

# Complexation Reactions and Titrations

**Complexation reactions** are widely used in analytical chemistry. One of the earliest uses of these reactions was for titrating cations.

In addition, many complexes are colored or absorb ultraviolet radiation; the formation of these complexes is often the basis for spectrophotometric determinations.

Some complexes are sparingly soluble and can be used in gravimetric analysis or for precipitation titrations as discussed early.

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.

## 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.

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.

**Coordination number** The number of covalent bonds that a cation tends to form with electron donors.

- 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,  $\text{Cu}(\text{NH}_3)_4^{+2}$ ; a neutral complex with glycine,  $\text{Cu}(\text{NH}_2\text{CH}_2\text{COO})_2$ ; and an anionic complex with chloride ion,  $\text{CuCl}_4^{-2}$

## Complexation Reactions and Titrations

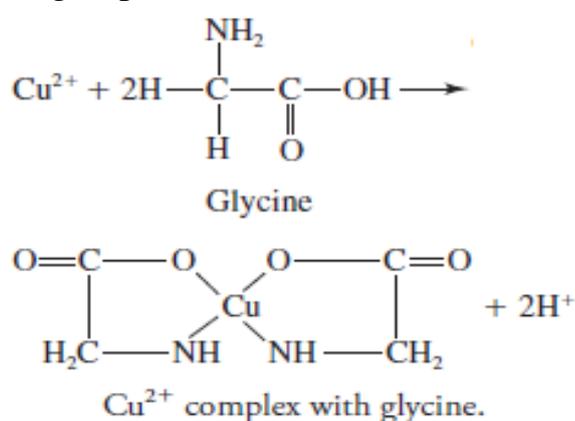
Titrations based on complex formation, sometimes called **Complexometric titrations**.

A titration in which the reaction between the analyte and titrant is a complexation reaction.

The truly remarkable growth in their analytical application, based on a particular class of coordination compounds called **chelates**,

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.

For example the copper complex of glycine is an example. In this complex, copper bonds to both the oxygen of the carboxyl group and the nitrogen of the amine group:



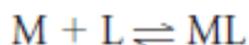
A ligand that has a single donor group, such as ammonia, is called **unidentate**

(single-toothed), whereas one such as glycine, which has two groups available for covalent bonding, is called **bidentate**.

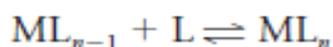
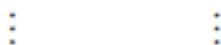
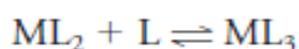
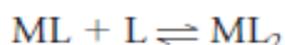
Tridentate, tetradentate, pentadentate, and hexadentate chelating agents are also known.

### Complexation Equilibria

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

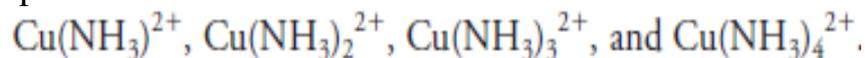


Complexation reactions occur in a stepwise fashion and the reaction above is often followed by additional reactions:



## Complexation Reactions and Titrations

For example, Cu(II), with a maximum coordination number of 4, can form complexes with ammonia that have the formulas



With the bidentate ligand glycine (gly), the only complexes that form are  $\text{Cu}(\text{gly})^{+2}$  and  $\text{Cu}(\text{gly})_2^{+2}$ .

### Complexation Titrations Curves

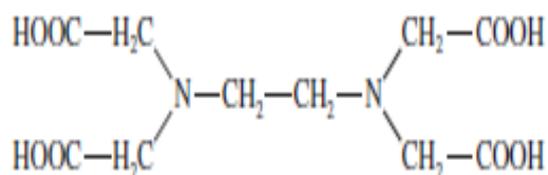
Complexometric titration curves are usually a plot of  $\text{pM} = -\log [\text{M}]$  as a function of the volume of titrant added. Usually in complexometric titrations, the ligand is the titrant, and the metal ion is the analyte, although occasionally the roles are reversed.

