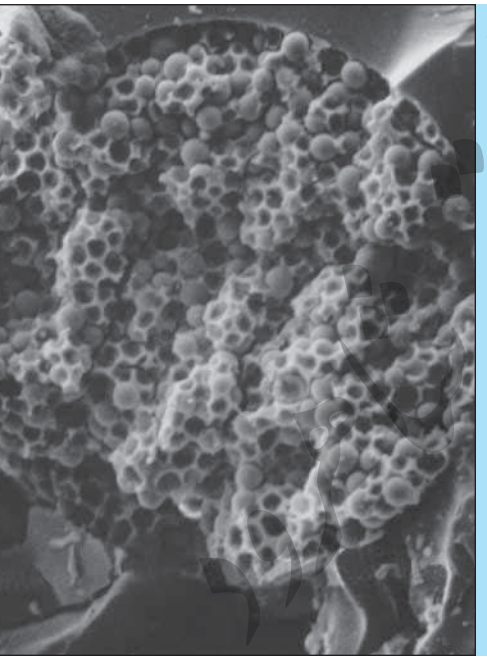
CHAPTER 17

Complexation and Precipitation Reactions and Titrations



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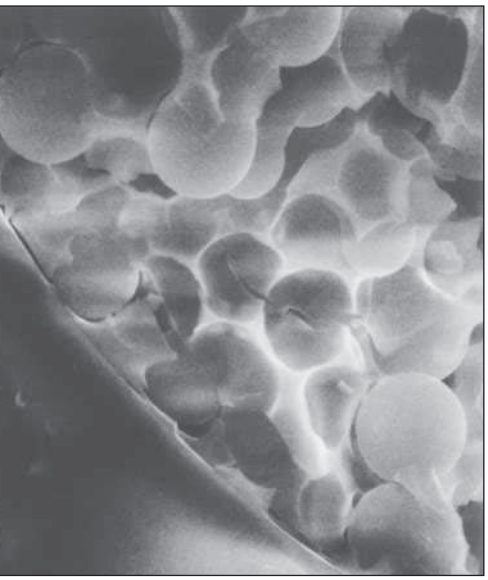
Complexation and precipitation reactions are important in many areas of science and everyday life as discussed in this chapter. Black-and-white photography is one such area. Although digital photography has come to dominate consumer areas, film photography is still important in many applications. Shown here are photomicrographs of a capillary chromatography column at ×1300 (top) and ×4900 (bottom) magnification. Black-and-white film consists of an emulsion of finely divided AgBr coated on a polymer strip. Exposure to light from the scanning electron microscope causes reduction of some of the Ag^+ ions to Ag atoms and corresponding oxidation of Br^- to Br atoms. These atoms remain in the crystal lattice of AgBr as invisible defects, or the so-called latent image. Developing reduces many more Ag^+ ions to Ag atoms in the granules of AgBr containing Ag atoms from the original latent image. Development produces a visible negative image where dark regions of Ag atoms represent areas where light has exposed the film. The fixing step removes the unexposed AgBr by forming the highly stable silver thiosulfate complex $[Ag(S_2O_3)_2]^{2-}$. The black metallic silver of the negative remains.

$$AgBr(s) + 2S_2O_3^{2-}(aq) \rightarrow [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)$$

After the negative has been fixed, a positive image is produced by projecting light through the negative onto photographic paper. (M. T. Dulay, R. P. Kulkarni, and R. N. Zare, *Anal. Chem.*, **1998**, 70, 5103, **DOI**: 10.1021/ac9806456. ©American Chemical Society. Courtesy of R. N. Zare, Stanford University.)



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Complexation reactions are widely used in analytical chemistry. One of the earliest uses of these reactions was for titrating cations, a major topic of this chapter. In addition, many complexes are colored or absorb ultraviolet radiation; the formation of these complexes is often the basis for spectrophotometric determinations (see Chapter 26). Some complexes are sparingly soluble and can be used in gravimetric analysis (see Chapter 12) or for precipitation titrations as discussed in this chapter. 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**, must have at least one pair of unshared electrons available for bond formation. Water, ammonia, and halide ions

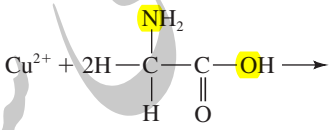
are common inorganic ligands. In fact most metal ions in aqueous solution actually exist as aquo complexes. Copper(II), for example, in aqueous solution is readily complexed by water molecules to form species such as $Cu(H_2O)_4^{2+}$. We often simplify such complexes in chemical equations by writing the metal ion as if it were uncomplexed Cu^{2+}. We should remember, however, that most metal ions are actually aquo complexes in aqueous solution.

A **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, which are then shared by the two.

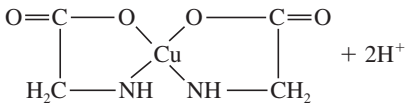
The number of covalent bonds that a cation tends to form with electron donors is its **coordination number**. Typical values for coordination numbers are two, four, and six. The species formed as a result of coordination can be electrically positive, neutral, or negative. For example, copper(II), which has a coordination number of four, forms a cationic ammine complex, $Cu(NH_3)_4^{2+}$; a neutral complex with glycine, $Cu(NH_2CH_2COO)_2$; and an anionic complex with chloride ion, $CuCl_4^{2-}$.

Titrations based on complex formation, sometimes called **complexometric titrations**, have been used for more than a century. The truly remarkable growth in their analytical application, based on a particular class of coordination compounds called **chelates**, began in the 1940s. 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:

Chelate is pronounced *kee'late* and is derived from the Greek word for claw.



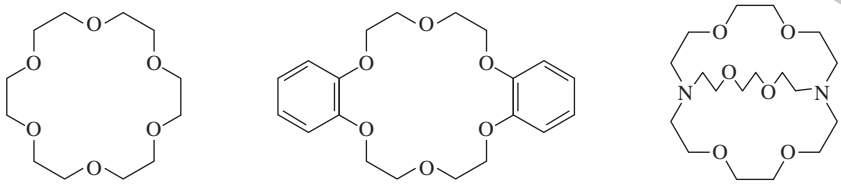
Glycine



Cu^{2+} complex with glycine.

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.

Dentate comes from the Latin word *dentatus* and means having toothlike projections.



18-crown-6 dibenzo-18-crown-6 cryptand 2,2,2

Crown ethers and cryptands.

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. Some macrocyclic compounds form three dimensional cavities that can just accommodate appropriately sized metal ions. Ligands known as **cryptands** are examples. Selectivity occurs to a large extent

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

because of the size and shape of the cycle or cavity relative to that of the metal ion, although the nature of the heteroatoms and their electron densities, the compatibility of the donor atoms with the metal ion, and several other factors also play important roles.

17A-1 Complexation Equilibria

The **selectivity** of a ligand for one metal ion over another refers to the stability of the complexes formed. The higher the formation constant of the metal-ligand complex, the better the selectivity of the ligand for the metal relative to similar complexes formed with other metals.

Complexation reactions involve a metal-ion M reacting with a ligand L to form a complex ML, as shown in Equation 17-1:

$$M + L \rightleftharpoons ML \tag{17-1}$$

where we have omitted the charges on the ions in order to be general. Complexation reactions occur in a stepwise fashion and the reaction above is often followed by additional reactions:

$$ML + L \rightleftharpoons ML_2 \tag{17-2}$$

$$ML_2 + L \rightleftharpoons ML_3 \tag{17-3}$$

$$\vdots \qquad \vdots$$

$$ML_{n-1} + L \rightleftharpoons ML_n \tag{17-4}$$

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. For example, Cu(II), with a maximum coordination number 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 $Cu(gly)_2{}^{2+}$.

The equilibrium constants for complex formation reactions are generally written as formation constants, as discussed in Chapter 9. Thus, each of the reactions 17-1 through 17-4 is associated with a stepwise formation constant K_1 through K_4. For example, $K_1 = [ML]/[M][L]$, $K_2 = [ML_2]/[ML][L]$, and so on. We can also write the equilibria as the sum of individual steps. These have overall formation constants designated by the symbol β_n. Therefore,

$$M + L \rightleftharpoons ML \qquad \beta_1 = \frac{[ML]}{[M][L]} = K_1 \tag{17-5}$$

$$M + 2L \rightleftharpoons ML_2 \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2} = K_1K_2 \tag{17-6}$$

$$M + 3L \rightleftharpoons ML_3 \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3} = K_1K_2K_3 \tag{17-7}$$

$$\vdots \qquad \vdots$$

$$M + nL \rightleftharpoons ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n} = K_1K_2\cdots K_n \tag{17-8}$$

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, α_M is the fraction of the total metal present at equilibrium in the free metal form, α_{ML} is the fraction in the ML form, and so on. As derived in Feature 17-1, the alpha values are given by

$$\alpha_M = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \cdots + \beta_n[L]^n} \quad (17\text{-}9)$$

$$\alpha_{ML} = \frac{\beta_1[L]}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \cdots + \beta_n[L]^n} \quad (17\text{-}10)$$

$$\alpha_{ML_2} = \frac{\beta_2[L]^2}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \cdots + \beta_n[L]^n} \quad (17\text{-}11)$$

$$\alpha_{ML_n} = \frac{\beta_n[L]^n}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \cdots + \beta_n[L]^n} \quad (17\text{-}12)$$

FEATURE 17-1

Calculation of Alpha Values for Metal Complexes

The alpha values for metal-ligand complexes can be derived as we did for polyfunctional acids in Section 15H. The alphas are defined as

$$\alpha_M = \frac{[M]}{c_M}; \quad \alpha_{ML} = \frac{[ML]}{c_M};$$

$$\alpha_{ML_2} = \frac{[ML_2]}{c_M}; \quad \alpha_{ML_n} = \frac{[ML_n]}{c_M}$$

The total metal concentration c_M can be written

$$c_M = [M] + [ML] + [ML_2] + \cdots + [ML_n]$$

From the overall formation constants (Equations 17-5 through 17-8), the concentrations of the complexes can be expressed in terms of the free metal concentration [M] to give

$$\begin{aligned} c_M &= [M] + \beta_1[M][L] + \beta_2[M][L]^2 + \cdots + \beta_n[M][L]^n \\ &= [M]\{1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_n[L]^n\} \end{aligned}$$

Now, α_M can be found as

$$\begin{aligned} \alpha_M = \frac{[M]}{c_M} &= \frac{[M]}{[M] + \beta_1[M][L] + \beta_2[M][L]^2 + \cdots + \beta_n[M][L]^n} \\ &= \frac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \cdots + \beta_n[L]^n} \end{aligned}$$

Note that the form on the right is Equation 17-9. We can find α_{ML} from

$$\begin{aligned} \alpha_{ML} = \frac{[ML]}{c_M} &= \frac{\beta_1[M][L]}{[M] + \beta_1[M][L] + \beta_2[M][L]^2 + \cdots + \beta_n[M][L]^n} \\ &= \frac{\beta_1[L]}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \cdots + \beta_n[L]^n} \end{aligned}$$

The rightmost form of this equation is identical to Equation 17-10. The other alpha values in Equations 17-11 and 17-12 can be found in a similar manner.

Note that these expressions are analogous to the α expressions we wrote for polyfunctional acids and bases except that the equations here are written in terms of formation equilibria while those for acids or bases are written in terms of dissociation equilibria. Also, the master variable is the ligand concentration [L] instead of the hydronium ion concentration. The denominators are the same for each α value. Plots of the α values versus p[L] are known as **distribution diagrams**.

Spreadsheet Summary In the first exercise in Chapter 9 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed., α values for the Cu(II)/NH_3 complexes are calculated and used to plot distribution diagrams. The α values for the Cd(II)/Cl^- system are also calculated.

17A-2 The Formation of Insoluble Species

In the cases discussed in the previous section, the complexes formed are soluble in solution. 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 Cl^- to Ag^+ results in the insoluble AgCl precipitate. Addition of a large excess of Cl^- produces soluble species $AgCl_2^-$, $AgCl_3^{2-}$, and $AgCl_4^{3-}$.

In contrast to complexation equilibria, which are most often treated as formation reactions, solubility equilibria are normally treated as dissociation reactions, as discussed in Chapter 9. In general, for a sparingly soluble salt M_xA_y in a saturated solution, we can write

$$M_xA_y(s) \rightleftharpoons xM^{y+}(aq) + yA^{x-}(aq) \qquad K_{sp} = [M^{y+}]^x[A^{x-}]^y \tag{17-13}$$

where K_{sp} is the solubility product. Hence, for BiI_3, the solubility product is written, $K_{sp} = [Bi^{3+}][I^-]^3$.

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_2L, . . . H_nL for which again the charges have been omitted for generality. Adding

acid to a solution containing M and L reduces the concentration of free L available to complex with M and thus decreases the effectiveness of L as a complexing agent (Le Chatelier's principle). For example, ferric ions (Fe^{3+}) form complexes with oxalate ($C_2O_4^{2-}$, which we abbreviate as ox^{2-}) with formulas $[Fe(ox)]^+$, $[Fe(ox)_2]^-$, and $[Fe(ox)_3]^{3-}$. Oxalate can protonate to form Hox^- and H_2ox. In basic solution, where most of the oxalate is present as ox^{2-} before complexation with Fe^{3+}, the ferric/oxalate complexes are very stable. Adding acid, however, protonates the oxalate ion, which in turn causes dissociation of the ferric complexes.

For a diprotic acid, like oxalic acid, the fraction of the total oxalate-containing species in any given form, ox^{2-}, Hox^-, and H_2ox, is given by an alpha value (recall Section 15H). Since

$$c_T = [H_2ox] + [Hox^-] + [ox^{2-}] \tag{17-14}$$

we can write the alpha values, α_0, α_1, and α_2, as

$$\alpha_0 = \frac{[H_2ox]}{c_T} = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{17-15}$$

$$\alpha_1 = \frac{[Hox^-]}{c_T} = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{17-16}$$

$$\alpha_2 = \frac{[ox^{2-}]}{c_T} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{17-17}$$

Since we are interested in the free oxalate concentration, we will be most concerned with the highest α value, here α_2. From Equation 17-17, we can write

$$[ox^{2-}] = c_T\alpha_2 \tag{17-18}$$

در محیط اسیدی ترآلفا2 و در نتیجه غلظت اگزالات آزاد کاهش می یابد.

Note that, as the solution gets more acidic, the first two terms in the denominator of Equation 17-17 dominate, and α_2 and the free oxalate concentration decrease. When the solution is very basic, the last term dominates, α_2 becomes nearly unity, and $[ox^{2-}] \approx c_T$, indicating that nearly all the oxalate is in the ox^{2-} form in basic solution.

