CHAPTER 11
EDTA TITRATIONS

11-1. The chelate effect is the observation that multidentate ligands form more stable metal complexes than do similar, monodentate ligands.

11-2. $\alpha_{Y^{4-}}$ gives the fraction of all free EDTA in the form Y^{4-}.

(a) At pH 3.50:

$$\alpha_{Y^{4-}} = \frac{10^{-0.0}10^{-1.5}10^{-2.00}10^{-2.69}10^{-6.13}10^{-10.37}}{(10^{-3.50})^6 + (10^{-3.50})^5 10^{-0.0} + ... + 10^{-0.0}10^{-1.5}...10^{-10.37}} = 2.7 \times 10^{-10}$$

(b) At pH 10.50:

$$\alpha_{Y^{4-}} = \frac{10^{-0.0}10^{-1.5}10^{-2.00}10^{-2.69}10^{-6.13}10^{-10.37}}{(10^{-10.50})^6 + (10^{-10.50})^5 10^{-0.0} + ... + 10^{-0.0}10^{-1.5}...10^{-10.37}} = 0.57$$

11-3. (a) $K_f' = \alpha_{Y^{4-}} K_f = 0.041 \times 10^{8.79} = 2.5 \times 10^7$

(b) $\qquad\qquad Mg^{2+} \ + \ EDTA \ \rightleftharpoons \ MgY^{2-}$

$\qquad\qquad\quad x \qquad\quad x \qquad\quad 0.050 - x$

$$\frac{0.050 - x}{x^2} = 2.5 \times 10^7 \Rightarrow [Mg^{2+}] = 4.5 \times 10^{-5} \text{ M}$$

11-4. $[Ca^{2+}] = 10^{-9.00}$ M, so essentially all calcium in solution is CaY^{2-}.

$$[CaY^{2-}] = \frac{1.95 \text{ g}}{(200.12 \text{ g/mol}) (0.500 \text{ L})} = 0.019\,49 \text{ M}$$

$$K_f' = (0.041)(10^{10.65}) = \frac{[CaY^{2-}]}{[EDTA][Ca^{2+}]} = \frac{(1.949 \times 10^{-2})}{[EDTA](10^{-9.00})}$$
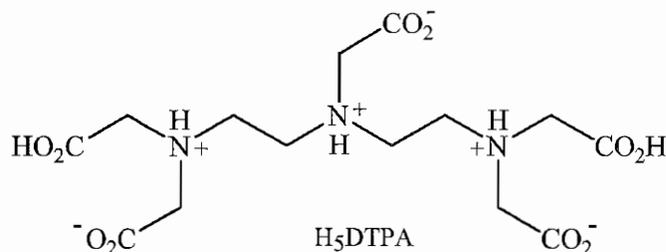
$$\Rightarrow [EDTA] = 0.010\,6 \text{ M}$$

Total EDTA needed $= $ mol CaY^{2-} + mol free EDTA

$\qquad\qquad\qquad = (0.019\,49 \text{ M}) (0.500 \text{ L}) + (0.010\,6 \text{ M}) (0.500 \text{ L}) = 0.015\,0_4$ mol

$\qquad\qquad\qquad = 5.60$ g $Na_2EDTA \cdot 2 H_2O$

11-5.

Neutral H_5DTPA has 2 carboxylic acid protons and 3 ammonium protons. We are not given the pK_a values, but, by analogy with EDTA, we expect carboxyl pK_a values to be below ~3 and ammonium pK_a values to be above ~6. At pH 14, we expect all acidic protons of DTPA to be dissociated, so the predominant

species will be DTPA^{5-}. At pH 3-4, nitrogen should be protonated, but carboxyl groups should be deprotonated. The predominant species is probably H$_3$DTPA^{2-}.

For HSO$_4^-$, pK_a = 2.0. At pH 14 and at pH 3, sulfate is in the form SO$_4^{2-}$.

At pH 14, DTPA^{5-} is apparently a strong enough ligand to chelate Ba^{2+} and dissolve BaSO$_4(s)$. At pH 3-4, H$_3$DTPA^{2-} is not a strong enough ligand to dissolve BaSO$_4(s)$. An equivalent statement is that H$^+$ at a concentration of 10^{-3}-10^{-4} M competes with Ba^{2+} for binding sites on DTPA, but H$^+$ at a concentration of 10^{-14} M does not compete with Ba^{2+} for binding sites on DTPA.

Now that you have seen my reasoning, I'll provide some more information. The pK_a values for DTPA, beginning with the fully protonated H$_8$DTPA^{3+}, are

H$_8$DTPA^{3+}	pK_1 = -0.1	CO$_2$H		H$_4$DTPA$^-$	pK_5 = 2.7	CO$_2$H
H$_7$DTPA^{2+}	pK_2 = 0.7	CO$_2$H		H$_3$DTPA^{2-}	pK_6 = 4.3	NH$^+$
H$_6$DTPA$^+$	pK_3 = 1.6	CO$_2$H		H$_2$DTPA^{3-}	pK_7 = 8.6	NH$^+$
H$_5$DTPA	pK_4 = 2.0	CO$_2$H		HDTPA^{4-}	pK_8 = 10.5	NH$^+$

As pH is lowered from 14, the three nitrogen atoms are 50% protonated at pH 10.5, 8.6, and 4.3. The third nitrogen atom is not quite fully protonated at pH 3-4. The predominant species is H$_3$DTPA^{2-}, as I guessed correctly. The species H$_4$DTPA$^-$ and H$_2$DTPA^{3-} are also present to some extent in the pH range 3-4.

11-6. (a) mmol EDTA = mmol M^{n+}

$(V_e)(0.050\,0\text{ M}) = (100.0\text{ mL})(0.050\,0\text{ M}) \Rightarrow V_e = 100.0\text{ mL}$

(b) $[M^{n+}] = \left(\dfrac{1}{2}\right) \cdot (0.050\,0\text{ M}) \cdot \left(\dfrac{100}{150}\right) = 0.016\,7\text{ M}$

           fraction   original   dilution
       remaining   concentration   factor

(c) 0.041 (Table 11-1)
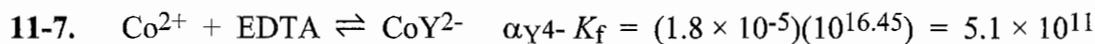
(d) $K_f' = (0.041)(10^{12.00}) = 4.1 \times 10^{10}$

(e) $[MY^{n-4}] = (0.050\,0\text{ M})\left(\dfrac{100}{200}\right) = 0.025\,0\text{ M}$