### Aminocarboxylic Acid Titrations

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

### 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.

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

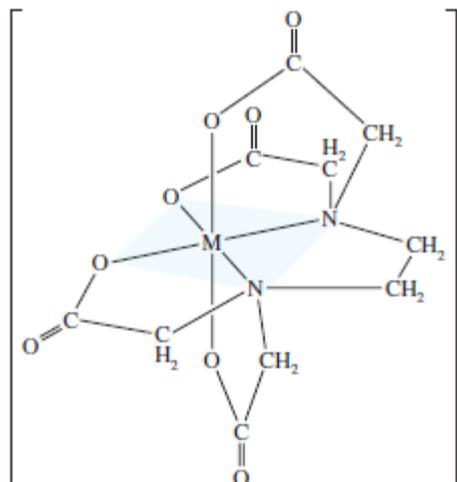
### Chemistry and Properties of EDTA

EDTA is a Lewis acid, has six binding sites (the four carboxylate groups and the two amino groups), providing six pairs of electrons.

The resulting metal–ligand complex, in which EDTA forms a cage-like

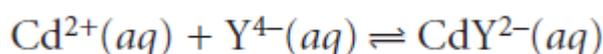
## Complexation Reactions and Titrations

structure around the metal ion (Figure below), is very stable. The actual number of coordination sites depends on the size of the metal ion; however, all metal–EDTA complexes have a 1:1 stoichiometry.



### Metal-EDTA Formation Constants

To illustrate the formation of a metal–EDTA complex consider the reaction between Cd<sup>2+</sup> and EDTA



where Y<sup>4-</sup> is a shorthand notation for the chemical form of EDTA shown in Figure 9.25. The formation constant for this reaction

$$K_f = \frac{[\text{CdY}^{2-}]}{[\text{Cd}^{2+}][\text{Y}^{4-}]} = 2.9 \times 10^{16}$$

is quite large, suggesting that the reaction's equilibrium position lies far to the right. Formation constants for other metal–EDTA complexes are found in

### EDTA Is a Weak Acid

Besides its properties as a ligand, EDTA is also a weak acid. The fully protonated form of EDTA, H<sub>6</sub>Y<sup>2+</sup>, is a hexaprotic weak acid with successive pK<sub>a</sub> values of

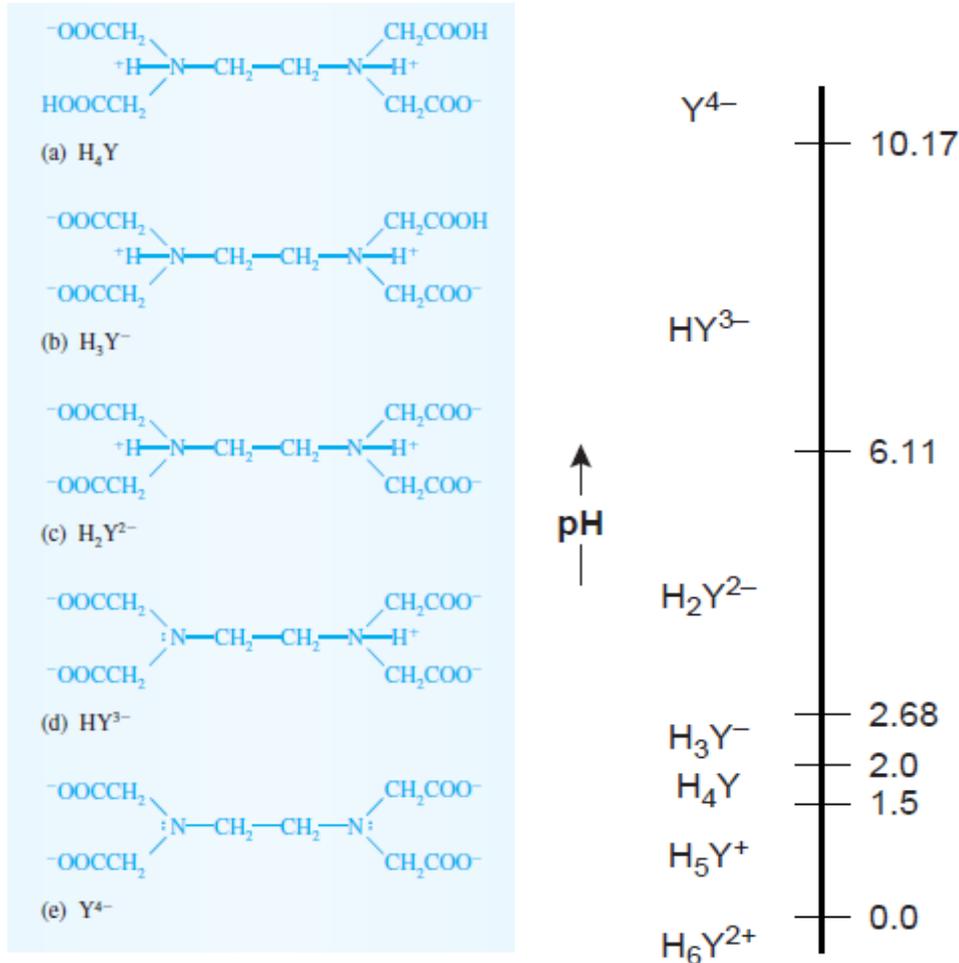
pK<sub>a1</sub> = 0.0, pK<sub>a2</sub> = 1.5, pK<sub>a3</sub> = 2.0, pK<sub>a4</sub> = 2.68, pK<sub>a5</sub> = 6.11, pK<sub>a6</sub> = 10.17

