Chapter 17
Complexation & Precipitation Reactions and Titrations
Complexation and precipitation reactions are important in many areas of science and everyday life. 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 \( \times 1300 \) (top) and \( \times 4900 \) (bottom) magnification.

Black-and-white film consists of an emulsion of finely divided AgBr coated on a polymer strip. Exposure to light from SEM 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 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. This produces a visible negative image, in which 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.

\[
\text{AgBr(s)} + 2 \text{S}_2\text{O}_3^{2-} \rightarrow [\text{Ag(S}_2\text{O}_3)_2]^{3-} \text{(aq)} + \text{Br}^- \text{(aq)}
\]

Black metallic silver of the negative remains.

After the negative has been fixed, a positive image is produced by projecting light through the negative onto photographic paper.
17A Formation of complex

Many metal ions can accept unshared pairs of electrons from an anion or molecule to form coordinate covalent bonds. The molecule or ion species containing atom which donates the electrons is called a ligand or complexing agent. The ion which accepts the donated electrons is called the central ion or central atom. And the product resulting from a reaction between a metal ion and a ligand is referred to as a coordination compound or complex ion.

Central atom

[CoCl(NH₃)₅]Cl₂

Ligands (unidentate)

Ionization sphere

Coordination sphere

Metal ions are Lewis acids, ligands are Lewis bases.

Ag⁺ + 2 :C≡N:⁻ = [N≡C—Ag—C≡N]⁻

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

The number of covalent bonds that a cation tends to form with electron donors is its **coordination number**. Typical values for coordination numbers are two, four, and six. The species formed as a result of coordination can be electrically positive, neutral, or negative. For example, copper(II), which has a coordination number of four, forms a cationic ammine complex, $\text{Cu(NH}_3)_4^{2+}$; a neutral complex with glycine, $\text{Cu(NH}_2\text{CH}_2\text{COO)}_2$; and an anionic complex with chloride ion, $\text{CuCl}_4^{2+}$. 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:

$$\text{Cu}^{2+} + 2\text{H} - \text{C} - \text{C} - \text{OH} \rightarrow \text{Cu}^{2+} \text{complex with glycine.}$$
The coordination number is the maximum of atoms or groups that can combine, in the coordination sphere, with central atom. Ligands containing a single donor atom are called monodentate; those which shares more than one pair of electrons are said to be bi-, tri-, poly-dentate. The complex can have either a positive or a negative charge, or it can be neutral.

Ex.  
\[
\text{HgI}_2 + 2\text{I}^- = \text{HgI}_4^{2-}
\]
\[
[\text{Cu(H}_2\text{O)}_4]^{2+} + 4 \text{NH}_3 = [\text{Cu(NH}_3)_4]^{2+} + 4 \text{H}_2\text{O}
\]
\[
[\text{Ag(CN)}_2]^- \quad [\text{Cu(CN)}_3]^{2-} \quad [\text{Fe(SCN)}]^{2+}
\]

cf. Analogous ions such SO\textsubscript{4}\textsuperscript{2-}, CrO\textsubscript{4}\textsuperscript{2-}, are not regarded as complex.

We should remember that uncoordinated metal ions do not exist in polar solvents.

A complex can contain more than one central metal ion. In such a case a ligand which is simultaneously attached to two or more metal ions binds the metal ions into single complex. A mononuclear complex contains a single metal ion; a binuclear complex contains two central metal ions, and so forth.
## Common monodentate ligands

<table>
<thead>
<tr>
<th>Neutral</th>
<th>Anionic</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>F$^-$, Cl$^-$, Br$^-$, I$^-$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>SCN$^-$, CN$^-$</td>
</tr>
<tr>
<td>RNH$_2$(aliphatic amines)</td>
<td>OH$^-$, RCOO$^-$, S$^{2-}$</td>
</tr>
<tr>
<td>Type</td>
<td>Name</td>
</tr>
<tr>
<td>-----------------</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td>Bidentate</td>
<td>Ethylenediamine(en)</td>
</tr>
<tr>
<td>Tetradentate</td>
<td>Triethylenetetraamine (Trien)</td>
</tr>
<tr>
<td></td>
<td>Nitrilotriacetic acid (NTA)</td>
</tr>
<tr>
<td></td>
<td>ATP</td>
</tr>
<tr>
<td>Hexadentate</td>
<td>Ethylenediaminetetraacetic acid (EDTA)</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cyclohexanediaminetetraacetic acid (CDTA)</td>
</tr>
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<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Octadentate</td>
<td>Diethylenetriaminepentaacetic acid (DTPA)</td>
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<td></td>
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</tbody>
</table>
# Classification of molecular complexes