Conditional Formation Constants

ثابت تشکیل مشروط (وابسته به pH)

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 Fe^{3+} with oxalate, for example, we can write the formation constant K_1 for the first complex as

$$K_1 = \frac{[Fe(ox)^+]}{[Fe^{3+}][ox^{2-}]} = \frac{[Fe(ox)^+]}{[Fe^{3+}]\alpha_2 c_T} \tag{17-19}$$

At a particular pH value, α_2 is constant, and we can combine K_1 and α_2 to yield a new conditional constant K_1':

$$K_1' = \alpha_2 K_1 = \frac{[Fe(ox)^+]}{[Fe^{3+}]c_T} \tag{17-20}$$

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, β values, for the higher complexes, $[Fe(ox)_2]^-$ and $[Fe(ox)_3]^{3-}$, can also be written as conditional constants.

Spreadsheet Summary Ligands that protonate are treated in Chapter 9 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed. Alpha values and conditional formation constants are calculated.

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, as discussed in Section 17B-2.

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 in complexometric titrations, the ligand is the titrant, and the metal ion is the analyte, although occasionally the roles are reversed. As we shall see later, 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 (recall Equations 17-1 through 17-4).

Tetradentate or hexadentate ligands are more satisfactory as titrants than ligands with fewer donor groups because their reactions with cations are more complete and because they tend to form 1:1 complexes.

The advantage of a single-step reaction is illustrated by the titration curves shown in **Figure 17-1**. Each of the titrations shown involves a reaction that has an overall equilibrium constant of 10^{20}. Curve *A* is computed for a reaction in which a metal-ion M having a coordination number of four reacts with a tetradentate ligand D to form the complex of MD (we have again omitted the charges on the two reactants for convenience). Curve *B* is for the reaction of M with a hypothetical bidentate ligand B to give MB_2 in two steps. The formation constant for the first step is 10^{12} and for the second

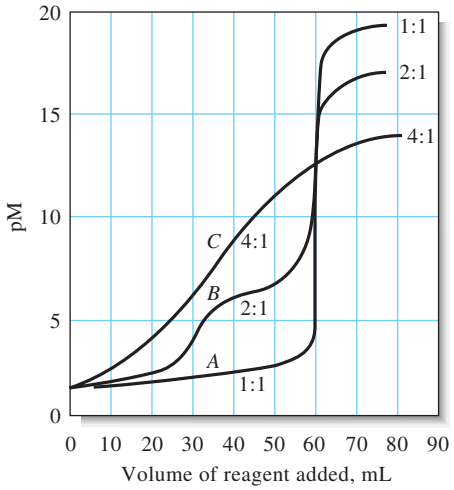


Figure 17-1 Titration curves for complexometric titrations. Titration of 60.0 mL of a solution that is 0.020 M in metal M with (A) a 0.020 M solution of the tetradentate ligand D to give MD as the product; (B) a 0.040 M solution of the bidentate ligand B to give MB_2; and (C) a 0.080 M solution of the unidentate ligand A to give MA_4. The overall formation constant for each product is 10^{20}.

FEATURE 17-2

Determination of Hydrogen Cyanide in Acrylonitrile Plant Streams

Acrylonitrile, $CH_2{=}CH{-}C{\equiv}N$, is an important chemical in the production of polyacrylonitrile. This thermoplastic was drawn into fine threads and woven into synthetic fabrics such as Orlon, Acrilan, and Creslan. Although acrylic fibers are no longer produced in the US, they are still made in many countries. Hydrogen cyanide is an impurity in the plant streams that carry aqueous acrylonitrile. The cyanide is commonly determined by titration with $AgNO_3$. The titration reaction is

$$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^-$$

In order to determine the end point of the titration, the aqueous sample is mixed with a basic solution of potassium iodide before the titration. Before the equivalence point, cyanide is in excess, and all the Ag^+ is complexed. As soon as all the cyanide has been reacted, the first excess of Ag^+ causes a permanent turbidity to appear in the solution because of the formation of the AgI precipitate according to

$$Ag^+ + I^- \rightarrow AgI(s)$$

10^8. Curve *C* involves a unidentate ligand, A, that forms MA_4 in four steps with successive formation constants of 10^8, 10^6, 10^4, and 10^2. These curves demonstrate that a much sharper end point is obtained with a reaction that takes place in a single step. For this reason, multidentate ligands are usually preferred for complexometric titrations.

The most widely used complexometric titration with a unidentate ligand is the titration of cyanide with silver nitrate, a method introduced by Liebig in the 1850s. This method involves the formation of soluble $Ag(CN)_2^-$, as discussed in Feature 17-2. Other common inorganic complexing agents and their applications are listed in **Table 17-1**.

Spreadsheet Summary The complexometric titration of Cd(II) with Cl^- is considered in Chapter 9 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed. A master equation approach is used.

17B-2 Precipitation Titrations

Precipitation titrations are based on reactions that yield ionic compounds of limited solubility. Precipitation titrimetry is one of the oldest analytical techniques, dating back to the mid-1800s. The slow rate at which most precipitates form, however, limits the number of precipitating agents that can be used in titrations to a handful. We limit our discussion here to the most widely used and important precipitating reagent, silver nitrate, which is used for the determination of the halogens, the

TABLE 17-1

Typical Inorganic Complex-Forming Titrations

Titrant	Analyte	Remarks
$Hg(NO_3)_2$	Br^-, Cl^-, SCN^-, CN^-, thiourea	Products are neutral Hg(II) complexes; various indicators used
$AgNO_3$	CN^-	Product is $Ag(CN)_2^-$; indicator is I^-; titrate to first turbidity of AgI
$NiSO_4$	CN^-	Product is $Ni(CN)_4^{2-}$; indicator is AgI; titrate to first turbidity of AgI
KCN	Cu^{2+}, Hg^{2+}, Ni^{2+}	Products are $Cu(CN)_4^{2-}$, $Hg(CN)_2$, and $Ni(CN)_4^{2-}$; various indicators used

halogenlike anions, mercaptans, fatty acids, and several divalent inorganic anions. 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 $AgNO_3$). Example 17-1 illustrates how p-functions are obtained for the preequivalence-point region, the postequivalence-point region, and the equivalence point for a typical precipitation titration.

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}.

$$[Cl^-] \approx c_{NaCl} = \frac{\text{original no. mmol } Cl^- - \text{no. mol } AgNO_3 \text{ added}}{\text{total volume of solution}}$$

$$= \frac{(50.00 \times 0.05000 - 10.00 \times 0.1000)}{50.00 + 10.00} = 0.02500 \text{ M}$$

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

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

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^- with Standard $AgNO_3$

	pAg	
Volume of $AgNO_3$	**50.00 mL of 0.0500 M NaCl with 0.1000 M $AgNO_3$**	**50.00 mL of 0.005 M NaCl with 0.0100 M $AgNO_3$**
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, $[Ag^+] = [Cl^-]$, and $[Ag^+][Cl^-] = K_{sp} = 1.82 \times 10^{-10} = [Ag^+]^2$

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

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

(c) Postequivalence-Point Region

At 26.00 mL of $AgNO_3$, Ag^+ is in excess so

$$[Ag^+] = c_{AgNO_3} = \frac{(26.00 \times 0.1000 - 50.00 \times 0.05000)}{76.00} = 1.32 \times 10^{-3}\ M$$

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

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

The effect of reagent and analyte concentration on titration curves can be seen in the data in Table 17-2 and the two curves shown in **Figure 17-2**. With 0.1000 M $AgNO_3$ (Curve *A*), the change in pAg in the equivalence-point region is large, about 2 pAg units. With the 0.01000 M reagent, the change is about 1 pAg unit, but still pronounced. An indicator that produces a signal in the 4.0 to 6.0 pAg region should give a minimal error for the stronger solution. For the more dilute chloride solution (Curve *B*), the change in pAg in the equivalence-point region would be drawn out over a fairly large volume of reagent (~3 mL as shown by the dashed lines in the

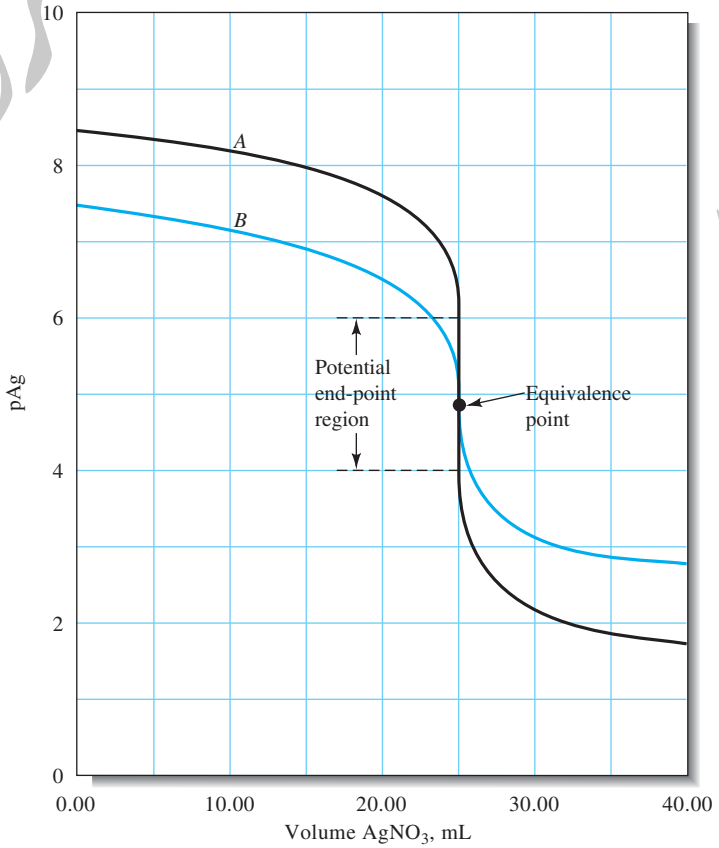


Figure 17-2 Titration curve for (*A*), 50.00 mL of 0.05000 M NaCl titrated with 0.1000 M $AgNO_3$, and (*B*), 50.00 mL of 0.00500 M NaCl titrated with 0.01000 M $AgNO_3$. Note the increased sharpness of the break at the end point with the more concentrated solution.

figure) so that to determine the end point accurately would be impossible. The effect here is analogous to that illustrated for acid/base titrations in Figure 14-4.

The Effect of Reaction Completeness on Titration Curves

Figure 17-3 illustrates the effect of solubility product on the sharpness of the end point for titrations with 0.1 M silver nitrate. Note that the change in pAg at the equivalence point becomes greater as the solubility products become smaller, that is, as the reaction between the analyte and silver nitrate becomes more complete. By choosing an indicator that changes color in the pAg region of 4 to 6, titration of chloride ions should be possible with a minimal titration error. Note that ions forming precipitates with solubility products much larger than about 10^{-10} do not yield satisfactory end points.

A useful relationship can be derived by taking the negative logarithm of both sides of a solubility-product expression. Thus, for silver chloride,

$$-\log K_{sp} = -\log ([Ag^+][Cl^-])$$
$$= -\log [Ag^+] - \log [Cl^-]$$

$$pK_{sp} = pAg + pCl$$

This expression is similar to the acid-base expression for pK_w

$$pK_w = pH + pOH$$

Titration Curves for Mixtures of Anions

The methods developed in Example 17-1 for constructing precipitation titration curves can be extended to mixtures that form precipitates of different solubilities. To illustrate, consider 50.00 mL of a solution that is 0.0500 M in iodide ion and 0.0800 M in chloride ion titrated with 0.1000 M silver nitrate. The curve for the initial stages of this titration is identical to the curve shown for iodide in Figure 17-3 because silver chloride, with its much larger solubility product, does not begin to precipitate until well into the titration.

It is interesting to determine how much iodide is precipitated before appreciable amounts of silver chloride form. With the appearance of the smallest amount of solid silver chloride, the solubility-product expressions for both precipitates apply, and division of one by the other provides the useful relationship

$$\frac{K_{sp}(AgI)}{K_{sp}(AgCl)} = \frac{\cancel{[Ag^+]}[I^-]}{\cancel{[Ag^+]}[Cl^-]} = \frac{8.3 \times 10^{-17}}{1.82 \times 10^{-10}} = 4.56 \times 10^{-7}$$

$$[I^-] = (4.56 \times 10^{-7})[Cl^-]$$

From this relationship, we see that the iodide concentration decreases to a tiny fraction of the chloride ion concentration before silver chloride begins to precipitate.

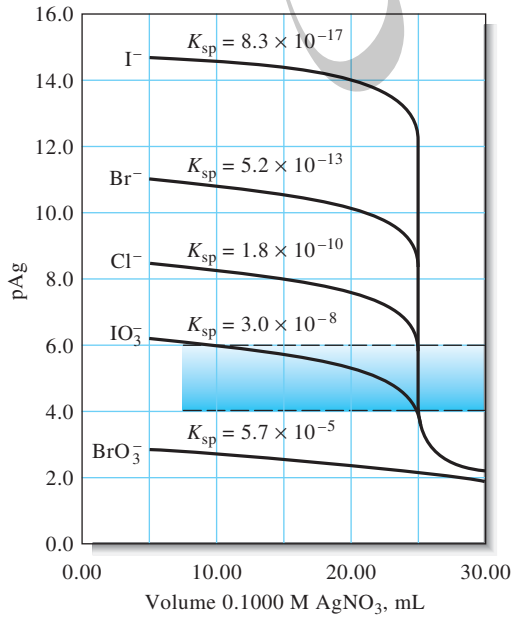


Figure 17-3 Effect of reaction completeness on precipitation titration curves. For each curve, 50.00 mL of a 0.0500 M solution of the anion was titrated with 0.1000 M $AgNO_3$. Note that smaller values of K_{sp} give much sharper breaks at the end point.