$\dfrac{[MY^{n-4}]}{[M^{n+}][EDTA]} = \dfrac{0.025\,0-x}{x^2} = 4.1 \times 10^{10} \Rightarrow x = [M^{n+}] = 7.8 \times 10^{-7}\text{ M}$

(f) $[EDTA] = (0.050\,0\text{ M})\left(\dfrac{10.0}{210.0}\right) = 2.38 \times 10^{-3}\text{ M}$

$[MY^{n-4}] = (0.050\,0\text{ M})\left(\dfrac{100.0}{210.0}\right) = 2.38 \times 10^{-2}\text{ M}$

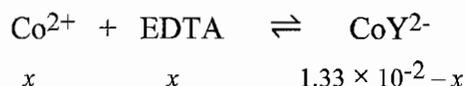$\dfrac{[MY^{n-4}]}{[M^{n+}][EDTA]} = \dfrac{(2.38 \times 10^{-2})}{[M^{n+}](2.38 \times 10^{-3})} = 4.1 \times 10^{10} \Rightarrow [M^{n+}] = 2.4 \times 10^{-10}\text{ M}$

11-7. $Co^{2+} + EDTA \rightleftharpoons CoY^{2-}$ $\alpha_{Y^{4-}} K_f = (1.8 \times 10^{-5})(10^{16.45}) = 5.1 \times 10^{11}$

$$V_e = (25.00)\left(\frac{0.020\,26\,M}{0.038\,55\,M}\right) = 13.14\,mL$$

(a)   <u>12.00 mL</u>: $[Co^{2+}] = \left(\frac{13.14 - 12.00}{13.14}\right)(0.020\,26\,M)\left(\frac{25.00}{37.00}\right)$

$$= 1.19 \times 10^{-3}\,M \Rightarrow pCo^{2+} = 2.93$$

(b)   <u>V_e</u>: Formal concentration of CoY^{2-} is $\left(\frac{25.00}{38.14}\right)(0.020\,26\,M) = 1.33 \times 10^{-2}\,M$

$$\begin{array}{ccccc} Co^{2+} & + & EDTA & \rightleftharpoons & CoY^{2-} \\ x & & x & & 1.33 \times 10^{-2} - x \end{array}$$

$$\frac{1.33 \times 10^{-2} - x}{x^2} = \alpha_{Y^{4-}} K_f \Rightarrow x = 1.6 \times 10^{-7}\,M \Rightarrow pCo^{2+} = 6.79$$

(c)   <u>14.00 mL</u>:   Formal concentration of CoY^{2-} is $\left(\frac{25.00}{39.00}\right)(0.020\,26\,M)$

$$= 1.30 \times 10^{-2}\,M$$

Formal concentration of EDTA is $\left(\frac{14.0 - 13.14}{39.00}\right)(0.038\,55\,M) = 8.50 \times 10^{-4}\,M$

$$[Co^{2+}] = \frac{[CoY^{2-}]}{[EDTA]\,K_f'} = \frac{1.30 \times 10^{-2}}{8.50 \times 10^{-4}\,(5.1 \times 10^{11})} = 3.0 \times 10^{-11}\,M$$

$$\Rightarrow pCo^{2+} = 10.52$$

11-8.   Titration reaction: $Mn^{2+} + EDTA \rightleftharpoons MnY^{2-}$

$$K_f' = \alpha_{Y^{4-}} K_f = \;\; = (4.2 \times 10^{-3})(10^{13.89}) = 3.3 \times 10^{11}$$

The equivalence point is 50.0 mL.   Sample calculations:

<u>20.0 mL</u>: The fraction of Mn^{2+} that has reacted is 2/5 and the fraction remaining is 3/5.

$$[Mn^{2+}] = \left(\frac{30.0}{50.0}\right)(0.020\,0\,M)\left(\frac{25.0}{45.0}\right) = 6.67 \times 10^{-3}\,M \Rightarrow pMn^{2+} = 2.18$$

<u>50.0 mL</u>: The formal concentration of MnY^{2-} is

$$[MnY^{2-}] = \left(\frac{25.0}{75.0}\right)(0.020\,0\,M) = 0.006\,67\,M$$

$$\begin{array}{ccccc} Mn^{2+} & + & EDTA & \rightleftharpoons & MnY^{2-} \\ x & & x & & 0.006\,67 - x \end{array}$$

$$\frac{0.006\,67 - x}{x^2} = \alpha_{Y^{4-}} K_f \Rightarrow x = 1.4 \times 10^{-7} \Rightarrow pMn^{2+} = 6.85$$
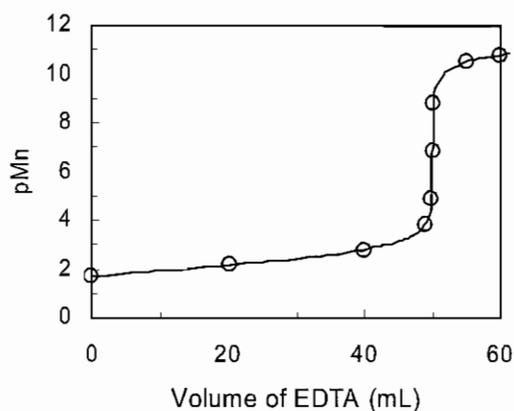
<u>60.0 mL</u>: There are 10.0 mL of excess EDTA.

$$[\text{EDTA}] = \left(\frac{10.0}{85.0}\right)(0.010\,0\ \text{M}) = 1.176 \times 10^{-3}\ \text{M}$$

$$[\text{MnY}^{2-}] = \left(\frac{25.0}{85.0}\right)(0.020\,0\ \text{M}) = 5.88 \times 10^{-3}\ \text{M}$$

$$[\text{Mn}^{2+}] = \frac{[\text{MnY}^{2-}]}{[\text{EDTA}]K_f'} = 1.5 \times 10^{-11} \Rightarrow \text{pMn}^{2+} = 10.82$$

Volume (mL)	pMn^{2+}	Volume	pMn^{2+}	Volume	pMn^{2+}
0	1.70	49.0	3.87	50.1	8.82
20.0	2.18	49.9	4.87	55.0	10.51
40.0	2.81	50.0	6.85	60.0	10.82

11-9. Titration reaction: $\text{Ca}^{2+} + \text{EDTA} \rightleftharpoons \text{CaY}^{2-}$

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

The equivalence point is 50.0 mL.   Sample calculations:

<u>20.0 mL</u>: The fraction of EDTA consumed is 2/5.

