Ch. 11: EDTA Titrations

Outline:

- 11-1 Metal-chelate complexes.

- 11-2 EDTA

- 11-3 EDTA titration curves

- 11-5 Auxiliary Complexing Agents

- 11-6 Metal-Ion Indicators

- 11-7 EDTA titration techniques

- This is Chapter 12 in the 7th edition.

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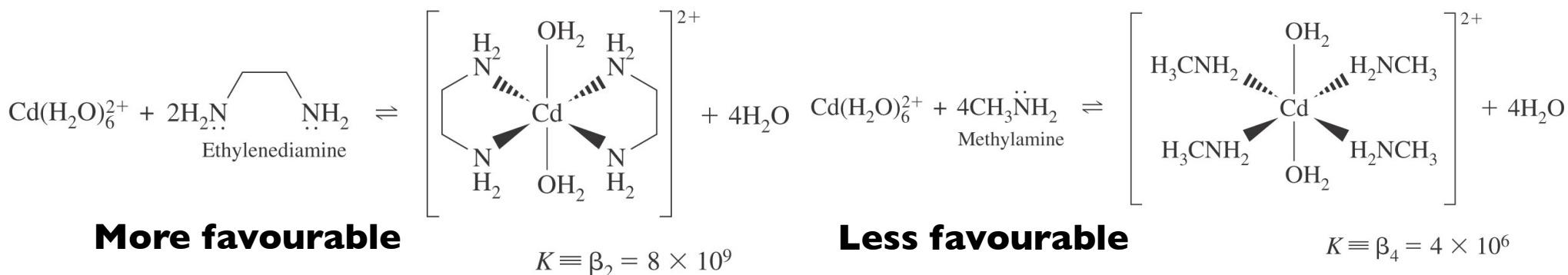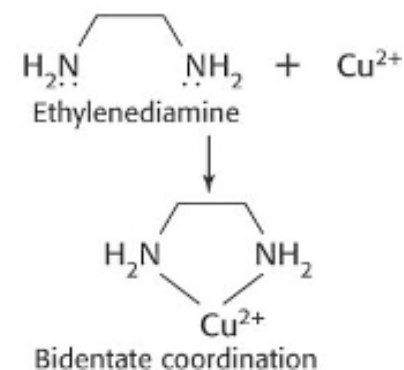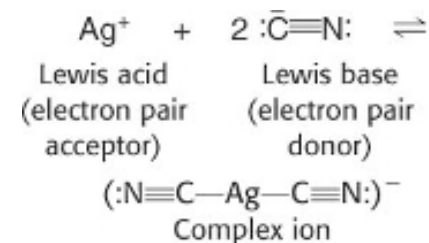
Metal-Chelate Complexes

Metal ions are *Lewis acids*, accepting electron pairs from electron-donating ligands that are *Lewis bases*. Most transition metals bind six (or more) ligand atoms.

Monodentate: ligand binds to a metal ion through only one atom (e.g., CN^-),

Bidentate: ligand binds to a metal ion through two atoms (e.g., ethylenediamine, $H_2NCH_2CH_2NH_2$, binds at the lone pairs of the N atoms).

*Multidentate*: ligand binds to a metal ion through two or more atoms, also known as a *chelating ligand*.

$Ag^+ \quad + \quad 2 :\bar{C}{\equiv}N: \quad \rightleftharpoons$

Lewis acid   Lewis base
(electron pair   (electron pair
acceptor)   donor)

$(:N{\equiv}C{-}Ag{-}C{\equiv}N:)^-$
Complex ion

$H_2N \qquad NH_2 \; + \; Cu^{2+}$
Ethylenediamine

$H_2N \qquad NH_2$
Cu^{2+}
Bidentate coordination

Chelate effect: the ability of multidentate ligands to form more stable metal complexes than those formed by similar monodentate ligands.

$$Cd(H_2O)_6^{2+} + 2H_2N{-}NH_2 \rightleftharpoons \left[\begin{array}{c} H_2 \; OH_2 \; H_2 \\ N \quad | \quad N \\ Cd \\ N \quad | \quad N \\ H_2 \; OH_2 \; H_2 \end{array} \right]^{2+} + 4H_2O$$

Ethylenediamine

More favourable

$K \equiv \beta_2 = 8 \times 10^9$

$$Cd(H_2O)_6^{2+} + 4CH_3\ddot{N}H_2 \rightleftharpoons \left[\begin{array}{c} OH_2 \\ H_3CNH_2 \quad | \quad H_2NCH_3 \\ Cd \\ H_3CNH_2 \quad | \quad H_2NCH_3 \\ OH_2 \end{array} \right]^{2+} + 4H_2O$$

Methylamine

Less favourable

$K \equiv \beta_4 = 4 \times 10^6$
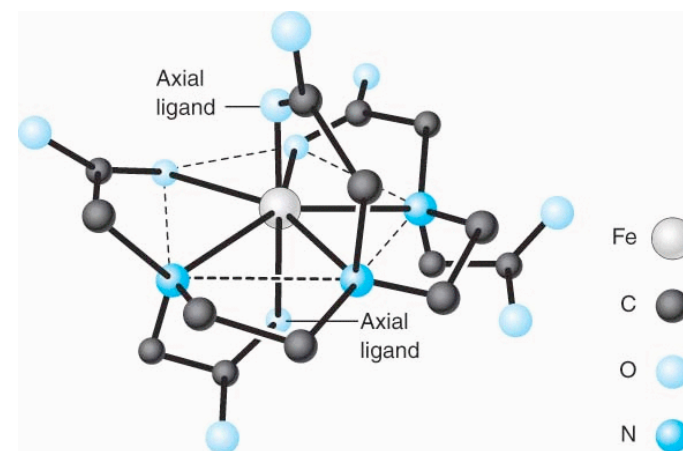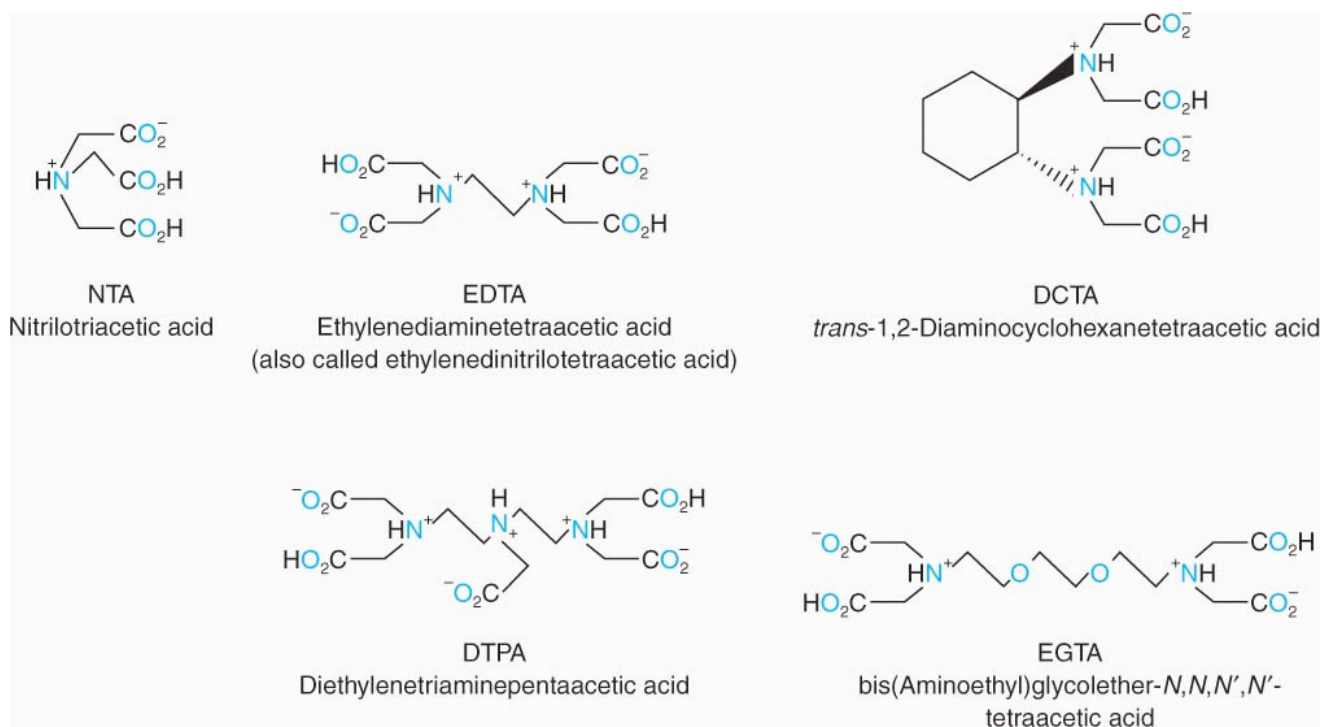
Metal-Chelate Complexes, 2

An important *tetradentate* ligand is *adenosine triphosphate* (ATP), which binds to divalent metal ions (such as Mg^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+}) through four of their six coordination positions. The fifth and sixth positions are occupied by water molecules. The biologically active form of ATP is generally the Mg^{2+} complex. Metal-chelate complexes are ubiquitous in biology.