<table>
<thead>
<tr>
<th>I. Type of bonding or interaction</th>
<th>III. Type of structure of complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge transfer</td>
<td>Self associated aggregate</td>
</tr>
<tr>
<td>Hydrogen bonding</td>
<td>Micelle</td>
</tr>
<tr>
<td>Hydrophobic interaction</td>
<td>Inclusion complex</td>
</tr>
<tr>
<td>Stacking interaction</td>
<td>Clathrate</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>II. Type or structure of interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small molecule-small molecule complex</td>
</tr>
<tr>
<td>Small molecule-macromolecule complex</td>
</tr>
<tr>
<td>Drug-protein binding</td>
</tr>
<tr>
<td>Enzyme-substrate complex</td>
</tr>
<tr>
<td>Drug-receptor complex</td>
</tr>
<tr>
<td>Antigen-antibody complex</td>
</tr>
</tbody>
</table>
Macrocycles: Cyclic organic compounds

Molecular model of 18-crown-6. This crown ether can form strong complexes with alkali metal ions. The formation constant of the $\text{Na}^+$, $\text{K}^+$ and $\text{Rb}^+$ complexes are in the $10^5$ to $10^6$ range.
Crown Ethers are cyclic polyethers discovered by Pederson in 1967. Structures of three typical ethers are given below. The common names of these ethers include a number as a prefix to designate the total number of atoms in the ring and a number as a suffix to designate the number of oxygen atoms in the ring. Thus, 15-crown-5 is comprised of 15 atoms in the ring, 5 of which are O and 10 of which are C. Pederson shared the Nobel Prize in Chemistry in 1987 with Cram and Lehn for work in this area.

The characteristic chemistry of crown ethers involves complexation of the ether oxygens with various ionic species. This is termed "host-guest" chemistry, with the ether as host and the ionic species as guest. Crown ethers may be used as phase-transfer catalysts and as agents to promote solubility of inorganic salts in organic solutions.

Crown Ether Complexation

Martin Jones
http://www.molecules.org/experiments/jones/jones.html
The cyclodextrine molecule. Topology of the β-cyclodextrin (7-membered sugar ring molecule) ring.

No hydroxyl group is present within the toroid cavity which, accordingly, has a hydrophobic character. As a consequence, the ability of the BCD to form inclusion complexes in aqueous solution derives from its cavity, the interior of which is less polar than water.
17A-1 Complexation Equilibria

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

\[ M + L \rightleftharpoons ML \]  \hspace{1cm} (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:

\[ ML + L \rightleftharpoons ML_2 \]  \hspace{1cm} (17-2)

\[ ML_2 + L \rightleftharpoons ML_3 \]  \hspace{1cm} (17-3)

\[ \vdots \]

\[ ML_{n-1} + L \rightleftharpoons ML_n \]  \hspace{1cm} (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$_3$)$_2^{2+}$, Cu(NH$_3$)$_3^{2+}$, Cu(NH$_3$)$_4^{2+}$, and Cu(NH$_3$)$_4^{2+}$. With the bidentate ligand glycine (gly), the only complexes that form are Cu(gly)$_2^{2+}$ and Cu(gly)$_3^{2+}$.

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.
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.

\[
Cd(H_2O)_6^{2+} \quad \text{with two molecules of ethylenediamine}
\]

\[
Cd(H_2O)_6^{2+} + 2H_2N\cdot\cdot\cdotNH_2 \Leftrightarrow \left(\begin{array}{cc}
\text{H}_2N & \text{H}_2N \\
\text{N} & \text{N} \\
\text{H}_2 & \text{H}_2 \\
\end{array}\right)_{2+} + 4H_2O
\]

\[\Delta H = -55.6 \text{KJ/mol}\]
\[\Delta S = -2 \text{J/(mol K)}\]

\[K = 8 \times 10^9\]

A reaction is favorable if \(\Delta G < 0\).

\[
Cd(H_2O)_6^{2+} \quad \text{with four molecules of methylamine}
\]

\[
Cd(H_2O)_6^{2+} + 4CH_3\cdot\cdot\cdotNH_2 \Leftrightarrow \left(\begin{array}{cc}
\text{H}_3CNH_2 & \text{H}_2NCH_3 \\
\text{H}_3CNH_2 & \text{H}_2NCH_3 \\
\text{OH}_2 & \text{OH}_2 \\
\end{array}\right)_{2+} + 4H_2O
\]

\[\Delta H = -58 \text{ KJ/mol}\]
\[\Delta S = -71 \text{ J/(mol K)}\]

\[K = 4 \times 10^6\]
The Chelate Effect

A central metal ion bonds to a multidentate ligand in more than one location to form a ring structure. Such compounds are called chelates. Generally, ring formation results in increased stability of the complex. This generalization is called the **chelate effect**. The stability of the multidendate complex is mainly an **entropy effect**.

① The chelate effect is the ability of multidentate ligands to form more stable metal complexes than those formed by similar monodentate ligands.