So, for all practical purposes, silver chloride forms only after 25.00 mL of titrant have been added in this titration. At this point, the chloride ion concentration is approximately

$$c_{Cl^-} \approx [Cl^-] = \frac{50.00 \times 0.0800}{50.00 + 25.00} = 0.0533\ M$$

Substituting into the previous equation yields

$$[I^-] = 4.56 \times 10^{-7}[Cl^-] = 4.56 \times 10^{-7} \times 0.0533 = 2.43 \times 10^{-8}\ M$$

The percentage of iodide unprecipitated at this point can be calculated as follows:

$$\text{amount } I^- \text{ unprecipitated} = (75.00\ \cancel{mL})(2.43 \times 10^{-8}\ \text{mmol } I^-/\cancel{mL}) = 1.82 \times 10^{-6}\ \text{mmol}$$

$$\text{original amount } I^- = (50.00\ \cancel{mL})(0.0500\ \text{mmol}/\cancel{mL}) = 2.50\ \text{mmol}$$

$$\text{percentage } I^- \text{ unprecipitated} = \frac{1.82 \times 10^{-6}}{2.50} \times 100\% = 7.3 \times 10^{-5}\%$$

Thus, to within about 7.3×10^{-5} percent of the equivalence point for iodide, no silver chloride forms. Up to this point, the titration curve is indistinguishable from that for iodide alone, as shown in **Figure 17-4**. The data points for the first part of the titration curve, shown by the solid line, were computed on this basis.

As chloride ion begins to precipitate, however, the rapid decrease in pAg ends abruptly at a level that can be calculated from the solubility product for silver chloride and the computed chloride concentration (0.0533 M):

$$[Ag^+] = \frac{K_{sp}(AgCl)}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.0533} = 3.41 \times 10^{-9}\ M$$

$$pAg = -\log(3.41 \times 10^{-9}) = 8.47$$

The sudden end to the sharp decrease in $[Ag^+]$ can be clearly seen in Figure 17-4 at pAg = 8.47. Further additions of silver nitrate decrease the chloride ion concentration, and the curve then becomes that for the titration of chloride by itself.

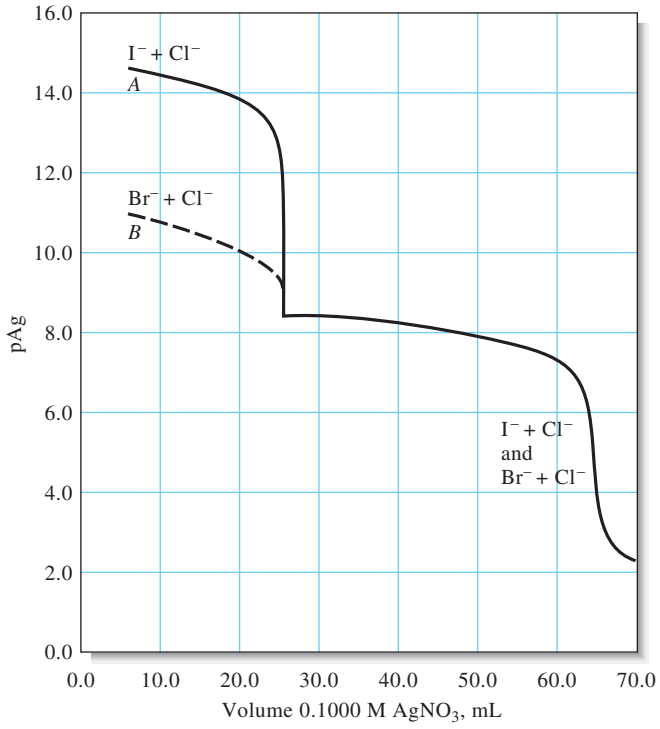


Figure 17-4 Titration curves for 50.00 mL of a solution 0.0800 M in Cl^- and 0.0500 M in I^- or Br^-.

For example, after 30.00 mL of titrant have been added,

$$c_{Cl^-} = [Cl^-] = \frac{50.00 \times 0.0800 + 50.00 \times 0.0500 - 30.00 \times 0.100}{50.00 + 30.00} = 0.0438\,M$$

In this expression, the first two terms in the numerator give the number of millimoles of chloride and iodide, respectively, and the third term is the number of millimoles of titrant. Therefore,

$$[Ag^+] = \frac{1.82 \times 10^{-10}}{0.0438} = 4.16 \times 10^{-9}\,M$$

$$pAg = 8.38$$

The remainder of the data points for this curve can be computed in the same way as for a curve of chloride by itself.

Curve *A* in Figure 17-4, which is the titration curve for the chloride/iodide mixture just considered, is a composite of the individual curves for the two anionic species. Two equivalence points are evident. Curve *B* is the titration curve for a mixture of bromide and chloride ions. Note that the change associated with the first equivalence point becomes less distinct as the solubilities of the two precipitates approach one another. In the bromide/chloride titration, the initial pAg values are lower than they are in the iodide/chloride titration because the solubility of silver bromide exceeds that of silver iodide. Beyond the first equivalence point, however, where chloride ion is being titrated, the two titration curves are identical.

Titration curves similar to those in Figure 17-4 can be obtained experimentally by measuring the potential of a silver electrode immersed in the analyte solution (see Section 21C). These curves can then be use to determine the concentration of each of the ions in mixtures of two halide ions.

End Points for Argentometric Titrations

Chemical, potentiometric, and amperometric end points are used in titrations with silver nitrate. In this section, we describe one of the chemical indicator methods. In potentiometric titrations, the potential difference between a silver electrode and a reference electrode is measured as a function of titrant volume. Titration curves similar to those shown in Figures 17-2, 17-3, and 17-4 are obtained. Potentiometric titrations are discussed in Section 21C. In amperometric titrations, the current generated between a pair of silver electrodes is measured and plotted as a function of titrant volume. Amperometric methods are considered in Section 23B-4.

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. For example, in Figure 17-3, we see that the titration of iodide with any indicator providing a signal in the pAg range of about 4.0 to 12.0 should give a satisfactory end point. Note that, in contrast, the end-point signal for the titration of chloride would be limited to a pAg of about 4.0 to 6.0.

The Volhard Method. The Volhard method is one of the most common argentometric methods. In this method, silver ions are titrated with a standard solution of thiocyanate ion:

$$Ag^+ + SCN^- \rightleftharpoons AgSCN(s)$$

Iron(III) serves as the indicator. The solution turns red with the first slight excess of thiocyanate ion due to the formation of $Fe(SCN)^{2+}$.

The most important application of the Volhard method is the indirect determination of halide ions. 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. The strongly acidic environment of the Volhard titration is a distinct advantage over other titrations of halide ions because such ions as carbonate, oxalate, and arsenate do not interfere. The silver salts of these ions are soluble in acidic media but only slightly soluble in neutral media.

Silver chloride is more soluble than silver thiocyanate. As a result, in chloride determinations using the Volhard method, the reaction

$$AgCl(s) + SCN^- \rightleftharpoons AgSCN(s) + Cl^-$$

occurs to a significant extent near the end of the back-titration. This reaction causes the end point to fade and results in overconsumption of thiocyanate ion. The resulting low results for chloride can be overcome by filtering the silver chloride before undertaking the back-titration. Filtration is not required for other halides because they form silver salts that are less soluble than silver thiocyanate.

Other Argentometric Methods. In the **Mohr method**, sodium chromate serves as the indicator for the argentometric titration of chloride, bromide, and cyanide ions. Silver ions react with chromate to form the brick-red silver chromate (Ag_2CrO_4) precipitate in the equivalence-point region. The Mohr method is now rarely used because Cr(VI) is a carcinogen.

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. Ideally, the adsorption or desorption occurs near the equivalence point and results not only in a color change but also in the transfer of color from the solution to the solid or vice versa.

Adsorption indicators were first described by K. Fajans, a Polish chemist in 1926. Titrations involving adsorption indicators are rapid, accurate, and reliable, but their application is limited to the few precipitation titrations that form colloidal precipitates rapidly.

Spreadsheet Summary In Chapter 9 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed., we plot a curve for the titration of NaCl with $AgNO_3$. A stoichiometric approach is first used and then a master equation approach is explored. Finally, the problem is inverted, and the volume needed to achieve a given pAg value is computed.

17C ORGANIC COMPLEXING AGENTS

Several different organic complexing agents have become important in analytical chemistry because of their 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.

Many organic reagents are useful in converting metal ions into forms that can be readily extracted from water into an immiscible organic phase. Extractions are widely used to separate metals of interest from potential interfering ions and for achieving a concentrating effect by transfer of the metal into a phase of smaller volume. Extractions are applicable to much smaller amounts of metals than precipitations, and they avoid problems associated with coprecipitation. Separations by extraction are considered in Section 31C.

Several of the most widely used organic complexing agents for extractions are listed in Table 17-3. Some of these same reagents normally form insoluble species

TABLE 17-3

Organic Reagents for Extracting Metals

Reagent	Metal Ions Extracted	Solvents
8-Hydroxyquinoline	Zn^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, many others	Water → Chloroform ($CHCl_3$)
Diphenylthiocarbazone (dithizone)	Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, many others	Water → $CHCl_3$ or CCl_4
Acetylacetone	Fe^{3+}, Cu^{2+}, Zn^{2+}, U(VI), many others	Water → $CHCl_3$, CCl_4, or C_6H_6
Ammonium pyrrolidine dithiocarbamate	Transition metals	Water → Methyl isobutyl ketone
Tenoyltrifluoroacetone	Ca^{2+}, Sr^{2+}, La^{3+}, Pr^{3+} other rare earths	Water → Benzene
Dibenzo-18-crown-6	Alkali metals, some alkaline earths	Water → Benzene

with metal ions in aqueous solution. However, in extraction applications, the solubility of the metal chelate in the organic phase keeps the complex from precipitating in the aqueous phase. 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, as shown in Equation 17-21.

$$n\text{HX}(org) + \text{M}^{n+}(aq) \rightleftharpoons \text{MX}_n(org) + n\text{H}^+(aq) \qquad (17\text{-}21)$$

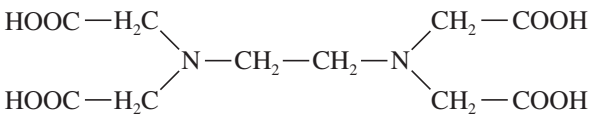
Another important application of organic complexing agents is in forming stable complexes that bind a metal and prevent it from interfering in a determination. Such complexing agents are called **masking agents** and are discussed in Section 17D-8. Organic complexing agents are also widely used in spectrophotometric determinations of metal ions (see Chapter 26). In this instance, the metal-ligand complex is either colored or absorbs ultraviolet radiation. Organic complexing agents are also commonly used in electrochemical determinations and in molecular fluorescence spectrometry.

17D AMINOCARBOXYLIC ACID TITRATIONS

Tertiary amines that also contain carboxylic acid groups form remarkably stable chelates with many metal ions.[1] Gerold Schwarzenbach, a Swiss chemist, first recognized their potential as analytical reagents in 1945. Since his original work, investigators throughout the world have described applications of these compounds to the volumetric determination of most of the metals in the periodic table.

17D-1 Ethylenediaminetetraacetic Acid (EDTA)

Ethylenediaminetetraacetic acid, which is also called (ethylenedinitrilo)tetraacetic acid and which is commonly shortened to EDTA, is the most widely used complexometric titrant. EDTA has the structural formula



Structural formula of EDTA.

[1]See for example, R. Pribil, *Applied Complexometry*, New York: Pergamon, 1982; A. Ringbom and E. Wanninen, in *Treatise on Analytical Chemistry*, 2nd ed., I. M. Kolthoff and P. J. Elving, eds., Part I, Vol. 2, Chap, 11, New York: Wiley, 1979.

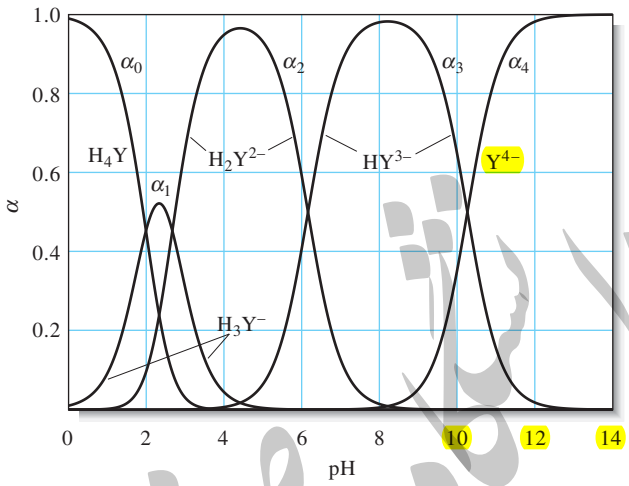


Figure 17-5 Composition of EDTA solutions as a function of pH. Note that the fully protonated form, H_4Y is only a major component in very acidic solutions (pH < 3). Throughout the pH range of 3 to 10, the species H_2Y^{2-} and HY^{3-} are predominant. The fully unprotonated form Y^{4-} is a significant component only in very basic solutions (pH > 10).

The EDTA molecule has six potential sites for bonding a metal ion: the four carboxyl groups and the two amino groups, each of the latter with an unshared pair of electrons. Thus, EDTA is a hexadentate ligand.

EDTA, a hexadentate ligand, is among the most important and widely used reagents in titrimetry.

Acidic Properties of EDTA

The dissociation constants for the acidic groups in EDTA are $K_1 = 1.02 \times 10^{-2}$, $K_2 = 2.14 \times 10^{-3}$, $K_3 = 6.92 \times 10^{-7}$, and $K_4 = 5.50 \times 10^{-11}$. Note that the first two constants are of the same order of magnitude. This similarity suggests that the two protons involved dissociate from opposite ends of the rather long molecule. Because the protons are several atoms apart, the negative charge resulting from the first dissociation does not greatly influence the removal of the second proton. Note, however, that the dissociation constants of the other two protons are much smaller and different from one another. These protons are closer to the negatively charged carboxylate ions resulting from the dissociations of the first two protons, and they are more difficult to remove from the ion because of electrostatic attraction.

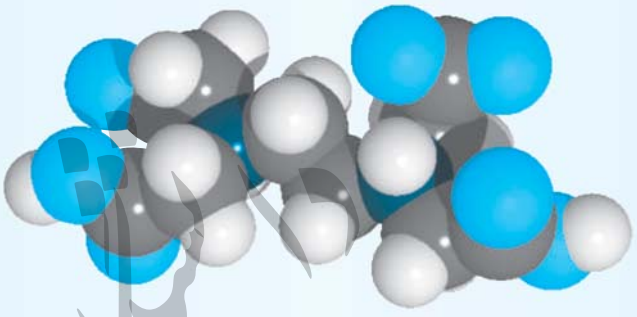
The various EDTA species are often abbreviated H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-}. Feature 17-3 describes the EDTA species and shows their structural formulas. **Figure 17-5** illustrates how the relative amounts of these five species vary as a function of pH. Note that the species H_2Y^{2-} predominates from pH 3 to 6.

