

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.

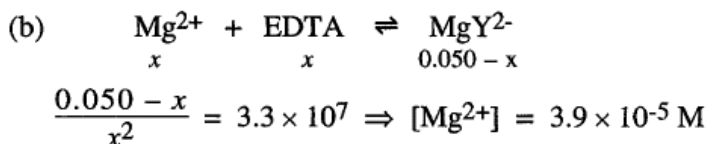
13-2. $\alpha_{Y^{4-}}$ gives the fraction of all free EDTA in the form Y^{4-} .

(a) At pH 3.50:

$$\alpha_{Y^{4-}} = \frac{10^{-0.0}10^{-1.5}\dots10^{-10.24}}{(10^{-3.50})^6 + (10^{-3.50})^510^{-0.0} + \dots + 10^{-0.0}10^{-1.5}\dots10^{-10.24}} = 3.4 \times 10^{-10}$$

(b) At pH 10.50, $\alpha_{Y^{4-}} = 0.64$

13-3. (a) $K_f' = \alpha_{Y^{4-}} K_f = 0.054 \times 10^{8.79} = 3.3 \times 10^7$



13-5. (a) mmol EDTA = mmol M^{n+}

$$(V_e)(0.0500 \text{ M}) = (100.0 \text{ mL})(0.0500 \text{ M}) \Rightarrow V_e = 100.0 \text{ mL}$$

(b)
$$[\text{M}^{n+}] = \left(\frac{1}{2}\right) \cdot (0.0500 \text{ M}) \cdot \left(\frac{100}{150}\right) = 0.0167 \text{ M}$$

fraction
original
dilution
remaining
concentration
factor

(c) 0.054 (Table 13-1)

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

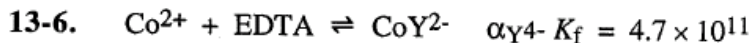
(e) $[\text{MY}^{n-4}] = (0.0500 \text{ M})\left(\frac{100}{200}\right) = 0.0250 \text{ M}$

$$\frac{[\text{MY}^{n-4}]}{[\text{M}^{n+}][\text{EDTA}]} = \frac{0.0250 - x}{x^2} = 5.4 \times 10^{10} \Rightarrow x = [\text{M}^{n+}] = 6.8 \times 10^{-7} \text{ M}$$

(f) $[\text{EDTA}] = (0.0500 \text{ M})\left(\frac{10.0}{210.0}\right) = 2.38 \times 10^{-3} \text{ M}$

$$[\text{MY}^{n-4}] = (0.0500 \text{ M})\left(\frac{100.0}{210.0}\right) = 2.38 \times 10^{-2} \text{ M}$$

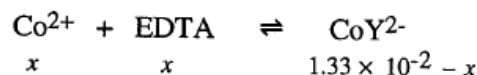
$$\frac{[\text{MY}^{n-4}]}{[\text{M}^{n+}][\text{EDTA}]} = \frac{(2.38 \times 10^{-2})}{[\text{M}^{n+}](2.38 \times 10^{-3})} = 5.4 \times 10^{10} \Rightarrow [\text{M}^{n+}] = 1.9 \times 10^{-10} \text{ M}$$



$$V_e = (25.00) \left(\frac{0.02026 \text{ M}}{0.03855 \text{ M}} \right) = 13.14 \text{ mL}$$

(a) 12.00 mL: $[\text{Co}^{2+}] = \left(\frac{13.14 - 12.00}{13.14} \right) (0.02026 \text{ M}) \left(\frac{25.00}{37.00} \right)$
 $= 1.19 \times 10^{-3} \text{ M} \Rightarrow \text{pCo}^{2+} = 2.93$

(b) V_e : Formal concentration of CoY^{2-} is $\left(\frac{25.00}{38.14} \right) (0.02026 \text{ M}) = 1.33 \times 10^{-2} \text{ M}$

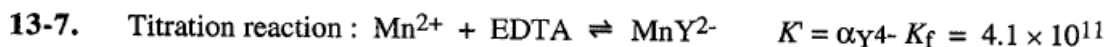


$$\frac{1.33 \times 10^{-2} - x}{x^2} = \alpha_{\text{Y}^{4-}} K_f \Rightarrow x = 1.68 \times 10^{-7} \text{ M} \Rightarrow \text{pCo}^{2+} = 6.77$$

(c) 14.00 mL: Formal concentration of CoY^{2-} is $\left(\frac{25.00}{39.00} \right) (0.02026 \text{ M})$
 $= 1.30 \times 10^{-2} \text{ M}$

Formal concentration of EDTA is $\left(\frac{14.0 - 13.14}{39.00} \right) (0.03855 \text{ M}) = 8.50 \times 10^{-4} \text{ M}$

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



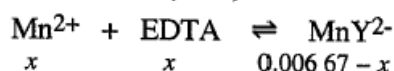
The equivalence point is 50.0 mL. Sample calculations:

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

$$[\text{Mn}^{2+}] = \left(\frac{30.0}{50.0} \right) (0.0200 \text{ M}) \left(\frac{25.0}{45.0} \right) = 6.67 \times 10^{-3} \text{ M} \Rightarrow \text{pMn}^{2+} = 2.18$$

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

$$[\text{MnY}^{2-}] = \left(\frac{25.0}{75.0} \right) (0.0200 \text{ M}) = 0.00667 \text{ M}$$



$$\frac{0.00667 - x}{x^2} = \alpha_{Y^{4-}} K_f \Rightarrow x = 1.28 \times 10^{-7} \Rightarrow \text{pMn}^{2+} = 6.89$$