② The chelate effect can be understood from thermodynamics. The two tendencies that drive a chemical reaction are decreasing enthalpy and increasing entropy
We can also write the equilibria as the sum of individual steps. These have **overall formation constants** designated by the symbol $\beta_n$. Therefore,

\[
\begin{align*}
M + L & \rightleftharpoons ML & \beta_1 &= \frac{[ML]}{[M][L]} = K_1 & (17-5) \\
M + 2L & \rightleftharpoons ML_2 & \beta_2 &= \frac{[ML_2]}{[M][L]^2} = K_1K_2 & (17-6) \\
M + 3L & \rightleftharpoons ML_3 & \beta_3 &= \frac{[ML_3]}{[M][L]^3} = K_1K_2K_3 & (17-7) \\
\vdots & & & \vdots & \\
M + nL & \rightleftharpoons ML_n & \beta_n &= \frac{[ML_n]}{[M][L]^n} = K_1K_2 \cdots K_n & (17-8)
\end{align*}
\]

Except for the first step, the overall formation constants are products of the stepwise formation constants for the individual steps leading to the product.
For a given species like the free metal M, we can calculate an alpha value, which is the fraction of the total metal concentration in that form. Thus, $\alpha_M$ is the fraction of the total metal present at equilibrium in the free metal form, $\alpha_{ML}$ is the fraction in the ML form, and so on. As derived in Feature 17-1, the alpha values are given by

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

(17-9)

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

(17-10)

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

(17-11)

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

(17-12)
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

\[
c_M = [M] + \beta_1[M][L] + \beta_2[M][L]^2 + \cdots + \beta_n[M][L]^n
\]

\[
= [M]\{1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_n[L]^n\}
\]
Now, \( \alpha_M \) can be found as

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

Note that the form on the right is Equation 17-9. We can find \( \alpha_{ML} \) from

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

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 \( a \) 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 \( a \) value. Plots of the \( a \) values versus \( p[L] \) are known as distribution diagrams.
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 $\text{Cl}^-$ to $\text{Ag}^+$ results in the insoluble $\text{AgCl}$ precipitate. Addition of a large excess of $\text{Cl}^-$ produces soluble species $\text{AgCl}_2^-$, $\text{AgCl}_3^{2-}$, and $\text{AgCl}_4^{3-}$.

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

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

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

The formation of soluble complexes can be used to control the concentration of free metal ions in solution and thus control their reactivity. For example, we can prevent a metal ion from precipitating or taking part in another reaction by forming a stable complex, which decreases the free metal-ion concentration. The control of solubility by complex formation is also used to achieve the separation of one metal ion from another. If the ligand is capable of protonation, as discussed in the next section, even more control can be accomplished by a combination of complexation and pH adjustment.
**12A-3  Ligands that can protonate**

**Complexation with protonating ligands**

Fe$^{3+}$ ions form complexes with oxalate ($C_2O_4^{2-}$ : Ox$^{2-}$) with formulas (FeOx)$^+$, (FeOx$_2$)$^-$ and (FeOx$_3$)$^{3-}$. Oxalic acid can protonate to form HOx$^-$ and H$_2$Ox.

\[
C_T = [H_2Ox] + [HOx^-] + [Ox^{2-}] \quad (17-14)
\]

\[
\alpha_0 = [H_2Ox] / C_T = [H^+]^2 / \{[H^+] + K_{a1}[H^+] + K_{a1}K_{a2} \} \quad (17-15)
\]

\[
\alpha_1 = [HOx^-] / C_T = K_{a1}[H^+]^2 / \{[H^+] + K_{a1}[H^+] + K_{a1}K_{a2} \} \quad (17-16)
\]

\[
\alpha_2 = [Ox^{2-}] / C_T = K_{a1}K_{a2} / \{[H^+] + K_{a1}[H^+] + K_{a1}K_{a2} \} \quad (17-17)
\]

\[
[Ox^{2-}] = C_T \alpha_2 \quad (17-18)
\]

**Conditional formation constant ; effective formation constant**

\[
K_{f1} = [FeOx^+] / [Fe^{3+}][Ox^{2-}] = [FeOx^+] / [Fe^{3+}] C_T \alpha_2 \quad (17-19)
\]

\[
K_{f1}' = [FeOx^+] / [Fe^{3+}] C_T = 1 / K_{f1} \alpha_2 \quad (17-20)
\]

At any given pH, we can find $\alpha_2$ and $K_{f1}'$.

$K_{f}'$ is the effective formation constant at the fixed pH of the solution.
17B  Titrations with Inorganic Complexing Agents

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).
The advantage of a single-step reaction is illustrated by the titration curves shown in Figure 17-1. 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.