FEATURE 17-3

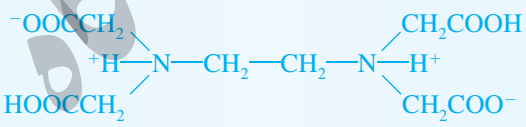
Species Present in a Solution of EDTA

When it is dissolved in water, EDTA behaves like an amino acid, such as glycine (see Features 14-5 and 15-2). With EDTA, however, a double zwitterion forms, which has the structure shown in Figure 17F-1a. Note that the net charge on this species is zero and that it contains four acidic protons, two associated with two of the carboxyl groups and the other two with the two amine groups. For simplicity, we usually abbreviate the double zwitterion as H_4Y, where Y^{4-} is the fully deprotonated form of Figure 17F-1e. The first and second steps in the dissociation process involve successive loss of protons from the two carboxylic acid groups; the third and fourth steps involve dissociation of the protonated amine groups. The structural formulas of H_3Y^-, H_2Y^{2-}, and HY^{3-} are shown in **Figure 17F-1b, c,** and **d**.

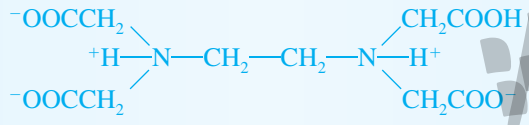
(*continued*)



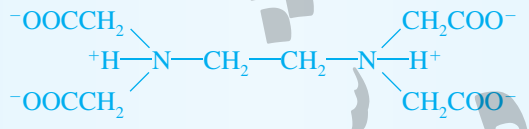
Molecular model of the H_4Y zwitterion.



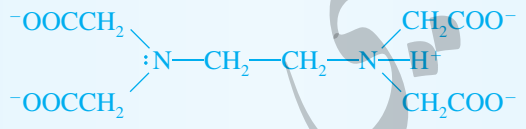
(a) H_4Y



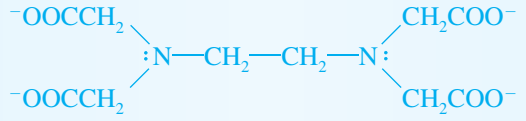
(b) H_3Y^-



(c) H_2Y^{2-}



(d) HY^{3-}



(e) Y^{4-}

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 and the dihydrate of the sodium salt, $Na_2H_2Y \cdot 2H_2O$, are commercially available in reagent quality. The free acid can serve as a primary standard after it has been dried for several hours at 130°C to 145°C. However, the free acid is not very soluble in water and must be dissolved in a small amount of base for complete solution.

More commonly, the dihydrate, $Na_2H_2Y \cdot 2H_2O$, is used to prepare standard solutions. Under normal atmospheric conditions, the dihydrate contains 0.3% moisture in excess of the stoichiometric water of hydration. For all but the most exacting work, this excess is sufficiently reproducible to permit use of a corrected mass of the salt in the direct preparation of a standard solution. If necessary, the pure dihydrate can be prepared by drying at 80°C for several days in an atmosphere of 50% relative humidity. Alternatively, an approximate concentration can be prepared and then standardized against primary standard $CaCO_3$.

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.

Several compounds that are chemically related to EDTA have also been investigated. Since these do not seem to offer significant advantages, we shall limit our discussion here to the properties and applications of EDTA.

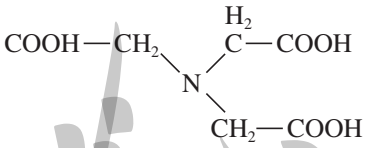
17D-2 Complexes of EDTA and Metal Ions

Solutions of EDTA are particularly valuable as titrants because the 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

$$Ag^{+} + Y^{4-} \rightleftharpoons AgY^{3-}$$

$$Al^{3+} + Y^{4-} \rightleftharpoons AlY^{-}$$

Nitrilotriacetic acid (NTA) is the second most common aminopolycarboxylic acid used for titrations. It is a tetradentate chelating agent and has the structure



Structural formula of NTA.

In general, we can write the reaction of the EDTA anion with a metal ion M^{n+} as $M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+}$.

EDTA is a remarkable reagent not only because it forms chelates with all cations but also because most of these chelates are sufficiently stable for titrations. This great stability undoubtedly results from the several complexing sites within the molecule that give rise to a cagelike structure in which the cation is effectively surrounded and isolated from solvent molecules. One of the common structures for metal/EDTA complexes is shown in **Figure 17-6**. The ability of EDTA to form complexes with metals is responsible for its widespread use as a preservative in foods and in biological samples as discussed in Feature 17-4.

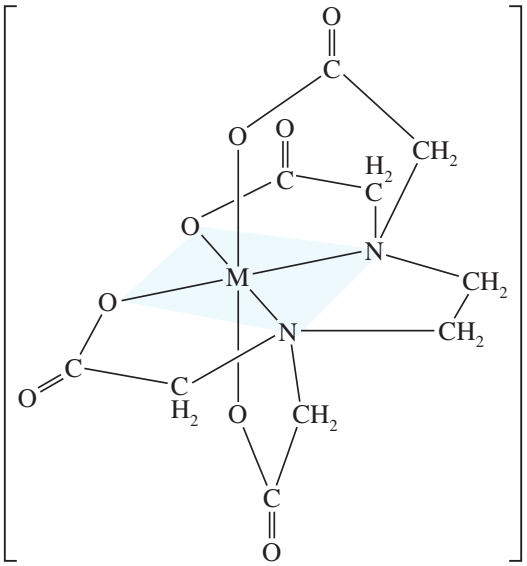


Figure 17-6 Structure of a metal/EDTA complex. Note that EDTA behaves here as a hexadentate ligand in that six donor atoms are involved in bonding the divalent metal cation.

TABLE 17-4

Formation Constants for EDTA Complexes

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

Table 17-4 lists formation constants K_{MY} for common EDTA complexes. Note that the constant refers to the equilibrium involving the fully unprotonated species Y^{4-} with the metal ion:

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+} \qquad K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}][Y^{4-}]} \tag{17-22}$$

17D-3 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. In the early stage of a titration, values for pM are readily computed by assuming that the equilibrium concentration of M^{n+} is equal to its analytical concentration, which is found from stoichiometric data.

FEATURE 17-4

EDTA as a Preservative

Trace quantities of metal ions can efficiently catalyze the air oxidation of many of the compounds present in foods and biological samples (for example, proteins in blood). To prevent such oxidation reactions, it is important to inactivate or remove even trace amounts of metal ions. Processed foods can readily pick up trace quantities of metal ions while in contact with various metallic containers (kettles and vats) during the processing stages. EDTA is an excellent preservative for foods and is a common ingredient of such commercial food products as mayonnaise, salad dressings, and oils. When EDTA is added to foods, it so tightly binds most metal ions that they are unable to catalyze the air oxidation reaction. EDTA and other similar chelating agents are often called **sequestering agents** because of their ability to remove or inactivate metal ions. In addition to EDTA, some other common sequestering agents are salts of citric and phosphoric acid. These agents can protect the unsaturated side chains of triglycerides and other components against air oxidation. Such oxidation reactions are responsible for making fats and oils turn rancid. Sequestering agents are also added to prevent oxidation of easily oxidized compounds, such as ascorbic acid.

It is important to add EDTA to preserve biological samples that are to be stored for long periods. As in foods, EDTA forms very stable complexes with metal ions and prevents them from catalyzing air oxidation reactions that can lead to decomposition of proteins and other compounds. During the murder trial of celebrity and former football player O. J. Simpson, the use of EDTA as a preservative became an important point of evidence. The prosecution team contended that if blood evidence had been planted on the back fence at his former wife's home, EDTA should be present, but if the blood were from the murderer, no preservative should be seen. Analytical evidence, obtained by using a sophisticated instrumental system (liquid chromatography combined with tandem mass spectrometry), did show traces of EDTA, but the amounts were very small and subject to differing interpretations.[2]

[2]D. Margolick, "FBI Disputes Simpson Defense on Tainted Blood," *New York Times*, July 26, 1995, p. A12.

Calculation of $[M^{n+}]$ at and beyond the equivalence point requires the use of Equation 17-22. In this region of the titration curve, it is difficult and time consuming to apply Equation 17-22 if the pH is unknown and variable because both $[MY^{(n-4)+}]$ and $[M^{n+}]$ are pH dependent. Fortunately, EDTA titrations are always performed in solutions that are buffered to a known pH to avoid interferences by other cations or to ensure satisfactory indicator behavior. Calculating $[M^{n+}]$ in a buffered solution containing EDTA is a relatively straightforward procedure provided the pH is known. In this computation, we use the alpha value for H_4Y, α_4 (see Section 15H).

$$\alpha_4 = \frac{[Y^{4-}]}{c_T} \tag{17-23}$$

where c_T is the total molar concentration of *uncomplexed* EDTA.

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

Note that, at a given pH, α_4, the fraction of total EDTA in the unprotonated form, is constant.

Conditional Formation Constants

To obtain the conditional formation constant for the equilibrium shown in Equation 17-22, we substitute $\alpha_4 c_T$ from Equation 17-23 for $[Y^{4-}]$ in the formation constant expression (right side of Equation 17-22):

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+} \qquad K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]\alpha_4 c_T} \tag{17-24}$$

Combining the two constants α_4 and K_{MY} yields the conditional formation constant K'_{MY}

$$K'_{MY} = \alpha_4 K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]c_T} \tag{17-25}$$

where K'_{MY} is a constant *only at the pH for which α_4 is applicable.*

Conditional formation constants are pH dependent.

Conditional constants are easily computed once the pH is known. They may be used to calculate the equilibrium concentration of the metal ion and the complex at the equivalence point and where there is an excess of reactant. Note that replacement of $[Y^{4-}]$ with c_T in the equilibrium-constant expression greatly simplifies calculations because c_T is easily determined from the reaction stoichiometry whereas $[Y^{4-}]$ is not.

Computing α_4 Values for EDTA Solutions

An expression for calculating α_4 at a given hydrogen ion concentration is obtained by the method given in Section 15-H (see Feature 15-3). Thus, α_4 for EDTA is

$$\alpha_4 = \frac{K_1K_2K_3K_4}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4} \tag{17-26}$$

$$\alpha_4 = \frac{K_1K_2K_3K_4}{D} \tag{17-27}$$

where K_1, K_2, K_3, and K_4 are the four dissociation constants for H_4Y, and D is the denominator of Equation 17-26.

The alpha values for the other EDTA species are calculated in a similar manner and are found to be

$\alpha_0 = [H^+]^4/D$
$\alpha_1 = K_1[H^+]^3/D$
$\alpha_2 = K_1K_2[H^+]^2/D$
$\alpha_3 = K_1K_2K_3[H^+]/D$

Only α_4 is needed in calculating titration curves.

	A	B	C	D	E
1	Cacluation of α_4 for EDTA				
2		*K* values	pH	*D* values	α_4
3	K_1	1.02E-02	1.0	1.10E-04	7.52E-18
4	K_2	2.14E-03	2.0	2.24E-08	3.71E-14
5	K_3	6.92E-07	3.0	3.30E-11	2.51E-11
6	K_4	5.50E-11	4.0	2.30E-13	3.61E-09
7			5.0	2.34E-15	3.54E-07
8			6.0	3.69E-17	2.25E-05
9			7.0	1.73E-18	4.80E-04
10			8.0	1.54E-19	5.39E-03
11			9.0	1.60E-20	5.21E-02
12			10.0	2.34E-21	0.35
13			11.0	9.82E-22	0.85
14			12.0	8.46E-22	0.98
15			13.0	8.32E-22	1.00
16			14.0	8.31E-22	1.00
17					
18					
19	Documentation				
20	Cell D3=(10^-C3)^4+B$3*(10^-C3)^3+B$3*B$4*(10^-C3)^2+B$3*B$4*B$5*(10^-C3)+B$3*B$4*B$5*B$6				
21	Cell E3=B$3*B$4*B$5*B$6/D3				

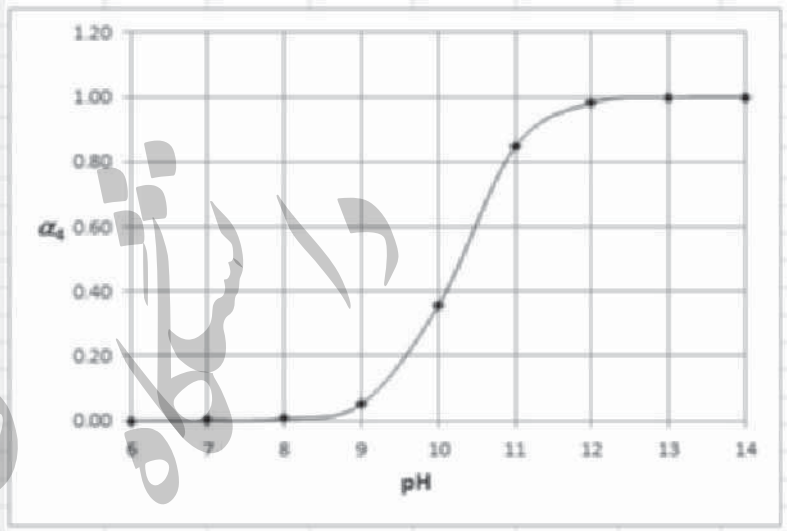


Figure 17-7 Spreadsheet to calculate α_4 for EDTA at selected pH values. Note that the acid dissociation constants for EDTA are entered in column B (labels in column A). Next the pH values for which the calculations are to be done are entered in column C. The formula for calculating the denominator *D* in Equations 17-26 and 17-27 is placed into cell D3 and copied into D4 through D16. The final column E contains the equation for calculating the α_4 values as given in Equation 17-27. The graph shows a plot of α_4 versus pH over the pH range of 6 to 14.

Figure 17-7 shows an Excel spreadsheet for calculating α_4 at selected pH values according to Equations 17-26 and 17-27. Note the wide variation of α_4 with pH. This variation allows the effective complexing ability of EDTA to be dramatically changed by varying the pH. Example 17-2 illustrates how the concentration of Y^{4-} is calculated for a solution of known pH.

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, α_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, we are interested in finding the cation concentration as a function of the amount of titrant (EDTA) added. Prior to the equivalence point, the cation is in excess, and its concentration can be found from the reaction stoichiometry. At the equivalence point and in the postequivalence-point region, however, the conditional formation constant of the complex must be used to calculate the cation concentration. Example 17-3 demonstrates how the cation concentration can be found in a solution of an EDTA complex. Example 17-4 illustrates this calculation when excess EDTA is present.