60.0 mL : There are 10.0 mL of excess EDTA.

$$[\text{EDTA}] = \left(\frac{10.0}{85.0}\right)(0.0100 \text{ M}) = 1.176 \times 10^{-3} \text{ M}$$

$$[\text{MnY}^{2-}] = \left(\frac{25.0}{85.0}\right)(0.0200 \text{ M}) = 5.88 \times 10^{-3} \text{ M}$$

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

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: $\text{Ca}^{2+} + \text{EDTA} \rightleftharpoons \text{CaY}^{2-}$ $K_f' = \alpha_{Y^{4-}} K_f = 1.76 \times 10^{10}$

The equivalence point is 50.0 mL. Sample calculations :

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

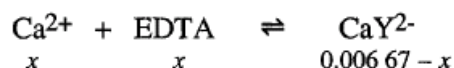
$$[\text{EDTA}] = \left(\frac{30.0}{50.0}\right)(0.0200 \text{ M}) \left(\frac{25.0}{45.0}\right) = 0.00667 \text{ M}$$

$$[\text{CaY}^{2-}] = \left(\frac{20.0}{50.0}\right)(0.0200 \text{ M}) \left(\frac{25.0}{45.0}\right) = 0.00444 \text{ M}$$

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

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

$$[\text{CaY}^{2-}] = \left(\frac{25.0}{75.0}\right)(0.0200 \text{ M}) = 0.00667 \text{ M}$$



$$\frac{0.00667 - x}{x^2} = \alpha_{Y^{4-}} K_f \Rightarrow x = 6.16 \times 10^{-7} \text{ M} \Rightarrow \text{pCa}^{2+} = 6.21$$

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

$$[\text{Ca}^{2+}] = \left(\frac{0.1}{75.1}\right)(0.0100 \text{ M}) = 1.33 \times 10^{-5} \text{ M} \Rightarrow \text{pCa}^{2+} = 4.88$$

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) $\beta_2 = K_1 K_2 = \beta_1 K_2 \Rightarrow K_2 = \beta_2 / \beta_1 = 10^{3.63} / 10^{2.23} = 10^{1.40} = 25$

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

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

$\alpha_{\text{Y}^{4-}} = 0.85$ 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 $\beta_4 = 1.07 \times 10^{12}$.

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

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

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

Equivalence point = 50.00 mL

(a) At 0 mL, the total concentration of copper is $C_{\text{Cu}^{2+}} = 0.00100 \text{ M}$ and

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

(b) At 1.00 mL, $C_{\text{Cu}^{2+}} = \left(\frac{49.00}{50.00}\right) (0.00100 \text{ M}) \left(\frac{50.00}{51.00}\right) = 9.61 \times 10^{-4} \text{ M}$

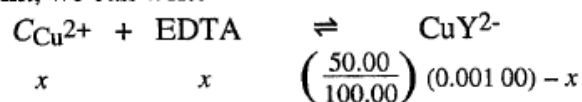
fraction remaining original concentration dilution factor

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

(c) At 45.00 mL, $C_{\text{Cu}^{2+}} = \left(\frac{5.00}{50.00}\right) (0.00100) \left(\frac{50.00}{95.00}\right) = 5.26 \times 10^{-5} \text{ M}$

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

(d) At the equivalence point, we can write



$$\frac{0.000500 - x}{x^2} = 4.5 \times 10^{10} \Rightarrow x = C_{\text{Cu}^{2+}} = 1.05 \times 10^{-7} \text{ M}$$

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

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

$$[\text{EDTA}] = \left(\frac{5.00}{105.00} \right) (0.00100 \text{ M}) = 4.76 \times 10^{-5} \text{ M}$$

$$[\text{CuY}^{2-}] = \left(\frac{50.00}{105.00} \right) (0.00100 \text{ M}) = 4.76 \times 10^{-4} \text{ M}$$

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

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

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 $[\text{L}] = 0.100 \text{ M}$, $\beta_1 = 1.7 \times 10^2$ and $\beta_2 = 4.3 \times 10^3$, we get

$$\alpha_{\text{ML}} = 0.28 \text{ and } \alpha_{\text{ML}_2} = 0.70$$

13-17. Let T = transferrin



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

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

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

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

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

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

$$19.44 = \frac{(0.8 - 2[\text{Fe}_2\text{T}])^2}{\{1 - (0.8 - 2[\text{Fe}_2\text{T}]) - [\text{Fe}_2\text{T}]\} [\text{Fe}_2\text{T}]}$$

solve
 \Rightarrow $[\text{Fe}_2\text{T}] = 0.0773$
quadratic
equation

Using this value for $[\text{Fe}_2\text{T}]$ in Eqns. (A) and (B) gives $[\text{FeT}] = 0.645$ and $[\text{T}] = 0.2773$. Now we also know that $\frac{k_{1a}}{k_{1b}} = \frac{[\text{Fe}_a\text{T}]}{[\text{Fe}_b\text{T}]} = 6.0$, which tells us that $[\text{Fe}_a\text{T}] = \left(\frac{6.0}{7.0}\right)[\text{FeT}] = 0.5532$ and $[\text{Fe}_b\text{T}] = \left(\frac{1.0}{7.0}\right)[\text{FeT}] = 0.0922$.

The final result is $[\text{T}] = 0.277$; $[\text{Fe}_a\text{T}] = 0.553$; $[\text{Fe}_b\text{T}] = 0.092$;
 $[\text{Fe}_2\text{T}] = 0.077$.

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