Auxiliary Complexing agents:

11-14. State the purpose of an auxiliary complexing agent and give an example of its use.

Ans:

An auxiliary complexing agent forms a weak complex with analyte ion, thereby keeping it in solution without interfering with the EDTA titration.

For Eg.

NH_3 keeps Zn^{2+} in solution at high pH.

11-15
~~13-14~~. According to Appendix I, Cu^{2+} forms two complexes with acetate:

$$Cu^{2+} + CH_3CO_2^- \rightleftharpoons Cu(CH_3CO_2)^+ \quad \beta_1\ (=K_1)$$

$$Cu^{2+} + 2CH_3CO_2^- \rightleftharpoons Cu(CH_3CO_2)_2\,(aq) \quad \beta_2$$

(a) Referring to Box 6-2, find K_2 for the reaction.

$$Cu(CH_3CO_2)^+ + CH_3CO_2^- \rightleftharpoons Cu(CH_3CO_2)_2\,(aq) \quad K_2$$

(b) Consider 1.00 L of solution prepared by mixing 1.00×10^{-4} mol $Cu(ClO_4)_2$ and 0.100 mol CH_3CO_2Na. Use Equation 13-16 to find the fraction of copper in the form Cu^{2+}.

Soln

(a)

$$Cu(CH_3CO_2)^+ + CH_3CO_2^- \overset{K_2}{\rightleftharpoons} Cu(CH_3CO_2)_{2\,(aq)}$$

$$MX + X \overset{k_2}{\rightleftharpoons} MX_2$$

$$\therefore K_2 = \frac{[MX_2]}{[MX][X]}$$

For Cu^{2+}

$\log \beta_1 = 2.23$

$\log \beta_2 = 3.63$

$\therefore \beta_1 = 10^{2.23}$

$\beta_2 = 10^{3.63}$

$$\therefore \beta_2 = k_1 k_2$$

$$\boxed{\therefore \beta_n = k_1 k_2 \ldots k_n}$$

$$\beta_2 = \beta_1 k_2$$

$$\boxed{\because \beta_1 = k_1}$$

$$\therefore k_2 = \frac{\beta_2}{\beta_1}$$

$$k_2 = \frac{10^{3.63}}{10^{2.23}}$$

$$\boxed{k_2 = 25.12}$$

$\therefore k_2 = 25$

(b) Fraction of copper in the form Cu^{2+}.

$$\alpha_{Cu^{2+}} = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2}$$

$$= \frac{1}{1 + 10^{2.23}(0.100) + 10^{3.63}(0.100)^2}$$

$$\boxed{\alpha_{Cu^{2+}} = 0.017}$$

$[L] = 0.100\ M$

$\beta_1 = 10^{2.23}$

$\beta_2 = 10^{3.63}$

11-16.
13. Calculate pCu^{2+} at each of the following points in the titration of 50.00 mL of 0.00100M Cu^{2+} with 0.001 00 M EDTA at pH 11.00 in a solution whose NH_3 concentration is somehow fixed at 0.100M.

(a) 0 mL (b) 1.00 mL (c) 45.00 mL

(d) 50.00 mL (e) 55.00 mL.

Soln

The titration reaction is

$$Cu^{2+} + Y^{4-} \rightleftharpoons CuY^{2-} \quad K_f = 10^{18.80} = 6.3\times10^{18}$$

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

For Cu^{2+} and NH_3, (From Appendix I)

$\log \beta_1 = 3.99$

$\log \beta_2 = 7.33$

$\log \beta_3 = 10.06$

$\log \beta_4 = 12.03$

Therefore

$\beta_1 = 9.8 \times 10^3$

$[L] = 0.100\ M$

$\beta_2 = 2.1 \times 10^7$

$\beta_3 = 1.15 \times 10^{10}$

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

$\therefore$ Fraction of Cu^{2+}

$$\alpha_{Cu^{2+}} = \frac{1}{1 + \beta_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3 + \beta_4 [L]^4}$$

$$= \frac{1}{1 + (9.8 \times 10^3)(0.100) + (2.1 \times 10^7)(0.100)^2 + (1.15 \times 10^{10})(0.100)^3 + (1.07 \times 10^{12})(0.100)^4}$$

$$\alpha_{Cu^{2+}} = 8.4 \times 10^{-9}$$

$$K_f' = \alpha_{Y^{4-}} \cdot K_f$$

$$= (0.85)(6.3\times10^{18})$$

$$\boxed{K_f' = 5.4\times10^{18}}$$

$\because \alpha_{Y^{4-}} = 0.85$ at $pH = 11.0$

$K_f = 6.3\times10^{18}$.