(a)   (b)
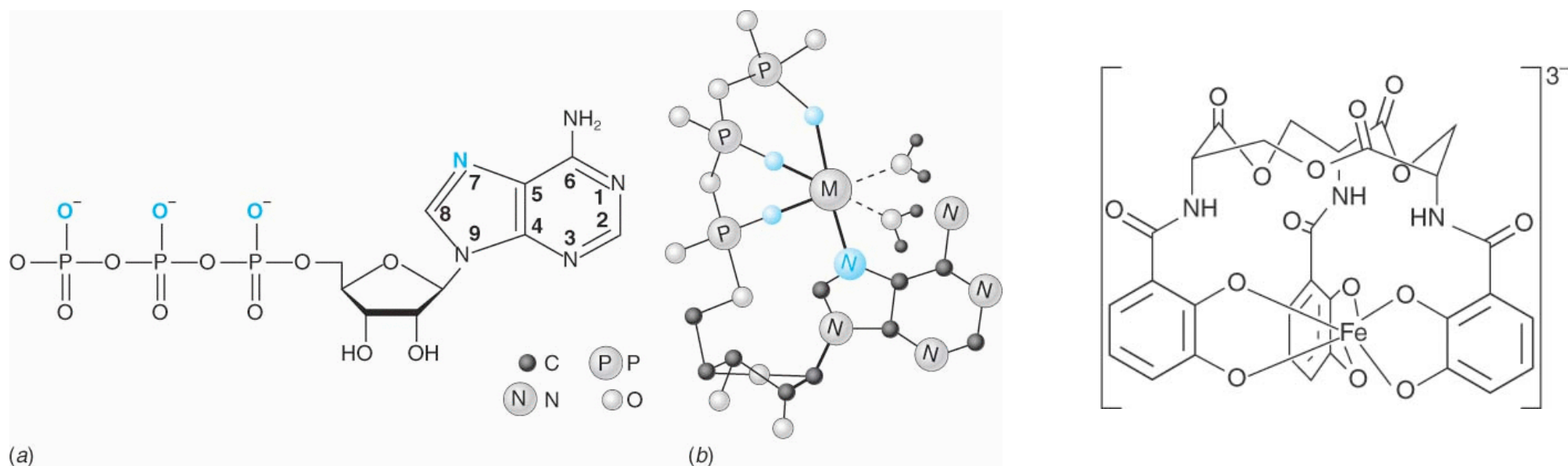
Bacteria such as *E. coli* and *Salmonella enterica* in your gut excrete a powerful iron chelator called *enterobactin* to scavenge iron that is essential for bacterial growth. The iron-enterobactin complex is recognized at specific sites on the bacterial cell surface and taken into the cell. Iron is then released inside the bacterium by enzymatic disassembly of the chelator. To fight bacterial infection, your immune system produces a protein called *siderocalin* to sequester and inactivate enterobactin.

Metal-Chelate Complexes, 3

Aminocarboxylic acids are *synthetic chelating agents*. Amine N atoms and carboxylate O atoms are potential ligand atoms in these molecules. When these molecules bind to a metal ion, the ligand atoms lose their protons. A medical application of the ligand DTPA is illustrated by the tightly bound complex Gd^{3+}-DTPA, which is injected into humans at a concentration of ~0.5 mM to provide contrast in magnetic resonance imaging.
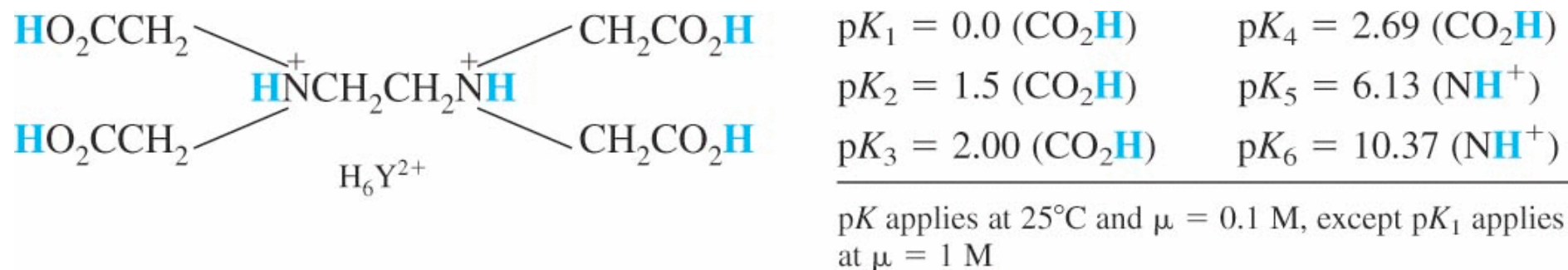

NTA
Nitrilotriacetic acid

EDTA
Ethylenediaminetetraacetic acid
(also called ethylenedinitrilotetraacetic acid)

DCTA
trans-1,2-Diaminocyclohexanetetraacetic acid

DTPA
Diethylenetriaminepentaacetic acid

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

Structure of Fe(DTPA)$^{2-}$ found in the salt Na$_2$[Fe(DTPA)] 2H$_2$O. The seven-coordinate pentagonal bipyramidal coordination environment of the iron atom features 3 N and 2 O ligands in the equatorial plane (dashed lines) and two axial O ligands.

A titration based on complex formation is called a *complexometric titration*. Ligands other than NTA form strong 1:1 complexes with all metal ions except univalent ions such as Li^+, Na^+ and K^+. The stoichiometry is 1:1 regardless of the charge on the ion.

EDTA

EDTA is, by far, the most widely used chelator in analytical chemistry. By direct titration or through an indirect sequence of reactions, <u>virtually every element of the periodic table can be measured with EDTA</u>.

$$pK_1 = 0.0 \ (CO_2H) \qquad pK_4 = 2.69 \ (CO_2H)$$
$$pK_2 = 1.5 \ (CO_2H) \qquad pK_5 = 6.13 \ (NH^+)$$
$$pK_3 = 2.00 \ (CO_2H) \qquad pK_6 = 10.37 \ (NH^+)$$

pK applies at 25°C and $\mu = 0.1$ M, except pK_1 applies at $\mu = 1$ M

EDTA is a *hexaprotic* system, designated H_6Y^{2+}. The first four pK values apply to carboxyl protons, and the last two are for the ammonium protons. The neutral acid is *tetraprotic*, with the formula H_4Y.

Preparation and usage: H_4Y can be dried at 140°C for 2 h and used as a *primary standard*. It can be dissolved by adding NaOH solution from a plastic container. NaOH solution from a glass bottle should not be used because it contains alkaline earth metals leached from the glass. Reagent-grade $Na_2H_2Y \cdot 2H2O$ contains ~0.3% excess water. It may be used in this form with suitable correction for the mass of excess water or dried to the composition $Na_2H_2Y \cdot 2H_2O$ at 80°C. The certified reference material $CaCO_3$ can be used to standardize EDTA or to verify the composition of standard EDTA.

EDTA: Acidic & Basic Properties

The fraction of EDTA in each of its protonated forms is plotted below.

