13-1. The chelate effect is the observation that multidentate ligands form more stable metal complexes than do similar, monodentate ligands. This happens because the entropy change when one multidentate ligand binds to a metal is greater than the entropy when many smaller ligands are bound.

13-2. α_{Y4-} gives the fraction of all free EDTA in the form Y^{4-}.

(a) At pH 3.50:

$$\alpha_{Y4-} = \frac{10^{-0.0}10^{-1.5}...10^{-10.24}}{(10^{-3.50})^6+(10^{-3.50})^5 10^{-0.0}+...+10^{-0.0}10^{-1.5}...10^{-10.24}} = 3.4 \times 10^{-10}$$

(b) At pH 10.50, $\alpha_{Y4-} = 0.64$

13-3. (a) $K_f' = \alpha_{Y4-} K_f = 0.054 \times 10^{8.79} = 3.3 \times 10^7$

(b)
$$\underset{x}{Mg^{2+}} + \underset{x}{EDTA} \rightleftharpoons \underset{0.050 - x}{MgY^{2-}}$$

$$\frac{0.050 - x}{x^2} = 3.3 \times 10^7 \Rightarrow [Mg^{2+}] = 3.9 \times 10^{-5} \text{ M}$$

13-5. (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)
$$[M^{n+}] = \underset{\text{fraction remaining}}{\left(\frac{1}{2}\right)} \cdot \underset{\text{original concentration}}{(0.050\,0 \text{ M})} \cdot \underset{\text{dilution factor}}{\left(\frac{100}{150}\right)} = 0.016\,7 \text{ M}$$

(c) 0.054 (Table 13-1)

(d) $K_f' = (0.054)(10^{12.00}) = 5.4 \times 10^{10}$

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

$$\frac{[MY^{n-4}]}{[M^{n+}][EDTA]} = \frac{0.025\,0 - x}{x^2} = 5.4 \times 10^{10} \Rightarrow x = [M^{n+}] = 6.8 \times 10^{-7} \text{ M}$$

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

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

$$\frac{[MY^{n-4}]}{[M^{n+}][EDTA]} = \frac{(2.38 \times 10^{-2})}{[M^{n+}](2.38 \times 10^{-3})} = 5.4 \times 10^{10} \Rightarrow [M^{n+}] = 1.9 \times 10^{-10} \text{ M}$$

13-6. Co^{2+} + EDTA ⇌ CoY^{2-} $\alpha_{Y^{4-}} K_f = 4.7 \times 10^{11}$

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

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

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

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

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

$$\frac{1.33 \times 10^{-2} - x}{x^2} = \alpha_{Y^{4-}} K_f \Rightarrow x = 1.68 \times 10^{-7}\text{ M} \Rightarrow pCo^{2+} = 6.77$$

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

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

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

$$[Co^{2+}] = \frac{[CoY^{2-}]}{[EDTA]\,K_f'} = 3.3 \times 10^{-11}\text{ M} \Rightarrow pCo^{2+} = 10.49$$

13-7. Titration reaction : Mn^{2+} + EDTA ⇌ MnY^{2-} $K' = \alpha_{Y^{4-}} K_f = 4.1 \times 10^{11}$

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.

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

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

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

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

$$\frac{0.006\,67 - x}{x^2} = \alpha_{Y^{4-}} K_f \Rightarrow x = 1.28 \times 10^{-7} \Rightarrow pMn^{2+} = 6.89$$

60.0 mL : There are 10.0 mL of excess EDTA.

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

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

$$[Mn^{2+}] = \frac{[MnY^{2-}]}{[EDTA]K_f'} = 1.20 \times 10^{-11} \Rightarrow pMn^{2+} = 10.92$$

Volume (mL)	pMn^{2+}	Volume	pMn^{2+}	Volume	pMn^{2+}
0	1.70	49.0	3.87	50.1	8.92
20.0	2.18	49.9	4.87	55.0	10.62
40.0	2.81	50.0	6.90	60.0	10.92

13-8. Titration reaction: $Ca^{2+} + EDTA \rightleftharpoons CaY^{2-}$ $\quad K_f' = \alpha_{Y^{4-}} K_f = 1.76 \times 10^{10}$

The equivalence point is 50.0 mL. Sample calculations :

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

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

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

$$[Ca^{2+}] = \frac{[CaY^{2-}]}{[EDTA]K_f'} = 3.79 \times 10^{-11} \Rightarrow pCa^{2+} = 10.42$$

50.0 mL : The formal concentration of CaY^{2-} is

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

$$\underset{x}{Ca^{2+}} + \underset{x}{EDTA} \rightleftharpoons \underset{0.006\,67 - x}{CaY^{2-}}$$

$$\frac{0.006\,67 - x}{x^2} = \alpha_{Y^{4-}} K_f \Rightarrow x = 6.16 \times 10^{-7}\ M \Rightarrow pCa^{2+} = 6.21$$

50.1 mL : 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	8.56	50.1	4.88
20.0	10.42	49.9	7.55	55.0	3.20
40.0	9.64	50.0	6.21	60.0	2.93

13-13. 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.