EXAMPLE 17-3

$[Ni^{2+}]=?$

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

Solution

در این محلول $[Ni^{2+}]$ از تفکیک جزئی کمپلکس ایجاد می شود.

From Table 17-4,

$$Ni^{2+} + Y^{4-} \rightleftharpoons NiY^{2-} \qquad K_{NiY} = \frac{[NiY^{2-}]}{[Ni^{2+}][Y^{4-}]} = 4.2 \times 10^{18}$$

The equilibrium concentration of 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 Ni^{2+} concentration. Thus,

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

به دلیل تفکیک جزئی کمپلکس

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

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

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

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

Substitution of this equality into Equation 17-25 gives

$$K'_{NiY} = \frac{[NiY^{2-}]}{[Ni^{2+}]c_T} = \frac{[NiY^{2-}]}{[Ni^{2+}]^2} = \alpha_4 K_{NiY}$$

(a) The spreadsheet in Figure 17-7 indicates that α_4 is 2.51×10^{-11} at pH 3.0. If we substitute this value and the concentration of NiY^{2-} into the equation for K'_{MY}, we get

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

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

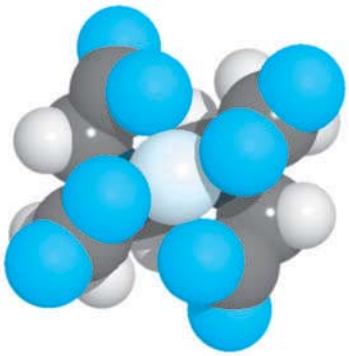
(b) At pH 8.0, α_4, and thus the conditional constant, is much larger. Therefore,

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

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

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

رابطه بین pH و پایداری کمپلکس ؟



Molecular model of NiY^{2-}. This complex is typical of the strong complexes that EDTA forms with metal ions. The formation constant of the Ni^{2+} complex is 4.2×10^{18}.

Note that for both pH 3.0 and pH 8.0, our assumption that $[Ni^{2+}] \ll 0.0150$ M is valid.

EXAMPLE 17-4

Calculate the concentration of Ni^{2+} in a solution that was prepared by mixing 50.0 mL of 0.0300 M 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 Ni^{2+} originally present. Thus,

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

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

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

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

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

$$c_T = c_{EDTA} = 0.0100\ M$$

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

مشابه مثال قبل است فقط C_T تفاوت دارد

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

Using the value of α_4 at pH 3.0 from Figure 17-7, we obtain

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

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

17D-4 EDTA Titration Curves

The principles illustrated in Examples 17-3 and 17-4 can be used to generate the titration curve for a metal ion with EDTA in a solution of fixed pH. Example 17-5 demonstrates how a spreadsheet can be used to construct the titration curve.

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 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 Ca^{2+} in cell B3 and the initial 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 α_4 value for EDTA at pH 10 (see Figure 17-7). If we substitute into Equation 17-25, we get

$$K'_{CaY} = \frac{[CaY^{2-}]}{[Ca^{2+}]c_T} = \alpha_4 K_{CaY}$$

$$= 0.35 \times 5.0 \times 10^{10} = 1.75 \times 10^{10}$$

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

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The initial $[Ca^{2+}]$ 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 $[Ca^{2+}]$ 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 Ca^{2+} is equal to the untitrated excess of the cation plus any 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,

	A	B	C	D	E
1	EDTA Titration of Ca^{2+} at pH 10.0				
2	K'_{CaY}	1.75E+10		Initial $c_{Ca^{2+}}$	0.00500
3	Vol. Ca^{2+}, mL	50.00		c_{EDTA}	0.0100
4	Vol. EDTA, mL	$[Ca^{2+}]$, M	$[CaY^{2-}]$	c_T	pCa
5	0.00	0.00500			2.30
6	5.00	3.64E-03			2.44
7	10.00	2.50E-03			2.60
8	15.00	1.54E-03			2.81
9	20.00	7.14E-04			3.15
10	24.00	1.35E-04			3.87
11	25.00	4.36E-07	0.003333		6.36
12	26.00	1.43E-09	0.003289	0.000132	8.85
13	30.00	2.86E-10	0.003125	0.000625	9.54
14	35.00	1.43E-10	0.002941	0.001176	9.85
15	40.00	9.52E-11	0.002778	0.001667	10.02
16	45.00	7.14E-11	0.002632	0.002105	10.15
17	50.00	5.71E-11	0.0025	0.002500	10.24
18	55.00	4.76E-11	0.002381	0.002857	10.32
19	60.00	4.08E-11	0.002273	0.003182	10.39
20	Documentation				
21	Cell B6=(B3*E2-A6*E3)/(B3+A6)				
22	Cell B11=SQRT(((B3*E2)/(B3+A11))/B2)				
23	Cell B12=C12/(D12*B2)				
24	Cell C11=(B3*E2)/(B3+A11)				
25	Cell D12=(A12*E3-B3*E2)/(B3+A12)				
26	Cell E5=-LOG(B5)				
27					

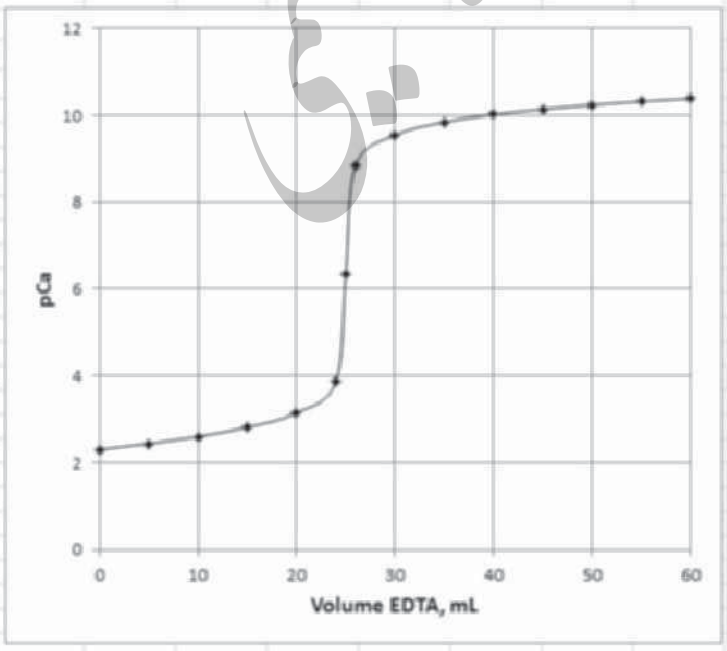

Figure 17-8 Spreadsheet for the titration of 50.00 mL of 0.00500 M Ca^{2+} with 0.0100 M EDTA in a solution buffered at pH 10.0.

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

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

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 $[Ca^{2+}]$ 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.

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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 CaY^{2-}:

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

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

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

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

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

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

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

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Postequivalence-Point pCa

Beyond the equivalence point, analytical concentrations of 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

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

$$c_{EDTA} = \frac{(26.0 \times 0.0100)\ \text{mL} - (50.0 \times 0.00500)\ \text{mL}}{76.0\ \text{mL}}$$

As an approximation,

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

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 $[CaY^{2-}]$ 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

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

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

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

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

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

Hence, the $[Ca^{2+}]$ in cell B12 is computed from the values in cells C12 and D12. We copy this formula into cells B13 through B19, and plot the titration curve shown in Figure 17-8.

Spreadsheet Summary The alpha values for EDTA are calculated and used to plot a distribution diagram in Chapter 9 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed. The titration of the tetraprotic acid EDTA with base is also considered.

Curve *A* in **Figure 17-9** is a plot of data for the titration in Example 17-5. Curve *B* is the titration curve for a solution of magnesium ion under identical conditions. The formation constant for the EDTA complex of magnesium is smaller than that

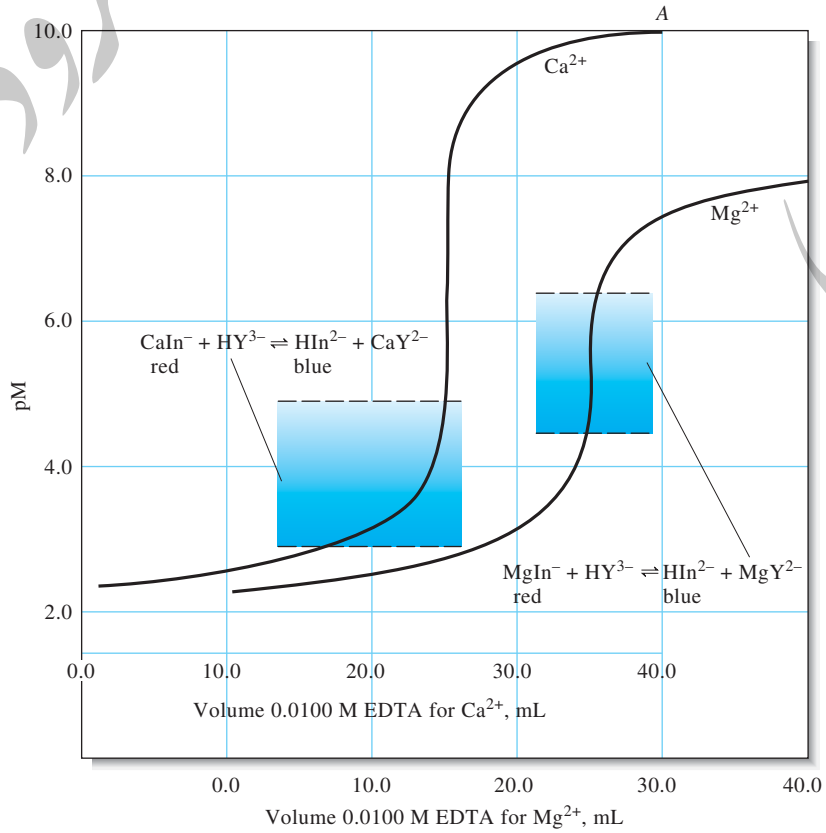

Figure 17-9 EDTA titration curves for 50.0 mL of 0.00500 M Ca^{2+} ($K'_{CaY} = 1.75 \times 10^{10}$) and Mg^{2+} ($K'_{MgY} = 1.72 \times 10^{8}$) at pH 10.0. Note that because of the larger formation constant, the reaction of calcium ion with EDTA is more complete, and a larger change occurs in the equivalence-point region. The shaded areas show the transition range for the indicator Eriochrome Black T.

اثر pH

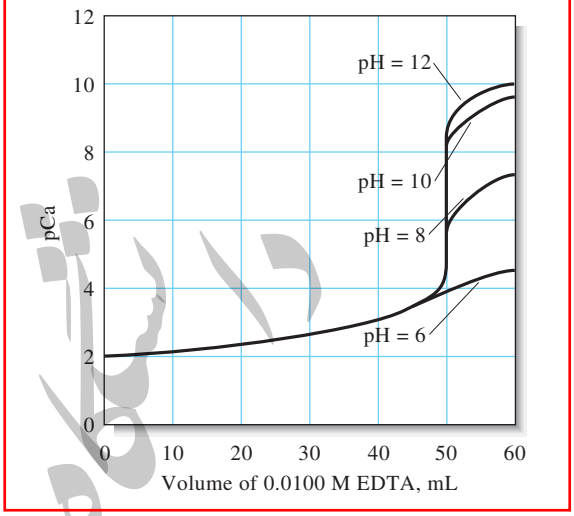

Figure 17-10 Influence of pH on the titration of 0.0100 M Ca^{2+} with 0.0100 M EDTA. Note that the end point becomes less sharp as the pH decreases because the complex-formation reaction is less complete under these circumstances.

of the calcium complex and this produces a smaller change in the p-function in the equivalence-point region.

Figure 17-10 shows titration curves for calcium ion in solutions buffered to various pH levels. Recall that α_4, and hence K'_{CaY}, becomes smaller as the pH decreases. As the conditional formation constant becomes less favorable, there is a smaller change in pCa in the equivalence-point region. Figure 17-10 shows that an adequate end point in the titration of calcium requires that the pH be greater than about 8.0. As shown in **Figure 17-11**, however, cations with larger formation constants provide sharp end points even in acidic media. If we assume that the conditional constant should be at least 10^6 to obtain a satisfactory end point with a 0.01 M solution of the metal ion, we can calculate the minimum pH needed.[3] **Figure 17-12** shows this minimum pH for a satisfactory end point in the titration of various metal ions in the absence of competing complexing agents. Note that a moderately acidic environment is satisfactory for many divalent heavy-metal cations and that a strongly acidic medium can be tolerated in the titration of such ions as iron(III) and indium(III).

Spreadsheet Summary We construct the titration curve for the titration of Ca^{2+} with EDTA by both a stoichiometric approach and a master equation approach in Chapter 9 of *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed. The effect of pH on the shape and end point of the titration curve is examined.

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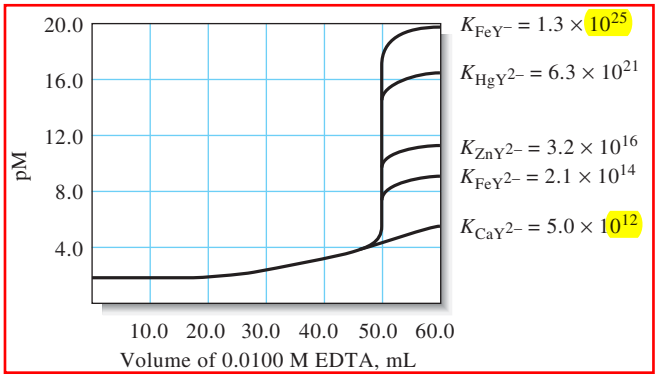


Figure 17-11 Titration curves for 50.0 mL of 0.0100 M solutions of various cations at pH 6.0.

