EDTA Titrations

- A chelating ligand is a molecule, acting as a Lewis base, that attaches to a metal ion
- Most metal ions can bind six ligands
- Monodentate ligands attach at only one site on the metal ion

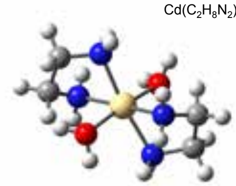
$Cu(NH_3)_4(NO_2)_2^{2+}$

$Mo(CO)_6$

EDTA Titrations

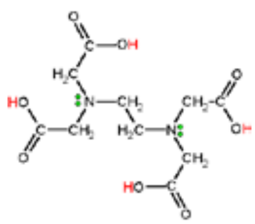
- Multidentate ligands attach at two or more sites on the metal ion

$Cd(C_2H_8N_2)_2(H_2O)_2^{2+}$



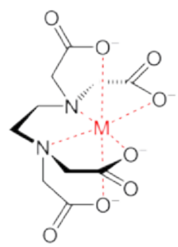
EDTA Titrations

- EDTA = ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$)



EDTA Titrations

- EDTA can attach to a metal ion at up to six sites



EDTA Titrations

- In solution, EDTA is a hexaprotic acid, H_6Y^{2+}:

HOOCCH$_2$ CH$_2$COOH

$\overset{+}{H}$NCH$_2$CH$_2\overset{+}{N}$H

HOOCCH$_2$ CH$_2$COOH

H are acidic hydrogens

pK_1 = 0.0 (carboxylic)	pK_4 = 2.69 (carboxylic)
pK_2 = 1.5 (carboxylic)	pK_5 = 6.13 (amine)
pK_3 = 2.00 (carboxylic)	pK_6 = 10.37 (amine)

EDTA Titrations

- The completely deprotonated form of EDTA is written Y^{4-}:

OOCCH$_2$ CH$_2$COO

$\overset{+}{N}$CH$_2$CH$_2\overset{+}{N}$

OOCCH$_2$ CH$_2$COO

- The fraction of EDTA in the Y^{4-} form, $\alpha_{Y^{4-}}$ is:

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

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

[EDTA] = concentration of all *free* EDTA—not complexed to metal ion

EDTA Titrations

- The form of EDTA varies as a function of pH

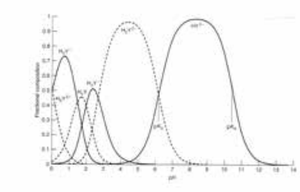


Figure 12-7 or 11-7

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

Table 12-1 or 11-1

EDTA Titrations

- The formation constant, K_f, for a EDTA-metal complex is expressed in terms of Y^{4-}

  $M^{n+} + Y^{4-} \leftrightarrow MY^{n-4}$

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

EDTA Titrations

- However, $[Y^{4-}]$ depends on pH and total [EDTA], so we express a new conditional formation constant, K'_f, as

  $M^{n+} + Y^{4-} \leftrightarrow MY^{n-4}$

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

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

Also called the effective formation constant

EDTA Titrations

- An auxiliary complexing agent is a ligand that binds the metal in a complex to hinder formation of hydroxide precipitate—maintains the metal in solution under basic conditions
- The auxiliary complexing agent is chosen such that the formation constant for this complex is smaller than that for EDTA—when EDTA is added, the metal EDTA complex will form

EDTA Titrations

- Let the auxiliary complexing agent be L:

  $M + L \leftrightarrow ML$ $\qquad \beta_1 = [ML]/[M][L]$

  $M + 2L \leftrightarrow ML_2$ $\qquad \beta_2 = [ML_2]/[M][L]^2$

- The fraction of metal remaining in solution as uncomplexed ion is given by

  $\alpha_M = [M]/C_M$

  $C_M = [M] + [ML] + [ML_2]$

$$[ML] = \beta_1[M][L] \qquad [ML_2] = \beta_2[M][L]^2$$

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

$$\alpha_M = \frac{[M]}{[M]\{1 + \beta_1[L] + \beta_2[L]^2\}} = \frac{1}{\{1 + \beta_1[L] + \beta_2[L]^2\}}$$

EDTA Titrations

- This results in a new conditional formation constant:

  $K''_f = \alpha_M \alpha_{Y^{4-}} K_f$

- Example (p 239 or p 248)

Titrate 50.0 mL of 0.00100 M Zn^{2+} with 0.00100 M EDTA buffered at pH = 10.00 in the presence of 0.100 M NH_3. Determine pZn^{2+} after addition of 20.0 mL, 50.0 mL, and 60.0 mL EDTA.