EDTA: Acidic & Basic Properties, 2

As in Chapter 9, we can define a fraction of dissociation, α, for each species as the fraction of EDTA in that form. For example, $\alpha_{Y^{4-}}$ is defined as

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[H_6Y^{2+}] + [H_5Y^{+}] + [H_4Y] + [H_3Y^{-}] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]}$$

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

where [EDTA] is the total concentration of all free (non-complexed) EDTA species in the solution. Following the derivation in Section 9-5 (8th edition), $\alpha_{Y^{4-}}$ is given by

$$\alpha_{Y^{4-}} = \frac{K_1K_2K_3K_4K_5K_6}{D}$$

pH	$\alpha_{Y^{4-}}$
0	1.3×10^{-23}
1	1.4×10^{-18}
2	2.6×10^{-14}
3	2.1×10^{-11}
4	3.0×10^{-9}
5	2.9×10^{-7}
6	1.8×10^{-5}
7	3.8×10^{-4}
8	4.2×10^{-3}
9	0.041
10	0.30
11	0.81
12	0.98
13	1.00
14	1.00

where $D = [H^+]^6 + [H^+]^5 K_1 + [H^+]^4 K_1 K_2 + [H^+]^3 K_1 K_2 K_3 + [H^+]^2 K_1 K_2 K_3 K_4 + [H^+] K_1 K_2 K_3 K_4 K_5 + K_1 K_2 K_3 K_4 K_5 K_6$.
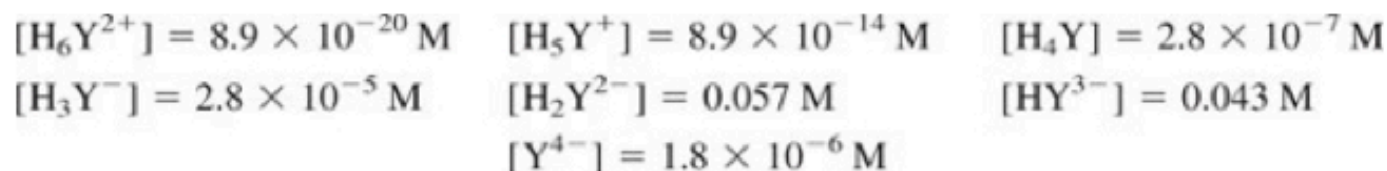
EDTA: Acidic & Basic Properties, 3

What does α_{Y4-} mean?

EXAMPLE **What does α_{Y4-} mean?**

The fraction of all free EDTA in the form Y^{4-} is called α_{Y4-}. At pH 6.00 and a formal concentration of 0.10 M, the composition of an EDTA solution is

$$[H_6Y^{2+}] = 8.9 \times 10^{-20} \text{ M} \quad [H_5Y^+] = 8.9 \times 10^{-14} \text{ M} \quad [H_4Y] = 2.8 \times 10^{-7} \text{ M}$$

$$[H_3Y^-] = 2.8 \times 10^{-5} \text{ M} \quad [H_2Y^{2-}] = 0.057 \text{ M} \quad [HY^{3-}] = 0.043 \text{ M}$$

$$[Y^{4-}] = 1.8 \times 10^{-6} \text{ M}$$

Find α_{Y4-}.

Solution α_{Y4-} is the fraction in the form Y^{4-}:

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[H_6Y^{2+}] + [H_5Y^+] + [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]}$$

$$= \frac{1.8 \times 10^{-6}}{(8.9 \times 10^{-20}) + (8.9 \times 10^{-14}) + (2.8 \times 10^{-7}) + (2.8 \times 10^{-5}) + (0.057) + (0.043) + (1.8 \times 10^{-6})}$$

$$= 1.8 \times 10^{-5}$$

Test Yourself At what pH does $\alpha_{Y4-} = 0.50$? (**Answer**: pH = pK_6 = 10.37)
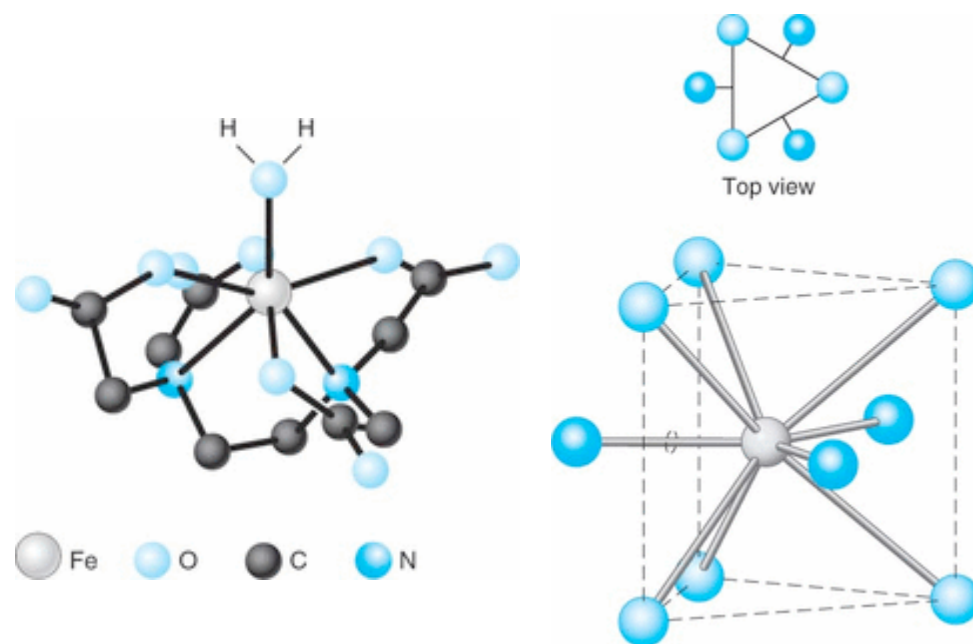
EDTA Complexes

The equilibrium constant for the reaction of a metal with a ligand is called the *formation constant*, K_f, or the *stability constant*:

$$\text{Formation constant:} \qquad M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4} \qquad K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}$$

In many transition metal complexes, EDTA engulfs the metal ion, forming the six-coordinate species. If you build a space-filling model of a six-coordinate metal-EDTA complex, you find strain in the chelate rings. This strain is relieved when the O ligands are drawn back toward the N atoms. Such distortion opens up a seventh coordination position, which can be occupied by H_2O. In some complexes, such as Ca(EDTA)(H2O)$_2^{2-}$, the metal ion is so large that it accommodates eight ligand atoms. Larger metal ions require more ligand atoms. Even if H_2O is attached to the metal ion, K_f is still given by the equation above.

Fe   O   C   N

(Left) Seven-coordinate geometry of Fe(EDTA)(H$_2$O)$^-$. Other metal ions that form seven-coordinate EDTA complexes include Fe^{2+}, Mg^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ru^{3+}, Cr^{3+}, Co^{3+}, V^{3+}, Ti^{3+}, In^{3+}, Sn^{4+}, Os^{4+} and Ti^{4+}. (Right) Tricapped trigonal prismatic structure of many Ln(III) and An(III) complexes.

EDTA Complexes, 2

Formation constants for most EDTA complexes are large and tend to be larger for more positively charged cations.