[3] C. N. Reilley and R. W. Schmid, *Anal. Chem.*, **1958**, *30*, 947, **DOI**: 10.1021/ac60137a022

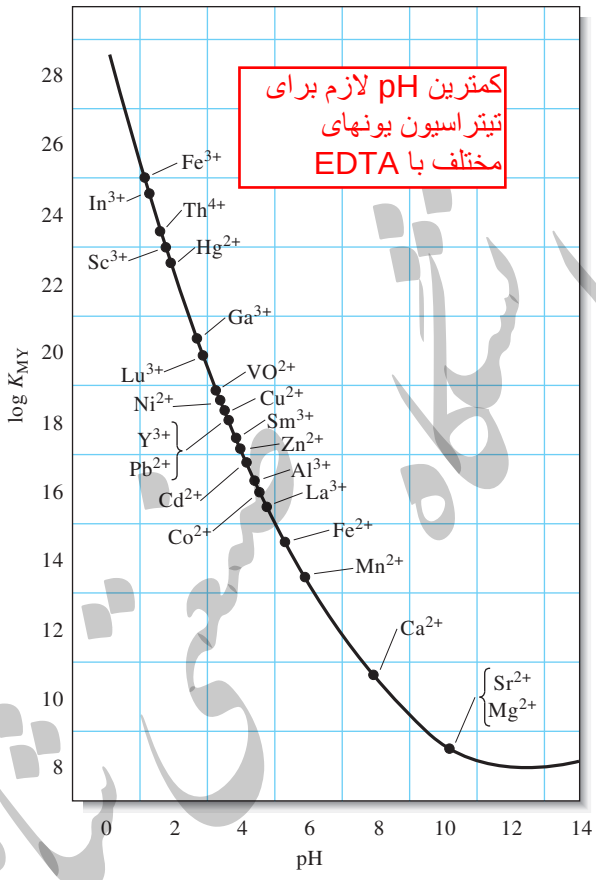


Figure 17-12 Minimum pH needed for satisfactory titration of various cations with EDTA. (Reprinted (adapted) with permission from C. N. Reilley and R. W. Schmid, *Anal. Chem.*, **1958**, *30*, 947, **DOI**: 10.1021/ac60137a022. Copyright 1958 American Chemical Society.)

17D-5 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. When we encounter this problem, an auxiliary complexing agent is needed to keep the cation in solution. For example, zinc(II) is usually titrated in a medium that has fairly high concentrations of ammonia and ammonium chloride. These species buffer the solution to a pH that ensures complete reaction between cation and titrant. In addition, ammonia forms ammine complexes with zinc(II) and prevents formation of the sparingly soluble zinc hydroxide, particularly in the early stages of the titration. A somewhat more realistic description of the reaction is then

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

Often, auxiliary complexing agents must be used in EDTA titrations to prevent precipitation of the analyte as a hydrous oxide. Such reagents cause the end points to be less sharp.

The solution also contains such other zinc/ammonia species as $Zn(NH_3)_3^{2+}$, $Zn(NH_3)_2^{2+}$ and $Zn(NH_3)^{2+}$. Calculation of pZn in a solution that contains ammonia must take these species into account as shown in Feature 17-5. Qualitatively, complexation of a cation by an auxiliary complexing reagent causes preequivalence pM values to be larger than in a comparable solution without the reagent.

Figure 17-13 shows 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. Note that, when the ammonia concentration is higher, the change in pZn near the equivalence point decreases. For this reason, the

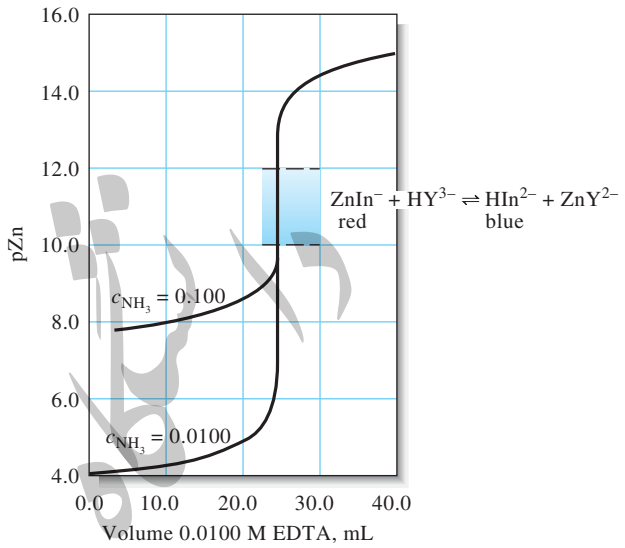


Figure 17-13 Influence of ammonia concentration on the end point for the titration of 50.0 mL of 0.00500 M Zn^{2+}. Solutions buffered to pH 9.00. The shaded region shows the transition range for Eriochrome Black T. Note that ammonia decreases the change in pZn in the equivalence-point region.

concentration of auxiliary complexing reagents should always be kept to the minimum required to prevent precipitation of the analyte. Note that the auxiliary complexing agent does not affect pZn beyond the equivalence point. On the other hand, keep in mind that α_4, and thus pH, plays an important role in defining this part of the titration curve (see Figure 17-10).

FEATURE 17-5

EDTA Titration Curves When a Complexing Agent Is Present

We can describe the effects of an auxiliary complexing reagent by a procedure similar to that used to determine the influence of pH on EDTA titration curves. In this case, we define a quantity α_M that is analogous to α_4:

$$\alpha_M = \frac{[M^{n+}]}{c_M} \tag{17-28}$$

where c_M is the sum of the concentrations of all species containing the metal ion that are *not* combined with EDTA. For solutions containing zinc(II) and ammonia, then

$$c_M = [Zn^{2+}] + [Zn(NH_3)^{2+}] + [Zn(NH_3)_2{}^{2+}] + [Zn(NH_3)_3{}^{2+}] + [Zn(NH_3)_4{}^{2+}] \tag{17-29}$$

The value of α_M can be expressed in terms of the ammonia concentration and the formation constants for the various ammine complexes as we describe for a general metal-ligand reaction in Feature 17-1. The result is an equation analogous to Equation 17-9:

$$\alpha_M = \frac{1}{1 + \beta_1[NH_3] + \beta_2[NH_3]^2 + \beta_3[NH_3]^3 + \beta_4[NH_3]^4} \tag{17-30}$$

Finally, we obtain a conditional constant for the equilibrium between EDTA and zinc(II) in an ammonia/ammonium chloride buffer by substituting Equation 17-28 into Equation 17-25 and rearranging

$$K''_{ZnY} = \alpha_4\alpha_M K_{ZnY} = \frac{[ZnY^{2-}]}{c_M c_T} \tag{17-31}$$

The new conditional constant K''_{ZnY} applies at a single concentration of ammonia as well as at a single pH.

To show how Equations 17-28 to 17-31 can be used to construct a titration curve, we can calculate the pZn of solutions prepared by adding 20.0, 25.0, and 30.0 mL of 0.0100 M EDTA to 50.0 mL of 0.00500 M Zn^{2+}. Assume that both the Zn^{2+} and EDTA solutions are 0.100 M in NH_3 and 0.175 M in NH_4Cl to provide a constant pH of 9.0.

In Appendix 4, we find that the logarithms of the stepwise formation constants for the four zinc complexes with ammonia are 2.21, 2.29, 2.36, and 2.03. Thus,

$$\beta_1 = \text{antilog } 2.21 = 1.62 \times 10^2$$

$$\beta_2 = \text{antilog } (2.21 + 2.29) = 3.16 \times 10^4$$

$$\beta_3 = \text{antilog } (2.21 + 2.29 + 2.36) = 7.24 \times 10^6$$

$$\beta_4 = \text{antilog } (2.21 + 2.29 + 2.36 + 2.03) = 7.76 \times 10^8$$

Calculating the Conditional Constant

A value for α_M can be calculated from Equation 17-30 by assuming that the molar and analytical concentrations of ammonia are the same; thus, for $[NH_3] \approx c_{NH_3} = 0.100$ M,

$$\alpha_M = \frac{1}{1 + 162 \times 0.100 + 3.16 \times 10^4 \times (0.100)^2 + 7.24 \times 10^6 \times (0.100)^3 + 7.76 \times 10^8 \times (0.100)^4}$$

$$= 1.17 \times 10^{-5}$$

A value for K_{ZnY} is found in Table 17-4, and α_4 for pH 9.0 is given in Figure 17-7. Substituting into Equation 17-31, we find

$$K''_{ZnY} = 5.21 \times 10^{-2} \times 1.17 \times 10^{-5} \times 3.12 \times 10^{16} = 1.9 \times 10^{10}$$

Calculating pZn after Adding 20.0 mL of EDTA

At this point, only part of the zinc has been complexed by EDTA. The remainder is present as Zn^{2+} and the four ammine complexes. By definition, the sum of the concentrations of these five species is c_M. Therefore,

$$c_M = \frac{50.00 \text{ mL} \times 0.00500 \text{ M} - 20.0 \text{ mL} \times 0.0100 \text{ M}}{70.00 \text{ mL}} = 7.14 \times 10^{-4} \text{ M}$$

Substitution of this value into Equation 17-28 gives

$$[Zn^{2+}] = c_M \alpha_M = (7.14 \times 10^{-4})(1.17 \times 10^{-5}) = 8.35 \times 10^{-9} \text{ M}$$

$$\text{pZn} = 8.08$$

Calculating pZn after Adding 25.0 mL of EDTA

Twenty-five milliliters is the equivalence point, and the analytical concentration of ZnY^{2-} is

$$c_{ZnY^{2-}} = \frac{50.00 \times 0.00500}{50.0 + 25.0} = 3.33 \times 10^{-3} \text{ M}$$

(*continued*)

The sum of the concentrations of the various zinc species not combined with EDTA equals the sum of the concentrations of the uncomplexed EDTA species:

$$c_M = c_T$$

And

$$[ZnY^{2-}] = 3.33 \times 10^{-3} - c_M \approx 3.33 \times 10^{-3}\ M$$

Substituting this value into Equation 17-31, we have

$$K''_{ZnY} = \frac{3.33 \times 10^{-3}}{(c_M)^2} = 1.9 \times 10^{10}$$

$$c_M = 4.19 \times 10^{-7}\ M$$

With Equation 17-28, we find that

$$[Zn^{2+}] = c_M\alpha_M = (4.19 \times 10^{-7})(1.17 \times 10^{-5}) = 4.90 \times 10^{-12}\ M$$

$$pZn = 11.31$$

Calculating pZn after Adding 30.0 mL of EDTA

Because the solution now contains excess EDTA,

$$c_{EDTA} = c_T = \frac{30.0 \times 0.0100 - 50.0 \times 0.00500}{80.0} = 6.25 \times 10^{-4}\ M$$

and since essentially all of the original Zn^{2+} is now complexed,

$$c_{ZnY^{2-}} = [ZnY^{2-}] = \frac{50.00 \times 0.00500}{80.0} = 3.12 \times 10^{-3}\ M$$

Rearranging Equation 17-31 gives

$$c_M = \frac{[ZnY^{2-}]}{c_T K''_{ZnY}} = \frac{3.12 \times 10^{-3}}{(6.25 \times 10^{-4})(1.9 \times 10^{10})} = 2.63 \times 10^{-10}\ M$$

and, from Equation 17-28,

$$[Zn^{2+}] = c_M\alpha_M = (2.63 \times 10^{-10})(1.17 \times 10^{-5}) = 3.08 \times 10^{-15}\ M$$

$$pZn = 14.51$$

17D-6 Indicators for EDTA Titrations

Nearly 200 organic compounds have been investigated as indicators for metal ions in EDTA titrations. The most common indicators are given by Dean.[4] In general, these indicators are organic dyes that form colored chelates with metal ions in a pM range that is characteristic of the particular cation and dye. The complexes are often intensely colored and can be detected visually at concentrations in the range of 10^{-6} to 10^{-7} M.

[4] J. A. Dean, *Analytical Chemistry Handbook*, New York: McGraw-Hill, 1995, p. 3.95.

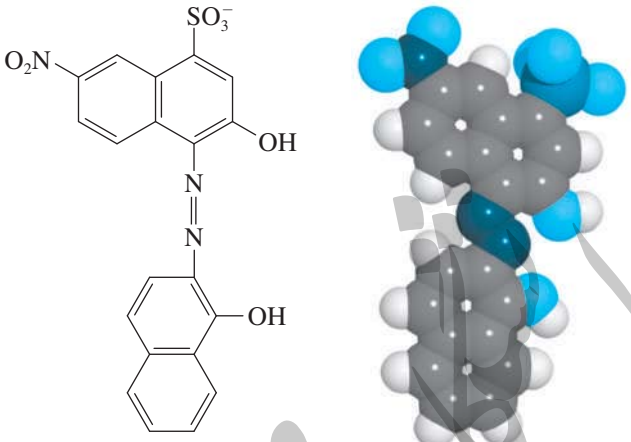


Figure 17-14 Structure and molecular model of Eriochrome Black T. The compound contains a sulfonic acid group that completely dissociates in water and two phenolic groups that only partially dissociate.

Eriochrome Black T is a typical metal-ion indicator that is used in the titration of several common cations. The structural formula of Eriochrome Black T is shown in **Figure 17-14**. Its behavior as a weak acid is described by the equations

$$\underset{}{H_2O} + \underset{\text{red}}{H_2In^-} \rightleftharpoons \underset{\text{blue}}{HIn^{2-}} + H_3O^+ \qquad K_1 = 5 \times 10^{-7}$$

$$\underset{}{H_2O} + \underset{\text{blue}}{HIn^{2-}} \rightleftharpoons \underset{\text{orange}}{In^{3-}} + H_3O^+ \qquad K_2 = 2.8 \times 10^{-12}$$

Note that the acids and their conjugate bases have different colors. Thus, Eriochrome Black T behaves as an acid/base indicator as well as a metal-ion indicator.

The metal complexes of Eriochrome Black T are generally red, as is H_2In^-. Thus, for metal-ion detection, it is necessary to adjust the pH to 7 or above so that the blue form of the species, HIn^{2-}, predominates in the absence of a metal ion. Until the equivalence point in a titration, the indicator complexes the excess metal ion so that the solution is red. With the first slight excess of EDTA, the solution turns blue as a result of the reaction

$$\underset{\text{red}}{MIn^-} + HY^{3-} \rightleftharpoons \underset{\text{blue}}{HIn^{2-}} + MY^{2-}$$

Eriochrome Black T forms red complexes with more than two dozen metal ions, but the formation constants of only a few are appropriate for end-point detection. As shown in Example 17-6, the applicability of a given indicator for an EDTA titration can be determined from the change in pM in the equivalence-point region, provided the formation constant for the metal-indicator complex is known.[5]

EXAMPLE 17-6

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

$$HIn^{2-} + H_2O \rightleftharpoons In^{3-} + H_3O^+ \qquad K_2 = \frac{[H_3O^+][In^{3-}]}{[HIn^{2-}]} = 2.8 \times 10^{-12}$$

(*continued*)

[5]C. N. Reilley and R. W. Schmid, *Anal. Chem.*, **1959**, *31*, 887, **DOI**: 10.1021/ac60137a022.