13-14. (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) $\alpha_{Cu^{2+}} = \dfrac{1}{1+\beta_1[L]+\beta_2[L]^2} = \dfrac{1}{1+10^{2.23}(0.100) + 10^{3.63}(0.100)^2} = 0.017$

13-15. $Cu^{2+} + Y^{4-} \rightleftharpoons CuY^{2-} \qquad K_f = 10^{18.80} = 6.3 \times 10^{18}$

$\alpha_{Y^{4-}} = 0.85$ at pH 11.00 (Table 13-1)

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 $\beta_4 = 1.07 \times 10^{12}$.

$$\alpha_{Cu^{2+}} = \frac{1}{1+\beta_1(0.100)+\beta_2(0.100)^2+\beta_3(0.100)^3+\beta_4(0.100)^4} = 8.4 \times 10^{-9}$$

$K_f' = \alpha_{Y^{4-}} K_f = 5.4 \times 10^{18}$

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

Equivalence point = 50.00 mL

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

$$[Cu^{2+}] = \alpha_{Cu^{2+}} C_{Cu^{2+}} = 8.4 \times 10^{-12} \text{ M} \Rightarrow pCu^{2+} = 11.08$$

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

$$[Cu^{2+}] = \alpha_{Cu^{2+}} C_{Cu^{2+}} = 8.1 \times 10^{-12} \text{ M} \Rightarrow pCu^{2+} = 11.09$$

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

$$[Cu^{2+}] = \alpha_{Cu^{2+}} C_{Cu^{2+}} = 4.4 \times 10^{-13} \text{ M} \Rightarrow pCu^{2+} = 12.35$$

(d) At the equivalence point, we can write

$C_{Cu^{2+}}$	+ EDTA	$\rightleftharpoons$	CuY^{2-}
x	x		$\left(\frac{50.00}{100.00}\right)(0.001\,00) - x$

$$\frac{0.000\,500 - x}{x^2} = 4.5 \times 10^{10} \Rightarrow x = C_{Cu^{2+}} = 1.05 \times 10^{-7} \text{ M}$$

$$[Cu^{2+}] = \alpha_{Cu^{2+}} C_{Cu^{2+}} = 8.9 \times 10^{-16} \text{ M} \Rightarrow pCu^{2+} = 15.06$$

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

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

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

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

$$\Rightarrow [\text{Cu}^{2+}] = 1.85 \times 10^{-18}\text{ M} \Rightarrow \text{pCu}^{2+} = 17.73$$

13-16. (a) $$\alpha_{\text{ML}} = \frac{[\text{ML}]}{C_\text{M}} = \frac{\beta_1[\text{M}][\text{L}]}{[\text{M}]\{1+\beta_1[\text{L}] + \beta_2[\text{L}]^2\}} = \frac{\beta_1[\text{L}]}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2}$$

$$\alpha_{\text{ML}_2} = \frac{[\text{ML}_2]}{C_\text{M}} = \frac{\beta_2[\text{M}][\text{L}]^2}{[\text{M}]\{1+\beta_1[\text{L}] + \beta_2[\text{L}]^2\}} = \frac{\beta_2[\text{L}]^2}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2}$$

(b) For $[\text{L}] = 0.100$ M, $\beta_1 = 1.7 \times 10^2$ and $\beta_2 = 4.3 \times 10^3$, we get $\alpha_{\text{ML}} = 0.28$ and $\alpha_{\text{ML}_2} = 0.70$

13-17. Let T = transferrin

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

$Fe^{3+} + FeT \overset{K_2}{\rightleftharpoons} Fe_2T$ $\qquad K_2 = \dfrac{[\text{Fe}_2\text{T}]}{[\text{Fe}^{3+}][\text{FeT}]}$

(b) $$K_1 = \frac{[\text{Fe}_\text{a}\text{T}] + [\text{Fe}_\text{b}\text{T}]}{[\text{Fe}^{3+}][\text{T}]} = \frac{[\text{Fe}_\text{a}\text{T}]}{[\text{Fe}^{3+}][\text{T}]} + \frac{[\text{Fe}_\text{b}\text{T}]}{[\text{Fe}^{3+}][\text{T}]} = k_{1\text{a}} + k_{1\text{b}}$$

$$\frac{1}{K_2} = \frac{[\text{Fe}^{3+}]([\text{Fe}_\text{a}\text{T}] + [\text{Fe}_\text{b}\text{T}])}{[\text{Fe}_2\text{T}]} = \frac{[\text{Fe}^{3+}][\text{Fe}_\text{a}\text{T}]}{[\text{Fe}_2\text{T}]} + \frac{[\text{Fe}^{3+}][\text{Fe}_\text{b}\text{T}]}{[\text{Fe}_2\text{T}]} = \frac{1}{k_{2\text{b}}} + \frac{1}{k_{2\text{a}}}$$

(c) $$k_{1\text{a}}\,k_{2\text{b}} = \frac{\cancel{[\text{Fe}_\text{a}\text{T}]}}{[\text{Fe}^{3+}][\text{T}]}\;\frac{[\text{Fe}_2\text{T}]}{[\text{Fe}^{3+}]\cancel{[\text{Fe}_\text{a}\text{T}]}} = \frac{\cancel{[\text{Fe}_\text{b}\text{T}]}}{[\text{Fe}^{3+}][\text{T}]}\;\frac{[\text{Fe}_2\text{T}]}{[\text{Fe}^{3+}]\cancel{[\text{Fe}_\text{b}\text{T}]}} = k_{1\text{b}}\,k_{2\text{a}}$$

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

$$19.44 = \frac{[\text{FeT}]^2}{(1 - [\text{FeT}] - [\text{Fe}_2\text{T}])\,[\text{Fe}_2\text{T}]} \qquad \text{(D)}$$

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

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

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 $\frac{k_{1a}}{k_{1b}} = \frac{[Fe_aT]}{[Fe_bT]} = 6.0$, which tells us that $[Fe_aT] = \left(\frac{6.0}{7.0}\right)[FeT] = 0.553\,2$ and $[Fe_bT] = \left(\frac{1.0}{7.0}\right)[FeT] = 0.092\,2$.

The final result is $[T] = 0.27_7$; $[Fe_aT] = 0.55_3$; $[Fe_bT] = 0.09_2$;
$[Fe_2T] = 0.07_7$.

13-24 Hin^{2-}, red, blue