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.95	V^{3+}	25.9^a	Tl^{3+}	35.3
Na^+	1.86	Cr^{3+}	23.4^a	Bi^{3+}	27.8^a
K^+	0.8	Mn^{3+}	25.2	Ce^{3+}	15.93
Be^{2+}	9.7	Fe^{3+}	25.1	Pr^{3+}	16.30
Mg^{2+}	8.79	Co^{3+}	41.4	Nd^{3+}	16.51
Ca^{2+}	10.65	Zr^{4+}	29.3	Pm^{3+}	16.9
Sr^{2+}	8.72	Hf^{4+}	29.5	Sm^{3+}	17.06
Ba^{2+}	7.88	VO^{2+}	18.7	Eu^{3+}	17.25
Ra^{2+}	7.4	VO_2^+	15.5	Gd^{3+}	17.35
Sc^{3+}	23.1^a	Ag^+	7.20	Tb^{3+}	17.87
Y^{3+}	18.08	Tl^+	6.41	Dy^{3+}	18.30
La^{3+}	15.36	Pd^{2+}	25.6^a	Ho^{3+}	18.56
V^{2+}	12.7^a	Zn^{2+}	16.5	Er^{3+}	18.89
Cr^{2+}	13.6^a	Cd^{2+}	16.5	Tm^{3+}	19.32
Mn^{2+}	13.89	Hg^{2+}	21.5	Yb^{3+}	19.49
Fe^{2+}	14.30	Sn^{2+}	18.3^b	Lu^{3+}	19.74
Co^{2+}	16.45	Pb^{2+}	18.0	Th^{4+}	23.2
Ni^{2+}	18.4	Al^{3+}	16.4	U^{4+}	25.7
Cu^{2+}	18.78	Ga^{3+}	21.7		
Ti^{3+}	21.3	In^{3+}	24.9		

NOTE: The stability constant is the equilibrium constant for the reaction $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$. Values in table apply at 25°C and ionic strength 0.1 M unless otherwise indicated.

a. 20°C, ionic strength = 0.1 M.   b. 20°C, ionic strength = 1 M.

SOURCE: A. E. Martell, R. M. Smith, and R. J. Motekaitis, NIST Critically Selected Stability Constants of Metal Complexes, NIST Standard Reference Database 46, Gaithersburg, MD, 2001.

Conditional Formation Constant

The formation constant $K_f = [MY^{n-4}]/[M^{n+}][Y^{4-}]$ describes the reaction between Y^{4-} and a metal ion. As seen in the fractional composition diagram, most EDTA is not Y^{4-} below pH 10.37. The species HY^{3-}, H_2Y^{2-}, and so on, predominate at lower pH. From the definition $\alpha_{Y^{4-}} = [Y^{4-}]/[EDTA]$, we can express the concentration of Y^{4-} as

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

where [EDTA] is the total concentration of all unbound EDTA species. K_f is written as:

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]} = \frac{[MY^{n-4}]}{[M^{n+}]\alpha_{Y^{4-}}[EDTA]}$$

If the pH is fixed (e.g., buffer), then the K_f and $\alpha_{Y^{4-}}$ are combined

$$K_f' = K_f\alpha_{Y^{4-}} = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

into the *conditional* (or *effective*) *formation constant*, which describes the formation of MY^{n-4} at any particular pH. Note: we can also use a modified form of this equation to treat situations where MY^{n-4} is not the dominant species. The conditional formation constant allows us to look at EDTA complex formation as if the uncomplexed EDTA is all in one form:

$$M^{n+} + EDTA \rightleftharpoons MY^{n-4} \qquad K_f' = \alpha_{Y^{4-}}K_f$$
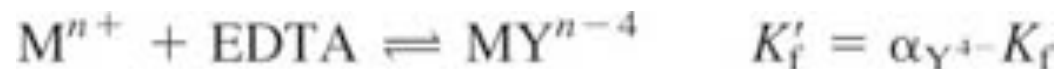
(*written example*)

Conditional Formation Constant, 2

You can see from the CaY^{2-} example that a metal-EDTA complex becomes less stable at lower pH. For a titration reaction to be effective, it must go "to completion" (say, 99.9%), which means that the equilibrium constant is large—the analyte and titrant are essentially completely reacted at the equivalence point.

pH can be used to select which metals will be titrated by EDTA and which will not. Metals with higher formation constants can be titrated at lower pH. **e.g.,** If a solution containing both Fe^{3+} and Ca^{2+} is titrated at pH 4, Fe^{3+} is titrated without interference from Ca^{2+}.
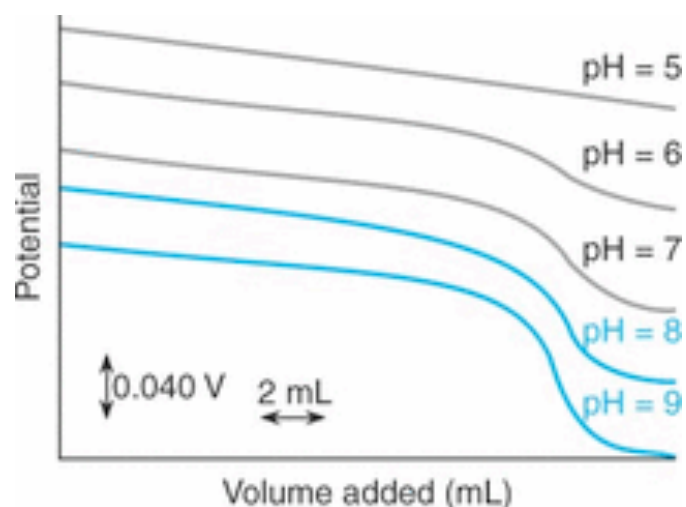
Titration of Ca^{2+} with EDTA as a function of pH. As the pH is lowered, the end point becomes less distinct. The potential was measured with mercury and calomel electrodes.

pH affects the titration of Ca^{2+} with EDTA. Below pH $\approx$ 8, the end point is not sharp enough to allow accurate determination. The conditional formation constant for CaY^{2-} is just too small for "complete" reaction at low pH.

EDTA Titration Curves

The titration reaction is

$$M^{n+} + EDTA \rightleftharpoons MY^{n-4} \qquad K'_f = \alpha_{Y^{4-}} K_f$$
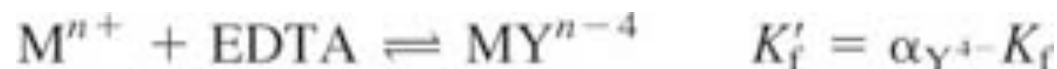
If K'_f is large, we can consider the reaction to be complete at each point in the titration. The titration curve is a graph of pM (= $-\log[M^{n+}]$) versus the volume of added EDTA. The curve is analogous to plotting pH versus volume of titrant in an acid-base titration. There are three natural regions of the titration curve.
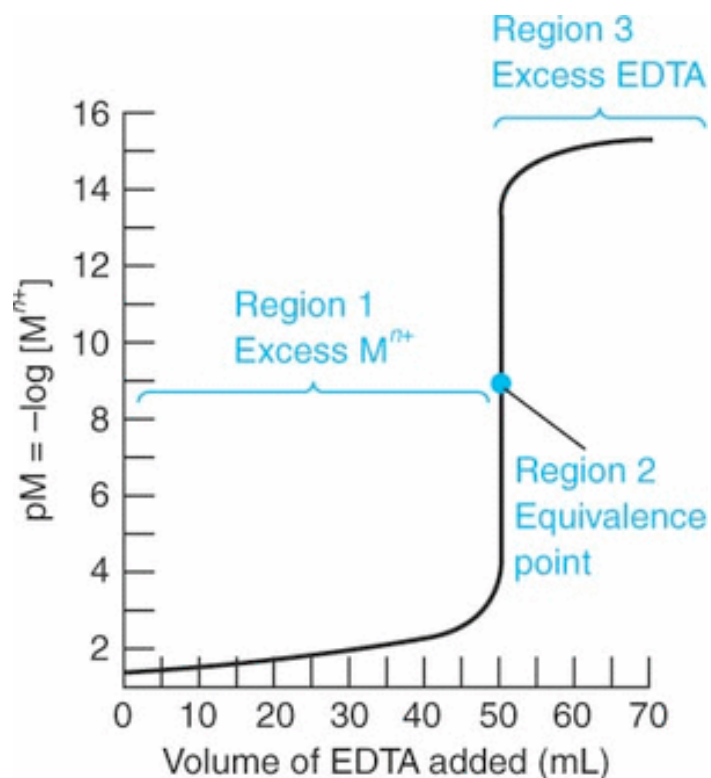
Three regions in an EDTA titration illustrated for reaction of 50.0 mL of 0.0500 M M^{n+} with 0.0500 M EDTA, assuming $K'_f = 1.15 \times 10^{16}$. The concentration of free M^{n+} decreases as the titration proceeds.

EDTA Titration Curves, 2

Region 1: Before the EP

In this region, there is excess M^{n+} left in solution after the EDTA has been consumed. The concentration of free metal ion is equal to the concentration of excess, unreacted M^{n+}. The dissociation of MY^{n-4} is negligible.

