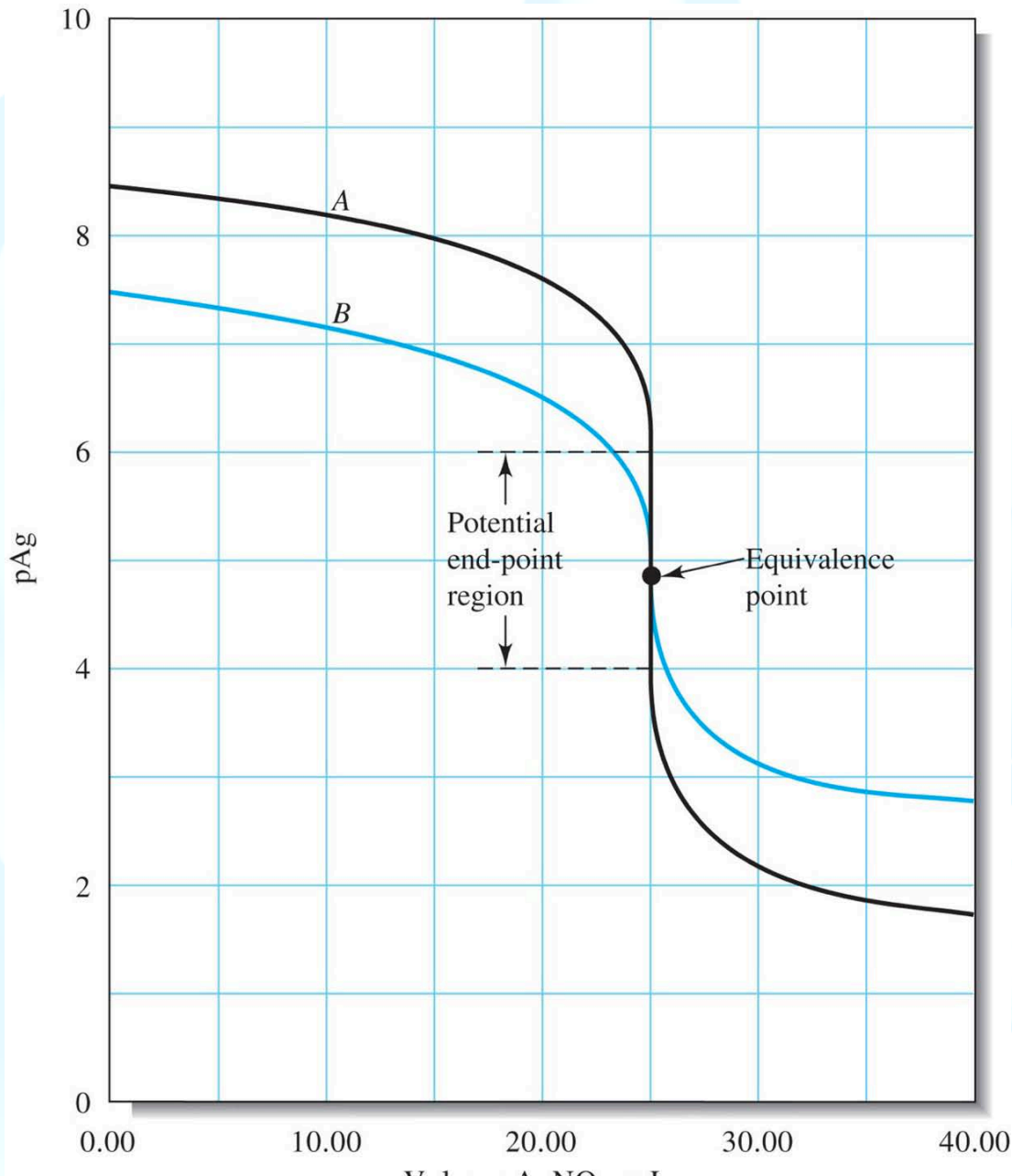


Figure 17-2 Titration curve for (A), 50.00 mL of 0.05000 M NaCl titrated with 0.1000 M AgNO<sub>3</sub>, and (B), 50.00 mL of 0.00500 M NaCl titrated with 0.01000 M AgNO<sub>3</sub>.

## The Effect of Reaction Completeness on Titration Curves

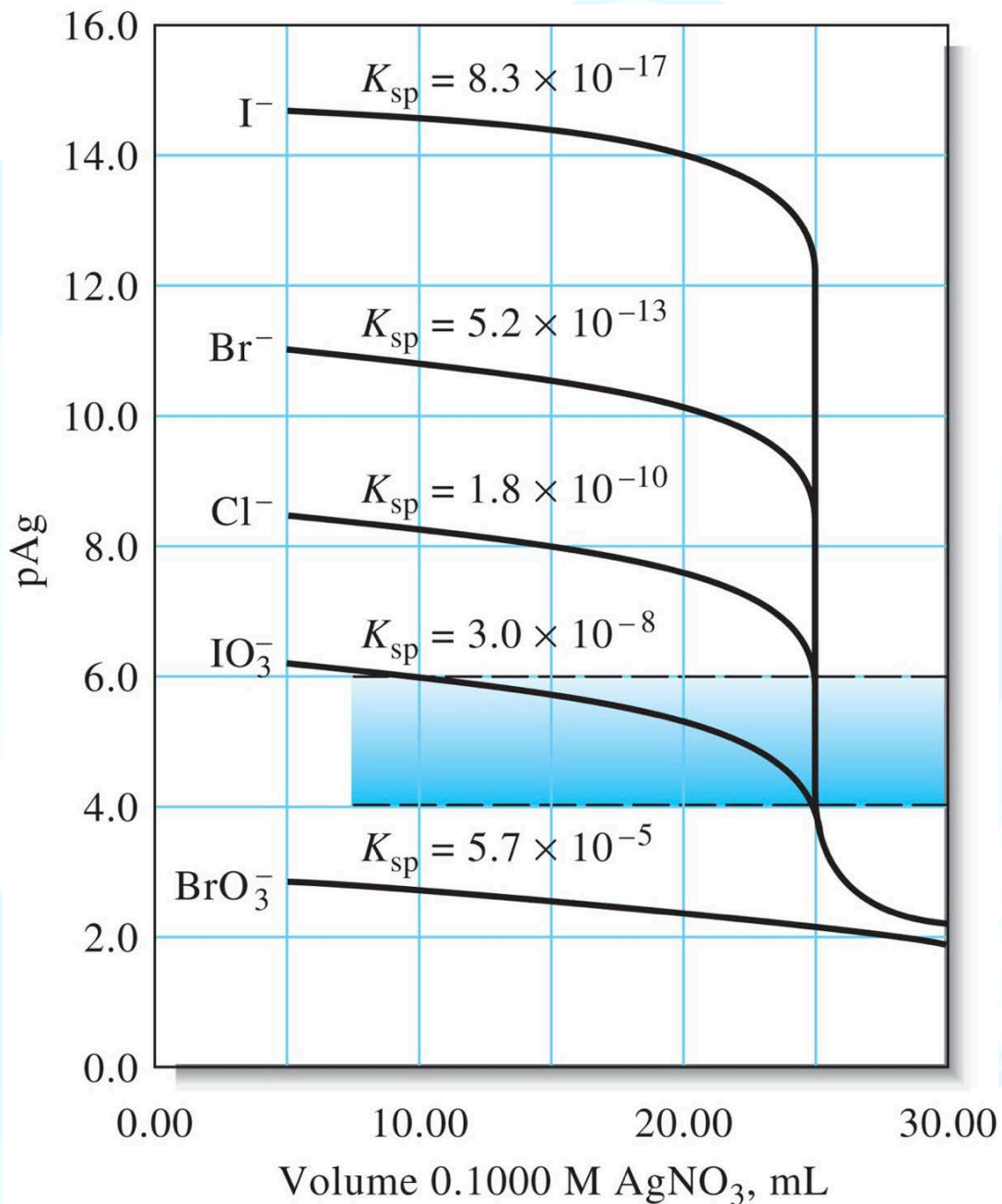


Figure 17-3 Effect of reaction completeness on precipitation titration curves. For each curve, 50.00 mL of a 0.0500 M solution of the anion was titrated with 0.1000 M  $\text{AgNO}_3$ .