The first four values are for the carboxyl protons, and the remaining two values are for the ammonium protons. A ladder diagram for EDTA is shown in Figure below.

The species Y<sup>4-</sup> becomes the predominate form of EDTA at pH levels greater than 10.17. It is only for pH levels greater than 12 that Y<sup>4-</sup> becomes the only significant form of EDTA.

## Complexation Reactions and Titrations

The various EDTA species are often abbreviated  $H_4Y$ ,  $H_3Y^{-1}$ ,  $H_2Y^{-2}$ ,  $HY^{-3}$ , and  $Y^{-4}$ . Feature below describes the EDTA species and shows their structural formulas.



### Conditional Metal-Ligand Formation Constants

Recognizing EDTA's acid-base properties is important. The formation constant for  $CdY^{2-}$  in equation above assumes that EDTA is present as  $Y^{4-}$ . If we restrict the pH to levels greater than 12, then equation above provides an adequate description of the formation of  $CdY^{2-}$ . For pH levels less than 12, however,  $K_f$  overestimates the stability of the  $p$   $CdY^{2-}$  complex.

At any pH a mass balance requires that the total concentration of unbound EDTA equal the combined concentrations of each of its forms.

$$C_{EDTA} = [H_6Y^{2+}] + [H_5Y^{+}] + [H_4Y] + [H_3Y^{-}] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

To correct the formation constant for EDTA's acid-base properties, we must account for the fraction,  $\alpha_{Y^{4-}}$ , of EDTA present as  $Y^{4-}$ .

## Complexation Reactions and Titrations

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{C_{EDTA}}$$

**Table 9.12** Values of  $\alpha_{Y^{4-}}$  for Selected pHs

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
2	$3.7 \times 10^{-14}$	8	$5.4 \times 10^{-3}$
3	$2.5 \times 10^{-11}$	9	$5.2 \times 10^{-2}$
4	$3.6 \times 10^{-9}$	10	0.35
5	$3.5 \times 10^{-7}$	11	0.85
6	$2.2 \times 10^{-5}$	12	0.98
7	$4.8 \times 10^{-4}$	13	1.00

**Table 9.13** Conditional Formation Constants for  $CdY^{2-}$

pH	$K'_f$	pH	$K'_f$
2	$1.1 \times 10^3$	8	$1.6 \times 10^{14}$
3	$7.3 \times 10^5$	9	$1.5 \times 10^{15}$
4	$1.0 \times 10^8$	10	$1.0 \times 10^{16}$
5	$1.0 \times 10^{10}$	11	$2.5 \times 10^{16}$
6	$6.4 \times 10^{11}$	12	$2.8 \times 10^{16}$
7	$1.4 \times 10^{13}$	13	$2.9 \times 10^{16}$

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\alpha_{Y^{4-}}C_{EDTA}}$$

$$K'_f = \alpha_{Y^{4-}} \times K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]C_{EDTA}}$$

where  $K'_f$  is a **conditional formation constant** whose value depends on the pH.