Region 2: At the EP

There is exactly as much EDTA as metal in the solution. We can treat the solution as if it had been made by dissolving pure MY^{n-4}. Some free M^{n+} is generated by the slight dissociation of MY^{n-4}.

$$MY^{n-4} \rightleftharpoons M^{n+} + EDTA$$

where EDTA represents EDTA in all uncomplexed forms.

Region 3: After the EP

Now there is excess EDTA, and virtually all the metal ion is in the form MY^{n-4}. The concentration of free EDTA can be equated to the concentration of excess EDTA added after the equivalence point.

Titration Calculations

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

$$Ca^{2+} + EDTA \rightarrow CaY^{2-}$$

$$K_f' = \alpha_{Y^{4-}} K_f = (0.30)(10^{10.65}) = 1.3_4 \times 10^{10}$$

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

Calculated titration curves for Ca^{2+} and Sr^{2+} show a distinct break at the EP, where the slope is greatest. The Ca^{2+} end point is more distinct than that of Sr^{2+} because the K_f' for CaY^{2-} is greater than that of SrY^{2-}. If the pH is lowered, the conditional formation constant decreases (because $\alpha_{Y^{4-}}$ decreases), and the end point becomes less distinct. The pH cannot be raised arbitrarily high, because metal hydroxide might precipitate.
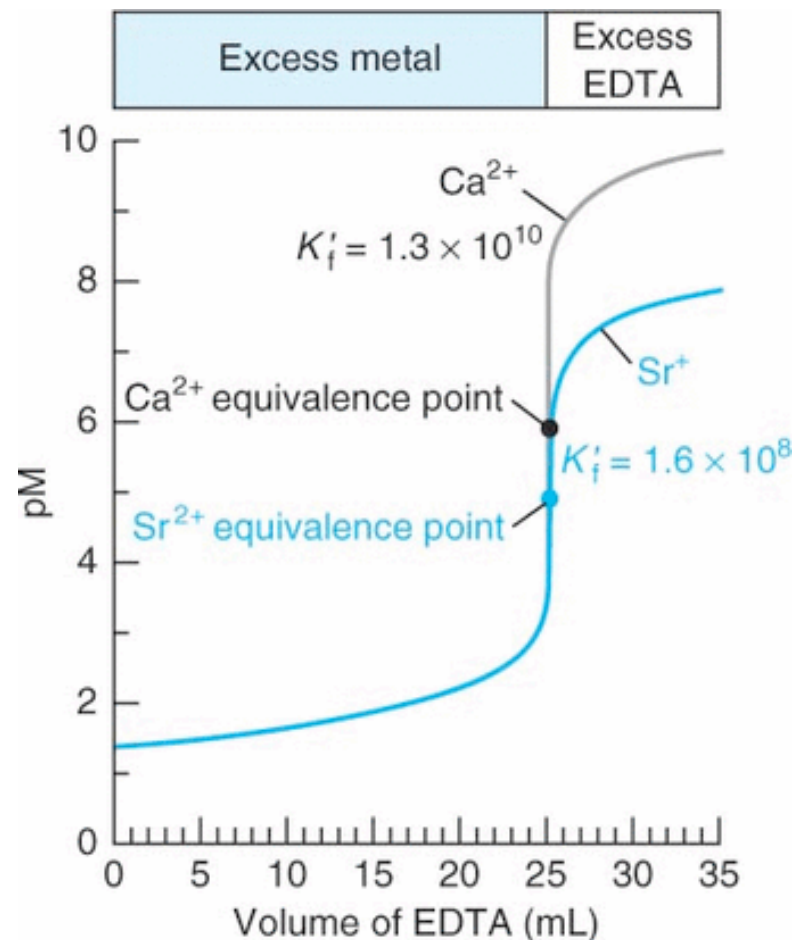
Auxiliary Complexing Agents

EDTA titration conditions in this chapter were selected to prevent metal hydroxide precipitation at the chosen pH. To permit many metals to be titrated in alkaline solutions with EDTA, we use an *auxiliary complexing agent*. This reagent is a ligand, such as ammonia, tartrate, citrate or triethanolamine, that binds the metal strongly enough to prevent metal hydroxide from precipitating but weakly enough to give up the metal when EDTA is added. **e.g.,** Zn^{2+} is usually titrated in ammonia buffer, which fixes the pH and complexes the metal ion to keep it in solution.

Tartaric acid

Citric acid

$N(CH_2CH_2OH)_3$
Triethanolamine
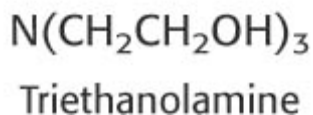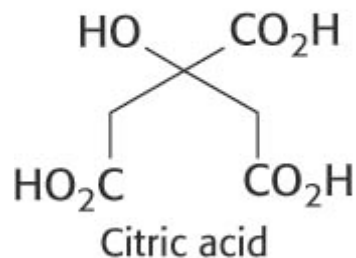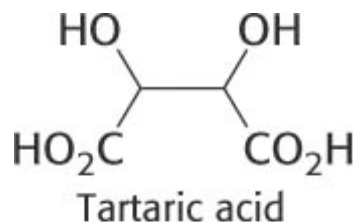
Metal-Ligand Equilibria

Consider a metal ion that forms two complexes with the auxiliary complexing ligand L:

$$M + L \rightleftharpoons ML \qquad \beta_1 = \frac{[ML]}{[M][L]}$$

$$M + 2L \rightleftharpoons ML_2 \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

The equilibrium constants, β_i, are called *overall* or *cumulative formation constants*. The fraction of metal ion in the uncomplexed state, M, can be expressed as

$$\alpha_M = \frac{[M]}{M_{tot}}$$

where M_{tot} is the total concentration of all forms of M (M, ML, and ML_2 in this case). The mass balance for metal is

$$M_{tot} = [M] + [ML] + [ML_2]$$

The equations above allow us to say $[ML] = \beta_1[M][L]$ and $[ML_2] = \beta_2[M][L]^2$. Therefore,

$$M_{tot} = [M] + \beta_1[M][L] + \beta_2[M][L]^2$$
$$= [M]\{1 + \beta_1[L] + \beta_2[L]^2\}$$

Metal-Ligand Equilibria, 2

Substituting this last result into α_M gives:

$$\text{Fraction of free metal ion:} \quad \alpha_M = \frac{[M]}{[M]\{1 + \beta_1[L] + \beta_2[L]^2\}} = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2}$$

EXAMPLE   **Ammonia Complexes of Zinc**

Zn^{2+} and NH_3 form the complexes $Zn(NH_3)^{2+}$, $Zn(NH_3)_2^{2+}$, $Zn(NH_3)_3^{2+}$, and $Zn(NH_3)_4^{2+}$. If the concentration of free, *unprotonated* NH_3 is 0.10 M, find the fraction of zinc in the form Zn^{2+}. (At any pH, there will also be some NH_4^+ in equilibrium with NH_3.)

Solution   **Appendix I** gives formation constants for the complexes $Zn(NH_3)^{2+}$ ($\beta_1 = 10^{2.18}$), $Zn(NH_3)_2^{2+}$ ($\beta_2 = 10^{4.43}$), $Zn(NH_3)_3^{2+}$ ($\beta_3 = 10^{6.74}$), and $Zn(NH_3)_4^{2+}$ ($\beta_4 = 10^{8.70}$). The appropriate form of **Equation 11-16** is

$$\alpha_{Zn^{2+}} = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \beta_4[L]^4} \qquad (11\text{-}17)$$

Equation 11-17 gives the fraction of zinc in the form Zn^{2+}. Putting in [L] = 0.10 M and the four values of β_i gives $\alpha_{Zn^{2+}} = 1.8 \times 10^{-5}$, which means there is very little free Zn^{2+} in the presence of 0.10 M NH_3.