# Titration Curves for Mixtures of Anions

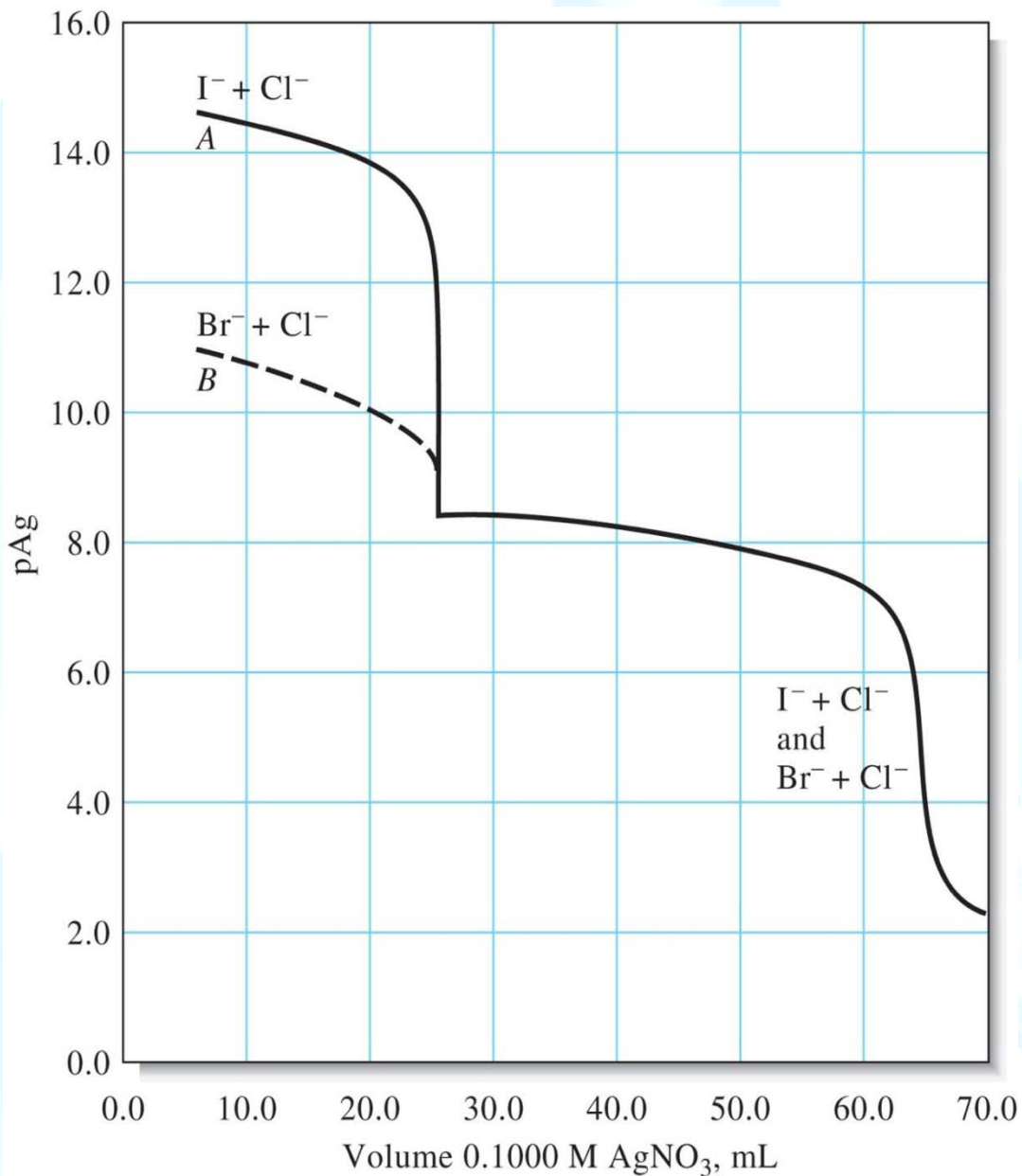


Figure 17-4 Titration curves for 50.00 mL of a solution 0.0800 M in Cl<sup>-</sup> and 0.0500 M in I<sup>-</sup> or Br<sup>-</sup>.

## *End Points for Argentometric Titrations*

- Chemical, potentiometric, and amperometric end points are used in titrations with silver nitrate.
- In potentiometric titrations, the potential difference between a silver electrode and a reference electrode is measured as a function of titrant volume.
- Chemical indicators produce a color change or occasionally the appearance or disappearance of turbidity in the solution being titrated.

The requirements for an indicator for a precipitation titration are that:

- (1) the color change should occur over a limited range in p-function of the titrant or the analyte and
- (2) the color change should take place within the steep portion of the titration curve for the analyte.

## The Volhard method :

- The Volhard method is one of the most common argentometric methods.
- In this method, a measured excess of standard silver nitrate solution is added to the sample,



- and the excess silver is determined by back-titration with a standard thiocyanate solution



- Iron(III) serves as the indicator. The solution turns red with the first slight excess of thiocyanate ion due to the formation of  $\text{Fe(SCN)}^{+2}$ .
- It is the most important application in the indirect determination of halide ions.
- The strongly acidic environment of Volhard method is advantageous because such ions like carbonate, oxalate, arsenate do not interfere, the silver salts of these ions are soluble in acidic medium.
- There is a problem though. Silver chloride is more soluble than thiocyanate, therefore, during titration thiocyanate can replace chlorides in the existing precipitate:



In order to prevent SCN overconsumption, AgCl should be precipitated, before the backtitration.



## Other Argentometric methods

### Mohr Method

➤ In the Mohr method, sodium chromate serves as the indicator for the argentometric titration of chloride, bromide, and cyanide ions.

➤ After all halides are ppt'ed by the addition of  $\text{AgNO}_3$



➤ Excess silver ions react with chromate to form the brick-red silver chromate ( $\text{Ag}_2\text{CrO}_4$ ) precipitate in the equivalence-point region.

➤ **The Fajans method** uses an adsorption indicator, an organic compound that adsorbs onto or desorbs from the surface of the solid in a precipitation titration.

➤ The adsorption or desorption occurs near the equivalence point and results in a color change as well as in the transfer of color from the solution to the solid or vice versa.



$\text{Ag}_2\text{CrO}_4 \rightleftharpoons \text{Cr(IV)}$   
carcinogen

## 17C Organic complexing agents

- These have inherent sensitivity and potential selectivity in reacting with metal ions.
- Organic reagents are particularly useful in:
  - precipitating metals,
  - in binding metals so as to prevent interferences,
  - in extracting metals from one solvent to another, and
  - in forming complexes that absorb light for spectrophotometric determinations.
- The most useful organic reagents form *chelate complexes* with metal ions.
- In many cases, the pH of the aqueous phase is used to achieve some control over the extraction process since most of the reactions are pH dependent
- Another important application of organic complexing agents is in forming stable complexes that bind a metal and prevent it from interfering in a determination. Such complexing agents are called **masking agents**

**TABLE 17-3**

### Organic Reagents for Extracting Metals

Reagent	Metal Ions Extracted	Solvents
8-Hydroxyquinoline	Zn <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Al <sup>3+</sup> , many others	Water → Chloroform (CHCl <sub>3</sub> )
Diphenylthiocarbazone (dithizone)	Cd <sup>2+</sup> , Co <sup>2+</sup> , Cu <sup>2+</sup> , Pb <sup>2+</sup> , many others	Water → CHCl <sub>3</sub> or CCl <sub>4</sub>
Acetylacetone	Fe <sup>3+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup> , U(VI), many others	Water → CHCl <sub>3</sub> , CCl <sub>4</sub> , or C <sub>6</sub> H <sub>6</sub>
Ammonium pyrrolidine dithiocarbamate	Transition metals	Water → Methyl isobutyl ketone
Tenoyltrifluoroacetone	Ca <sup>2+</sup> , Sr <sup>2+</sup> , La <sup>3+</sup> , Pr <sup>3+</sup> other rare earths	Water → Benzene
Dibenzo-18-crown-6	Alkali metals, some alkaline earths	Water → Benzene

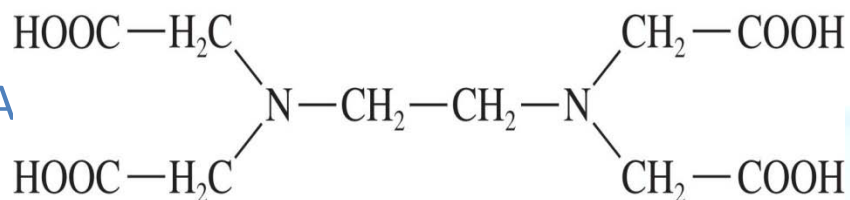
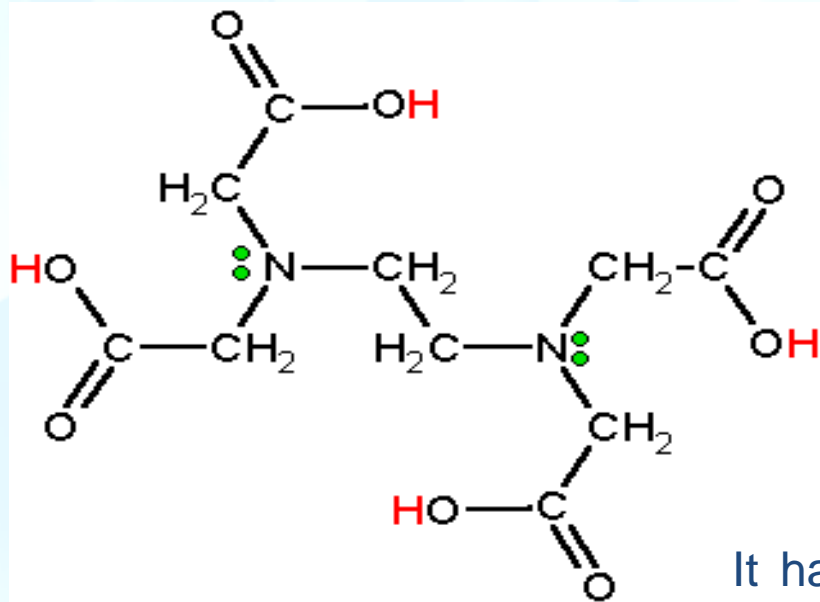
# 17D AMINOCARBOXYLIC ACID TITRATIONS

Tertiary amines that also contain carboxylic acid groups form remarkably stable chelates with many metal ions.

