

## Auxiliary Complexing agents:

①

~~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.

$\text{NH}_3$  keeps  $\text{Zn}^{2+}$  in solution at high  $\text{pH}$ .

2

11-15

~~13-14~~ According to Appendix I,  $\text{Cu}^{2+}$  forms two complexes with acetate:



(a) Referring to Box 6-2, find  $k_2$  for the reaction.

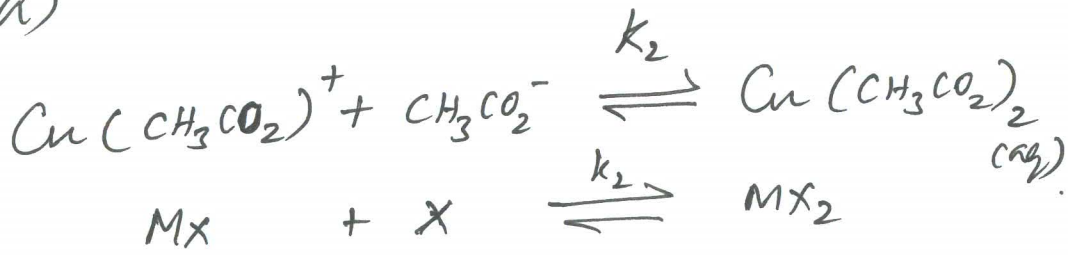


(b) Consider 1.00L of solution prepared by mixing  $1.00 \times 10^{-4}$  mol  $\text{Cu}(\text{ClO}_4)_2$  and 0.100 mol  $\text{CH}_3\text{CO}_2\text{Na}$ . Use Equation 13-16 to find the fraction of copper in the form  $\text{Cu}^{2+}$ .

(3)

Soln

(a)



$$\therefore K_2 = \frac{[\text{MX}_2]}{[\text{MX}][\text{X}]}$$

$$\therefore \beta_2 = k_1 k_2$$

$$\beta_2 = \beta_1 k_2$$

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

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

$$k_2 = 25.12$$

$$\therefore k_2 = 25$$

For  $\text{Cu}^{2+}$

$$\log \beta_1 = 2.23$$

$$\log \beta_2 = 3.63$$

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

$$\beta_2 = 10^{3.63}$$

$$\beta_n = k_1 k_2 \dots k_n$$

$$\therefore \beta_1 = k_1$$

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

(4)

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

$$= \frac{1}{1 + 10^{2.23}(0.100) + 10^{8.63}(0.100)^2}$$

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

$$[\text{L}] = 0.100 \text{ M}$$

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

$$\beta_2 = 10^{8.63}$$

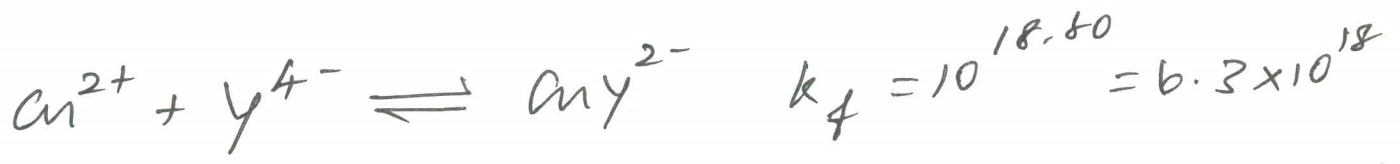
11-16. Calculate  $p_{Cu^{2+}}$  at each of the following 5

Points in the titration of 50.00 mL of 0.00100 M  $Cu^{2+}$  with 0.00100 M EDTA at pH 11.00 in a solution whose  $NH_3$  concentration is somehow fixed at 0.100 M.

- (a) 0 mL                      (b) 1.00 mL                      (c) 45.00 mL  
(d) 50.00 mL                      (e) 55.00 mL.

Soln

The titration reaction is



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

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

$$\log \beta_1 = 3.99$$

$$\log \beta_2 = 7.33$$

$$\log \beta_3 = 10.06$$

$$\log \beta_4 = 12.03$$

(6)

Therefore

$$\beta_1 = 9.8 \times 10^3$$

$$[L] = 0.100 \text{ M}$$

$$\beta_2 = 2.1 \times 10^7$$

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

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

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

1

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

1

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

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

(7)

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

$$= (0.85) (6.3 \times 10^{18})$$

$$K_f' = 5.4 \times 10^{18}$$

$$\therefore \alpha_{Y^{4-}} = 0.85 \text{ at } pH_{11.0}$$

$$K_f = 6.3 \times 10^{18}$$

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

$$= (0.85) \cdot (8.4 \times 10^{-9}) (6.3 \times 10^{18})$$

$$K_f'' = 4.5 \times 10^{10}$$

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

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

$$K_f = 6.3 \times 10^{18}$$

Equivalence point = 50.00 mL

$$\begin{aligned} \therefore 50.00 \text{ mL} \times 0.001 \text{ M} \\ \underbrace{\hspace{1cm}}_{Ca^{2+}} \\ = 0.001 \times \underbrace{V_e}_{EDTA} \\ V_e = 50.00 \text{ mL} \end{aligned}$$



(8)

(A) At 0 mL.