Test Yourself   Find $\alpha_{Zn^{2+}}$ if free, unprotonated $[NH_3]$ = 0.02 M. (**Answer:** 0.007 2)

Titration in Presence of Complexing Agent

Now consider a titration of Zn^{2+} by EDTA in the presence of NH_3. We need a new conditional formation constant to account for the fact that only some of the EDTA is in the form Y^{4-} and only some of the zinc not bound to EDTA is in the form Zn^{2+}:

$$K_f'' = \alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f$$

where

$$\alpha_{Zn^{2+}} = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \beta_4[L]^4} \qquad \alpha_{Y^{4-}} = \frac{K_1 K_2 K_3 K_4 K_5 K_6}{D}$$

For particular values of pH and $[NH_3]$, we can compute K_f'' and proceed with titration calculations as we did earlier, substituting K_f'' for K_f'.

An assumption in this process is that EDTA is a much stronger complexing agent than ammonia, so essentially all EDTA binds Zn^{2+} until the metal ion is consumed.

Titration in Presence of Complexing Agent, 2

EXAMPLE **EDTA Titration in the Presence of Ammonia**

Consider the titration of 50.0 mL of 1.00×10^{-3} M Zn^{2+} with 1.00×10^{-3} M EDTA at pH 10.00 in the presence of 0.10 M NH_3. (This is the concentration of NH_3. There is also NH_4^+ in the solution.) The equivalence point is at 50.0 mL. Find pZn^{2+} after addition of 20.0, 50.0, and 60.0 mL of EDTA.

Solution In **Equation 11-17**, we found that $\alpha_{Zn^{2+}} = 1.8 \times 10^{-5}$. **Table 11-1** tells us that $\alpha_{Y^{4-}} = 0.30$. With K_f from **Table 11-2**, the conditional formation constant is

$$K_f'' = \alpha_{Zn^{2+}}\alpha_{Y^{4-}}K_f = (1.8 \times 10^{-5})(0.30)(10^{16.5}) = 1.7 \times 10^{11}$$

(a) Before the equivalence point—20.0 mL: Because the equivalence point is 50.0 mL, the fraction of Zn^{2+} remaining is 30.0/50.0. The dilution factor is 50.0/70.0. Therefore, the concentration of zinc not bound to EDTA is

$$C_{Zn^{2+}} = \left(\frac{30.0}{50.0}\right)(1.00 \times 10^{-3}\,M)\left(\frac{50.0}{70.0}\right) = 4.3 \times 10^{-4}\,M$$

However, nearly all zinc not bound to EDTA is bound to NH_3. The concentration of free Zn^{2+} is

$$[Zn^{2+}] = \alpha_{Zn^{2+}}C_{Zn^{2+}} = (1.8 \times 10^{-5})(4.3 \times 10^{-4}) = 7.7 \times 10^{-9}\,M$$
$$\Rightarrow pZn^{2+} = -\log[Zn^{2+}] = 8.11$$

Let's try a reality check. The product $[Zn^{2+}][OH^-]^2$ is $[10^{-8.11}][10^{-4.00}]^2 = 10^{-16.11}$, which does not exceed the solubility product of $Zn(OH)_2$ ($K_{sp} = 10^{-15.52}$).

Titration in Presence of Complexing Agent, 3

(b) *At the equivalence point—50.0 mL:* At the equivalence point, the dilution factor is 50.0/100.0, so $[ZnY^{2-}] = (50.0/100.0)(1.00 \times 10^{-3}$ M$) = 5.00 \times 10^{-4}$ M. We then create a table of concentrations:

	$C_{Zn^{2+}} + EDTA \rightleftharpoons$		ZnY^{2-}
Initial concentration (M)	0	0	5.00×10^{-4}
Final concentration (M)	x	x	$5.00 \times 10^{-4} - x$

$$K_f'' = 1.7 \times 10^{11} = \frac{[ZnY^{2-}]}{[C_{Zn^{2+}}][EDTA]} = \frac{5.00 \times 10^{-4} - x}{x^2}$$

$$\Rightarrow x = C_{Zn^{2+}} = 5.4 \times 10^{-8} \, M$$

$$[Zn^{2+}] = \alpha_{Zn^{2+}} C_{Zn^{2+}} = (1.8 \times 10^{-5})(5.4 \times 10^{-8}) = 9.7 \times 10^{-13} \, M$$

$$\Rightarrow pZn^{2+} = -\log[Zn^{2+}] = 12.01$$

Titration in Presence of Complexing Agent, 4
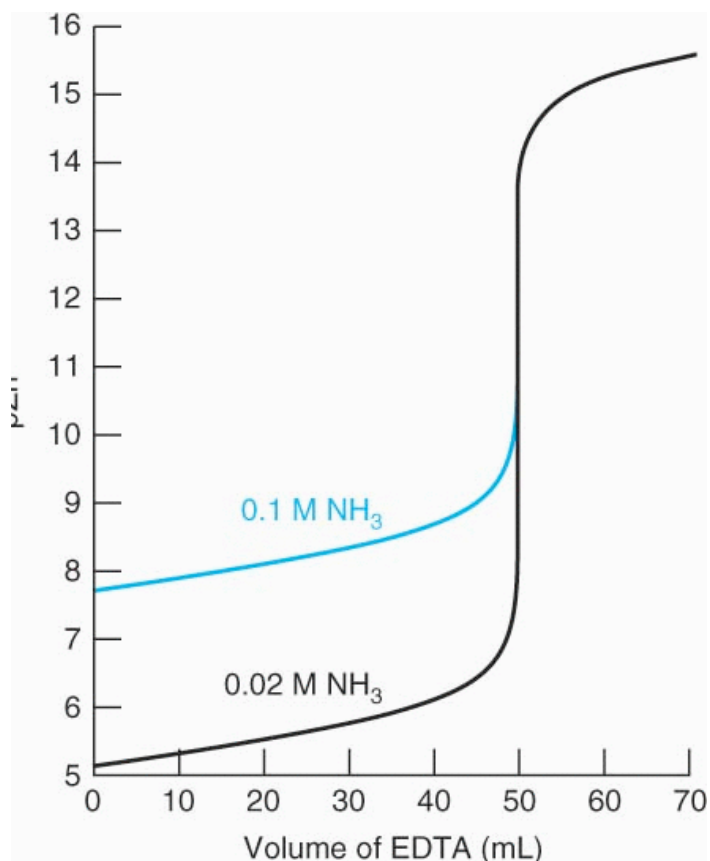
Titration curves for the reaction of 50.0 mL of 1.00×10^{-3} M Zn^{2+} with 1.00×10^{-3} M EDTA at pH 10.00 in the presence of two different concentrations of NH_3. The greater the concentration of NH_3, the smaller the change of pZn^{2+} near the equivalence point. The auxiliary ligand must be kept below the level that would obliterate the end point of the titration.

(c) *After the equivalence point—60.0 mL:* Almost all zinc is in the form ZnY^{2-}. With a dilution factor of 50.0/110.0 for zinc, we find

$$[ZnY^{2-}] = \left(\frac{50.0}{110.0}\right)(1.00 \times 10^{-3} \, M) = 4.5 \times 10^{-4} \, M$$

We also know the concentration of excess EDTA, whose dilution factor is 10.0/110.0:

$$[EDTA] = \left(\frac{10.0}{110.0}\right)(1.00 \times 10^{-3} \, M) = 9.1 \times 10^{-5} \, M$$

Once we know $[ZnY^{2-}]$ and [EDTA], we can use the equilibrium constant to find $[Zn^{2+}]$:

$$\frac{[ZnY^{2-}]}{[Zn^{2+}][EDTA]} = \alpha_{Y^{4-}} K_f = K_f' = (0.30)(10^{16.5}) = 9.5 \times 10^{15}$$

$$\frac{[4.5 \times 10^{-4}]}{[Zn^{2+}][9.1 \times 10^{-5}]} = 9.5 \times 10^{15} \Rightarrow [Zn^{2+}] = 5.3 \times 10^{-16} \, M$$

$$\Rightarrow pZn^{2+} = 15.28$$

After the equivalence point, the problem does not depend on the presence of NH_3, because we know both $[ZnY^{2-}]$ and [EDTA].

Metal Ion Indicators

The most common way to detect the end point in EDTA titrations is with a metal ion indicator. Alternatives include a mercury electrode and an ion-selective electrode (Chapter 14, 8th Ed.). A pH electrode will follow the course of the titration in unbuffered solution, because H_2Y^{2-} releases $2H^+$ when it forms a metal complex.