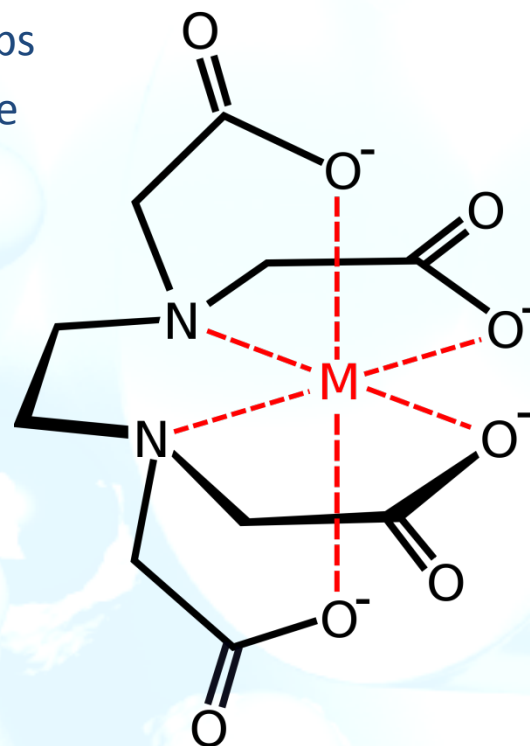
## 17D-1 Ethylenediaminetetraacetic Acid (EDTA)

- EDTA is the most widely used complexometric titrant.

-It is a polyprotic acid containing four carboxylic acid groups (acidic hydrogens are red) and two amine groups with lone pair electrons (green dots).



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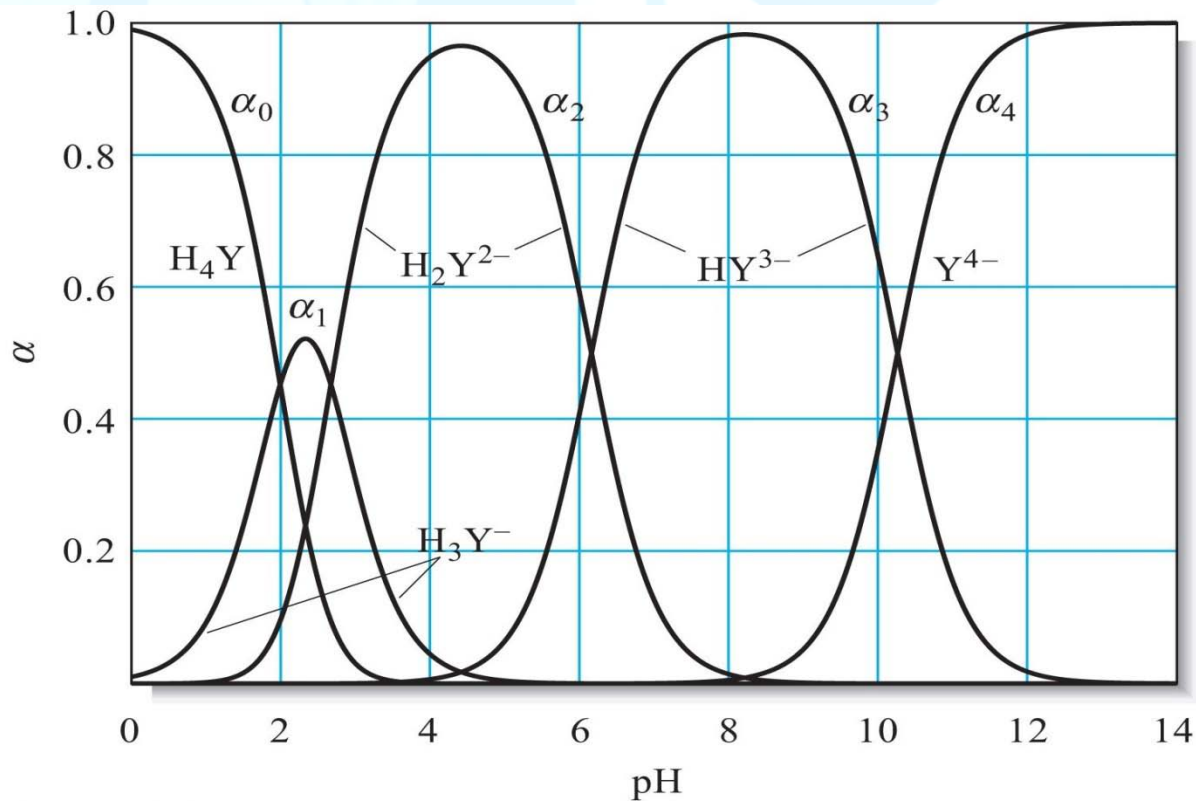


It has six potential sites for bonding a metal ion: four carboxyl groups and the two amino groups.

The fully protonated form,  $H_4Y$  is only a major component in very acidic solutions ( $pH < 3$ ).

In the pH range of 3 to 10, the species  $H_2Y^{2-}$  and  $HY^{3-}$  are predominant.

The fully unprotonated form  $Y^{4-}$  is a significant component only in very basic solutions ( $pH > 10$ ).



*Acidic Properties of EDTA*  
The dissociation constants for the acidic groups in EDTA are

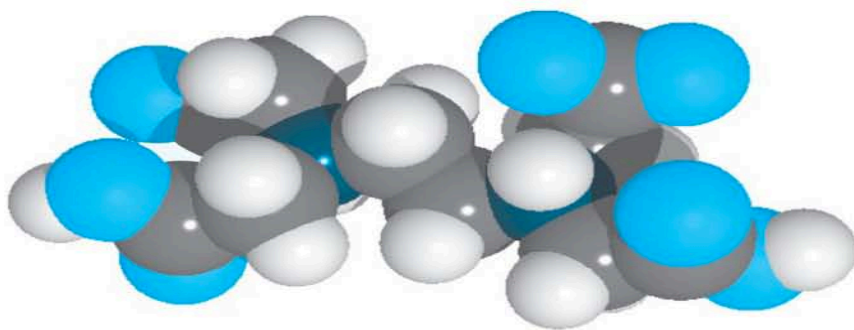
$$K_1 = 1.02 \times 10^{-2},$$

$$K_2 = 2.14 \times 10^{-3},$$

$$K_3 = 6.92 \times 10^{-7},$$

$$K_4 = 5.50 \times 10^{-11}.$$

Figure 17-5 Composition of EDTA solutions as a function of pH.



Molecular model of the  $H_4Y$  zwitterion.



(a)  $H_4Y$



(b)  $H_3Y^-$



(c)  $H_2Y^{2-}$



(d)  $HY^{3-}$



### Figure 17F-1 Structure of $H_4Y$ and its dissociation products.

Note that the fully protonated species  $H_4Y$  exist as a double zwitterion with the amine nitrogens and two of the carboxylic acid groups protonated.

The first two protons dissociate from the carboxyl groups, while the last two come from the amine groups.



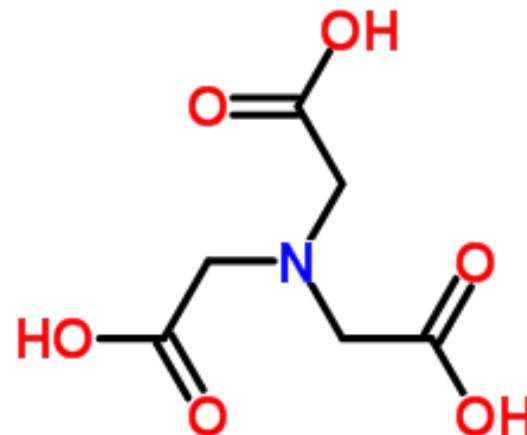
## Reagents for EDTA Titrations

The free acid  $H_4Y$  can serve as a primary standard after it has been dried for several hours at  $130\text{ }^\circ\text{C}$  to  $145\text{ }^\circ\text{C}$ .

The dihydrate,  $Na_2H_2Y \cdot 2H_2O$ , is commonly used to prepare standard solutions.

Standard EDTA solutions can be prepared by dissolving weighed quantities of  $Na_2H_2Y \cdot 2H_2O$  and diluting to the mark in a volumetric flask.

Nitrilotriacetic acid (NTA) is the second most common amino-polycarboxylic acid used for titrations. It is a tetradentate chelating agent.