The total concentration of Copper is

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

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

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

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

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

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

$$\boxed{p_{\text{Cu}^{2+}} = 11.08}$$

$$\left. \begin{array}{l} \therefore \\ \alpha_{\text{Cu}^{2+}} = 8.4 \times 10^{-9} \\ C_{\text{Cu}^{2+}} = 0.001 \text{ M} \end{array} \right\}$$



(9)

(b) At 1.00 mL

$$C_{\text{Cu}^{2+}} = \left( \frac{49.00 \text{ mL}}{50.00 \text{ mL}} \right) (0.00100 \text{ M}) \left( \frac{50.00 \text{ mL}}{51.00 \text{ mL}} \right)$$

Fraction remaining                      original concentration of  $\text{Cu}^{2+}$                       dilution factor.

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

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

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

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

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

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

$$\boxed{\therefore p^{\text{Cu}^{2+}} = 11.09}$$

(C) At 45.00 mL.

$$C_{\text{Cu}^{2+}} = \left( \frac{5.00 \text{ mL}}{50.00 \text{ mL}} \right) (0.00100) \left( \frac{50.00}{95.00} \right)$$

$\downarrow$  Fraction Remaining       $\downarrow$  Original Concentration of  $\text{Cu}^{2+}$        $\downarrow$  Dilution Factor

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

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

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

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

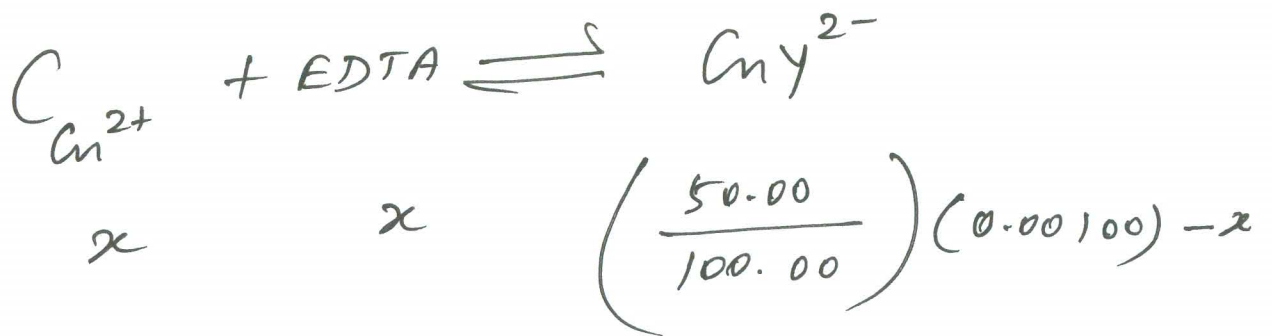
$$\therefore p_{\text{Cu}^{2+}} = -\log [\text{Cu}^{2+}]$$

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

$$\therefore p_{\text{Cu}^{2+}} = 12.35$$

(11)

d) At the equivalence point, we can write



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

$$\therefore K_f = 4.5 \times 10^{10}$$

$$\therefore x = C_{\text{Cu}^{2+}} = 1.05 \times 10^{-7} \text{ M}$$

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

$$= (8.4 \times 10^{-9}) \cdot (1.05 \times 10^{-7} \text{ M})$$

$$[\text{Cu}^{2+}] = \cancel{8.4} \cdot 9 \times 10^{-16} \text{ M}$$

$$\therefore p_{\text{Cu}^{2+}} = -\log (8.9 \times 10^{-16}) = 15.06$$

$$\boxed{\therefore p_{\text{Cu}^{2+}} = 15.06}$$

(c) At. 55.00 mL.

Past the equivalence point at 55.00 mL  
we can say

$$[EDTA] = \left( \frac{5.00}{105.00} \right) (0.00100 M)$$

$\downarrow$  Dilution Factor                       $\downarrow$  Original Concentration of EDTA.

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

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

$\swarrow$  original volume of  $Cu^{2+}$                        $\nwarrow$  Original concentration of  $Cu^{2+}$   
 $\nwarrow$  Total volume of the solution

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

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

(13)

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

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

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

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

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

$$= 17.73$$

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

$$K_f' = 5.4 \times 10^{18}$$

11-17 ~~11-17~~ Consider the derivation of the fraction  $\alpha_M$  in Equation 13-16. (14)

(a) Derive the following expressions for the fractions  $\alpha_{ML}$  and  $\alpha_{ML_2}$ :

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

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

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

Soln

(a)



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

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

where

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

$\alpha_{ML}$  - fraction of metal ligand complex.

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

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

~~$\alpha$~~



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

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

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



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

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

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

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

$$\therefore [L] = 0.100 \text{ M}$$

$$\log \beta_1 = 2.23$$

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

$$\log \beta_2 = 3.63$$

$$\beta_2 = 10^{3.63}$$

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

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

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

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