(b) that the formation constant for $MgIn^-$ is

$$Mg^{2+} + In^{3-} \rightleftharpoons MgIn^- \qquad K_f = \frac{[MgIn^-]}{[Mg^{2+}][In^{3-}]} = 1.0 \times 10^7$$

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

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 $[MgIn^-]/[HIn^{2-}]$ changes from 10 to 0.10. The product of K_2 for the indicator and K_f for $MgIn^-$ contains this ratio:

$$\frac{[MgIn^-][H_3O^+]}{[HIn^{2-}][Mg^{2+}]} = 2.8 \times 10^{-12} \times 1.0 \times 10^7 = 2.8 \times 10^{-5}$$

Substituting 1.0×10^{-10} for $[H_3O^+]$ and 10 and 0.10 for the ratio yields, the range of $[Mg^{2+}]$ over which the color change occurs is

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

$$pMg = 5.4 \pm 1.0$$

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

Transition ranges for magnesium and calcium are indicated on the titration curves in Figure 17-9. The curves show that, Eriochrome Black T is ideal for the titration of magnesium, but it is unsatisfactory for calcium. Note that the formation constant for $CaIn^-$ is only about 1/40 that for $MgIn^-$. Because of the lower formation constant, significant conversion of $CaIn^-$ to HIn^{2-} occurs well before equivalence. A similar calculation shows that Eriochrome Black T is also well suited for the titration of zinc with EDTA (see Figure 17-13).

A limitation of Eriochrome Black T is that its solutions decompose slowly with standing. Solutions of Calmagite (see **Figure 17-15**), an indicator that for all practical purposes is identical in behavior to Eriochrome Black T, do not appear to suffer this disadvantage. Many other metal indicators have been developed for EDTA

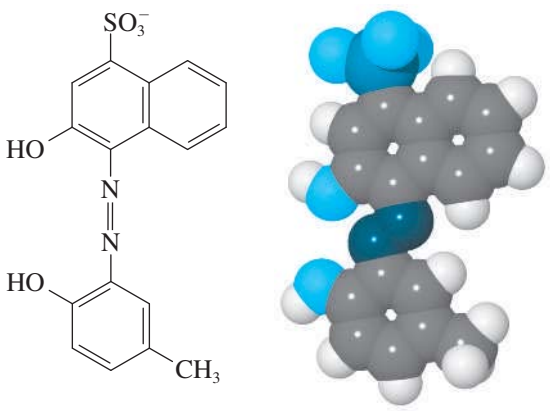


Figure 17-15 Structural formula and molecular model of Calmagite. Note the similarity to Eriochrome Black T (see Figure 17-14).

titrations.[6] In contrast to Eriochrome Black T, some of these indicators can be used in strongly acidic media.

17D-7 Titration Methods Involving EDTA

Next, we describe several different types of titration methods that can be used with EDTA.

Direct titration procedures with a metal-ion indicator that responds to the analyte are the easiest and most convenient to use. Methods that incorporate an added metal ion are also used.

Direct Titration

Many of the metals in the periodic table can be determined by titration with standard EDTA solutions. Some methods are based on indicators that respond to the analyte itself, while others are based on an added metal ion.

Methods Based on Indicators for the Analyte. Dean[7] lists nearly 40 metal ions that can be determined by direct titration with EDTA using metal-ion indicators. Indicators that respond to the metal directly cannot be used in all cases either because an indicator with an appropriate transition range is not available or because the reaction between the metal ion and EDTA is so slow as to make titration impractical.

Methods Based on Indicators for an Added Metal Ion. In cases where a good, 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. For example, indicators for calcium ion are generally less satisfactory than those we have described for magnesium ion. Consequently, a small amount of magnesium chloride is often added to an EDTA solution that is to be used for the determination of calcium. In this case, Eriochrome Black T can be used as indicator. In the initial stages of the titration, magnesium ions are displaced from the EDTA complex by calcium ions and are free to combine with the Eriochrome Black T, therefore imparting a red color to the solution. When all of the calcium ions have been complexed, however, the liberated magnesium ions again combine with the EDTA until the end point is observed. This procedure requires standardization of the EDTA solution against primary-standard calcium carbonate.

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. Electrodes of this type are described in Section 21D-1.

Spectrophotometric Methods. Measurement of UV/visible absorption can also be used to determine the end points of titrations (see Section 26A-4). In these cases, a spectrophotometer responds to the color change in the titration rather than relying on a visual determination of the end point.

Back-Titration Methods

Back-titrations 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. A measured excess of standard EDTA solution is added to the analyte solution. After the reaction is judged complete, the excess EDTA is back-titrated with a standard

[6]See, for example, J. A. Dean, *Analytical Chemistry Handbook*, New York: McGraw-Hill, 1995, pp. **3**.94–**3**.96.
[7]J. A. Dean, ibid, pp. 3.104–3.109.

magnesium or zinc ion solution to an Eriochrome Black T or Calmagite end point.[8] For this procedure to be successful, it is necessary that the magnesium or zinc ions form an EDTA complex that is less stable than the corresponding analyte complex.

Back-titration procedures are used when no suitable indicator is available, when the reaction between analyte and EDTA is slow, or when the analyte forms precipitates at the pH required for its titration.

Back-titration is also useful for analyzing samples that contain anions that could form precipitates with the analyte under the analytical conditions. The excess EDTA complexes the analyte and prevents precipitate formation.

Displacement Methods

In displacement titrations, 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:

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

where M^{2+} represents the analyte cation. The liberated Mg^{2+} or, in some cases Zn^{2+}, is then titrated with a standard EDTA solution.

17D-8 The Scope of EDTA Titrations

Complexometric titrations with EDTA have been applied to the determination of virtually every metal cation with the exception of the alkali metal ions. Because EDTA complexes most cations, the reagent might appear at first glance to be totally lacking in selectivity. In fact, however, considerable control over interferences can be realized by pH regulation. For example, trivalent cations can usually be titrated without interference from divalent species by maintaining the solution at a pH of about 1 (see Figure 17-12). At this pH, the less stable divalent chelates do not form to any significant extent, but trivalent ions are quantitatively complexed.

Similarly, 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. Eriochrome Black T serves as an indicator for the cadmium or zinc end points without interference from magnesium because the indicator chelate with magnesium is not formed at this pH.

A **masking agent** is a complexing agent that reacts selectively with a component in a solution to prevent that component from interfering in a determination.

Finally, interference from a particular cation can sometimes be eliminated by adding a suitable **masking agent**, an auxiliary ligand that preferentially forms highly stable complexes with the potential interfering ion.[9] Thus, cyanide ion is often used as a masking agent to permit the titration of magnesium and calcium ions in the presence of ions such as cadmium, cobalt, copper, nickel, zinc, and palladium. All of these ions form sufficiently stable cyanide complexes to prevent reaction with EDTA. Feature 17-6 illustrates how masking and demasking reagents are used to improve the selectivity of EDTA reactions.

[8]For a discussion of the back-titration procedure, see C. Macca and M. Fiorana, *J. Chem. Educ.*, **1986**, *63*, 121, **DOI**: 10.1021/ed063p121.

[9]For further information, see D. D. Perrin, *Masking and Demasking of Chemical Reactions*, New York: Wiley-Interscience, 1970; J. A. Dean, *Analytical Chemistry Handbook,* New York: McGraw-Hill, 1995, pp. 3.92–3.111.

FEATURE 17-6

Enhancing the Selectivity of EDTA Titrations with Masking and Demasking Agents

Lead, magnesium, and zinc can be determined in a single sample by two titrations with standard EDTA and one titration with standard Mg^{2+}. The sample is first treated with an excess of NaCN, which masks Zn^{2+} and prevents it from reacting with EDTA:

$$Zn^{2+} + 4CN^- \rightleftharpoons Zn(CN)_4^{2-}$$

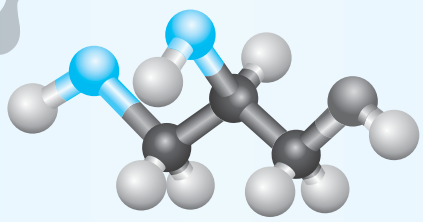
The Pb^{2+} and Mg^{2+} are then titrated with standard EDTA. After the equivalence point has been reached, a solution of the complexing agent BAL (2-3-dimercapto-1-propanol, $CH_2SHCHSHCH_2OH$), which we will write as $R(SH)_2$, is added to the solution. This bidentate ligand reacts selectively to form a complex with Pb^{2+} that is much more stable than PbY^{2-}:

$$PbY^{2-} + 2R(SH)_2 \rightarrow Pb(RS)_2 + 2H^+ + Y^{4-}$$

The liberated Y^{4-} is then titrated with a standard solution of Mg^{2+}. Finally, the zinc is demasked by adding formaldehyde:

$$Zn(CN)_4^{2-} + 4HCHO + 4H_2O \rightarrow Zn^{2+} + 4HOCH_2CN + 4OH^-$$

The liberated Zn^{2+} is then titrated with the standard EDTA solution.



Molecular model of BAL (2,3-dimercapto-1-propanol, $CH_2SHCHSHCH_2OH$).

Suppose the initial titration of Mg^{2+} and Pb^{2+} required 42.22 mL of 0.02064 M EDTA. Titration of the Y^{4-} liberated by the BAL consumed 19.35 mL of 0.007657 M Mg^{2+}. After addition of formaldehyde, the liberated Zn^{2+} was titrated with 28.63 mL of the EDTA solution. Calculate the percent of the three elements if a 0.4085-g sample was used.

$$\text{amount } (Pb^{2+} + Mg^{2+}) \text{ in mmol} = 42.22 \times 0.02064 = 0.87142$$

The second titration gives the amount of Pb^{2+}. Thus,

$$\text{amount } Pb^{2+} \text{ in mmol} = 19.35 \times 0.007657 = 0.14816$$

$$\text{amount } Mg^{2+} \text{ in mmol} = 0.87142 - 0.14816 = 0.72326$$

Finally, from the third titration, we obtain

$$\text{amount } Zn^{2+} \text{ in mmol} = 28.63 \times 0.02064 = 0.59092$$

(continued)

To obtain the percentages, we write

$$\frac{0.14816 \text{ mmol Pb} \times 0.2072 \text{ g Pb/mmol Pb}}{0.4085 \text{ g sample}} \times 100\% = 7.515\% \text{ Pb}$$

$$\frac{0.72326 \text{ mmol Mg} \times 0.024305 \text{ g Mg/mmol Mg}}{0.4085 \text{ g sample}} \times 100\% = 4.303\% \text{ Mg}$$

$$\frac{0.59095 \text{ mmol Zn} \times 0.06538 \text{ g Zn/mmol Zn}}{0.4085 \text{ g sample}} \times 100\% = 9.459\% \text{ Zn}$$

17D-9 Determination of Water Hardness

Hard water contains calcium, magnesium, and heavy metal ions that form precipitates with soap (but not detergents).

Historically, water "hardness" was defined in terms of the capacity of cations in the water to replace the sodium or potassium ions in soaps and form sparingly soluble products that cause "scum" in the sink or bathtub. Most multiply charged cations share this undesirable property. In natural waters, however, the concentrations of calcium and magnesium ions generally far exceed those of any other metal ion. Consequently, hardness is now expressed in terms of the concentration of calcium carbonate that is equivalent to the total concentration of all the multivalent cations in the sample.

The determination of hardness is a useful analytical test that provides a measure of the quality of water for household and industrial uses. The test is important to industry because hard water, on being heated, precipitates calcium carbonate, which clogs boilers and pipes.

Water hardness is usually determined by an EDTA titration after the sample has been buffered to pH 10. Magnesium, which forms the least stable EDTA complex of all of the common multivalent cations in typical water samples, is not titrated until enough reagent has been added to complex all of the other cations in the sample. Therefore, a magnesium-ion indicator, such as Calmagite or Eriochrome Black T, can serve as indicator in water-hardness titrations. Often, a small concentration of the magnesium-EDTA chelate is incorporated in the buffer or in the titrant to ensure the presence of sufficient magnesium ions for satisfactory indicator action. Feature 17-7 gives an example of a kit for testing household water for hardness.

FEATURE 17-7

Test Kits for Water Hardness

Test kits for determining the hardness of household water are available at stores selling water softeners and plumbing supplies. They usually consist of a vessel calibrated to contain a known volume of water, a packet containing an appropriate amount of a solid buffer mixture, an indicator solution, and a bottle of standard EDTA, which is equipped with a medicine dropper. A typical kit is shown in **Figure 17F-2**. The number of drops of standard reagent needed to cause a color change is counted. The EDTA solution is usually prepared with a concentration such that one drop corresponds to one grain (about 0.065 g) of calcium carbonate per gallon of water. Home

water softeners that use ion-exchange processes to remove hardness are discussed in Feature 31-2.

Figure 17F-2 Typical kit for testing household water for hardness.

WEB WORKS

The disodium salt of EDTA ($Na_2H_2Y \cdot 2H_2O$) is widely used to prepare standard EDTA solutions. The free acid is also used, but it is not very soluble in water. Use a search engine to locate the Materials Safety Data Sheets for these reagents. What are the solubilities of the two reagents in water in g/100mL? What, if any, are the health effects of these chemicals? What is the J. T. Baker Safe-T-Data™ Rating for the disodium salt. What precautions are recommended when working with these reagents in the laboratory? How should the reagents or solutions containing them be disposed?

QUESTIONS AND PROBLEMS

17-1. Define
- *(a) ligand.
- (b) chelate.
- *(c) tetradentate chelating agent.
- (d) adsorption indicator.
- *(e) argentometric titration.
- (f) conditional formation constant.
- *(g) EDTA displacement titration.
- (h) water hardness.

17-2. Why are multidentate ligands preferable to unidentate ligands for complexometric titrations?

***17-3.** Describe three general methods for performing EDTA titrations. What are the advantages of each?

17-4. Write chemical equations and equilibrium-constant expressions for the stepwise formation of
- *(a) $Ag(S_2O_3)_2^{3-}$.
- (b) $Ni(CN)_4^{2-}$.
- (c) $Cd(SCN)_3^-$.

***17-5.** Explain how stepwise and overall formation constants are related.

17-6. Write chemical formulas for the following complex ions:
- (a) hexamminezinc(II)
- (b) dichloroargentate
- (c) disulfatocuprate(II)
- (d) trioxalotoferrate(III)
- (e) hexacyanoferrate(II)

***17-7.** In what respect is the Fajans method superior to the Volhard method for the titration of chloride ion?

17-8. Briefly explain why the sparingly soluble product must be removed by filtration before you back-titrate the excess silver ion in the Volhard determination of
- (a) chloride ion.
- (b) cyanide ion.
- (c) carbonate ion.