## Complexes of EDTA and Metal Ions

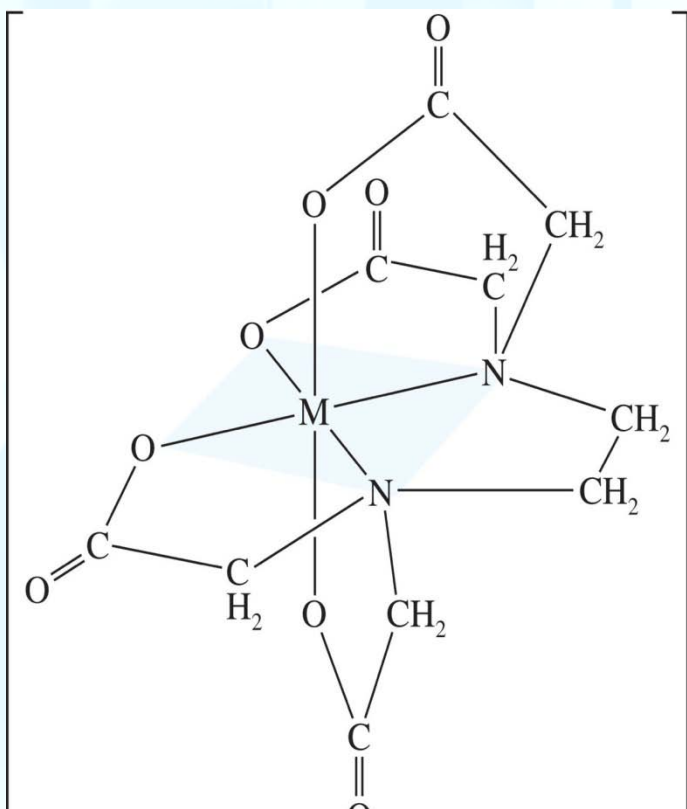
EDTA combines with metal ions in a 1:1 ratio **regardless of the charge on the cation**.

For example, the silver and aluminum complexes are formed by the reactions



It forms chelates with all cations; most of these chelates are sufficiently stable for titrations.

Structure of a metal/EDTA complex. Note that EDTA behaves as a hexadentate ligand.





**TABLE 17-4**

## Formation Constants for EDTA Complexes

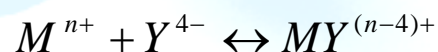
Cation	$K_{MY}^*$	$\log K_{MY}$	Cation	$K_{MY}$	$\log K_{MY}$
Ag <sup>+</sup>	$2.1 \times 10^7$	7.32	Cu <sup>2+</sup>	$6.3 \times 10^{18}$	18.80
Mg <sup>2+</sup>	$4.9 \times 10^8$	8.69	Zn <sup>2+</sup>	$3.2 \times 10^{16}$	16.50
Ca <sup>2+</sup>	$5.0 \times 10^{10}$	10.70	Cd <sup>2+</sup>	$2.9 \times 10^{16}$	16.46
Sr <sup>2+</sup>	$4.3 \times 10^8$	8.63	Hg <sup>2+</sup>	$6.3 \times 10^{21}$	21.80
Ba <sup>2+</sup>	$5.8 \times 10^7$	7.76	Pb <sup>2+</sup>	$1.1 \times 10^{18}$	18.04
Mn <sup>2+</sup>	$6.2 \times 10^{13}$	13.79	Al <sup>3+</sup>	$1.3 \times 10^{16}$	16.13
Fe <sup>2+</sup>	$2.1 \times 10^{14}$	14.33	Fe <sup>3+</sup>	$1.3 \times 10^{25}$	25.1
Co <sup>2+</sup>	$2.0 \times 10^{16}$	16.31	V <sup>3+</sup>	$7.9 \times 10^{25}$	25.9
Ni <sup>2+</sup>	$4.2 \times 10^{18}$	18.62	Th <sup>4+</sup>	$1.6 \times 10^{23}$	23.2

\*Constants are valid at 20°C and ionic strength of 0.1.

**Source:** G. Schwarzenbach, *Complexometric Titrations*, London: Chapman and Hall, 1957, p. 8.

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The constant  $K_{MY}$  refers to the equilibrium involving the fully unprotonated species  $Y^{4-}$  with the metal ion:



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

## Equilibrium Calculations Involving EDTA

A titration curve for the reaction of a cation  $M^{n+}$  with EDTA consists of a plot of pM ( $pM = -\log[M^{n+}]$ ) versus reagent volume.

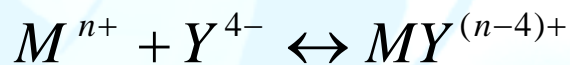
To calculate  $[M^{n+}]$  in a buffered solution containing EDTA, we use the alpha value for  $H_4Y$ :

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

$$c_T = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^{3-}] + [H_4Y]$$

### *Conditional Formation Constants*

To obtain the conditional formation constant, substitute  $\alpha_4 c_T$  for  $[Y^{4-}]$



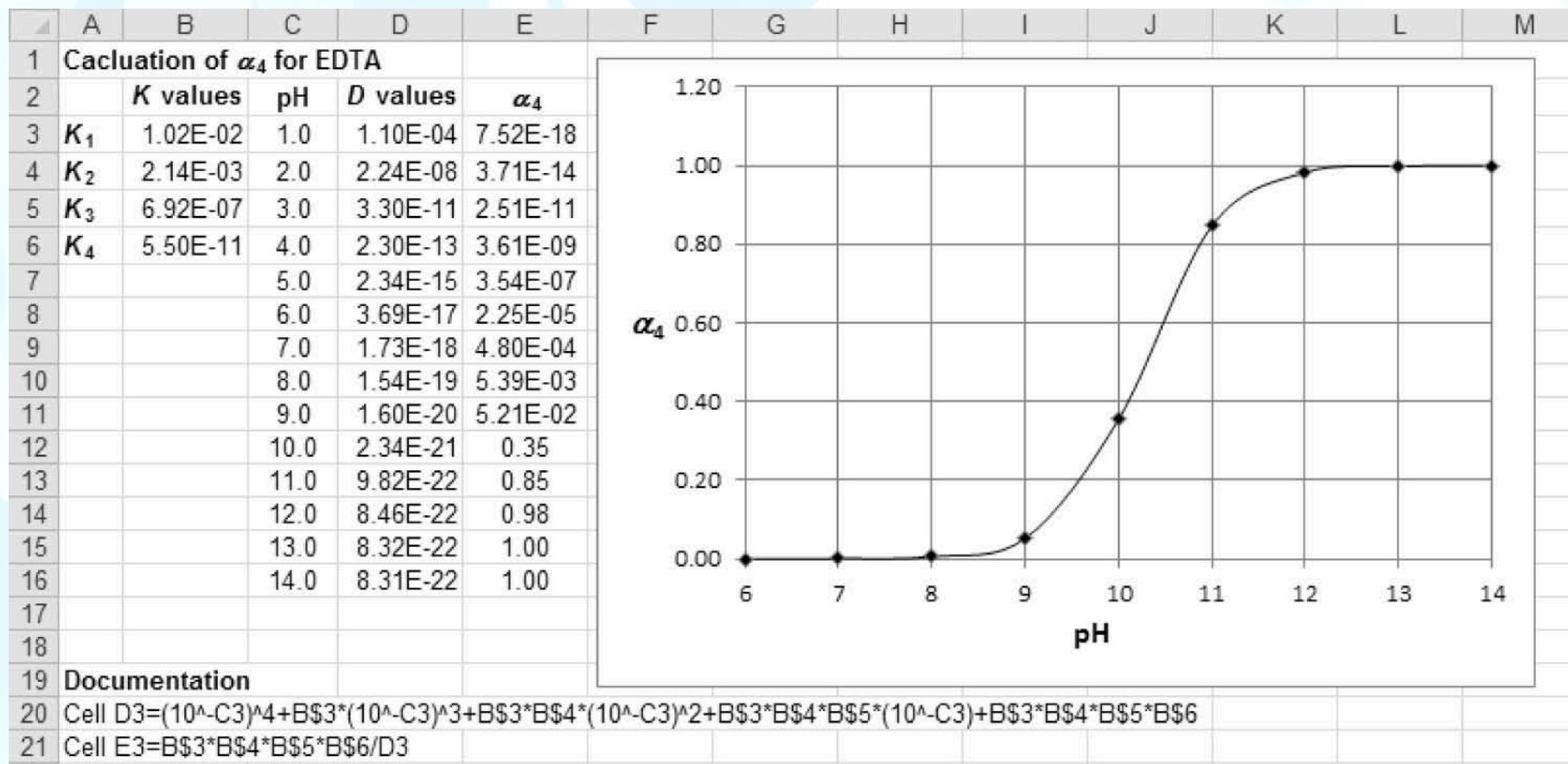
$$K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]\alpha_4 c_T}$$

$$K_{MY}^1 = \alpha_4 K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]c_T}$$

## Computing $\alpha_4$ Values for EDTA Solutions $\alpha_4$ for EDTA is

$$\alpha_4 = \frac{K_1 K_2 K_3 K_4}{[H^+]^4 + K_1 [H^+]^3 + K_1 K_2 [H^+]^2 + K_1 K_2 K_3 [H^+] + K_1 K_2 K_3 K_4} = \frac{K_1 K_2 K_3 K_4}{D}$$

Figure 17-7 Spreadsheet to calculate  $\alpha_4$  for EDTA at selected pH values.