**Figure 17-1** Titration curves for complexometric titrations. Titration of 60.0 ml of a solution that is 0.020M in M with

A) A 0.020M solution of the tetridentate ligand D to give MD as the product;

B) A 0.040M solution of the bidentate ligand B to give MB₂;

C) A 0.080M solution of the unidentate ligand A to give MA₄.

The overall formation constant for each product is $10^{20}$. 
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.
Acrylonitrile, \( \text{CH}_2\text{=CH-C\equiv N} \), is an important chemical in the production of poly-acrylonitrile. 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 \( \text{AgNO}_3 \). The titration reaction is

\[
\text{Ag}^+ + 2\text{CN}^- \rightarrow \text{Ag(CN)}_2^-
\]

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 \( \text{Ag}^+ \) is complexed. As soon as all the cyanide has been reacted, the first excess of \( \text{Ag}^+ \) causes a permanent turbidity to appear in the solution because of the formation of the \( \text{AgI} \) precipitate according to

\[
\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI}(s)
\]
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 halogenlike anions, mercaptans, fatty acids, and several divalent inorganic anions. Titrations with silver nitrate are sometimes called argentometric titrations.

**Precipitation titration**

Precipitation titrations are based on precipitation of the analyte with a precipitant.

**Precipitation**:

Precipitation is the conversion of a dissolved substance into insoluble form by chemical or physical means.
Ex. \( Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4 \) (white)

Detection of end point in precipitation titrations:

1) *Turbidimetry*:
   - stabilizer (glycerol-alcohol mixture)

2) *Indicator*:
   - rhodizonate + \( Ba^{2+} \) → Red ppt

*Turbidimetry*: The intensity (T) of light scattered by particles of precipitate is measured.
The shapes of a precipitation titration curve

**Titration curve**: a graph showing how the concentration, $pX$ of one the reactants varies as titrant is added

$$pX = - \log A_X = - \log[X] f_X$$

**Ex.**

\[0.05000M \text{ Ag}^+\]  

\[0.1000M \text{ I}^- \quad 25.00 \text{ ml}\]

Titration reaction:

\[\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI} \downarrow \quad K = (1 / K_{sp}) = 1.2 \times 10^{16}\]

\[K_{sp} = [\text{Ag}^+][\text{I}^-] = 8.3 \times 10^{-17}\]

**Equivalence point**:

\[0.05000M \times V_e \text{ ml} = 0.10000M \times 25.00\text{ml}\]

\[V_e = 50.00 \text{ ml} \quad K_{sp} = [\text{Ag}^+][\text{I}^-] = x^2 = 8.3 \times 10^{-17}\]

\[[\text{Ag}^+] = [\text{I}^-] = x = 9.1 \times 10^{-9} \quad p\text{Ag}^+ = 8.04\]

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 $p\text{Ag}$ versus volume of the silver reagent (usually AgNO$_3$).
Before the equivalence point: $V < V_e$

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{I}^-]} = \frac{8.3 \times 10^{-17}}{[\text{I}^-]}$$

$$[\text{I}^-] = \text{(fraction remaining) (original concentration) (dilution factor)}$$

$$= \frac{(V_e - V)}{V_e} [M] \frac{[V_i]}{(V_i + V)}$$

if $V = 10.00\text{ml}$,

$$[\text{I}^-] = \frac{(50.00 - 10.00)}{50.00} (0.1000\text{M}) \frac{25.00}{(25.00 + 10.00)} = 0.05714 \text{M}$$

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{I}^-]} = \frac{8.3 \times 10^{-17}}{0.05714} = 1.45 \times 10^{-15}$$

$$\therefore p\text{Ag}^+ = 14.84$$

After the equivalence point: $V > V_e$

$$[\text{Ag}^+] = \text{(original concentration) (dilution factor)}$$

$$= [M] \frac{(V - V_e)}{(V_i + V)}$$

if $V = 52.00\text{ml}$,

$$[\text{Ag}^+] = 0.05000\text{M} \times \frac{(52.00 - 50.00)}{(25.00 + 52.00)} = 1.30 \times 10^{-3}$$

$$\therefore p\text{Ag}^+ = 2.89$$
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 AgNO₃ after the addition of the following volumes of reagent: (a) in the pre-equivalence 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) Pre-equivalence-Point Data

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

$$[\text{Cl}^-] \approx c_{\text{NaCl}} = \frac{\text{original no. mmol Cl}^- - \text{no. mol AgNO}_3 \text{ added}}{\text{total volume of solution}}$$

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

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

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

Additional points in the pre-equivalence-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.
(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 AgNO₃, Ag⁺ is in excess so

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

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

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.