$$[\text{EDTA}] = \left(\frac{30.0}{50.0}\right)(0.020\,0\ \text{M})\left(\frac{25.0}{45.0}\right) = 0.006\,67\ \text{M}$$

$$[\text{CaY}^{2-}] = \left(\frac{20.0}{50.0}\right)(0.020\,0\ \text{M})\left(\frac{25.0}{45.0}\right) = 0.004\,44\ \text{M}$$

$$[\text{Ca}^{2+}] = \frac{[\text{CaY}^{2-}]}{[\text{EDTA}]K_f'} = 4.9_7 \times 10^{-11} \Rightarrow \text{pCa}^{2+} = 10.30$$

<u>50.0 mL</u>: The formal concentration of CaY^{2-} is

$$[CaY^{2-}] = \left(\frac{25.0}{75.0}\right)(0.020\,0\ M) = 0.006\,67\ M$$

$$\begin{array}{ccccc} Ca^{2+} & + & EDTA & \rightleftharpoons & CaY^{2-} \\ x & & x & & 0.006\,67 - x \end{array}$$
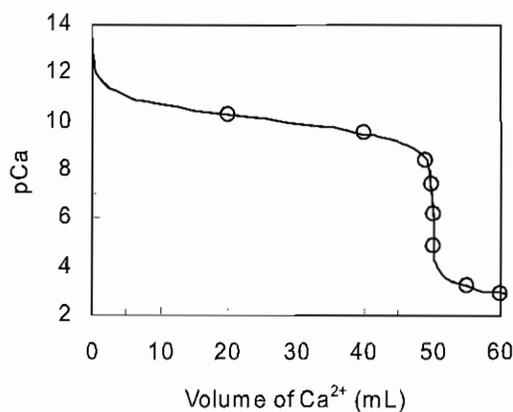
$$\frac{0.006\,67 - x}{x^2} = \alpha_{Y^{4-}}\, K_f \Rightarrow x = 7.0_5 \times 10^{-7}\ M \Rightarrow pCa^{2+} = 6.15$$

<u>50.1 mL</u>: There is an excess of 0.1 mL of Ca^{2+}.

$$[Ca^{2+}] = \left(\frac{0.1}{75.1}\right)(0.010\,0\ M) = 1.33 \times 10^{-5}\ M \Rightarrow pCa^{2+} = 4.88$$

Volume (mL)	pCa^{2+}	Volume	pCa^{2+}	Volume	pCa^{2+}
0	(∞)	49.0	8.44	50.1	4.88
20.0	10.30	49.9	7.43	55.0	3.20
40.0	9.52	50.0	6.15	60.0	2.93

11-10. There is more VO^{2+} than EDTA in this solution.

$$[VO^{2+}] = \left(\frac{0.10}{29.9}\right)(0.010\,0\ M) = 3.34 \times 10^{-5}\ M$$

$$[VOY^{2-}] = \left(\frac{9.90}{29.90}\right)(0.010\,0\ M) = 3.31 \times 10^{-3}\ M$$

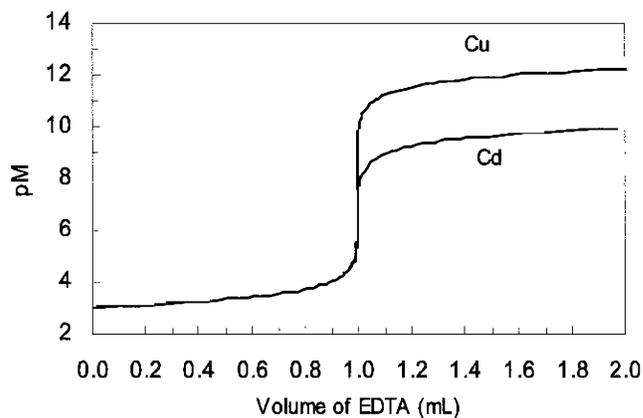K_f for $VOY^{2-} = 10^{18.7}$; pK_6 for $H_6Y^{2+} = 10.37$; pH = 4.00

$$[Y^{4-}] = \frac{[VOY^{2-}]}{[VO^{2+}]\, K_f} = 1.98 \times 10^{-17}\ M$$

$$[HY^{3-}] = \frac{[H^+][Y^{4-}]}{K_6} = 4.6 \times 10^{-11}\ M$$

11-11.

	A	B	C	D	E	F	G
1	Titration of V_M mL of C_M M Cu^{2+} with C(ligand) M EDTA						
2							
3	C_M =	pM	M	Phi	V(EDTA)		
4	0.001	3.0	1.00E-03	0.000	0.000		
5	V_M =	4.0	1.00E-04	0.891	0.891		
6	10	5.0	1.00E-05	0.989	0.989		
7	C(ligand) =	6.0	1.00E-06	0.999	0.999		
8	0.01	7.0	1.00E-07	1.000	1.000		
9	$K_f^{'}$ =	8.0	1.00E-08	1.000	1.000		
10	1.75E+12	9.0	1.00E-09	1.001	1.001		
11	$\alpha(Y^{4-})$=	10.0	1.00E-10	1.006	1.006		
12	2.90E-07	11.0	1.00E-11	1.057	1.057		
13	K_f =	12.0	1.00E-12	1.572	1.572		
14	6.0256E+18	12.3	5.01E-13	2.142	2.142		
15							
16	A10 = A12*A14						
17	C4 = 10^-B4						
18	D4 = (1+$A$10*C4-(C4+C4*C4*$A$10)/$A$4)/(C4*$A$10+(C4+C4*C4*$A$10)/$A$8)						
19	E4 = D4*$A$4*$A$6/$A$8						

11-12. The spreadsheet below gives representative calculations for the pH 7.