## EXAMPLE 17-2

Calculate the molar  $Y^{4-}$  concentration in a 0.0200 M EDTA solution buffered to a pH of 10.00.

### Solution

At pH 10.00,  $\alpha_4$  is 0.35 (see Figure 17-7). Thus,

$$[Y^{4-}] = \alpha_4 c_T = 0.35 \times 0.0200 \text{ M} = 7.00 \times 10^{-3} \text{ M}$$

## *Calculating the Cation Concentration in EDTA Solutions*

In an EDTA titration, prior to the equivalence point, the cation is in excess. Its concentration can be found from the reaction stoichiometry.

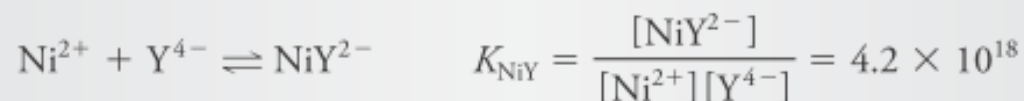
At the equivalence point and in the postequivalence-point region, *the conditional formation constant of the complex* must be used to calculate the cation concentration.

### EXAMPLE 17-3

Calculate the equilibrium concentration of  $\text{Ni}^{2+}$  in a solution with an analytical  $\text{NiY}^{2-}$  concentration of 0.0150 M at pH (a) 3.0 and (b) 8.0.

#### Solution

From Table 17-4,



The equilibrium concentration of  $\text{NiY}^{2-}$  is equal to the analytical concentration of the complex minus the concentration lost by dissociation. The concentration lost by dissociation is equal to the equilibrium  $\text{Ni}^{2+}$  concentration. Thus,

$$[\text{NiY}^{2-}] = 0.0150 - [\text{Ni}^{2+}]$$

If we assume that  $[\text{Ni}^{2+}] \ll 0.0150$ , an assumption that is almost certainly valid in light of the large formation constant of the complex, this equation simplifies to

$$[\text{NiY}^{2-}] \cong 0.0150$$

Since the complex is the only source of both  $\text{Ni}^{2+}$  and the EDTA species,

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

Substitution of this equality into Equation 17-25 gives

$$K'_{\text{NiY}} = \frac{[\text{NiY}^{2-}]}{[\text{Ni}^{2+}]c_{\text{T}}} = \frac{[\text{NiY}^{2-}]}{[\text{Ni}^{2+}]^2} = \alpha_4 K_{\text{NiY}}$$

(a) The spreadsheet in Figure 17-7 indicates that  $\alpha_4$  is  $2.51 \times 10^{-11}$  at pH 3.0. If we substitute this value and the concentration of  $\text{NiY}^{2-}$  into the equation for  $K'_{\text{MY}}$ , we get

$$\frac{0.0150}{[\text{Ni}^{2+}]^2} = 2.51 \times 10^{-11} \times 4.2 \times 10^{18} = 1.05 \times 10^8$$

$$[\text{Ni}^{2+}] = \sqrt{1.43 \times 10^{-10}} = 1.2 \times 10^{-5} \text{ M}$$

(b) At pH 8.0,  $\alpha_4$ , and thus the conditional constant, is much larger. Therefore,

$$K'_{\text{NiY}} = 5.39 \times 10^{-3} \times 4.2 \times 10^{18} = 2.27 \times 10^{16}$$

and, after we substitute this into the equation for  $K'_{\text{NiY}}$ , we find that

$$[\text{Ni}^{2+}] = \sqrt{\frac{0.0150}{2.27 \times 10^{16}}} = 8.1 \times 10^{-10} \text{ M}$$

#### EXAMPLE 17-4

Calculate the concentration of  $\text{Ni}^{2+}$  in a solution that was prepared by mixing 50.0 mL of 0.0300 M  $\text{Ni}^{2+}$  with 50.00 mL of 0.0500 M EDTA. The mixture was buffered to a pH of 3.0.

#### Solution

The solution has an excess of EDTA, and the analytical concentration of the complex is determined by the amount of  $\text{Ni}^{2+}$  originally present. Thus,

$$c_{\text{NiY}^{2-}} = 50.00 \text{ mL} \times \frac{0.0300 \text{ M}}{100 \text{ mL}} = 0.0150 \text{ M}$$

$$c_{\text{EDTA}} = \frac{(50.00 \times 0.0500) \text{ mmol} - (50.0 \times 0.0300) \text{ mmol}}{100.0 \text{ mL}} = 0.0100 \text{ M}$$

Again, we will assume that  $[\text{Ni}^{2+}] \ll [\text{NiY}^{2-}]$  so that

$$[\text{NiY}^{2-}] = 0.0150 - [\text{Ni}^{2+}] \approx 0.0150 \text{ M}$$

At this point, the total concentration of uncomplexed EDTA is given by its concentration,  $c_{\text{EDTA}}$ :

$$c_{\text{T}} = c_{\text{EDTA}} = 0.0100 \text{ M}$$

If we substitute this value in Equation 17-25, we get

$$K'_{\text{NiY}} = \frac{0.0150}{[\text{Ni}^{2+}] \times 0.0100} = \alpha_4 K_{\text{NiY}}$$

Using the value of  $\alpha_4$  at pH 3.0 from Figure 17-7, we obtain

$$[\text{Ni}^{2+}] = \frac{0.0150}{0.0100 \times 2.51 \times 10^{-11} \times 4.2 \times 10^{18}} = 1.4 \times 10^{-8} \text{ M}$$

Note again that our assumption that  $[\text{Ni}^{2+}] \ll [\text{NiY}^{2-}]$  is valid.



### EXAMPLE 17-5

Use a spreadsheet to construct the titration curve of pCa versus volume of EDTA for 50.0 mL of 0.00500 M  $\text{Ca}^{2+}$  titrated with 0.0100 M EDTA in a solution buffered to pH 10.0.

#### Solution

##### Initial Entries

The spreadsheet is shown in **Figure 17-8**. We enter the initial volume of  $\text{Ca}^{2+}$  in cell B3 and the initial  $\text{Ca}^{2+}$  concentration in E2. The EDTA concentration is entered into cell E3. The volumes for which pCa values are to be calculated are entered into cells A5 through A19. We also need the conditional formation constant for the CaY complex. This constant is obtained from the formation constant of the complex (Table 17-4) and the  $\alpha_4$  value for EDTA at pH 10 (see Figure 17-7). If we substitute into Equation 17-25, we get

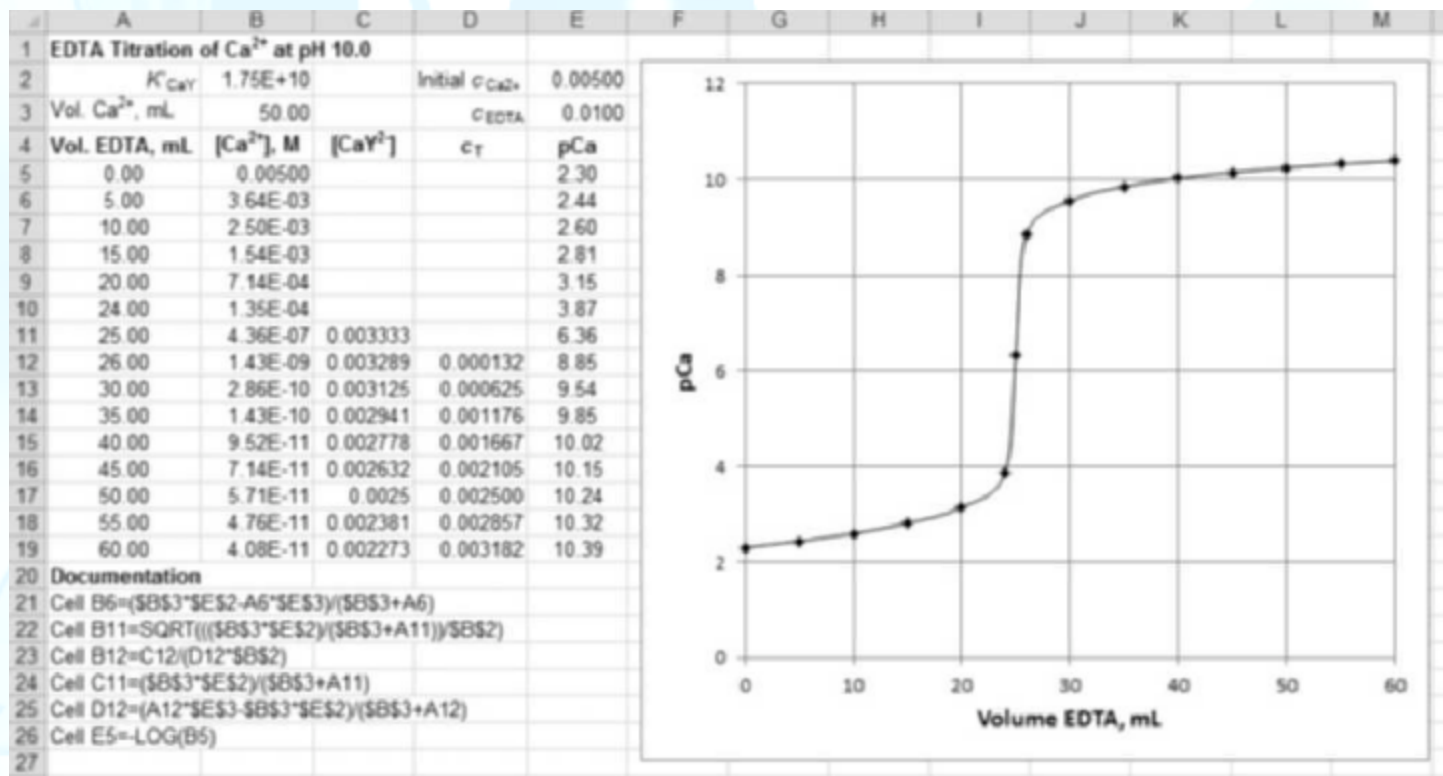
$$\begin{aligned}K'_{\text{CaY}} &= \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}]c_T} = \alpha_4 K_{\text{CaY}} \\ &= 0.35 \times 5.0 \times 10^{10} = 1.75 \times 10^{10}\end{aligned}$$