Reagent concentration

\[ [T], [A] \uparrow \Rightarrow e_T \downarrow \]

**Figure 17-2** Titration curve for
(A), 50.00 mL of 0.05000 M NaCl titrated with 0.1000 M AgNO₃, and
(B), 50.00 mL of 0.00500 M NaCl Titrated with 0.01000 M AgNO₃.
Note the **increased sharpness of the break at the end point with the more concentrated solution.**
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,

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

\[pK_{sp} = pAg + pCl\]
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 AgNO₃. Note that smaller values of $K_{sp}$ give much sharper breaks at the end point.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgI</td>
<td>$8.3 \times 10^{-17}$</td>
</tr>
<tr>
<td>AgBr</td>
<td>$5.0 \times 10^{-13}$</td>
</tr>
<tr>
<td>AgCl</td>
<td>$1.8 \times 10^{-10}$</td>
</tr>
<tr>
<td>AgIO₃</td>
<td>$3.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>AgBrO₃</td>
<td>$5.7 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Titration curves for mixtures of anion

Titrant (ex. Ag⁺)

Two precipitable ions
(ex. Cl⁻, I⁻)

Ex. 0.0500 M KI + 0.0800 M KCl
0.1000 M AgNO₃

\[ K_{sp \ AgI} \ll K_{sp \ AgCl} \]

\[ 8.3 \times 10^{-17} \quad 1.82 \times 10^{-10} \]

Coprecipitation

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

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

Figure 17-4 Titration curves for 50.0 ml of a solution 0.0800 M in Cl⁻ and 0.0500 M in I⁻ or Br⁻.
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

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

Substituting into the previous equation yields

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

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

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

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

percentage \( I^- \) unprecipitated = \[ \frac{1.82 \times 10^{-6}}{2.50} \times 100\% = 7.3 \times 10^{-5}\\% \]

Thus, to within about \( 7.3 \times 10^{-5} \) 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.
Thus, to within about $7.3 \times 10^{-5}$ 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):

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

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

The sudden end to the sharp decrease in $[\text{Ag}^+]$ 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.
For example, after 30.00 mL of titrant have been added,

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

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,

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

\[ p\text{Ag} = 8.38 \]

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

Detection techniques in precipitation titrations:

! Indicator ≡ Potentiometry  # Light scattering / turbidimetry of nephelometry

<table>
<thead>
<tr>
<th>Titration</th>
<th>Mohr</th>
<th>Volhard</th>
<th>Fajans</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration</td>
<td>$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \downarrow$</td>
<td>$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \downarrow$</td>
<td>$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \downarrow$</td>
</tr>
<tr>
<td>reaction</td>
<td>white</td>
<td>Back titration:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Ag}^+ + \text{SCN}^- \rightarrow \text{AgSCN} \downarrow$</td>
<td></td>
</tr>
<tr>
<td>End point</td>
<td>$2\text{Ag}^+ + \text{CrO}_4^{2-} \rightarrow \text{Ag}_2\text{CrO}_4 \downarrow$</td>
<td>$\text{SCN}^- + \text{Fe}^{3+} \rightarrow \text{FeSCN}^{2+}$</td>
<td>Electric double layer</td>
</tr>
<tr>
<td>reaction</td>
<td>red</td>
<td>soluble red</td>
<td>with adsorption Ind.</td>
</tr>
<tr>
<td></td>
<td>pH 7~10.5</td>
<td>K_f = $1.05 \times 10^3$</td>
<td>Dichlorofluorescein</td>
</tr>
<tr>
<td>Use</td>
<td>Cl$^-$, Br$^-$, CN$^-$</td>
<td>Cl$^-$, Br$^-$, I$^-$</td>
<td>Cl$^-$, Br$^-$, I$^-$, SCN$^-$</td>
</tr>
<tr>
<td>No use</td>
<td>I$^-$, SCN$^-$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Mohr method

AgCl $=\text{Ag}^+ + \text{Cl}^-$

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

$[\text{Ag}^+] = 1.35 \times 10^{-5}$ M

Ag$_2$CrO$_4 = 2\text{Ag}^+ + \text{CrO}_4^{2-}$

$[\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = K_{sp} = 1.2 \times 10^{-12}$

$[\text{CrO}_4^{2-}] = \frac{K_{sp}}{[\text{Ag}^+]^2} = \frac{1.2 \times 10^{-12}}{(1.35 \times 10^{-5})^2}$

$= 6.6 \times 10^{-3}$ M

Volhard method

Fe$^{3+} + \text{SCN}^- \leftrightarrow \text{FeSCN}^{2+}$ (red)

$K_f = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}] [\text{SCN}^-]} = 1.05 \times 10^3$
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.
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 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.

\[
nHX(\text{org}) + M^{n+}(aq) \rightleftharpoons MX_n(\text{org}) + nH^+(aq) \tag{17-21}
\]

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 titration

17D-1  EDTA  📝

Ethylenediaminetetraacetic acid (EDTA) is a hexadentate ligand

Hexatropic system:  $H_6Y^{2+}$  EDTA disodium salt  $Na_2H_2Y\cdot2H_2O$

$pK_1 = 0.0$

$pK_2 = 1.5$  Carbonyl protons

$pK_3 = 2.0$

$pK_4 = 2.66$

$pK_5 = 6.16$  Ammonium protons

$pK_6 = 10.24$
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).
Figure 17F-1 Structure of $\text{H}_4\text{Y}$ and its dissociation products. Note that the fully protonated species $\text{H}_4\text{Y}$ 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 $\text{H}_4\text{Y}$ and the dihydrate of the sodium salt, $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$, 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, $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$, 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 $\text{CaCO}_3$.