$$K_f'' = \alpha_{Y^{4-}} \cdot \alpha_{Cu^{2+}} \cdot K_f$$

$$= (0.85) \cdot (8.4\times10^{-9})(6.3\times10^{18})$$

$$\boxed{K_f'' = 4.5\times10^{10}}$$

$\because \alpha_{Y^{4-}} = 0.85$

$\alpha_{Cu^{2+}} = 8.4\times10^{-9}$

$K_f = 6.3\times10^{18}$

Equivalence point = 50.00 mL

$\because \underbrace{50.00\text{ mL} \times 0.001\text{ M}}_{Cu^{2+}}$

$= \underbrace{0.001 \times V_e}_{EDTA}$

$V_e = 50.00\text{ mL}$

(a) At 0 mL.

The total concentration of Copper is

$$C_{Cu^{2+}} = 0.00100\,M.$$

$$\therefore [Cu^{2+}] = \alpha_{Cu^{2+}} \cdot C_{Cu^{2+}}$$

$$= (8.4 \times 10^{-9}) \cdot (0.00100)$$

$$[Cu^{2+}] = 8.4 \times 10^{-12}$$

$\therefore$ $\alpha_{Cu^{2+}} = 8.4 \times 10^{-9}$

$C_{Cu^{2+}} = 0.001\,M$

$$\therefore pCu^{2+} = -\log(Cu^{2+})$$

$$= -\log(8.4 \times 10^{-12})$$

$$\therefore \boxed{pCu^{2+} = 11.08}$$

(b) At $\underline{\underline{1.00\ mL}}$

$$C_{Cu^{2+}} = \underbrace{\left[\frac{49.00\ mL}{50.00\ mL}\right]}_{\text{Fraction remaining}} \underbrace{(0.00100M)}_{\text{original concentration of } Cu^{2+}} \underbrace{\left(\frac{50.00\ mL}{51.00\ mL}\right)}_{\text{dilution factor.}}$$

$$C_{Cu^{2+}} = 9.61 \times 10^{-4} M$$

$$\therefore [Cu^{2+}] = \alpha_{Cu^{2+}} \cdot C_{Cu^{2+}}$$

$$= (8.4 \times 10^{-9}) \cdot (9.61 \times 10^{-4} M)$$

$$[Cu^{2+}] = 8.07 \times 10^{-12} M$$

$$\therefore pCu^{2+} = -\log [Cu^{2+}]$$

$$= -\log (8.1 \times 10^{-12}) = 11.09$$

$$\boxed{\therefore pCu^{2+} = 11.09}$$

(c) At <u>45.00 mL</u>.

$$C_{Cu^{2+}} = \underbrace{\left(\frac{5.00\ mL}{50.00\ mL}\right)}_{\text{Fraction remaining}} \underbrace{(0.00100)}_{\text{Original concentration of } Cu^{2+}} \underbrace{\left(\frac{50.00}{95.00}\right)}_{\text{Dilution Factor.}}$$

