

## EDTA titration curves.

①

Example:

Calculate the shape of the titration curve for the reaction of 50.0 mL of 0.0400 M  $\text{Ca}^{2+}$  (buffered to pH 10.00) with 0.0800 M EDTA:-



$$K_f' = \alpha_{Y^{4-}} K_f = (0.36)(4.9 \times 10^{10}) \\ = 1.8 \times 10^{10}$$

The equivalence volume is 25.0 mL. Because  $K_f'$  is large, it is reasonable to say that the reaction goes to completion with each addition of titrant. We want to make a graph in which  $p_{\text{Ca}^{2+}} (= -\log[\text{Ca}^{2+}])$  is plotted versus milliliters of added EDTA.

Soln.:

Region 1: Before the equivalence point:

Consider the addition of 5.0 mL of EDTA.

Because the equivalence point requires 25.0 mL of EDTA, one-fifth of the  $\text{Ca}^{2+}$  will be consumed

and four-fifths remains.

②

$$[Ca^{2+}] = \underbrace{\left( \frac{25.0 - 5.0}{25.0} \right)}_{\substack{\text{Fraction remaining} \\ (= 4/5)}} \underbrace{(0.0400)}_{\substack{\text{Original} \\ \text{Concentration} \\ \text{of } Ca^{2+}}} \underbrace{\left( \frac{50.0}{55.0} \right)}_{\substack{\text{Total volume} \\ \text{of solution}}} \underbrace{\quad}_{\substack{\text{Initial volume} \\ \text{of } Ca^{2+}}} \underbrace{\quad}_{\substack{\text{Dilution} \\ \text{factor}}}$$

$$[Ca^{2+}] = 0.0291 \text{ M}$$

$$\begin{aligned} \therefore p^{Ca^{2+}} &= -\log [Ca^{2+}] \\ &= -\log (0.0291) \end{aligned}$$

$$p^{Ca^{2+}} = 1.54$$

In a similar manner, we could calculate  $p^{Ca^{2+}}$  for any volume of EDTA less than 50.0 mL.

(3)

Region 2: At the equivalence point.

In this region virtually all the metal is in the form  $\text{CaY}^{2-}$ .

The concentration of  $\text{CaY}^{2-}$  is equal to the original concentration of  $\text{Ca}^{2+}$ , with a correction for dilution.

$$[\text{CaY}^{2-}] = (0.040 \text{ M}) \frac{(50.0)}{(75.0)}$$

Initial concentration of  $\text{Ca}^{2+}$

Initial volume of  $\text{Ca}^{2+}$

Total volume of solution.

$$[\text{CaY}^{2-}] = 0.0267 \text{ M}$$

(4)

The concentration of free  $\text{Ca}^{2+}$  is small and unknown. we can write.



Initial Concentration (M)	—	—	0.0267
Final Concentration (M)	$x$	$x$	$0.0267 - x$

$$\frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{EDTA}]} = K_f' = 1.8 \times 10^{10}$$

$$\frac{0.0267 - x}{x^2} = 1.8 \times 10^{10}$$

$$\therefore x = 1.2 \times 10^{-6} \text{ M}$$

$$\text{i.e. } [\text{Ca}^{2+}] = 1.2 \times 10^{-6} \text{ M}$$

$$\begin{aligned} \therefore p_{\text{Ca}^{2+}} &= -\log [\text{Ca}^{2+}] \\ &= -\log (1.2 \times 10^{-6}) \end{aligned}$$

$$\boxed{p_{\text{Ca}^{2+}} = 5.92}$$

$$\therefore x = \text{Ca}^{2+}$$

(5)

Region 3: After the equivalence point:

In this region, virtually all the metal is in the form  $\text{CaY}^{2-}$ , and there is excess, unreacted EDTA. The concentration of  $\text{CaY}^{2-}$  and excess EDTA are easily calculated.

For example, at 26.0 mL, there is 1.0 mL of excess EDTA.

$$[\text{EDTA}] = (0.0800) \left( \frac{1.0}{76.0} \right) = 1.05 \times 10^{-3} \text{ M}$$

Annotations for the EDTA calculation:

- Original concentration of EDTA points to 0.0800
- Volume of excess EDTA points to 1.0
- Total volume of solution points to 76.0
- Dilution factor points to the fraction  $\frac{1.0}{76.0}$

$$[\text{CaY}^{2-}] = (0.0400 \text{ M}) \left( \frac{50.0}{76.0} \right) = 2.63 \times 10^{-2} \text{ M}$$

Annotations for the  $\text{CaY}^{2-}$  calculation:

- Original concentration of  $\text{Ca}^{2+}$  points to 0.0400 M
- Original volume of  $\text{Ca}^{2+}$  points to 50.0
- Dilution factor points to the fraction  $\frac{50.0}{76.0}$
- Total volume of solution points to 76.0



(b)