	A	B	C	D	E	F
1	Titration of 10 mL of 1 mM Ca^{2+} with 1 mM EDTA vs pH					
2	pH 7					
3	C_M =	pM	M	Phi	V(ligand)	
4	0.001	3.000	1.00E-03	0.000	0.000	
5	V_M =	3.250	5.62E-04	0.280	2.801	
6	10	3.500	3.16E-04	0.520	5.196	
7	C(ligand) =	3.750	1.78E-04	0.698	6.982	
8	0.001	4.000	1.00E-04	0.819	8.186	
9	K_f' =	4.500	3.16E-05	0.940	9.404	
10	1.70E+07	5.000	1.00E-05	0.986	9.859	
11	$\alpha(Y^{4-})$ =	5.500	3.16E-06	1.012	10.121	
12	3.80E-04	6.000	1.00E-06	1.057	10.567	
13	K_f =	6.500	3.16E-07	1.185	11.855	
14	4.4668E+10	7.000	1.00E-07	1.589	15.887	
15	A10 = A12*A14					
16	C4 = 10^-B4					
17	D4 = (1+A$10*C4-(C4+C4*C4*A$10)/A$4)/(C4*A$10+(C4+C4*C4*A$10)/A$8)					
18	E4 = D4*A$4*A$6/A$8					
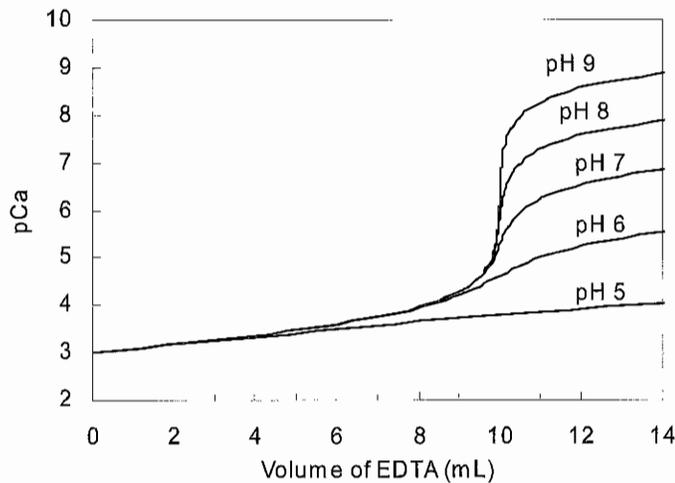
11-13.

	A	B	C	D	E	F	G
1	Titration of EDTA with metal						
2							
3	C_M =	pM	M	Phi	V_M		
4	0.08	14.640	2.29E-15	0.004	0.100		
5	V(ligand) =	12.844	1.43E-13	0.200	5.004		
6	50	12.418	3.82E-13	0.400	10.007		
7	C(ligand) =	12.066	8.59E-13	0.600	15.004		
8	0.04	11.640	2.29E-12	0.800	20.003		
9	K_f' =	10.860	1.38E-11	0.960	24.005		
10	1.75E+12	6.910	1.23E-07	1.000	25.000		
11	$\alpha(Y^{4-})$	2.978	1.05E-03	1.040	25.999		
12	2.90E-07	2.301	5.00E-03	1.200	30.000		
13	K_f =						
14	6.0256E+18						
15							
16	A10 = A12*A14						
17	C4 = 10^-B4						
18	D4 = (C4*\$A\$10+(C4+C4*C4*\$A\$10)/\$A\$8)/(1+\$A\$10*C4-(C4+C4*C4*\$A\$10)/\$A\$4)						
19	E4 = D4*\$A\$8*\$A\$6/\$A\$4						

11-14. An auxiliary complexing agent forms a weak complex with analyte ion, thereby keeping it in solution without interfering with the EDTA titration. For example, NH_3 keeps Zn^{2+} in solution at high pH, but is easily displaced by EDTA.

11-15. (a) $\beta_2 = K_1K_2 = \beta_1K_2 \Rightarrow K_2 = \beta_2/\beta_1 = 10^{3.63}/10^{2.23} = 10^{1.40} = 25$

(b) $\alpha_{Cu^{2+}} = \dfrac{1}{1+\beta_1[L] + \beta_2[L]^2} = \dfrac{1}{1 + 10^{2.23}(0.100)+10^{3.63}(0.100)^2} = 0.017$

11-16. $Cu^{2+} + Y^{4-} \rightleftharpoons CuY^{2-}$ $\qquad K_f = 10^{18.78} = 6.0_3 \times 10^{18}$

$\alpha_{Y^{4-}} = 0.81$ at pH 11.00 (Table 11-1)

For Cu^{2+} and NH_3, Appendix I gives $\log \beta_1 = 3.99$, $\log \beta_2 = 7.33$, $\log \beta_3 = 10.06$, and $\log \beta_4 = 12.03$. Therefore, $\beta_1 = 9.8 \times 10^3$, $\beta_2 = 2.1 \times 10^7$, $\beta_3 = 1.15 \times 10^{10}$, and $\beta_4 = 1.07 \times 10^{12}$.

$\alpha_{Cu^{2+}} = \dfrac{1}{1 + \beta_1(1.00) + \beta_2(1.00)^2 + \beta_3(1.00)^3 + \beta_4(1.00)^4} = 9.2_3 \times 10^{-13}$

$K_f' = \alpha_{Y^{4-}} K_f = 4.8_8 \times 10^{18}$

$K_f'' = \alpha_{Y^{4-}} \alpha_{Cu^{2+}} K_f = 4.5_1 \times 10^6$

Equivalence point = 50.00 mL

(a) At 0 mL, the total concentration of copper is $C_{Cu^{2+}} = 0.001\,00$ M and

$[Cu^{2+}] = \alpha_{Cu^{2+}} C_{Cu^{2+}} = 9.2_3 \times 10^{-16}$ M $\Rightarrow$ p$Cu^{2+} = 15.03$

(b)   At 1.00 mL, $C_{Cu^{2+}} = \left(\dfrac{49.00}{50.00}\right)(0.001\ 00\ M)\left(\dfrac{50.00}{51.00}\right) = 9.61 \times 10^{-4}\ M$
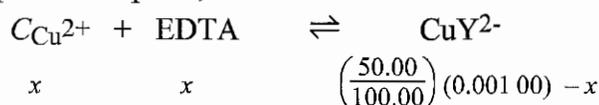
$\qquad\qquad\qquad\quad$ fraction $\qquad$ original $\qquad$ dilution
$\qquad\qquad\qquad\quad$ remaining $\;$ concentration $\;$ factor

$\qquad$ $[Cu^{2+}] = \alpha_{Cu^{2+}}\, C_{Cu^{2+}} = 8.8_7 \times 10^{-16}\ M \Rightarrow pCu^{2+} = 15.05$

(c)   At 45.00 mL, $C_{Cu^{2+}} = \left(\dfrac{5.00}{50.00}\right)(0.001\ 00)\left(\dfrac{50.00}{95.00}\right) = 5.26 \times 10^{-5}\ M$

$\qquad$ $[Cu^{2+}] = \alpha_{Cu^{2+}}\, C_{Cu^{2+}} = 5.0_4 \times 10^{-17}\ M \Rightarrow pCu^{2+} = 16.30$