This value is entered into cell B2. Since the conditional constant is to be used in further calculations, we do not round off to keep only significant figures at this point.

##### Preequivalence-Point Values for pCa

The initial  $[\text{Ca}^{2+}]$  at 0.00 mL titrant is just the value in cell E2. Hence, **=E2** is entered into cell B5. The initial pCa is calculated from the initial  $[\text{Ca}^{2+}]$  by taking the negative logarithm as shown in the documentation for cell E5. This formula is copied into cells E6 through E19. For the other entries prior to the equivalence point, the equilibrium concentration of  $\text{Ca}^{2+}$  is equal to the untitrated excess of the cation plus any  $\text{Ca}^{2+}$  resulting from dissociation of the complex. The latter concentration is equal to  $c_T$ . Usually,  $c_T$  is small relative to the analytical concentration of the uncomplexed calcium ion. For example, after 5.00 mL of EDTA has been added,

Figure 17-8 Spreadsheet for the titration of 50.00 mL of 0.00500 M  $\text{Ca}^{2+}$  with 0.0100 M EDTA in a solution buffered at pH 10.0.



$$[\text{Ca}^{2+}] = \frac{50.0 \text{ mL} \times 0.00500 \text{ M} - 5.00 \text{ mL} \times 0.0100 \text{ M}}{(50 + 5.00) \text{ mL}} + c_T$$

$$\approx \frac{50.0 \text{ mL} \times 0.00500 \text{ M} - 5.00 \text{ mL} \times 0.0100 \text{ M}}{55.00 \text{ mL}}$$

We thus enter into cell B6 the formula shown in the documentation section of the spreadsheet. The reader should verify that the spreadsheet formula is equivalent to the expression for  $[\text{Ca}^{2+}]$  given above. The volume of titrant (A6) is the only value that changes in this preequivalence-point region. The other preequivalence-point values of pCa are calculated by copying the formula in cell B6 into cells B7 through B10.

#### The Equivalence-Point pCa

At the equivalence point (25.00 mL of EDTA), we follow the method shown in Example 17-3 and first compute the analytical concentration of  $\text{CaY}^{2-}$ :

$$c_{\text{CaY}^{2-}} = \frac{(50.0 \times 0.00500) \text{ mmol}}{(50.0 + 25.0) \text{ mL}}$$

The only source of  $\text{Ca}^{2+}$  ions is the dissociation of the complex. It also follows that the  $\text{Ca}^{2+}$  concentration must be equal to the sum of the concentrations of the uncomplexed EDTA,  $c_T$ . Therefore,

$$[\text{Ca}^{2+}] = c_T, \text{ and } [\text{CaY}^{2-}] = c_{\text{CaY}^{2-}} - [\text{Ca}^{2+}] \approx c_{\text{CaY}^{2-}}$$

The formula for  $[\text{CaY}^{2-}]$  is entered into cell C11. Be sure to verify this formula for yourself. To obtain  $[\text{Ca}^{2+}]$ , we substitute into the expression for  $K'_{\text{CaY}}$ ,

$$K'_{\text{CaY}} = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}] c_T} \cong \frac{c_{\text{CaY}^{2-}}}{[\text{Ca}^{2+}]^2}$$

$$[\text{Ca}^{2+}] = \sqrt{\frac{c_{\text{CaY}^{2-}}}{K'_{\text{CaY}}}}$$

We enter into cell B11 the formula corresponding to this expression.

#### Postequivalence-Point pCa

Beyond the equivalence point, analytical concentrations of  $\text{CaY}^{2-}$  and EDTA are obtained directly from the stoichiometry. Since there is excess EDTA, a calculation similar to that in Example 17-4 is then performed. For example, after the addition of 26.0 mL of EDTA, we can write

$$c_{\text{CaY}^{2-}} = \frac{(50.0 \times 0.00500) \text{ mmol}}{(50.0 + 26.0) \text{ mL}}$$
$$c_{\text{EDTA}} = \frac{(26.0 \times 0.0100) \text{ mL} - (50.0 \times 0.00500) \text{ mL}}{76.0 \text{ mL}}$$

As an approximation,

$$[\text{CaY}^{2-}] = c_{\text{CaY}^{2-}} - [\text{Ca}^{2+}] \approx c_{\text{CaY}^{2-}} \approx \frac{(50.0 \times 0.00500) \text{ mmol}}{(50.0 + 26.0) \text{ mL}}$$

We note that this expression is the same as that previously entered into cell C11. Therefore, we copy that equation into cell C12. We also note that  $[\text{CaY}^{2-}]$  will be given by this same expression (with the volume varied) throughout the remainder of the titration. Hence, the formula in cell C12 is copied into cells C13 through C19. Also, we approximate

$$e_{\text{T}} = c_{\text{EDTA}} + [\text{Ca}^{2+}] \approx c_{\text{EDTA}} = \frac{(26.0 \times 0.0100) \text{ mL} - (50.0 \times 0.00500) \text{ mL}}{76.0 \text{ mL}}$$

We enter this formula into cell D12 and copy it into cells D13 through D16.

To calculate  $[\text{Ca}^{2+}]$ , we then substitute this approximation for  $e_{\text{T}}$  in the conditional formation-constant expression, and obtain

$$K'_{\text{CaY}} = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}] \times e_{\text{T}}} \cong \frac{c_{\text{CaY}^{2-}}}{[\text{Ca}^{2+}] \times c_{\text{EDTA}}}$$
$$[\text{Ca}^{2+}] = \frac{c_{\text{CaY}^{2-}}}{c_{\text{EDTA}} \times K'_{\text{CaY}}}$$

Figure 17-9 EDTA titration curves for 50.0 mL of 0.00500 M  $\text{Ca}^{2+}$  ( $K'_{\text{CaY}} = 1.75 \times 10^{10}$ ) and  $\text{Mg}^{2+}$  ( $K'_{\text{MgY}} = 1.72 \times 10^8$ ) at pH 10.0.