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

![Structural formula of NTA.](https://example.com/structural_formula.png)
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

\[
\text{Ag}^+ + Y^{4-} \rightleftharpoons \text{AgY}^{3-}
\]
\[
\text{Al}^{3+} + Y^{4-} \rightleftharpoons \text{AlY}^{-}
\]

In general, we can write the reaction of the EDTA anion with a metal ion \( M^{n+} \) as

\[
M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+}
\]

\[
K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}][Y^{4-}]} \quad (17-22)
\]
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.
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

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.

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 $H_4Y$, $\alpha_4$ (see Section 15H).

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

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, $\alpha_4$, 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):

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

Combining the two constants $\alpha_4$ 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 $\alpha_4$ is applicable.

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.

At any given pH, we can find $\alpha_4$ and $K'_{MY}$.

$K'_{MY}$ is the conditional formation constant at the fixed pH of the solution.
Computing $\alpha_4$ Values for EDTA Solutions

An expression for calculating $\alpha_4$ at a given hydrogen ion concentration is obtained by the method given in Section 15-H (see Feature 15-3). Thus, $\alpha_4$ for EDTA is

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

$$\alpha_4 = \frac{K_1K_2K_3K_4}{D} \quad (17-27)$$

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

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

Only $\alpha_4$ is needed in calculating titration curves.
Figure 17-7  Spreadsheet to calculate $\alpha_4$ 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 $\alpha_4$ values as given in Equation 17-27. The graph shows a plot of $\alpha_4$ versus pH over the pH range of 6 to 14. Note the wide variation of $\alpha_4$ with pH. This variation allows the effective complexing ability of EDTA to be dramatically changed by varying the 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, $\alpha_4$ is 0.35 (see Figure 17-7). Thus,

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

Example 17-2 illustrates how the concentration of $Y^{4-}$ is calculated for a solution of known pH.
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
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.

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 \(4.2 \times 10^{18}\).

**Solution**
From Table 17-4,

\[ \text{Ni}^{2+} + \text{Y}^{4-} \rightleftharpoons \text{NiY}^{2-} \]

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

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,

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

\[
[\text{NiY}^{2-}] \approx 0.0150
\]

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

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

Substitution of this equality into Equation 17-25 gives

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

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

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

\[
[\text{Ni}^{2+}] = \sqrt{1.43 \times 10^{-10}} = 1.2 \times 10^{-5} \text{ M}
\]
(b) At pH 8.0, $\alpha_4$, and thus the conditional constant, is much larger. Therefore,

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

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

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

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

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

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

Again, we will assume that [Ni\(^{2+}\)] \(\ll\) [Ni\(^{2+}\)] so that

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

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

\[
c_T = c_{\text{EDTA}} = 0.0100 \text{ M}
\]
If we substitute this value in Equation 17-25, we get

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

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

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

Note again that our assumption that \([\text{Ni}^{2+}] \ll [\text{NiY}^{2-}]\) is valid.
EXAMPLE 17-5

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

Titration reaction:

\[
Ca^{2+} + \text{EDTA} \rightleftharpoons Ca\text{Y}^{2-}
\]

\[
K'_{CaY} = \frac{[Ca\text{Y}^{2-}]}{[Ca^{2+}][\text{EDTA}]} = \frac{[Ca\text{Y}^{2-}]}{[Ca^{2+}]C_T} = \alpha_4 K_{CaY}
\]

\[
= 0.36 \times (5.0 \times 10^{10}) = 1.75 \times 10^{10}
\]

Equivalence point:

\[
0.00500 \text{ M} \times 50 \text{ mL} = 0.0100 \text{ M} \times V_e \text{ mL}
\]

\[
V_e = 25.0 \text{ mL}
\]
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 \(\alpha_4\) value for EDTA at pH 10 (see Figure 17-7). If we substitute into Equation 17-25, we get

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

\[
= 0.35 \times 5.0 \times 10^{10} = 1.75 \times 10^{10}
\]

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.
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.
Preequivalence-Point Values for pCa

The initial \([Ca^{2+}]\) at 0.00 mL titrant is just the value in cell E2. Hence, \(=\text{E2}\) 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,

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

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

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.
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 $K'_{CaY}$

