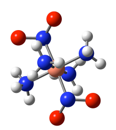
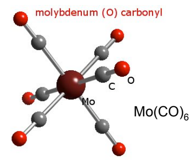
EDTA Titrations

- 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



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

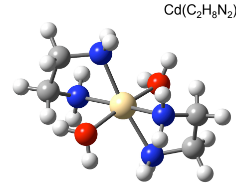


$Mo(CO)_6$

EDTA Titrations

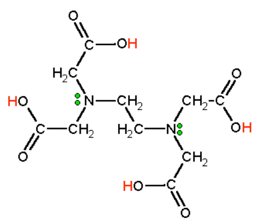
- Multidentate ligands attach at two or more sites on the metal ion

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



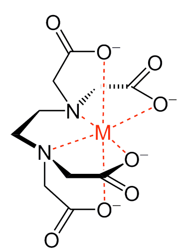
EDTA Titrations

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



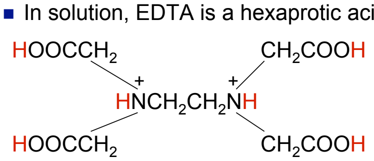
EDTA Titrations

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



EDTA Titrations

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

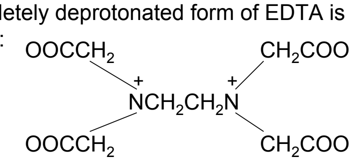


H are acidic hydrogens

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-}:



- 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

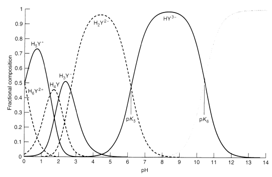


Figure 12-7

pH	α_{Y4-}
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

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], se we express a new conditional formation constant, K'_f, as

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

$$[Y^{4-}] = \alpha_{Y4-}[EDTA]$$

$$K'_f = \alpha_{Y4-}K_f = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

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 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:

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

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

- 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:

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

- Example (p 239)

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 α_{Zn2+}
2. Find α_{Y4-}
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)

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

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

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 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	$5.00 \times 10^{-4} - x$

$$K''_f = 1.7_0 x10^{11} = \frac{[ZnY^{2-}]}{C_{Zn^{2+}}[EDTA]} = \frac{5.00x10^{-4} - x}{x^2}$$ assume x is negligible in numerator

$x = C_{Zn^{2+}} = 5.4_1 x10^{-8}$ $[Zn^{2+}] = (1.7_9x10^{-5})(5.4_1x10^{-8}) = 9.6_8x10^{-13}$

$pZn^{2+} = 12.01$

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

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

$$= (0.30)(3.1_6 x10^{16}) = 9.4_9 x10^{15}$$

$$9.4_9 x10^{15} = \frac{4.55x10^{-4}}{[Zn^{2+}](9.09x10^{-5})} \Rightarrow [Zn^{2+}] = 5.2_7 x10^{-16}$$

$pZn^{2+} = 15.28$