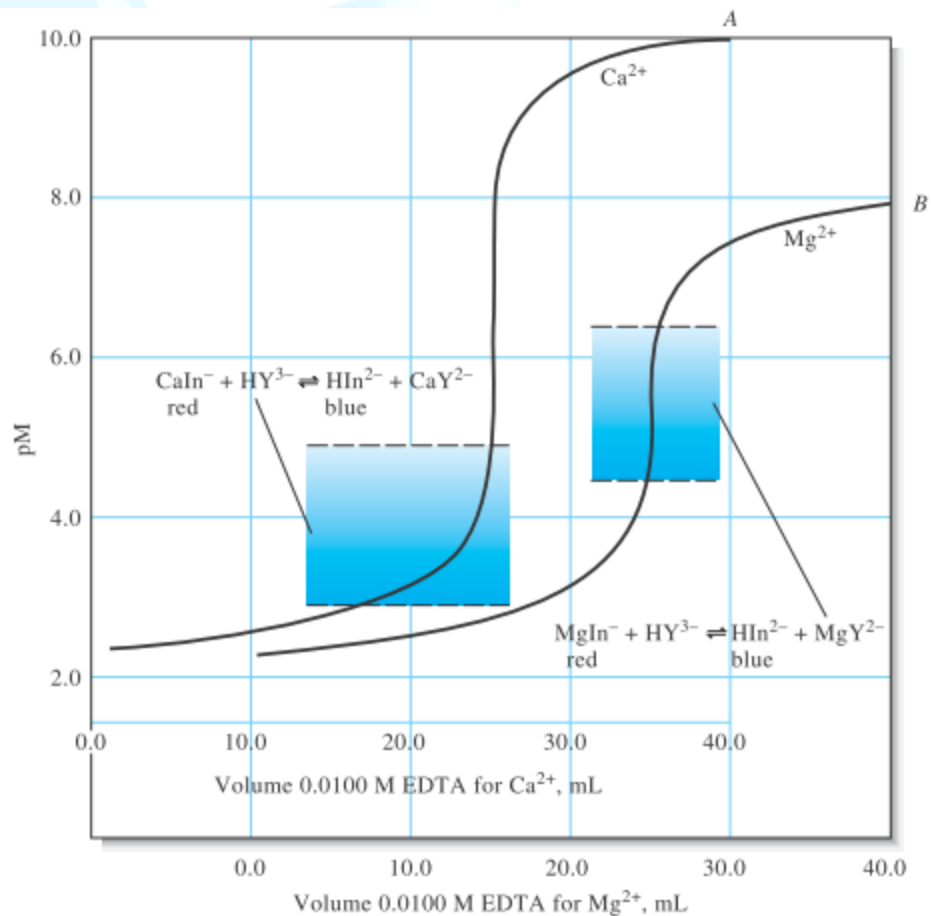
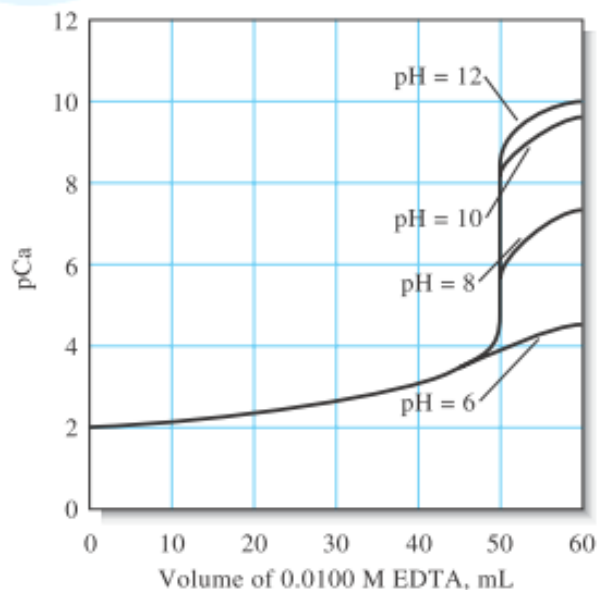


Figure 17-10 Influence of pH on the titration of 0.0100 M  $\text{Ca}^{+2}$  with 0.0100 M EDTA.



The titration curves for calcium ion in solutions buffered to various pH levels. As the conditional formation constant becomes less favorable, there is a smaller change in pCa in the equivalence-point region.

Figure 17-11 Titration curves for 50.0 mL of 0.0100 M solutions of various cations at pH 6.0.

Cations with larger formation constants provide sharp end points even in acidic media.

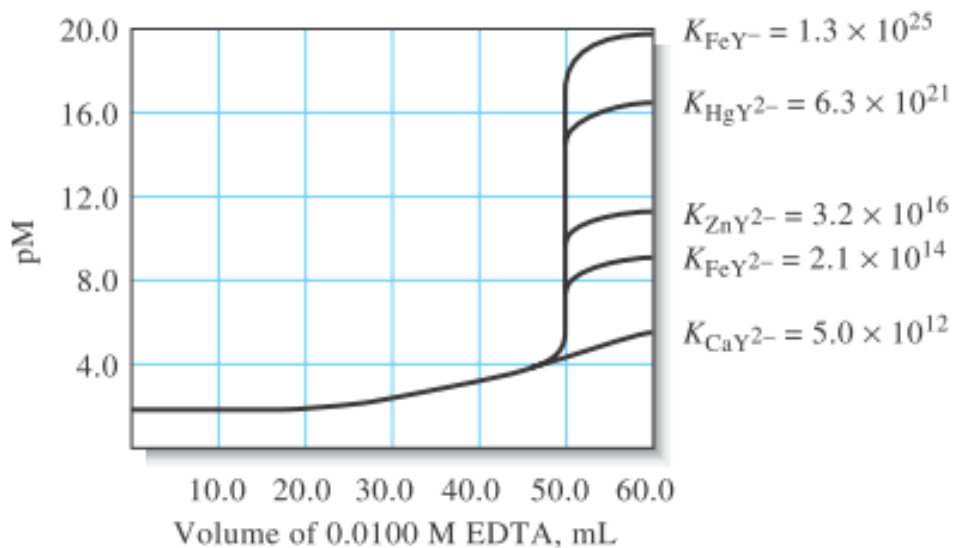
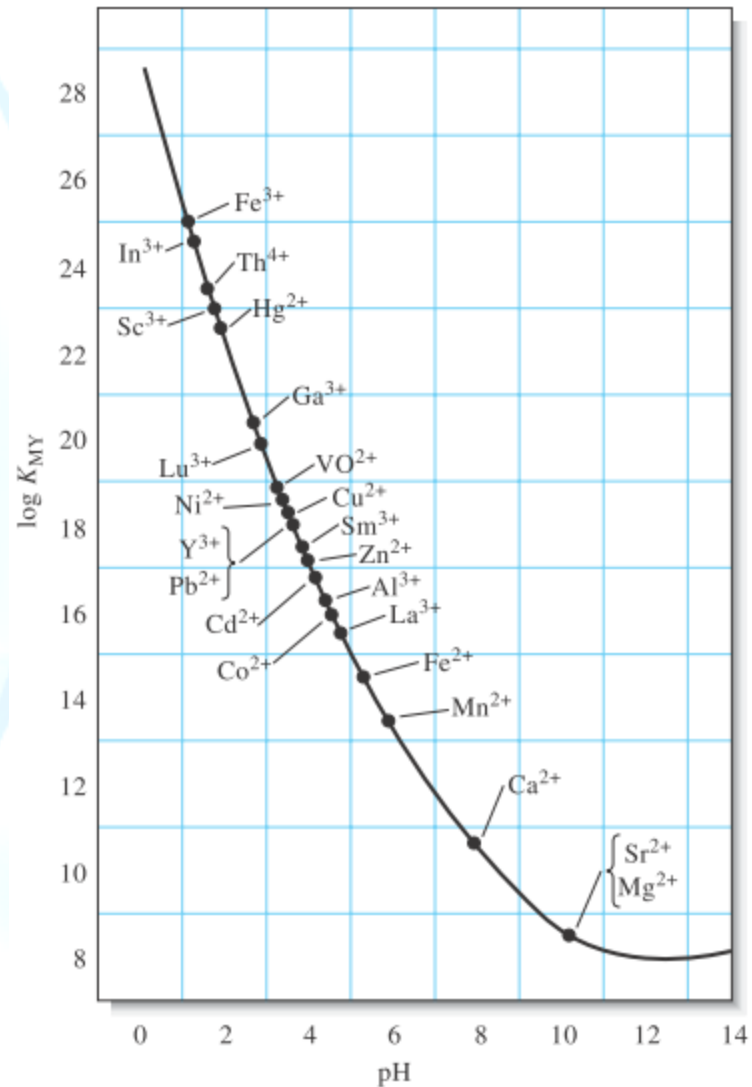




Figure 17-12 Minimum pH needed for satisfactory titration of various cations with EDTA.



# The Effect of Other Complexing Agents on EDTA Titration Curves

Many cations form hydrous oxide precipitates (hydroxides, oxides, or oxyhydroxides) when the pH is raised to the level required for their successful titration with EDTA.

An auxiliary complexing agent is needed to keep the cation in solution.

Zinc(II) is usually titrated in a medium that has fairly high concentrations of ammonia and ammonium chloride.



Here are two theoretical curves for the titration of zinc(II) with EDTA at pH 9.00. The equilibrium concentration of ammonia was 0.100 M for one titration and 0.0100 M for the other.