## Complexation Reactions and Titrations

### EDTA Must Compete with Other Ligands

To maintain a constant pH, we must add a buffering agent. If one of the buffer's components forms a metal–ligand complex with  $\text{Cd}^{2+}$ , then EDTA must compete with the ligand for  $\text{Cd}^{2+}$ .

For example, an  $\text{NH}_4^+/\text{NH}_3$  buffer includes the ligand  $\text{NH}_3$ , which forms several stable  $\text{Cd}^{2+}-\text{NH}_3$  complexes. EDTA forms a stronger complex with  $\text{Cd}^{2+}$  and will displace  $\text{NH}_3$ .

The presence of  $\text{NH}_3$ , however, decreases the stability of the  $\text{Cd}^{2+}$ –EDTA complex.

We can account for the effect of an **auxiliary complexing agent**, such as  $\text{NH}_3$ , in the same way we accounted for the effect of pH. Before adding EDTA, a mass balance on  $\text{Cd}^{2+}$  requires that the total concentration of  $\text{Cd}^{2+}$ ,  $C_{\text{Cd}}$ , be

$$C_{\text{Cd}} = [\text{Cd}^{2+}] + [\text{Cd}(\text{NH}_3)^{2+}] + [\text{Cd}(\text{NH}_3)_2^{2+}] + [\text{Cd}(\text{NH}_3)_3^{2+}] + [\text{Cd}(\text{NH}_3)_4^{2+}]$$

$$\alpha_{\text{Cd}^{2+}} = \frac{[\text{Cd}^{2+}]}{C_{\text{Cd}}}$$

$$K_f' = \alpha_{\text{Y}^{4-}} \times K_f = \frac{[\text{CdY}^{2-}]}{\alpha_{\text{Cd}^{2+}} C_{\text{Cd}} C_{\text{EDTA}}}$$

$$K_f'' = \alpha_{\text{Cd}^{2+}} \times \alpha_{\text{Y}^{4-}} \times K_f = \frac{[\text{CdY}^{2-}]}{C_{\text{Cd}} C_{\text{EDTA}}}$$

Where  $K_f''$  is a new conditional formation constant accounting for both pH and the presence of an **auxiliary complexing agent**.

### Complexometric EDTA Titration Curves

Calculate the titration curve for 50.0 mL of  $5.00 \times 10^{-3}$  M  $\text{Cd}^{2+}$  with 0.0100 M EDTA at a pH of 10 and in the presence of 0.0100 M  $\text{NH}_3$ . The formation constant for  $\text{Cd}^{2+}$ –EDTA is  $2.9 \times 10^{16}$ .

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## Complexation Reactions and Titrations

- Since the titration is carried out at a pH of 10, some of the EDTA is present in forms other than  $Y^{4-}$ .
- In addition, the presence of  $NH_3$  means that the EDTA must compete for the  $Cd^{2+}$ .
- To evaluate the titration curve, therefore, we must use the appropriate conditional formation constant.

From Tables, we find that  $\alpha_{Y^{4-}}$  is 0.35 at a pH of 10, and that  $\alpha_{Cd^{2+}}$  is 0.0881 when the concentration of  $NH_3$  is 0.0100 M. Using these values, we calculate that the conditional formation constant is

$$K_f' = \alpha_{Y^{4-}} \times \alpha_{Cd^{2+}} \times K_f = (0.35)(0.0881)(2.9 \times 10^{16}) = 8.9 \times 10^{14}$$

Because  $K_f'$  is so large, we treat the titration reaction as though it proceeds to completion.

$$\text{Moles EDTA} = \text{moles } Cd^{2+}$$

or

$$M_{EDTA}V_{EDTA} = M_{Cd}V_{Cd}$$

Solving for the volume of EDTA

$$V_{EDTA} = \frac{M_{Cd}V_{Cd}}{M_{EDTA}} = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{0.0100 \text{ M}} = 25.0 \text{ mL}$$

shows us that 25.0 mL of EDTA is needed to reach the equivalence point.