Metal ion indicators are compounds that change colour when they bind to a metal ion. <u>Useful indicators must bind metal less strongly than EDTA does</u> (must give up their metal ions to EDTA, otherwise, they are not very useful).

A typical titration is the reaction of Mg^{2+} with EDTA at pH 10 with *Calmagite* indicator.

$$MgIn + EDTA \rightarrow MgEDTA + In$$

Red   Colorless   Colorless   Blue

Start of the experiment: a small amount of indicator (**In**) is added to the colourless solution of Mg^{2+} to form a red complex.

As EDTA is added: **In** reacts first with free, colourless Mg2+.

At the EP: When free Mg^{2+} is used up, the last EDTA added before the equivalence point displaces indicator from the red **MgIn** complex.

After the EP: The change from the red **MgIn** to blue unbound **In** signals the end point.

Most metal ion indicators are also acid-base indicators. Because the colour of free indicator is pH dependent, <u>most indicators can be used only in certain pH ranges</u>.

Metal Ion Indicators, 2

| Name	Structure	pK_a	Color of free indicator	Color of metal ion complex
Calmagite	(H_2In^-)	$pK_2 = 8.1$ $pK_3 = 12.4$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Eriochrome black T	(H_2In^-)	$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Murexide	(H_4In^-)	$pK_2 = 9.2$ $pK_3 = 10.9$	H_4In^- red-violet H_3In^{2-} violet H_2In^{3-} blue	Yellow (with Co^{2+}, Ni^{2+}, Cu^{2+}); red with Ca^{2+}
Xylenol orange	(H_3In^{3-})	$pK_2 = 2.32$ $pK_3 = 2.85$ $pK_4 = 6.70$ $pK_5 = 10.47$ $pK_6 = 12.23$	H_5In^- yellow H_4In^{2-} yellow H_3In^{3-} yellow H_2In^{4-} violet HIn^{5-} violet In^{6-} violet	Red
Pyrocatechol violet	(H_3In^-)	$pK_1 = 0.2$ $pK_2 = 7.8$ $pK_3 = 9.8$ $pK_4 = 11.7$	H_4In red H_3In^- yellow H_2In^{2-} violet HIn^{3-} red-purple	Blue

Guide to EDTA titrations of common metals
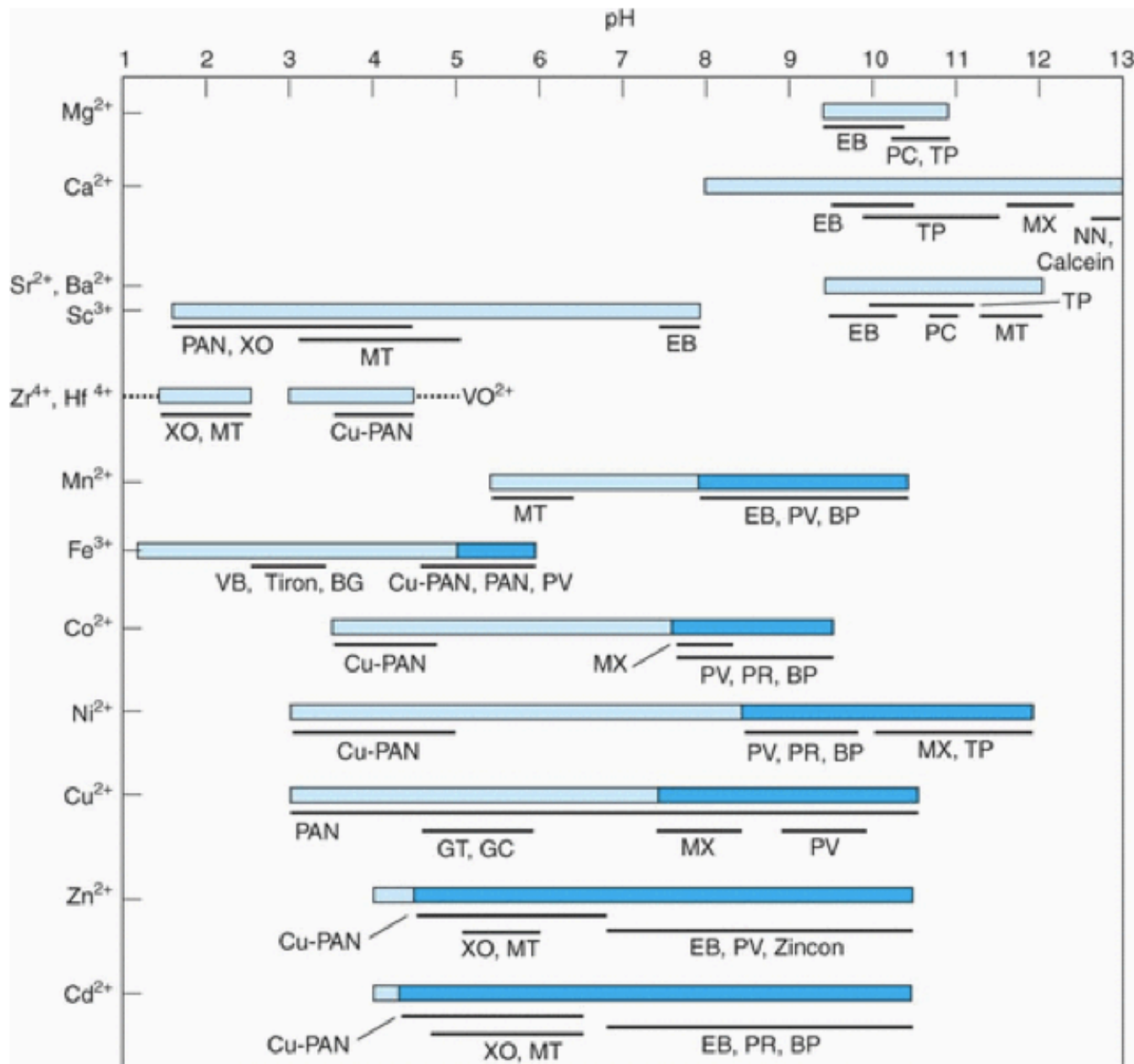
Abbreviations for indicators:
BG, Bindschedler's green leuco base
BP, Bromopyrogallol red
EB, Eriochrome black T
GC, Glycinecresol red
GT, Glycinethymol blue
MT, Methylthymol blue
MX, Murexide
NN, Patton & Reeder's dye
PAN, Pyridylazonaphthol
Cu-PAN, PAN plus Cu-EDTA
PC, o-Cresolphthalein complexone
PR, Pyrogallol red
PV, Pyrocatechol violet
TP, Thymolphthalein complexone
VB, Variamine blue B base
XO, Xylenol orange