***17-9.** Why does the charge on the surface of precipitate particles change sign at the equivalence point of a titration?

17-10. Outline a method for the determination of K^+ based on argentometry. Write balanced equations for the chemical reactions.

*17-11. Write equations in terms of the acid dissociation constants and $[H^+]$ for the highest alpha value for each of the following weak acid ligands:
(a) acetate (α_1).
(b) tartrate (α_2).
(c) phosphate (α_3).

17-12. Write conditional formation constants for 1:1 complexes of Fe(III) with each of the ligands in Problem 17-11. Express these constants in terms of the α value and the formation constant and in terms of concentrations as in Equation 17-20.

*17-13. Write a conditional overall formation constant for $[Fe(ox)_3]^{3-}$ in terms of α_2 for oxalic acid and the β value for the complex. Also express the conditional constant in terms of concentrations as in Equation 17-20.

17-14. Propose a complexometric method for the determination of the individual components in a solution containing In^{3+}, Zn^{2+}, and Mg^{2+}.

*17-15. Given an overall complex formation reaction of $M + nL \rightleftharpoons ML_n$, with an overall formation constant of β_n, show that the following relationship holds:

$$\log \beta_n = pM + npL - pML_n$$

17-16. Why is a small amount of MgY^{2-} often added to a water specimen that is to be titrated for hardness?

*17-17. An EDTA solution was prepared by dissolving 3.426 g of purified and dried $Na_2H_2Y_2 \cdot 2H_2O$ in sufficient water to give 1.000 L. Calculate the molar concentration, given that the solute contained 0.3% excess moisture (see Section 17D-1).

17-18. A solution was prepared by dissolving about 3.0 g of $NaH_2Y_2 \cdot 2H_2O$ in approximately 1 L of water and standardizing against 50.00-mL aliquots of 0.004423 M Mg^{2+}. An average titration of 30.27 mL was required. Calculate the molar concentration of the EDTA.

*17-19. A solution contains 1.569 mg of $CoSO_4$ (155.0 g/mol) per milliliter. Calculate
(a) the volume of 0.007840 M EDTA needed to titrate a 25.00-mL aliquot of this solution.
(b) the volume of 0.009275 M Zn^{2+} needed to titrate the excess reagent after addition of 50.00 mL of 0.007840 M EDTA to a 25.00-mL aliquot of this solution.
(c) the volume of 0.007840 M EDTA needed to titrate the Zn^{2+} displaced by Co^{2+} following addition of an unmeasured excess of ZnY^{2-} to a 25.00-mL aliquot of the $CoSO_4$ solution. The reaction is

$$Co^{2+} + ZnY^{2-} \rightarrow CoY^{2-} + Zn^{2+}$$

17-20. Calculate the volume of 0.0500 M EDTA needed to titrate
*(a) 29.13 mL of 0.0598 M $Mg(NO_3)_2$.
(b) the Ca in 0.1598 g of $CaCO_3$.
*(c) the Ca in a 0.4861-g mineral specimen that is 81.4% brushite, $CaHPO_4 \cdot 2H_2O$ (172.09 g/mol).
(d) the Mg in a 0.1795-g sample of the mineral hydromagnesite, $3MgCO_3Mg(OH)_2 \cdot 3H_2O$ (365.3 g/mol).
*(e) the Ca and Mg in a 0.1612-g sample that is 92.5% dolomite, $CaCO_3 \cdot MgCO_3$ (184.4 g/mol).

*17-21. The Zn in a 0.7457-g sample of foot powder was titrated with 22.57 mL of 0.01639 M EDTA. Calculate the percent Zn in this sample.

17-22. The Cr plating on a surface that measured 3.00 × 4.00 cm was dissolved in HCl. The pH was suitably adjusted, following which 15.00 mL of 0.01768 M EDTA were introduced. The excess reagent required a 4.30-mL back-titration with 0.008120 M Cu^{2+}. Calculate the average weight of Cr on each square centimeter of surface.

17-23. A silver nitrate solution contains 14.77 g of primary-standard $AgNO_3$ in 1.00 L. What volume of this solution will be needed to react with
*(a) 0.2631 g of NaCl?
(b) 0.1799 g of Na_2CrO_4?
*(c) 64.13 mg of Na_3AsO_4?
(d) 381.1 mg of $BaCl_2 \cdot 2H_2O$?
*(e) 25.00 mL of 0.05361 M Na_3PO_4?
(f) 50.00 mL of 0.01808 M H_2S?

17-24. What is the molar analytical concentration of a silver nitrate solution if a 25.00-mL aliquot reacts with each amount of solute listed in Problem 17-23?

17-25. What minimum volume of 0.09621 M $AgNO_3$ will be needed to assure an excess of silver ion in the titration of
*(a) an impure NaCl sample that weighs 0.2513 g?
(b) a 0.3462-g sample that is 74.52% (w/w) $ZnCl_2$?
*(c) 25.00 mL of 0.01907 M $AlCl_3$?

17-26. A Fajans titration of a 0.7908-g sample required 45.32 mL of 0.1046 M $AgNO_3$. Express the results of this analysis in terms of the percentage of
(a) Cl^-.
(b) $BaCl_2 \cdot H_2O$.
(c) $ZnCl_2 \cdot 2NH_4Cl$ (243.28 g/mol).

*17-27. The Tl in a 9.57-g sample of rodenticide was oxidized to the trivalent state and treated with an unmeasured excess of Mg/EDTA solution. The reaction is

$$Tl^{3+} + MgY^{2-} \rightarrow TlY^- + Mg^{2+}$$

Titration of the liberated Mg^{2+} required 12.77 mL of 0.03610 M EDTA. Calculate the percent Tl_2SO_4 (504.8 g/mol) in the sample.

17-28. An EDTA solution was prepared by dissolving approximately 4 g of the disodium salt in approximately 1 L of water. An average of 42.35 mL of this solution was required to titrate 50.00-mL aliquots of a standard

that contained 0.7682 g of $MgCO_3$ per liter. Titration of a 25.00-mL sample of mineral water at pH 10 required 18.81 mL of the EDTA solution. A 50.00-mL aliquot of the mineral water was rendered strongly alkaline to precipitate the magnesium at $Mg(OH)_2$. Titration with a calcium-specific indicator required 31.54 mL of the EDTA solution. Calculate

(a) the molar concentration of the EDTA solution.
(b) the concentration of $CaCO_3$ in the mineral water in ppm.
(c) the concentration of $MgCO_3$ in the mineral water in ppm.

*17-29. A 50.00-mL aliquot of a solution containing iron(II) and iron(III) required 10.98 mL of 0.01500 M EDTA when titrated at pH 2.0 and 23.70 mL when titrated at pH 6.0. Express the concentration of each solute in parts per million.

17-30. A 24-hr urine specimen was diluted to 2.000 L. After the solution was buffered to pH 10, a 10.00-mL aliquot was titrated with 23.57 mL of 0.004590 M EDTA. The calcium in a second 10.00-mL aliquot was isolated as $CaC_2O_4(s)$, redissolved in acid, and titrated with 10.53 mL of the EDTA solution. Assuming that 15 to 300 mg of magnesium and 50 to 400 mg of calcium per day are normal, did this specimen fall within these ranges?

*17-31. A 1.509-g sample of a Pb/Cd alloy was dissolved in acid and diluted to exactly 250.0 mL in a volumetric flask. A 50.00-mL aliquot of the diluted solution was brought to a pH of 10.0 with a NH_4^+/NH_3 buffer; the subsequent titration involved both cations and required 28.89 mL of 0.06950 M EDTA. A second 50.00-mL aliquot was brought to a pH of 10.0 with an HCN/NaCN buffer, which also served to mask the Cd^{2+}; 11.56 mL of the EDTA solution were needed to titrate the Pb^{2+}. Calculate the percent Pb and Cd in the sample.

17-32. A 0.6004-g sample of Ni/Cu condenser tubing was dissolved in acid and diluted to 100.0 mL in a volumetric flask. Titration of both cations in a 25.00-mL aliquot of this solution required 45.81 mL of 0.05285 M EDTA. Mercaptoacetic acid and NH_3 were then introduced; production of the Cu complex with the former resulted in the release of an equivalent amount of EDTA, which required a 22.85-mL titration with 0.07238 M Mg^{2+}. Calculate the percent Cu and Ni in the alloy.

*17-33. Calamine, which is used for relief of skin irritations, is a mixture of zinc and iron oxides. A 1.056-g sample of dried calamine was dissolved in acid and diluted to 250.0 mL. Potassium fluoride was added to a 10.00-mL aliquot of the diluted solution to mask the iron; after suitable adjustment of the pH, Zn^{2+} consumed 38.37 mL of 0.01133 M EDTA. A second 50.00-mL aliquot was suitably buffered and titrated with 2.30 mL of 0.002647 M ZnY^{2-} solution:

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

Calculate the percentages of ZnO and Fe_2O_3 in the sample.

*17-34. A 3.650-g sample containing bromate and bromide was dissolved in sufficient water to give 250.0 mL. After acidification, silver nitrate was introduced to a 25.00-mL aliquot to precipitate AgBr, which was filtered, washed, and then redissolved in an ammoniacal solution of potassium tetracyanonickelate(II):

$$Ni(CN)_4^{2-} + 2AgBr(s) \rightarrow 2Ag(CN)_2^- + Ni^{2+} + 2Br^-$$

The liberated nickel ion required 26.73 mL of 0.02089 M EDTA. The bromate in a 10.00-mL aliquot was reduced to bromide with arsenic(III) prior to the addition of silver nitrate. The same procedure was followed, and the released nickel ion was titrated with 21.94 mL of the EDTA solution. Calculate the percentages of NaBr and $NaBrO_3$ in the sample.

17-35. The potassium ion in a 250.0-mL sample of mineral water was precipitated with sodium tetraphenylborate:

$$K^+ + B(C_6H_5)_4^- \rightarrow KB(C_6H_5)(s)$$

The precipitate was filtered, washed, and redissolved in an organic solvent. An excess of the mercury(II)/EDTA chelate was added:

$$4HgY^{2-} + B(C_6H_4)_4^- + 4H_2O \rightarrow H_3BO_3 + 4C_6H_5Hg^+ + 4HY^{3-} + OH^-$$

The liberated EDTA was titrated with 29.64 mL of 0.05581 M Mg^{2+}. Calculate the potassium ion concentration in parts per million.

*17-36. Chromel is an alloy composed of nickel, iron, and chromium. A 0.6553-g sample was dissolved and diluted to 250.0 mL. When a 50.00-mL aliquot of 0.05173 M EDTA was mixed with an equal volume of the diluted sample, all three ions were chelated, and a 5.34-mL back-titration with 0.06139 M copper(II) was required. The chromium in a second 50.0-mL aliquot was masked through the addition of hexamethylenetetramine; titration of the Fe and Ni required 36.98 mL of 0.05173 M EDTA. Iron and chromium were masked with pyrophosphate in a third 50.0-mL aliquot, and the nickel was titrated with 24.53 mL of the EDTA solution. Calculate the percentages of nickel, chromium, and iron in the alloy.

17-37. A 0.3304-g sample of brass (containing lead, zinc, copper, and tin) was dissolved in nitric acid. The sparingly soluble $SnO_2 \cdot 4H_2O$ was removed by filtration, and the combined filtrate and washings were then diluted to 500.0 mL. A 10.00-mL aliquot was suitably buffered; titration of the lead, zinc, and copper in this aliquot required 34.78 mL of 0.002700 M EDTA. The copper in a 25.00-mL aliquot was masked with thiosulfate; the lead and zinc were then titrated with 25.62 mL of the EDTA solution. Cyanide ion was used to mask the copper and zinc in a 100-mL aliquot; 10.00 mL of the EDTA solution was needed to titrate the lead ion. Determine the composition of the brass sample; evaluate the percentage of tin by difference.

***17-38.** Calculate conditional constants for the formation of the EDTA complex of Fe^{2+} at a pH of (a) 6.0, (b) 8.0, and (c) 10.0.

17-39. Calculate conditional constants for the formation of the EDTA complex of Ba^{2+} at a pH of (a) 5.0, (b) 7.0, (c) 9.0, and (d) 11.0.

17-40. Construct a titration curve for 50.00 mL of 0.01000 M Sr^{2+} with 0.02000 M EDTA in a solution buffered to pH 11.0. Calculate pSr values after the addition of 0.00, 10.00, 24.00, 24.90, 25.00, 25.10, 26.00, and 30.00 mL of titrant.

17-41. Construct a titration curve for 50.00 mL of 0.0150 M Fe^{2+} with 0.0300 M EDTA in a solution buffered to pH 7.0. Calculate pFe values after the addition of 0.00, 10.00, 24.00, 24.90, 25.00, 25.10, 26.00, and 30.00 mL of titrant.

***17-42.** Titration of Ca^{2+} and Mg^{2+} in a 50.00-mL sample of hard water required 23.65 mL of 0.01205 M EDTA. A second 50.00-mL aliquot was made strongly basic with NaOH to precipitate Mg^{2+} as $Mg(OH)_2(s)$. The supernatant liquid was titrated with 14.53 mL of the EDTA solution. Calculate

(a) the total hardness of the water sample, expressed as ppm $CaCO_3$.
(b) the concentration of $CaCO_3$ in the sample in ppm.
(c) the concentration of $MgCO_3$ in the sample in ppm.

17-43. **Challenge Problem**: Zinc sulfide, ZnS, is sparingly soluble in most situations. With ammonia, Zn^{2+} forms four complexes, $Zn(NH_3)^{2+}$, $Zn(NH_3)_2^{2+}$, $Zn(NH_3)_3^{2+}$, and $Zn(NH_3)_4^{2+}$. Ammonia is, of course, a base, and S^{2-} is the anion of the weak diprotic acid, H_2S. Find the molar solubility of zinc sulfide in

(a) pH-7.0 water.
(b) a solution containing 0.100 M NH_3.
(c) a pH-9.00 ammonia/ammonium ion buffer with a total NH_3/NH_4^+ concentration of 0.100 M.
(d) the same solution as in part (c) except that it also contains 0.100 M EDTA.
(e) Use a search engine and locate a Materials Safety Data Sheet (MSDS) for ZnS. Determine what health hazards ZnS poses.
(f) Determine if there is a phosphorescent pigment containing ZnS. What activates the pigment to "glow in the dark"?
(g) Determine what uses ZnS has in making optical components. Why is ZnS useful for these components?