$$\boxed{C_{Cu^{2+}} = 5.26 \times 10^{-5}\ M.}$$

$$\therefore [Cu^{2+}] = \alpha_{Cu^{2+}} \cdot C_{Cu^{2+}}$$

$$= (8.4 \times 10^{-9}) \cdot (5.26 \times 10^{-5}\ M)$$

$$[Cu^{2+}] = 4.4 \times 10^{-13}\ M$$

$$\therefore pCu^{2+} = -\log[Cu^{2+}]$$

$$= -\log(4.4 \times 10^{-13}) = 12.35$$

$$\boxed{\therefore pCu^{2+} = 12.35}$$

d) At the equivalence point, we can write

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

$$x \qquad x \qquad \left(\frac{50.00}{100.00}\right)(0.00100) - x$$

$$\therefore \frac{0.00500 - x}{x^2} = 4.5\times10^{10}$$

$$\because K_f = 4.5\times10^{10}$$

$$\therefore x = C_{Cu^{2+}} = 1.05\times10^{-7} M$$

$$\therefore [Cu^{2+}] = \alpha_{Cu^{2+}} \cdot C_{Cu^{2+}}$$

$$= (8.4\times10^{-9}) \cdot (1.05\times10^{-7} M)$$

$$[Cu^{2+}] = 8.9\times10^{-16} M$$

$$\therefore pCu^{2+} = -\log(8.9\times10^{-16}) = 15.06$$

$$\boxed{\therefore pCu^{2+} = 15.06}$$

(e) At. 55.00 mL

Past the equivalence point at 55.00 mL

we can say

$$[EDTA] = \underbrace{\left(\frac{5.00}{105.00}\right)}_{\text{Dilution Factor}} \underbrace{(0.00100\,M)}_{\text{original Concentration of EDTA.}}$$

$$[EDTA] = 4.76 \times 10^{-5} M$$

original volume of Cu^{2+}

$$[CuY^{2-}] = \left(\frac{50.00}{105.00}\right)(0.00100\,M)$$

Original concentration of Cu^{2+}

Total volume of the solution

$$= 4.76 \times 10^{-4} M.$$

$$\therefore K_f' = \frac{[CuY^{2-}]}{[Cu^{2+}][EDTA]}$$

$$K'_f = \frac{(4.76 \times 10^{-4})}{[Cu^{2+}]\ (4.76 \times 10^{-5})}$$

$$\therefore K'_f = 5.4 \times 10^{18}$$

$$[Cu^{2+}] = \frac{(4.76 \times 10^{-4})}{(5.4 \times 10^{18})\ (4.76 \times 10^{-5})}$$

$$= 1.85 \times 10^{-18}\ M$$

$$\therefore [Cu^{2+}] = 1.85 \times 10^{-18}\ M$$

$$\therefore p^{Cu^{2+}} = -\log\ (1.85 \times 10^{-18})$$

$$= 17.73$$

$$\boxed{\therefore p^{Cu^{2+}} = 17.73}$$

11-17. Consider the derivation of the fraction α_M in Equation 13-16.

(a) Derive the following expressions for the fractions α_{ML} and α_{ML_2}:

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

$$\alpha_{ML_2} = \frac{\beta_2 [L]^2}{1 + \beta_1 [L] + \beta_2 [L]^2}$$

(b) Calculate the values of α_{ML} and α_{ML_2} for the conditions in problem 13-14.

Soln

(a) $$M + L \rightleftharpoons ML$$

$$\beta_1 = \frac{[ML]}{[M][L]} \; ; \; [ML] = \beta_1 [M][L]$$

$$\therefore \alpha_{ML} = \frac{[ML]}{c_M}$$

where

C_M - refers to the total concentration of all forms of M (= M, ML, ---)

α_{ML} - fraction of metal ligand Complex.

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

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

$$M + 2L \rightleftharpoons ML_2$$

$$\therefore \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$\therefore [ML_2] = \beta_2 [M][L]^2$$

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

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

(b) Calculate the values of α_{ML} and α_{ML_2} for the conditions in problem 13-14.

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

$$= \frac{(10^{2.23})(0.100)}{1 + (10^{2.23})(0.100) + (10^{3.63})(0.100)}$$

$\because [L] = 0.100\,m$

$\log \beta_1 = 2.23$

$\beta_1 = 10^{2.23}$

$\log \beta_2 = 3.63$

$\beta_2 = 10^{3.63}$

$$\boxed{\alpha_{ML} = 0.28}$$

$$\alpha_{ML_2} = \frac{\beta_2 [L]^2}{1 + \beta_1 [L] + \beta_2 [L]^2}$$

$$= \frac{(10^{3.63})(0.100)^2}{1 + (10^{2.23})(0.100) + (10^{3.63})(0.100)}$$

$$\boxed{\alpha_{ML_2} = 0.70}$$