Guide to EDTA titrations of common metals
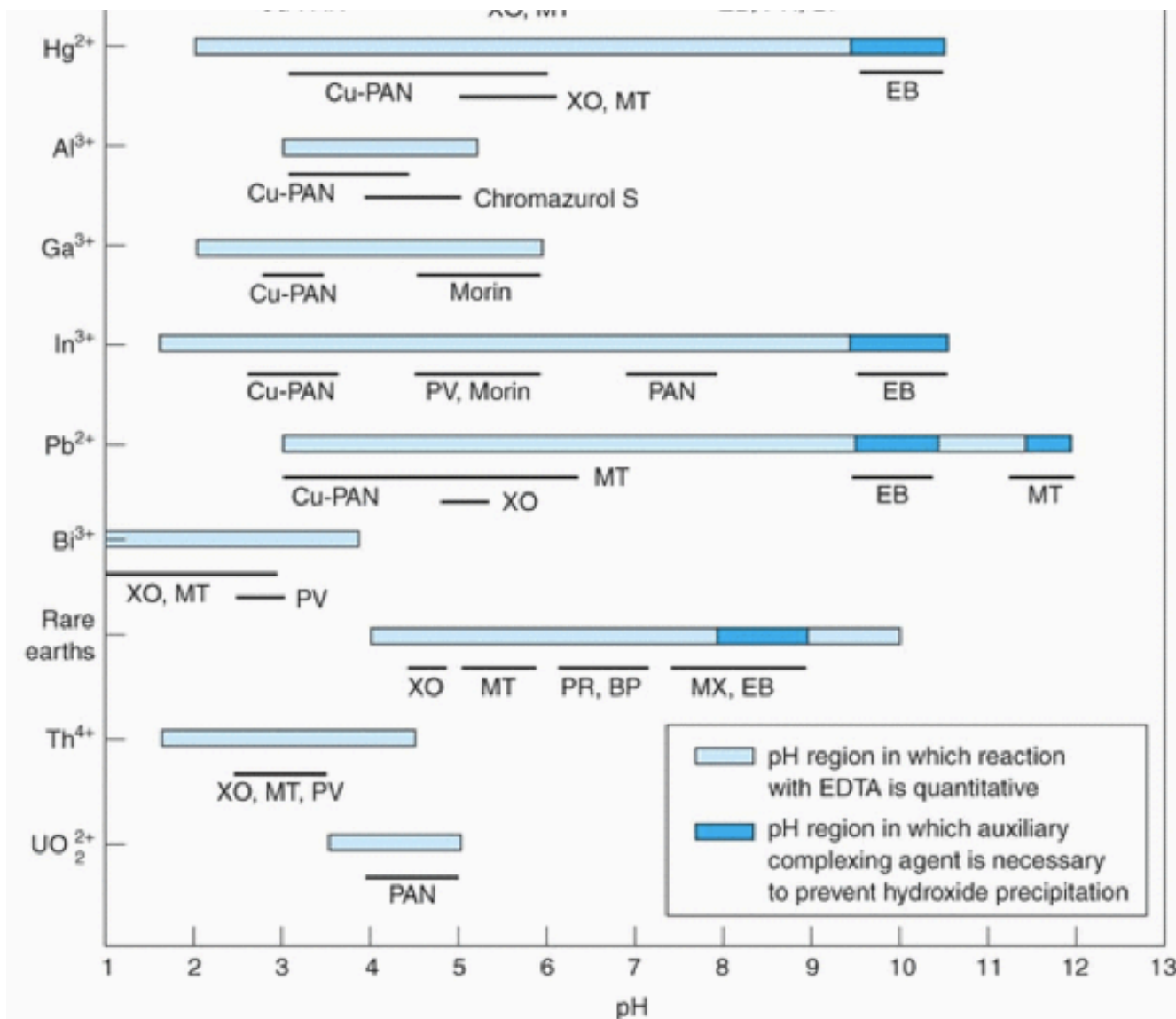
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MX, Murexide
NN, Patton & Reeder's dye
PAN, Pyridylazonaphthol
Cu-PAN, PAN plus Cu-EDTA
PC, o-Cresolphthalein complexone
PR, Pyrogallol red
PV, Pyrocatechol violet
TP, Thymolphthalein complexone
VB, Variamine blue B base
XO, Xylenol orange

EDTA Titration Techniques

1. **Direct titration**: Analyte is titrated with standard EDTA. Analyte is buffered to a pH at which the conditional formation constant for the metal-EDTA complex is large and the colour of the free indicator is distinctly different from that of the metal-indicator complex.

2. **Back titration**: A known excess of EDTA is added to the analyte. Excess EDTA is then titrated with a standard solution of a second metal ion. A back titration is necessary if analyte precipitates in the absence of EDTA, if it reacts too slowly with EDTA, or if it blocks the indicator. The metal ion for the back titration must not displace analyte from EDTA.

EXAMPLE   **A Back Titration**

Ni^{2+} can be analyzed by a back titration using standard Zn^{2+} at pH 5.5 with xylenol orange indicator. A solution containing 25.00 mL of Ni^{2+} in dilute HCl is treated with 25.00 mL of 0.052 83 M Na_2EDTA. The solution is neutralized with NaOH, and the pH is adjusted to 5.5 with acetate buffer. The solution turns yellow when a few drops of indicator are added. Titration with 0.022 99 M Zn^{2+} requires 17.61 mL to reach the red end point. What is the molarity of Ni^{2+} in the unknown?

Solution   The unknown was treated with 25.00 mL of 0.052 83 M EDTA, which contains (25.00 mL)(0.052 83 M) = 1.320 8 mmol of EDTA. Back titration required (17.61 mL) × (0.022 99 M) = 0.404 9 mmol of Zn^{2+}. Because 1 mol of EDTA reacts with 1 mol of any metal ion, there must have been

$$1.320\ 8 \text{ mmol EDTA} - 0.404\ 9 \text{ mmol Zn}^{2+} = 0.915\ 9 \text{ mmol Ni}^{2+}$$

The concentration of Ni^{2+} is 0.915 9 mmol/25.00 mL = 0.036 64 M.

EDTA Titration Techniques, 2

3. **Displacement titration**: Hg^{2+} does not have a satisfactory indicator, but a displacement titration is feasible. Hg^{2+} is treated with excess $Mg(EDTA)^{2-}$ to displace Mg^{2+}, which is titrated with standard EDTA.

$$M^{n+} + MgY^{2-} \rightarrow MY^{n-4} + Mg^{2+}$$
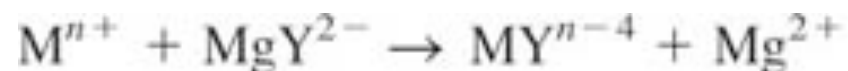
The conditional formation constant for $Hg(EDTA)^{2-}$ must be greater than that for $Mg(EDTA)^{2-}$, or else Mg^{2+} will not be displaced from $Mg(EDTA)^{2-}$.

4. **Indirect titration**: Anions that precipitate with certain metal ions can be analyzed with EDTA by indirect titration. For example, sulphate can be analyzed by precipitation with excess Ba^{2+} at pH 1. The BaSO4(s) is washed and then boiled with excess EDTA at pH 10 to bring Ba^{2+} back into solution as $Ba(EDTA)^{2-}$. Excess EDTA is back-titrated with Mg^{2+}.

Alternatively, an anion can be precipitated with excess standard metal ion. The precipitate is filtered and washed, and excess metal in the filtrate is titrated with EDTA. Anions such as CO_3^{2-}, CrO_4^{2-}, S^{2-} and SO_4^{2-} can be determined by indirect titration with EDTA

EDTA Titration Techniques, 3

5. **Masking**: A masking agent is a reagent that protects some component of the analyte from reaction with EDTA. For example, Al^{3+} in a mixture of Mg^{2+} and Al^{3+} can be measured by first masking the Al^{3+} with F^-, thereby leaving only the Mg^{2+} to react with EDTA.

The cyanide anion is one of the most common masking agents, masking Cd^{2+}, Zn^{2+}, Hg^{2+}, Co^{2+}, Cu^+, Ag^+, Ni^{2+}, Pd^{2+}, Pt^{2+}, Fe^{2+} and Fe^{3+}, but not Mg^{2+}, Ca^{2+}, Mn^{2+} or Pb^{2+}.

Demasking releases metal ion from a masking agent. Cyanide complexes can be demasked with formaldehyde:

$$M(CN)_m^{n-m} + mH_2CO + mH^+ \rightarrow mH_2C\overset{\displaystyle OH}{\underset{\displaystyle CN}{\diagup\!\!\!\diagdown}} + M^{n+}$$

Formaldehyde
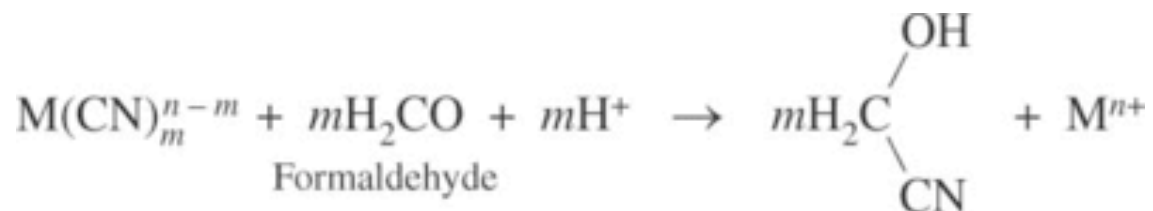
Selectivity afforded by masking, demasking, and pH control allows individual components of complex mixtures of metal ions to be analyzed by EDTA titration.