The concentration of  $\text{Ca}^{2+}$  is governed by

$$\frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{EDTA}]} = K_f' = 1.8 \times 10^{10}$$

$$\frac{[2.63 \times 10^{-2}]}{[\text{Ca}^{2+}][1.05 \times 10^{-3}]} = 1.8 \times 10^{10}$$

$$\therefore [\text{Ca}^{2+}] = 1.4 \times 10^{-9} \text{ M.}$$

$$\begin{aligned} \therefore p^{\text{Ca}^{2+}} &= -\log [\text{Ca}^{2+}] \\ &= -\log (1.4 \times 10^{-9}) \end{aligned}$$

$$\therefore p^{\text{Ca}^{2+}} = 8.85$$

EDTA titration curves:

18-6. The ion  $M^{n+}$  (100.0 mL of 0.0500 M metal ion buffered to pH 9.00) was titrated with 0.0500 M EDTA.

(a) What is the equivalence volume,  $V_e$ , in milliliters?

Ans

$$\text{mmol EDTA} = \text{mmol } M^{n+}$$

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

$$\Rightarrow V_e = 100.0 \text{ mL}$$

(b) Calculate the concentration of  $M^{n+}$  at

$$V = \frac{1}{2} V_e.$$

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

Fraction
Original  
Remaining
Concentration

(8)

(c) what fraction ( $\alpha_{Y^{4-}}$ ) of free EDTA is in the form  $Y^{4-}$  at pH 9.00?

At pH 9.00  $\alpha_{Y^{4-}}$  is 0.054 (from the

table 13-1).

(d) the formation constant ( $K_f$ ) is  $10^{12.00}$ .  
Calculate the value of the conditional formation constant  $K_f'$  ( $= \alpha_{Y^{4-}} K_f$ ).

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

$$\therefore K_f' = (0.054) (10^{12.00})$$

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

$$\therefore K_f = 10^{12.00}$$

$$\alpha_{Y^{4-}} \text{ at pH } 9.00 = 0.054$$

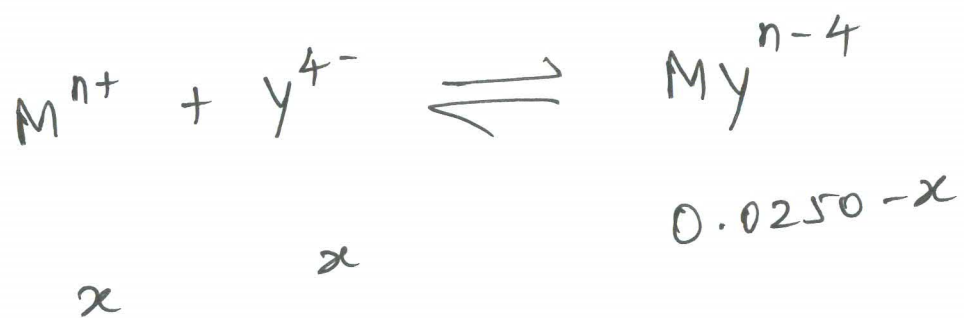


(9)

(e) Calculate the Concentration of  $M^{n+}$  at  $V=V_e$

Ans:

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



$$\therefore \frac{[My^{n-4}]}{[M^{n+}][EDTA]_{(or) Y^{4-}}} = \frac{0.0250 - x}{x^2} = 5.4 \times 10^{10}$$

$\therefore$   
From  
problem  
(d)  
 $K_f' = 5.4 \times 10^{10}$

$$\therefore x = 6.8 \times 10^{-7} M.$$

$$\therefore x = [M^{n+}] = 6.8 \times 10^{-7} M.$$

(f) What is the concentration of  $M^{n+}$  at  
 $V = 1.100 V_e$ ?

(10)

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

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

$$K_f' = \frac{[My^{n-4}]}{[M^{n+}][EDTA]} = \frac{(2.38 \times 10^{-2})}{[M^{n+}](2.38 \times 10^{-3})} = 5.4 \times 10^{10}$$

$$\therefore [M^{n+}] = \frac{(2.38 \times 10^{-2})}{(5.4 \times 10^{10})(2.38 \times 10^{-3})}$$

$$\boxed{[M^{n+}] = 1.9 \times 10^{-10} M}$$

11

11-7. Calculate  $p_{Co^{2+}}$  at each of the following points in the titration of 25.00 mL of 0.02026 M  $Co^{2+}$  by 0.03855 M EDTA at  $pH 6.00$ :  
(a) 12.00 mL ; (b)  $V_e$  ; (c) 14.00 mL.