Before the equivalence point

For example, after adding 5.0 mL of EDTA, the total concentration of  $Cd^{2+}$  is

$$\begin{aligned} C_{Cd} &= \frac{\text{moles excess } Cd^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd} - M_{EDTA}V_{EDTA}}{V_{Cd} + V_{EDTA}} \\ &= \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL}) - (0.0100 \text{ M})(5.0 \text{ mL})}{50.0 \text{ mL} + 5.0 \text{ mL}} = 3.64 \times 10^{-3} \text{ M} \end{aligned}$$

To calculate the concentration of free  $Cd^{2+}$  we use equation 9.14.

$$[Cd^{2+}] = \alpha_{Cd^{2+}} \times C_{Cd} = (0.0881)(3.64 \times 10^{-3} \text{ M}) = 3.21 \times 10^{-4} \text{ M}$$

Thus, pCd is

## Complexation Reactions and Titrations

$$p\text{Cd} = -\log[\text{Cd}^{2+}] = -\log(3.21 \times 10^{-4}) = 3.49$$

At the equivalence point, all the  $\text{Cd}^{2+}$  initially present is now present as  $\text{CdY}^{2-}$ . The concentration of  $\text{Cd}^{2+}$ , therefore, is determined by the dissociation of the  $\text{CdY}^{2-}$  complex. To find  $p\text{Cd}$  we must first calculate the concentration of the complex.

$$\begin{aligned} [\text{CdY}^{2-}] &= \frac{\text{initial moles Cd}^{2+}}{\text{total volume}} = \frac{M_{\text{Cd}}V_{\text{Cd}}}{V_{\text{Cd}} + V_{\text{EDTA}}} \\ &= \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 25.0 \text{ mL}} = 3.33 \times 10^{-3} \text{ M} \end{aligned}$$

Letting the variable  $x$  represent the concentration of  $\text{Cd}^{2+}$  due to the dissociation of the  $\text{CdY}^{2-}$  complex, we have

$$K_f'' = \frac{[\text{CdY}^{2-}]}{C_{\text{Cd}}C_{\text{EDTA}}} = \frac{3.33 \times 10^{-3} - x}{(x)(x)} = 8.94 \times 10^{14}$$

$$x = C_{\text{Cd}} = 1.93 \times 10^{-9} \text{ M}$$

Once again, to find the  $[\text{Cd}^{2+}]$  we must account for the presence of  $\text{NH}_3$ ; thus

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} \times C_{\text{Cd}} = (0.0881)(1.93 \times 10^{-9} \text{ M}) = 1.70 \times 10^{-10} \text{ M}$$

giving  $p\text{Cd}$  as 9.77.

After the equivalence point, EDTA is in excess, and the concentration of  $\text{Cd}^{2+}$  is determined by the dissociation of the  $\text{CdY}^{2-}$  complex. Examining the equation for the complex's conditional formation constant (equation 9.15), we see that to calculate  $C_{\text{Cd}}$  we must first calculate  $[\text{CdY}^{2-}]$  and  $C_{\text{EDTA}}$ . After adding 30.0 mL of EDTA, these concentrations are

$$\begin{aligned} [\text{CdY}^{2-}] &= \frac{\text{initial moles Cd}^{2+}}{\text{total volume}} = \frac{M_{\text{Cd}}V_{\text{Cd}}}{V_{\text{Cd}} + V_{\text{EDTA}}} \\ &= \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 30.0 \text{ mL}} = 3.13 \times 10^{-3} \text{ M} \end{aligned}$$

## Complexation Reactions and Titrations

$$C_{\text{EDTA}} = \frac{\text{moles excess EDTA}}{\text{total volume}} = \frac{M_{\text{EDTA}}V_{\text{EDTA}} - M_{\text{Cd}}V_{\text{Cd}}}{V_{\text{Cd}} + V_{\text{EDTA}}}$$
$$= \frac{(0.0100 \text{ M})(30.0 \text{ mL}) - (5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 30.0 \text{ mL}} = 6.25 \times 10^{-4} \text{ M}$$