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

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

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

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

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

As an approximation,

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

We note that this expression is the same as that previously entered into cell C11. Therefore, we copy that equation into cell C12. We also note that \([\text{CaY}^{2-}]\) will be given by this same expression (with the volume varied) throughout the remainder of the titration. Hence, the formula in cell C12 is copied into cells C13 through C19. Also, we approximate
\[ c_T = c_{\text{EDTA}} + [\text{Ca}^{2+}] \approx c_{\text{EDTA}} = \frac{(26.0 \times 0.0100) \text{ mL} - (50.0 \times 0.00500) \text{ mL}}{76.0 \text{ mL}} \]

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

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

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

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

Hence, the \([\text{Ca}^{2+}]\) 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.
Figure 17-9  EDTA titration curves for 50.0 mL of 0.00500 M Ca\(^{2+}\)
\((K'_{\text{CaY}} = 1.75 \times 10^{10})\) and Mg\(^{2+}\)
\((K'_{\text{MgY}} = 1.72 \times 10^{8})\) 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.
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.
Figure 17-11 Titration curves for 50.0 mL of 0.0100 M solutions of various cations at pH 6.0. Cations with larger formation constants provide sharp end points even in acidic media. 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.
Figure 17-12 Minimum pH needed for satisfactory titration of various cations with EDTA.
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.

At pH 10.00

\[
\text{Zn}^{2+} + 2 \text{OH}^- \rightarrow \text{Zn(OH)}_2 \downarrow \text{(ppt)} \quad \text{Ksp} = 3.0 \times 10^{-16}
\]

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

\[
\text{Zn(NH}_3\text{)}_4^{2+} + \text{HY}^{3-} \rightarrow \text{ZnY}^{2-} + 3\text{NH}_3 + \text{NH}_4^+
\]
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.
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 $\alpha_M$ that is analogous to $\alpha_4$:

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

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

$$c_M = [Zn^{2+}] + [Zn(NH_3)^{2+}] + [Zn(NH_3)_2^{2+}] + [Zn(NH_3)_3^{2+}] + [Zn(NH_3)_4^{2+}] \quad (17-29)$$
The value of $\alpha_M$ 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:

$$\alpha_M = \frac{1}{1 + \beta_1[\text{NH}_3] + \beta_2[\text{NH}_3]^2 + \beta_3[\text{NH}_3]^3 + \beta_4[\text{NH}_3]^4} \quad (17-30)$$

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

$$K_{ZnY}^{''} = \alpha_4 \alpha_M K_{ZnY} = \frac{[\text{ZnY}^2-]}{c_{M}c_{T}} \quad (17-31)$$
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$_4$Cl 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 $\alpha_M$ can be calculated from Equation 17-30 by assuming that the molar and analytical concentrations of ammonia are the same; thus, for $[\text{NH}_3] \approx c_{\text{NH}_3} = 0.100 \text{ M}$,

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

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

A value for $K_{\text{ZnY}}$ is found in Table 17-4, and $\alpha_4$ for pH 9.0 is given in Figure 17-7. Substituting into Equation 17-31, we find

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

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

$$pZn = 8.08$$
Calculating pZn after Adding 25.0 mL of EDTA

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

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

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

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

Substituting this value into Equation 17-31, we have

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

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

With Equation 17-28, we find that

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

$$pZn = 11.31$$
Calculating pZn after Adding 30.0 mL of EDTA

Because the solution now contains excess EDTA,

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

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

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

Rearranging Equation 17-31 gives

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

and, from Equation 17-28,

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

\[ pZn = 14.51 \]
16D-6 Indicators for EDTA Titrations

End point detection methods

1) Metal ion indicator

Compound whose color changes when it binds to a metal ion.

Ex. Eriochrome black T

\[ \text{Mg}^{2+} + \text{In} \rightarrow \text{MgIn} \]

\[ \text{MgIn} + \text{EDTA} \rightarrow \text{MgEDTA} + \text{In} \]

(Red) (Colorless) (Colorless) (Blue)

2) Mercury electrode

3) Glass(pH) electrode

4) Ion selective electrode
Metal ion indicators are compounds whose color changes when they bind to a metal ion. Useful indicators must bind metal less strongly than EDTA does.

A typical titration is illustrated by the reaction of Mg$^{2+}$ with EDTA, using **Eriochrome black T** as the indicator.

\[
\text{MgIn} + \text{EDTA} \rightarrow \text{MgEDTA} + \text{In}
\]

(red) (colorless) (colorless) (blue)
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

\[
\begin{align*}
H_2O + H_2In^- \rightleftharpoons HIn^{2-} + H_3O^+ & \quad K_1 = 5 \times 10^{-7} \\
H_2O + HIn^{2-} \rightleftharpoons In^{3-} + H_3O^+ & \quad K_2 = 2.8 \times 10^{-12}
\end{align*}
\]

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\textsubscript{2}In\textsuperscript{−}. 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\textsuperscript{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

\[
MIn^- + HY^{3-} \rightleftharpoons HIn^{2-} + MY^{2-}
\]

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
**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. (See Figure 17-9 and Figure 17-13.)