1. Find $\alpha_{Zn^{2+}}$
2. Find $\alpha_{Y^{4-}}$
3. Determine K''_f

EDTA Titrations

Titrate 50.0 mL of 0.00100 M Zn^{2+} with 0.00100 M EDTA buffered at pH = 10.00 in the presence of 0.100 M NH_3

1. Find $\alpha_{Zn^{2+}}$

   From Appendix I

   $Zn^{2+} + NH_3(aq) \leftrightarrow Zn(NH_3)^{2+}$ $\beta_1 = 1.5_1 \times 10^2$

   $Zn^{2+} + 2NH_3(aq) \leftrightarrow Zn(NH_3)_2^{2+}$ $\beta_2 = 2.6_9 \times 10^4$

   $Zn^{2+} + 3NH_3(aq) \leftrightarrow Zn(NH_3)_3^{2+}$ $\beta_3 = 5.5_0 \times 10^6$

   $Zn^{2+} + 4NH_3(aq) \leftrightarrow Zn(NH_3)_4^{2+}$ $\beta_4 = 5.0_1 \times 10^8$

$$\alpha_{Zn^{2+}} = \frac{1}{1 + (.100)(1.5x10^2) + (.100)^2(2.7x10^4) + (.100)^3(5.5x10^6) + (.100)^4(5.0x10^8)}$$

$$= 1.7_9 x10^{-5}$$

EDTA Titrations

Titrate 50.0 mL of 0.00100 M Zn^{2+} with 0.00100 M EDTA buffered at pH = 10.00 in the presence of 0.100 M NH_3

2. Find α_{Y4-}

   From Table 12-1, at pH = 10.00, $\alpha_{Y4-} = 0.30$

3. Determine K''_f

   $K''_f = \alpha_{Zn2+}\alpha_{Y4-}K_f$

   $K_f = 3.1_6 \times 10^{16}$ (Table 12-2 or 11-2)

   $K''_f = (1.7_9 \times 10^{-5})(0.30)(3.1_6 \times 10^{16})$

   $= 1.7_0 \times 10^{11}$

EDTA Titrations

Titrate 50.0 mL of 0.00100 M Zn^{2+} with 0.00100 M EDTA buffered at pH = 10.00 in the presence of 0.100 M NH_3

- The equivalence point is reached when 50.0 mL of EDTA solution have been added
- Before the equivalence point, essentially all EDTA added will react with Zn^{2+} to form complex—the amount of Zn^{2+} remaining in solution is determined by subtracting the moles of EDTA added from the initial moles of Zn^{2+}

  initial moles Zn^{2+}: (.00100 M)(.0500 L) = 5.00×10^{-5} mol

  At 20.0 mL EDTA added: (.00100 L)(.0200 L) = 2.00×10^{-5} mol

  Moles Zn^{2+} remaining: $5.00 \times 10^{-5} - 2.00 \times 10^{-5} = 3.00 \times 10^{-5}$ mol

  $C_{Zn^{2+}} = 3.00 \times 10^{-5}$ mol/.0700 L = 4.29×10^{-4} M

  However, most of the Zn^{2+} remaining is bound to NH_3—the free Zn^{2+} is given by $[Zn^{2+}]_{free} = \alpha_{Zn2+} C_{Zn^{2+}} = (1.7_9x10^{-5})(4.29x10^{-4})$

  $= 7.6_8 \times 10^{-9}$ $pZn^{2+} = 8.11$

EDTA Titrations

Titrate 50.0 mL of 0.00100 M Zn^{2+} with 0.00100 M EDTA buffered at pH = 10.00 in the presence of 0.100 M NH_3

- At the equivalence point, we can use an ICE table with proper dilution factors. Since K'_f is large, assume all reactants go to products, and then allow some of the products to go back to reactants

  $Zn^{2+} + Y^{4-} \leftrightarrow ZnY^{2-}$

  $[ZnY^{2-}] = 1.00 \times 10^{-3}$ M (50.0 mL/100.0 mL) = 5.00×10^{-4} M

	$C_{Zn^{2+}}$	EDTA	ZnY^{2-}
initial	0	0	5.00×10^{-4}
change	x	x	-x
final	x	x	$5.00 \times 10^{-4} - x$

$$K''_f = 1.7_0x10^{11} = \frac{[ZnY^{2-}]}{C_{Zn^{2+}}[EDTA]} = \frac{5.00x10^{-4} - x}{x^2}$$ assume x is negligible in numerator

$x = C_{Zn^{2+}} = 5.4_1x10^{-8}$ $[Zn^{2+}] = (1.7_9x10^{-5})(5.4_1x10^{-8}) = 9.6_8x10^{-13}$

$pZn^{2+} = 12.01$

EDTA Titrations

Titrate 50.0 mL of 0.00100 M Zn^{2+} with 0.00100 M EDTA buffered at pH = 10.00 in the presence of 0.100 M NH_3

- After the equivalence point, Zn^{2+} has all complexed with EDTA in the form ZnY^{2-}—no zinc-ammonia complex remains in solution because zinc complexes more strongly with EDTA than with NH_3

  For 60.0 mL EDTA solution added:

  $[ZnY^{2-}] = (1.00 \times 10^{-3}$ M)(50.0/110.0) = 4.55×10^{-4} M

  The excess EDTA is given by

  $[EDTA] = (1.00 \times 10^{-3}$ M)(60.0-50.0)/110.0 = 9.09×10^{-5} M

$$Zn^{2+} + Y^{4-} \longrightarrow ZnY^{2-} \qquad K'_f = \alpha_{Y^{4-}}K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][EDTA]}$$

$$= (0.30)(3.1_6x10^{16}) = 9.4_9x10^{15}$$

$$9.4_9x10^{15} = \frac{4.55x10^{-4}}{[Zn^{2+}](9.09x10^{-5})} \Rightarrow [Zn^{2+}] = 5.2_7x10^{-16}$$

$pZn^{2+} = 15.28$