(d)   At the equivalence point, we can write

$$C_{Cu^{2+}} \quad + \quad EDTA \quad \rightleftharpoons \quad CuY^{2-}$$

$\qquad\qquad$ $x \qquad\qquad\quad x \qquad\qquad\qquad \left(\dfrac{50.00}{100.00}\right)(0.001\ 00) - x$

$\dfrac{0.000\ 500 - x}{x^2} = K_f'' = 4.5_1 \times 10^6 \Rightarrow x = C_{Cu^{2+}} = 1.04 \times 10^{-5}\ M$

$\qquad$ $[Cu^{2+}] = \alpha_{Cu^{2+}}\, C_{Cu^{2+}} = 9.6_2 \times 10^{-18}\ M \Rightarrow pCu^{2+} = 17.02$

(e)   Past the equivalence point at 55.00 mL, we can say

$[EDTA] = \left(\dfrac{5.00}{105.00}\right)(0.001\ 00\ M) = 4.76 \times 10^{-5}\ M$

$[CuY^{2-}] = \left(\dfrac{50.00}{105.00}\right)(0.001\ 00\ M) = 4.76 \times 10^{-4}\ M$

$K_f' = \dfrac{[CuY^{2-}]}{[Cu^{2+}][EDTA]} = \dfrac{(4.76 \times 10^{-4})}{[Cu^{2+}]\,(4.76 \times 10^{-5})}$

$\Rightarrow [Cu^{2+}] = 2.05 \times 10^{-18}\ M \Rightarrow pCu^{2+} = 17.69$

11-17.   (a) $\alpha_{ML} = \dfrac{[ML]}{C_M} = \dfrac{\beta_1[M][L]}{[M]\{1+\beta_1[L]+\beta_2[L]^2\}} = \dfrac{\beta_1[L]}{1+\beta_1[L]+\beta_2[L]^2}$

$\qquad\qquad$ $\alpha_{ML_2} = \dfrac{[ML_2]}{C_M} = \dfrac{\beta_2[M][L]^2}{[M]\{1+\beta_1[L]+\beta_2[L]^2\}} = \dfrac{\beta_2[L]^2}{1+\beta_1[L]+\beta_2[L]^2}$

$\qquad$ (b)   For $[L] = 0.100\ M$, $\beta_1 = 1.7 \times 10^2$, and $\beta_2 = 4.3 \times 10^3$, we get
$\qquad\qquad$ $\alpha_{ML} = 0.28$ and $\alpha_{ML_2} = 0.70$.

11-18.   Let T = transferrin

$\qquad$ (a) $Fe^{3+} + T \overset{K_1}{\rightleftharpoons} FeT \qquad\qquad\qquad K_1 = \dfrac{[FeT]}{[Fe^{3+}][T]}$

$\qquad\qquad$ $Fe^{3+} + FeT \overset{K_2}{\rightleftharpoons} Fe_2T \qquad\qquad K_2 = \dfrac{[Fe_2T]}{[Fe^{3+}][FeT]}$

$\qquad$ (b) $K_1 = \dfrac{[Fe_aT]+[Fe_bT]}{[Fe^{3+}][T]} = \dfrac{[Fe_aT]}{[Fe^{3+}][T]} + \dfrac{[Fe_bT]}{[Fe^{3+}][T]} = k_{1a} + k_{1b}$

$$\frac{1}{K_2} = \frac{[Fe^{3+}]([Fe_aT] + [Fe_bT])}{[Fe_2T]} = \frac{[Fe^{3+}][Fe_aT]}{[Fe_2T]} + \frac{[Fe^{3+}][Fe_bT]}{[Fe_2T]} = \frac{1}{k_{2b}} + \frac{1}{k_{2a}}$$

(c) $k_{1a}\,k_{2b} = \dfrac{[Fe_aT]}{[Fe^{3+}][T]}\dfrac{[Fe_2T]}{[Fe^{3+}]\,[Fe_aT]} = \dfrac{[Fe_bT]}{[Fe^{3+}][T]}\dfrac{[Fe_2T]}{[Fe^{3+}]\,[Fe_bT]} = k_{1b}\,k_{2a}$

(d) Substituting from Eq. (A) into Eq. (C) gives

$$19.44 = \frac{[FeT]^2}{(1 - [FeT] - [Fe_2T])\,[Fe_2T]} \tag{D}$$

Substituting from Eq. (B) into Eq. (D) gives

$$19.44 = \frac{(0.8 - 2[Fe_2T])^2}{\{1-(0.8-2[Fe_2T]) - [Fe_2T]\}\,[Fe_2T]} \quad \overset{\text{solve}}{\underset{\substack{\text{quadratic}\\\text{equation}}}{\Rightarrow}} \quad [Fe_2T] = 0.077\,3$$

Using this value for $[Fe_2T]$ in Eqns. (A) and (B) gives $[FeT] = 0.645$ and $[T] = 0.277\,3$. Now we also know that $\dfrac{k_{1a}}{k_{1b}} = \dfrac{[Fe_aT]}{[Fe_bT]} = 6.0$, which tells us that $[Fe_aT] = \left(\dfrac{6.0}{7.0}\right)[FeT] = 0.553\,2$ and $[Fe_bT] = \left(\dfrac{1.0}{7.0}\right)[FeT] = 0.092\,2.$

Final result: $[T] = 0.27_7$, $[Fe_aT] = 0.55_3$, $[Fe_bT] = 0.09_2$, $[Fe_2T] = 0.07_7.$

11-19. In place of Equation 11-8, we write

$$M_{free} + EDTA \rightleftharpoons M(EDTA) \qquad\qquad K_f'' = \frac{[M(EDTA)]}{[M]_{free}\,[EDTA]}$$

where $[M]_{free}$ is the concentration of all metal not bound to EDTA. [EDTA] is the concentration of all EDTA not bound to metal. The mass balances are

Metal: $[M]_{free} + [M(EDTA)] = \dfrac{C_M V_M}{V_M + V_{EDTA}}$

EDTA: $[EDTA] + [M(EDTA)] = \dfrac{C_{EDTA} V_{EDTA}}{V_M + V_{EDTA}}$

These equations have the same form as the first three equations in Section 11-4, with K_f replaced by K_f'', [M] replaced by $[M]_{free}$, and [L] replaced by [EDTA]. The derivation therefore leads to Equation 11-11, with K_f replaced by K_f'', [M] replaced by $[M]_{free}$, and C_L replaced by C_{EDTA}.