**Figure 17-15** Structural formula and molecular model of *Calmagite*. Note the similarity to Eriochrome Black T (see Figure 17-14).
EXAMPLE 17-6

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

$$\text{HIn}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{In}^{3-} + \text{H}_3\text{O}^+ \quad K_2 = \frac{[\text{H}_3\text{O}^+][\text{In}^{3-}]}{[\text{HIn}^{2-}]} = 2.8 \times 10^{-12}$$

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

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

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

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

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

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

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

\[
p\text{Mg} = 5.4 \pm 1.0
\]

Proceeding in the same way, we find the range for \(p\text{Ca}\) to be \(3.8 \pm 1.0\).
Direct Titration

Methods Based on Indicators for the Analyte.

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 magnesium or zinc ion solution to an Eriochrome Black T or Calmagite end point. 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 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:

\[
\text{MgY}^{2-} + \text{M}^{2+} \rightarrow \text{MY}^{2-} + \text{Mg}^{2+}
\]

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

1) Direct titration: standard EDTA → analyte (appropriate pH) auxiliary complexing agent

2) Back titration:

   Analyte

   Excess EDTA

   standard Zn$^{2+}$ or Mg$^{2+}$

3) Displacement titration:

   Analyte

   Mg(EDTA)$^{2-}$

   Mg$^{2+}$

   standard EDTA
EDTA Titration Techniques

**Direct Titration**
- In a **direct titration**, analyte is titrated with standard EDTA.
- Conditional formation constant for the metal-EDTA complex is large.
- The color of the free indicator is distinctly different from that of the metal-indicator complex.

**Back Titration**
- In a **back titration**, a known excess of EDTA is added to the analyte. The excess EDTA is then titrated with a standard solution of a second metal ion.
- Necessary if the analyte precipitates in the absence of EDTA, if it reacts too slowly with EDTA under titration conditions, or if it blocks the indicator.
- The metal ion used in the back titration must not displace the analyte metal ion from its EDTA complex.
Displacement Titration

For metal ions that do not have a satisfactory indicator, a displacement titration maybe feasible.

Indirect Titration

Anions that precipitate with certain metal ions can be analyzed with EDTA by indirect titration.

Alternatively, an anion can be precipitated with excess metal ion. The precipitate is filtered and washed, and the excess metal ion in the filtrate is titrated with EDTA. Anions such as $\text{CO}_3^{2-}$, $\text{CrO}_4^{2-}$, $\text{S}^{2-}$, and $\text{SO}_4^{2-}$ can be determined by indirect titration with EDTA.

Masking

• A masking agent is a reagent that protects some component of the analyte from reaction with EDTA.

• Demasking release metal ion from a masking agent.
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.

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. 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.
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:

\[
\text{Zn}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Zn(CN)}_4^{2-}
\]

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\(_2\)SHCHSHCH\(_2\)OH), 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\(^{2-}\):

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

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

\[
\text{Zn(CN)}_4^{2-} + 4\text{HCHO} + 4\text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + 4\text{HOCH}_2\text{CN} + 4\text{OH}^-
\]

The liberated Zn\(^{2+}\) is then titrated with the standard EDTA solution.
Molecular model of BAL (2,3-dimercapto-1-propanol, CH₂SHCHSHCH₂OH).

Suppose the initial titration of Mg²⁺ and Pb²⁺ required 42.22 mL of 0.02064 M EDTA. Titration of the Y⁴⁻ liberated by the BAL consumed 19.35 mL of 0.007657 M Mg²⁺. After addition of formaldehyde, the liberated Zn²⁺ 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.

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

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

To obtain the percentages, we write

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

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

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

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

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.

**Application**

1) Calcium determination in food using EDTA titration
   
   AOAC Method 968.31

2) Water hardness (Ca, Mg)

3) Ca or Al content of drugs such as calcium pantothenate or alumina.
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.
Summary

Complex, complexometric titration, Chelate, chelating agent
Chelate effect: entropy effect
Coordination number, monodentate, multidentate, ligand
Formation constant: stability constant, Crown Ethers, beta-cyclodextrine
EDTA, Aminocarboxylic acid titration
Conditional formation constant, Auxiliary complexing agent
Metal ion indicator, Eriochrome black T, Calmagite
Masking, demasking
Turbidimetry, nephelometry, Titration curve, potentiometry, precipitation titration curve
Argentometry, Mohr, Volhard, Fajans method
Adsorption indicator, electric double layer, water hardness