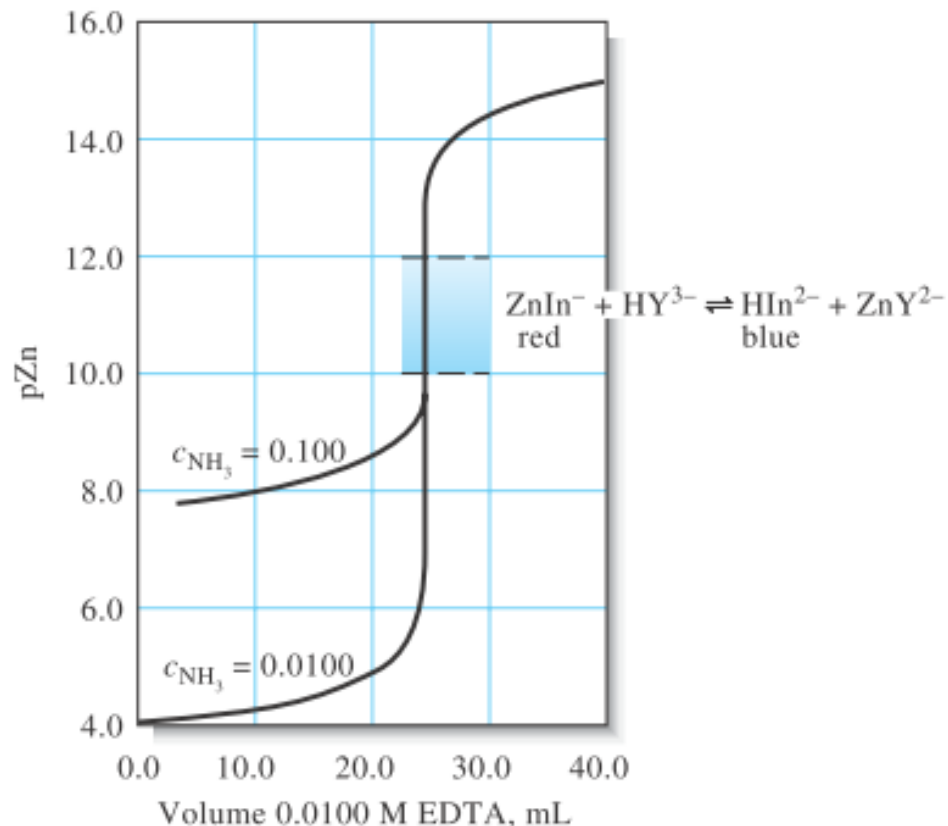


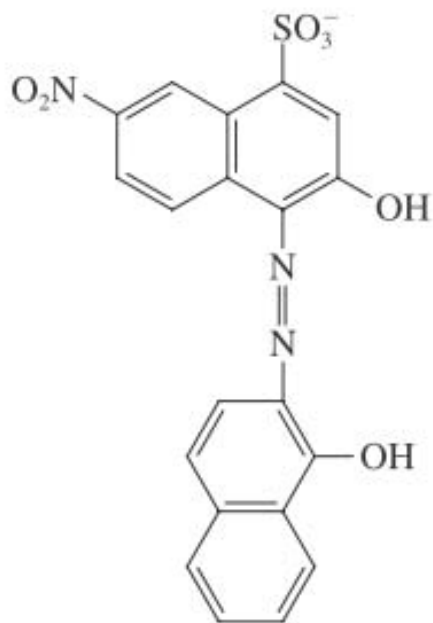
Figure 17-13 Influence of ammonia concentration on the end point for the titration of 50.0 mL of 0.00500 M  $\text{Zn}^{2+}$ .

## Indicators for EDTA Titrations

There are nearly 200 organic compounds that can be used as indicators for metal ions in EDTA titrations.

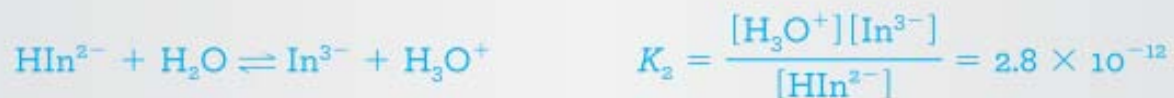
These indicators are organic dyes that form colored chelates with metal ions in a  $\mu\text{M}$  range that is characteristic of the particular cation and dye.

Eriochrome Black T is a typical metal-ion indicator.



### EXAMPLE 17-6

Determine the transition ranges for Eriochrome Black T in titrations of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  at pH 10.0, given (a) that the second acid dissociation constant for the indicator is



(b) that the formation constant for  $\text{MgIn}^-$  is



and (c) that the analogous formation constant for  $\text{Ca}^{2+}$  is  $2.5 \times 10^5$ .

#### Solution

We assume, as we did earlier (see Section 14A-1), that a detectable color change requires a tenfold excess of one or the other of the colored species, that is, a detectable color change is observed when the ratio  $[\text{MgIn}^-]/[\text{HIn}^{2-}]$  changes from 10 to 0.10. The product of  $K_2$  for the indicator and  $K_f$  for  $\text{MgIn}^-$  contains this ratio:

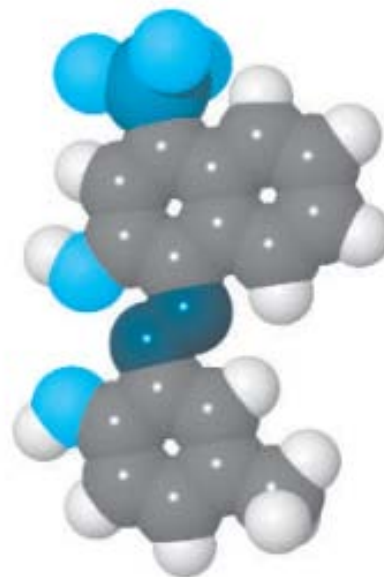
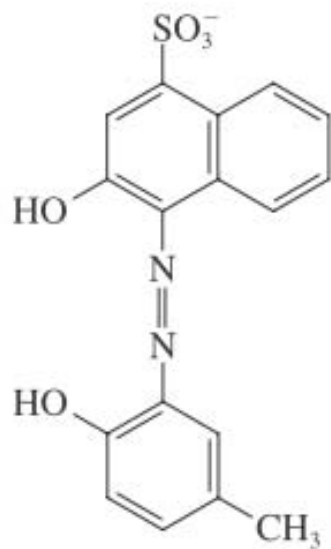
$$\frac{[\text{MgIn}^-][\text{H}_3\text{O}^+]}{[\text{HIn}^{2-}][\text{Mg}^{2+}]} = 2.8 \times 10^{-12} \times 1.0 \times 10^7 = 2.8 \times 10^{-5}$$

Substituting  $1.0 \times 10^{-10}$  for  $[\text{H}_3\text{O}^+]$  and 10 and 0.10 for the ratio yields, the range of  $[\text{Mg}^{2+}]$  over which the color change occurs is

$$[\text{Mg}^{2+}] = 3.6 \times 10^{-5} \quad \text{to} \quad 3.6 \times 10^{-7} \text{ M}$$
$$\text{pMg} = 5.4 \pm 1.0$$

Proceeding in the same way, we find the range for pCa to be  $3.8 \pm 1.0$ .

- A limitation of Eriochrome Black T is that its solutions decompose slowly with standing.
- Solutions of Calmagite (shown here) do not have this limitation but for all practical purposes is identical in behavior to Eriochrome Black T.



## Titration Methods Involving EDTA

*Direct Titration:* Most metals in the periodic table can be determined by titration with standard EDTA solutions.

1. Methods based on indicators for the analyte: Nearly 40 metal ions can be determined by direct titration with EDTA using metal-ion indicators.
2. Methods based on indicators for an added metal ion: When a direct indicator for the analyte is unavailable, a small amount of a metal ion for which a good indicator is available can be added. The metal ion must form a complex that is less stable than the analyte complex.
3. Potentiometric methods. Potential measurements can be used for end-point detection in the EDTA titration of those metal ions for which specific ion electrodes are available.
4. Spectrophotometric methods. Measurement of UV/visible absorption can be used.



## *Back-Titration Methods*

- These are useful for the determination of cations that form stable EDTA complexes and for which a satisfactory indicator is not available.
- The method is also useful for cations such as Cr(III) and Co(III) that react slowly with EDTA.
- It is useful for analyzing samples that contain anions that could form precipitates with the analyte under the analytical conditions.

## *Displacement Methods*

- An unmeasured excess of a solution containing the magnesium or zinc complex of EDTA is introduced into the analyte solution.

If the analyte forms a more stable complex than that of magnesium or zinc, the following displacement reaction occurs:



## The Scope of EDTA Titrations

- Titrations with EDTA have been applied to the determination of almost every metal cation because EDTA complexes most cations.
- Selectivity or considerable control over interferences can be realized by pH regulation.
- Trivalent cations can usually be titrated without interference from divalent species by maintaining the solution at a pH = 1.
- Ions such as cadmium and zinc, which form more stable EDTA chelates than does magnesium, can be determined in the presence of the magnesium by buffering the mixture to pH 7 before titration.
- Interference can also be eliminated by using a masking agent, an auxiliary ligand that preferentially forms highly stable complexes with the potential interfering ion.

## - Determination of Water Hardness

- Hard water contains calcium, magnesium, and heavy metal ions that form precipitates with soap.
- These cations in the water replace the sodium or potassium ions in soaps and form sparingly soluble products that cause “scum” in the sink or bathtub.
- In natural waters, the concentrations of calcium and magnesium ions generally far exceed those of any other metal ion.
- Hardness is expressed in terms of the concentration of calcium carbonate that is equivalent to the total concentration of all the multivalent cations in the sample.
- Water hardness is usually determined by an EDTA titration after the sample has been buffered to pH 10.
- A magnesium-ion indicator, such as Calmagite or Eriochrome Black T, can serve as indicator in water-hardness titrations.