11-20. (a)

	A	B	C	D	E	F
1	Titration of 50 mL of 0.001 M Zn^{2+} with 0.001 M EDTA/pH 10 with NH_3					
2						
3	$C_M =$	pM	M	$[M]_{tot}$	ϕ	V_{EDTA}
4	0.001	8.115	7.67E-09	4.29E-04	0.400	19.9814
5	$V_M =$	12.014	9.68E-13	5.41E-08	1.000	50.0000
6	50	15.278	5.27E-16	2.95E-11	1.200	59.9965
7	$C_{EDTA} =$					
8	0.001					
9	$K_f'' =$	A10 = A12*A16*10^A14				
10	1.70E+11	A12 = 1/(1+A20*A18+B20*A18^2+C20*A18^3+D20*A18^4)				
11	$\alpha(Zn^{2+}) =$					
12	1.79E-05	C4 = 10^-B4				
13	$\log K_f =$	D4 = C4/$A$12				
14	16.5	E4 = (1+$A$10*D4-(D4+D4^2*$A$10)/$A$4)/				
15	$\alpha(Y^{4-}) =$		(D4*$A$10+(D4+D4^2*$A$10)/$A$8)			
16	0.30	F4 = E4*$A$4*$A$6/$A$8				
17	$[NH_3] =$					
18	0.1					
19	$\beta_1 =$	$\beta_2 =$	$\beta_3 =$	$\beta_4 =$		
20	1.51E+02	2.69E+04	5.50E+06	5.01E+08		

(b)
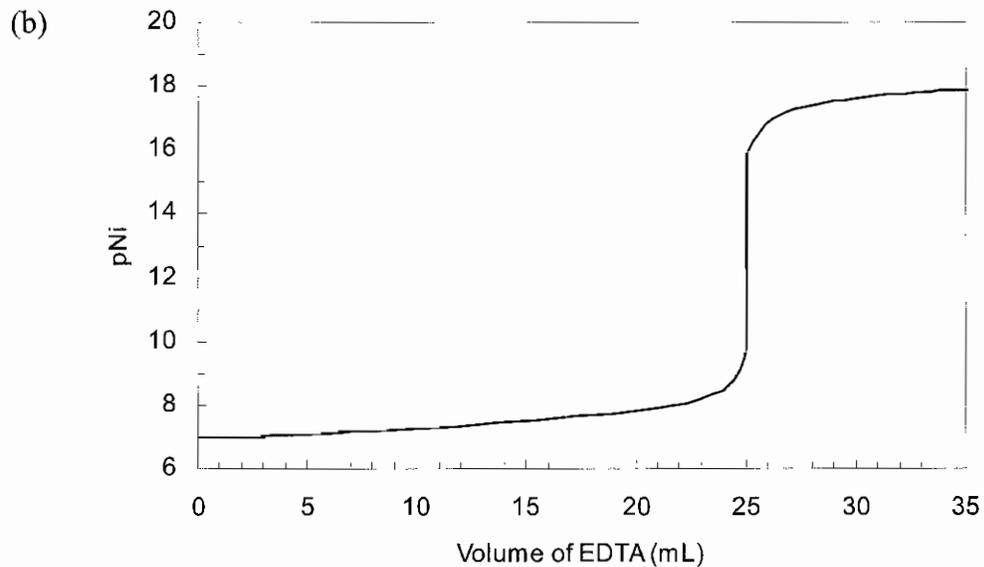
	A	B	C	D	E	F
1	Titration of 50 mL of 0.05 M Ni^{2+} with 0.1 M EDTA/pH 11/0.1 M Oxalate					
2						
3	C_M =	pM	M	$[M]_{tot}$	ϕ	V_{EDTA}
4	0.005	6.97	1.07E-07	4.94E-03	0.008	0.210
5	V_M =	7.00	1.00E-07	4.61E-03	0.054	1.342
6	50	7.20	6.31E-08	2.91E-03	0.324	8.106
7	C_{EDTA} =	7.50	3.16E-08	1.46E-03	0.618	15.461
8	0.01	8.00	1.00E-08	4.61E-04	0.868	21.696
9	K_f'' =	8.40	3.98E-09	1.83E-04	0.946	23.649
10	4.42E+13	8.80	1.58E-09	7.30E-05	0.978	24.456
11	$\alpha(Ni^{2+})$ =	9.50	3.16E-10	1.46E-05	0.996	24.891
12	2.17E-05	10.50	3.16E-11	1.46E-06	1.000	24.989
13	log K_f =	12.80	1.58E-13	7.30E-09	1.000	25.000
14	18.4	14.00	1.00E-14	4.61E-10	1.000	25.001
15	$\alpha(Y^{4-})$ =	15.00	1.00E-15	4.61E-11	1.000	25.012
16	0.81	16.00	1.00E-16	4.61E-12	1.005	25.123
17	$[Oxalate^{2-}]$ =	17.00	1.00E-17	4.61E-13	1.049	26.229
18	0.1	17.40	3.98E-18	1.83E-13	1.123	28.086
19	β_1 =	17.60	2.51E-18	1.16E-13	1.196	29.892
20	1.45E+05	17.80	1.58E-18	7.30E-14	1.310	32.753
21	β_2 =	17.90	1.26E-18	5.80E-14	1.390	34.760
22	3.16E+06	18.00	1.00E-18	4.61E-14	1.491	37.287
23						
24	A10 = A16*A12*10^A14					
25	A12 = 1/(1+A20*A18+A22*A18^2)					
26	C4 = 10^-B4					
27	D4 = C4/$A$12					
28	E4 = (1+$A$10*D4-(D4+D4*D4*$A$10)/$A$4)/					
29		(D4*$A$10+(D4+D4*D4*$A$10)/$A$8)				
30	F4 = E4*$A$4*$A$6/$A$8					

11-21. $[L] + [ML] + 2[ML_2] = \dfrac{C_L V_L}{V_M + V_L}$

$[L] + \alpha_{ML}\dfrac{C_M V_M}{V_M + V_L} + 2\alpha_{ML_2}\dfrac{C_M V_M}{V_M + V_L} = \dfrac{C_L V_L}{V_M + V_L}$

Multiply both sides by $V_M + V_L$:

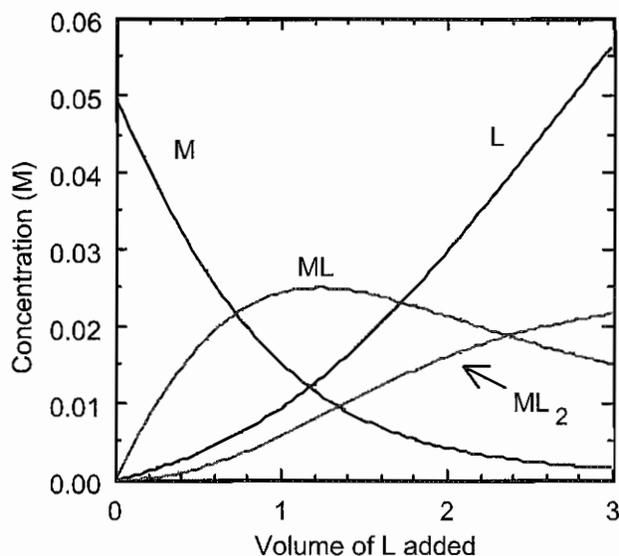$[L]V_M + [L]V_L + \alpha_{ML}C_M V_M + 2\alpha_{ML_2}C_M V_M = C_L V_L$

Collect terms $V_L ([L] - C_L) = V_M (-[L] - \alpha_{ML}C_M - 2\alpha_{ML_2}C_M)$

$\dfrac{V_L}{V_M} = \dfrac{[L] + \alpha_{ML}C_M + 2\alpha_{ML_2}C_M}{C_L - [L]}$

Divide the denominator by C_L and divide the numerator by C_M to obtain ϕ, the fraction of the way to the equivalence point:

$$\phi = \frac{C_L V_L}{C_M V_M} = \frac{\dfrac{[L]}{C_M} + \alpha_{ML} + 2\alpha_{ML_2}}{1 - \dfrac{[L]}{C_L}}$$

11-22.

	A	B	C	D	E	F	G	H	I	J	K
1	Copper-acetate complexes ML and ML$_2$										
2											
3	C_M =	pL	[L]	α_M	α_{ML}	α_{ML2}	ϕ	V(ligand)	[M]	[ML]	[ML$_2$]
4	0.05	4.0	0.0001	0.983	0.017	0.000	0.019	0.019	0.0491	0.0008	0.0000
5	V_M =	3.0	0.0010	0.852	0.145	0.004	0.172	0.172	0.0419	0.0071	0.0002
6	10	2.8	0.0016	0.781	0.210	0.008	0.260	0.260	0.0381	0.0103	0.0004
7	C(ligand)	2.6	0.0025	0.688	0.294	0.019	0.383	0.383	0.0331	0.0141	0.0009
8	0.5	2.4	0.0040	0.573	0.388	0.039	0.550	0.550	0.0272	0.0184	0.0019
9	β_1 =	2.2	0.0063	0.446	0.478	0.076	0.766	0.766	0.0207	0.0222	0.0035
10	170	2.0	0.0100	0.319	0.543	0.137	1.039	1.039	0.0145	0.0246	0.0062
11	β_2 =	1.9	0.0126	0.262	0.560	0.178	1.199	1.199	0.0117	0.0250	0.0080
12	4300	1.8	0.0158	0.209	0.564	0.226	1.377	1.377	0.0092	0.0248	0.0099
13		1.7	0.0200	0.164	0.556	0.280	1.579	1.579	0.0071	0.0240	0.0121
14		1.6	0.0251	0.125	0.535	0.340	1.808	1.808	0.0053	0.0226	0.0144
15		1.5	0.0316	0.094	0.504	0.403	2.073	2.073	0.0039	0.0209	0.0167
16		1.4	0.0398	0.069	0.464	0.467	2.385	2.385	0.0028	0.0187	0.0189
17		1.3	0.0501	0.049	0.419	0.532	2.761	2.761	0.0019	0.0164	0.0208
18		1.3	0.0562	0.041	0.396	0.563	2.981	2.981	0.0016	0.0152	0.0217
19											
20	C4 = 10^-B4						H4 = G4*$A$4*$A$6/$A$8				
21	D4 = 1/(1+$A$10*C4+$A$12*C4*C4)						I4 = D4*$A$4*$A$6/($A$6+H4)				
22	E4 = $A$10*C4/(1+$A$10*C4+$A$12*C4*C4)						J4 = E4*$A$4*$A$6/($A$6+H4)				
23	F4 = $A$12*C4*C4/(1+$A$10*C4+$A$12*C4*C4)						K4 = F4*$A$4*$A$6/($A$6+H4)				
24	G4 = (C4/$A$4+E4+2*F4)/(1-C4/$A$8)										

11-23. Only a small amount of indicator is employed. Most of the Mg^{2+} is not bound to the indicator. Free Mg^{2+} reacts with EDTA before MgIn reacts. Therefore, the concentration of MgIn is constant until all of Mg^{2+} has been consumed. Only when MgIn begins to react does the color change.

11-24. 1. With metal ion indicators
2. With a mercury electrode
3. With an ion-selective electrode
4. With a glass electrode

11-25. HIn^{2-}, wine red, blue

11-26. Buffer (a) (pH 6-7) will give a yellow $\rightarrow$ blue color change that will be easier to observe than the violet $\rightarrow$ blue change expected with the other buffers.

11-27. A back titration is necessary if the analyte precipitates in the absence of EDTA, if it reacts too slowly with EDTA, or if it blocks the indicator.

11-28. In a displacement titration, analyte displaces a metal ion from a complex. The displaced metal ion is then titrated. An example is the liberation of Ni^{2+} from $Ni(CN)_4^{2-}$ by the analyte Ag^+. The liberated Ni^{2+} is then titrated by EDTA to find out how much Ag^+ was present.

11-29. The Mg^{2+} in a solution of Mg^{2+} and Fe^{3+} can be titrated by EDTA if the Fe^{3+} is masked with CN^- to form $Fe(CN)_6^{3-}$, which does not react with EDTA.

11-30. Hardness refers to the total concentration of alkaline earth cations in water, which normally means $[Ca^{2+}] + [Mg^{2+}]$. Hardness gets its name from the reaction of these cations with soap to form insoluble curds. Temporary hardness, due to $Ca(HCO_3)_2$, is lost by precipitation of $CaCO_3(s)$ upon heating. Permanent hardness derived from other salts, such as $CaSO_4$, is not affected by heat.

11-31. $(50.0\ mL)(0.010\ 0\ mmol/mL) = 0.500\ mmol\ Ca^{2+}$, which requires 0.500 mmol EDTA $= 10.0$ mL EDTA.
0.500 mmol Al^{3+} requires the same amount of EDTA, 10.0 mL.