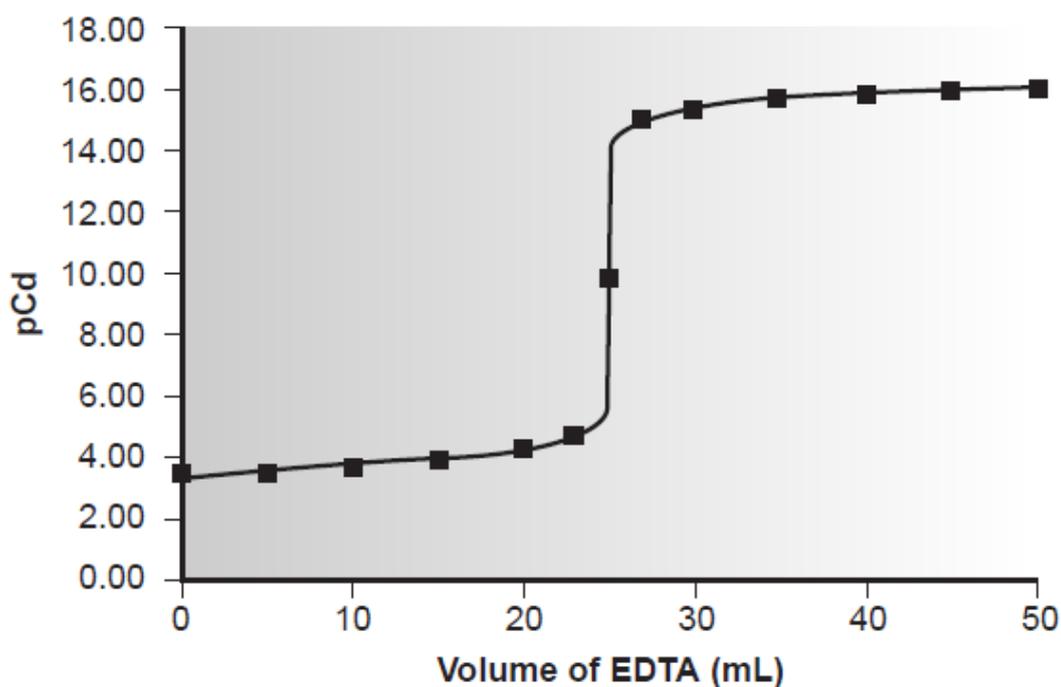
Substituting these concentrations into equation 9.15 and solving for  $C_{\text{Cd}}$  gives

$$\frac{[\text{CdY}^{2-}]}{C_{\text{Cd}}C_{\text{EDTA}}} = \frac{3.13 \times 10^{-3} \text{ M}}{C_{\text{Cd}}(6.25 \times 10^{-4})} = 8.94 \times 10^{14}$$

$$C_{\text{Cd}} = 5.60 \times 10^{-15} \text{ M}$$

Thus,

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} \times C_{\text{Cd}} = (0.0881)(5.60 \times 10^{-15} \text{ M}) = 4.93 \times 10^{-16} \text{ M}$$



## Complexation Reactions and Titrations

**Table 9.15** Data for Titration of  $5.00 \times 10^{-3}$  M  $\text{Cd}^{2+}$  with 0.0100 M EDTA at a pH of 10.0 and in the Presence of 0.0100 M  $\text{NH}_3$

Volume of EDTA (mL)	pCd
0.00	3.36
5.00	3.49
10.00	3.66
15.00	3.87
20.00	4.20
23.00	4.62
25.00	9.77
27.00	14.91
30.00	15.31
35.00	15.61
40.00	15.78
45.00	15.91
50.00	16.01

**Table 9.16** Selected Metallochromic Indicators

Indicator	Useful pH Range	Useful for
calmagite	9–11	Ba, Ca, Mg, Zn
Eriochrome Black T	7.5–10.5	Ba, Ca, Mg, Zn
Eriochrome Blue Black R	8–12	Ca, Mg, Zn, Cu
murexide	6–13	Ca, Ni, Cu
PAN	2–11	Cd, Cu, Zn
salicylic acid	2–3	Fe