11-32. mmol EDTA $=$ mmol $Ni^{2+} +$ mmol Zn^{2+}
$1.250\ \ =\ \ x\ \ +\ \ 0.250 \Rightarrow 1.000$ mmol Ni^{2+} in 50.0 mL $= 0.020\ 0$ M

11-33. The formula mass of $MgSO_4$ is 120.37. The 50.0 mL aliquot contains

$$\left(\frac{50.0 \text{ mL}}{500 \text{ mL}}\right)\left(\frac{0.450 \text{ g}}{120.37 \text{ g/mol}}\right) = 0.373\,8 \text{ mmol of } Mg^{2+}$$

37.6 mL of EDTA reacts with this much Mg^{2+}, so the EDTA solution contains 0.373 8 mmol / 37.6 mL = 9.943×10^{-3} mmol/mL. The formula mass of $CaCO_3$ is 100.09. 1.00 mL of EDTA will react with 9.943×10^{-3} mmol of $CaCO_3$ = 0.995 mg.

11-34. 30.10 mL Ni^{2+} reacted with 39.35 mL 0.013 07 M EDTA, so Ni^{2+} molarity is

$$[Ni^{2+}] = \frac{(39.35 \text{ mL})(0.013\,07 \text{ mol/L})}{30.10 \text{ mL}} = 0.017\,09 \text{ M}.$$

25.00 mL Ni^{2+} contains 0.427 2 mmol Ni^{2+}. 10.15 mL EDTA = 0.132 7 mmol EDTA. The Ni^{2+} which must have reacted with CN^- was 0.427 2 – 0.132 7 = 0.294 5 mmol. Cyanide reacting with Ni^{2+} must have been (4)(0.294 5 mmol) = 1.178 mmol. Original $[CN^-]$ = 1.178 mmol/12.73 mL = 0.092 54 M.

11-35. For 1.00 mL of unknown:

    25.00 mL of EDTA = 0.968 0 mmol

    $-$ 23.54 mL of Zn^{2+} = 0.500 7 mmol

    Co^{2+} + Ni^{2+} = 0.467 3 mmol

For 2.000 mL of unknown:

    25.00 mL of EDTA = 0.968 0 mmol

    $-$ 25.63 mL of Zn^{2+} = 0.545 2 mmol

    Ni^{2+} in 2.000 mL = 0.422 8 mmol

Co^{2+} in 2.000 mL of unknown = 2 (0.467 3) – 0.422 8 = 0.511 8 mmol. The Co^{2+} will react with 0.511 8 mmol of EDTA, leaving 0.968 0 – 0.511 8 = 0.456 2 mmol EDTA.   mL Zn needed $= \dfrac{0.456\,2 \text{ mmol}}{0.021\,27 \text{ mmol/mL}} = 21.45 \text{ mL}$

11-36.   Total EDTA = (25.0 mL) (0.045 2 M) = 1.130 mmol

    $-$ Mg^{2+} required = (12.4 mL) (0.012 3 M) = 0.153 mmol

    Ni^{2+} + Zn^{2+} = 0.977 mmol

Zn^{2+} = EDTA displaced by 2,3-dimercapto-1-propanol

$$= (29.2 \text{ mL}) (0.012 \text{ } 3 \text{ M}) = 0.359 \text{ mmol}$$

$$\Rightarrow \text{Ni}^{2+} = 0.977 - 0.359 = 0.618 \text{ mmol}; \quad [\text{Ni}^{2+}] = \frac{0.618 \text{ mmol}}{50.0 \text{ mL}} = 0.012 \text{ } 4 \text{ M}$$

$$[\text{Zn}^{2+}] = \frac{0.359 \text{ mmol}}{50.0 \text{ mL}} = 0.007 \text{ } 18 \text{ M}$$

11-37.   The precipitation reaction is $\text{Cu}^{2+} + \text{S}^{2-} \rightarrow \text{CuS } (s)$.

Total Cu^{2+} used $= (25.00 \text{ mL}) (0.043 \text{ } 32 \text{ M}) = 1.083 \text{ } 0 \text{ mmol}$

$\underline{\quad \text{Excess Cu}^{2+} \quad = (12.11 \text{ mL}) (0.039 \text{ } 27 \text{ M}) = 0.475 \text{ } 6 \text{ mmol} \quad}$

mmol of S^{2-} $\qquad\qquad\qquad\qquad\qquad = 0.607 \text{ } 4 \text{ mmol}$

$[\text{S}^{2-}] = 0.607 \text{ } 4 \text{ mmol}/25.00 \text{ mL} = 0.024 \text{ } 30 \text{ M}$

11-38.   mmol Bi in reaction $= (25.00 \text{ mL}) (0.086 \text{ } 40 \text{ M}) = 2.160 \text{ mmol}$

EDTA required $= (14.24 \text{ mL}) (0.043 \text{ } 7 \text{ M}) = 0.622 \text{ mmol}$

mmol Bi that reacted with Cs $= 2.160 - 0.622 = 1.538 \text{ mmol}$

Since 2 mol Bi react with 3 mol Cs to give $\text{Cs}_3\text{Bi}_2\text{I}_9$,

mmol Cs^+ in unknown $= \frac{3}{2}(1.538) = 2.307 \text{ mmol}$

$$[\text{Cs}^+] = \frac{2.307 \text{ mmol}}{25.00 \text{ mL}} = 0.092 \text{ } 28 \text{ M}.$$

11-39.   Total standard $\text{Ba}^{2+} + \text{Zn}^{2+}$ added to the sulfate was $(5.000 \text{ mL})(0.014 \text{ } 63 \text{ M}$ $\text{BaCl}_2) + (1.000 \text{ mL})(0.010 \text{ } 00 \text{ M ZnCl}_2) = 0.083 \text{ } 15 \text{ mmol}$. Total EDTA required was $(2.39 \text{ mL})(0.009 \text{ } 63 \text{ M}) = 0.023 \text{ } 0_2 \text{ mmol}$. Therefore, the original solid must have contained $0.083 \text{ } 15 - 0.023 \text{ } 0_2 = 0.060 \text{ } 1_3 \text{ mmol}$ sulfur (which made $0.060 \text{ } 1_3 \text{ mmol}$ sulfate that precipitated $0.060 \text{ } 1_3 \text{ mmol Ba}^{2+}$). The mass of sulfur was $(0.060 \text{ } 1_3 \text{ mmol})(32.066 \text{ mg/mmol}) = 1.92_8 \text{ mg}$. wt% S $= 100 \times$ $(1.92_8 \text{ mg S}/5.89 \text{ mg sphalerite}) = 32.7 \text{ wt\%}$. Theoretical wt% S in pure ZnS $=$ $100 \times (32.066 \text{ g S} / 97.46 \text{ g ZnS}) = 32.90 \text{ wt\%}$.