Soln



$$K_f = 4.7 \times 10^{11}$$

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

equivalence volume

(a) 12.00 mL:

$$[Co^{2+}] = \left( \frac{13.14 \text{ mL} - 12.00 \text{ mL}}{13.14 \text{ mL}} \right) \times (0.02026 \text{ M}) \left( \frac{25.00}{37.00} \right)$$

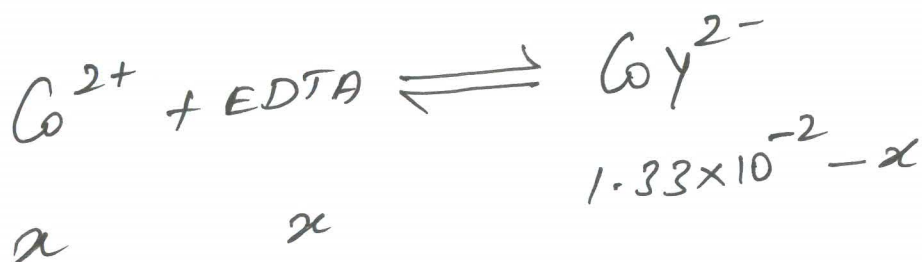
$$[Co^{2+}] = 1.19 \times 10^{-3} \text{ M}$$

$$\therefore p_{Co^{2+}} = -\log [Co^{2+}] = -\log (1.19 \times 10^{-3})$$

$p_{Co^{2+}} = 2.92$

(b)  $V_e$ :Formal Concentration of  $\text{CoY}^{2-}$  is

$$\left( \frac{25.00}{38.14} \right) (0.02026 \text{ M}) = 1.33 \times 10^{-2} \text{ M}$$



$$\therefore \frac{1.33 \times 10^{-2} - x}{x^2} = \alpha_{Y^{4-}} \cdot K_f$$

$$\therefore \frac{1.33 \times 10^{-2} - x}{x^2} = 4.7 \times 10^{11}$$

$$\therefore x = 1.68 \times 10^{-7} \text{ M}$$

$$\therefore x = [\text{Co}^{2+}] = 1.68 \times 10^{-7} \text{ M}$$

$$\begin{array}{l} \therefore \alpha_{Y^{4-}} \cdot K_f \\ = 4.7 \times 10^{11} \end{array}$$

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

$$= -\log (1.68 \times 10^{-7}) = 6.77$$

$$\therefore p\text{Co}^{2+} = 6.77$$

(c) 14.00 mL:Formal Concentration of  $\text{CoY}^{2-}$  is

$$\left( \frac{25.00}{39.00} \right) (0.02026 \text{ M}) = 1.30 \times 10^{-2} \text{ M}$$

Formal Concentration of EDTA is

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

$$K'_f = \frac{[\text{CoY}^{2-}]}{[\text{Co}^{2+}] [\text{EDTA}]}$$

$$\therefore [\text{Co}^{2+}] = \frac{[\text{CoY}^{2-}]}{[\text{EDTA}] K'_f}$$

$$[\text{Co}^{2+}] = \frac{(1.30 \times 10^{-2})}{(8.50 \times 10^{-4}) (4.7 \times 10^{11})}$$

$$[\text{Co}^{2+}] = 3.3 \times 10^{-11} \text{ M}$$

$$\therefore p\text{Co}^{2+} = -\log (3.3 \times 10^{-11}) = 10.48$$

$$\therefore \boxed{p\text{Co}^{2+} = 10.48}$$

$$\therefore [\text{CoY}^{2-}] = 1.30 \times 10^{-2} \text{ M}$$

$$[\text{EDTA}] = 8.50 \times 10^{-4} \text{ M}$$

$$K'_f = 4.7 \times 10^{11}$$

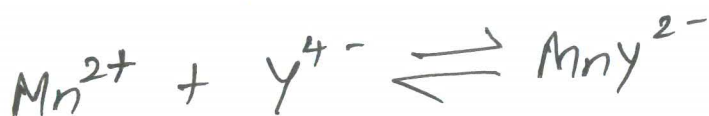


17-8. Consider the titration of 25.0 mL of 0.020 M  $MnSO_4$  with 0.010 M EDTA in a solution buffered to pH 8.00. Calculate  $pMn^{2+}$  at the following volumes of added EDTA and sketch the titration curve.

- |             |                    |                    |
|-------------|--------------------|--------------------|
| (a) 0 mL    | (b) <u>20.0 mL</u> | (c) 40.0 mL        |
| (d) 49.0 mL | (e) 49.9 mL        | (f) <u>50.0 mL</u> |
| (g) 50.1 mL | (h) 55.0 mL        | (i) <u>60.0 mL</u> |

Soln

Titration reaction:



The equivalence point is 50.0 mL

∴

(25.0 mL) (0.020 M  $MnSO_4$ )

= x (0.010 M EDTA)

∴ x = 50.0 mL

∴

(25.0 mL) (0.020 M  $MnSO_4$ )

= x (0.010 M EDTA)

∴ x = 50.0 mL

20.0 mL :

The fraction of  $Mn^{2+}$  that has reacted is  $\frac{2}{5}$  and the fraction remaining is  $\frac{3}{5}$ .

$$\therefore [Mn^{2+}] = \left( \frac{30.0}{50.0} \right) (0.0200 M) \left( \frac{25.0}{45.0} \right)$$

$\downarrow$  fraction remaining       $\downarrow$  original concentration of  $Mn^{2+}$        $\downarrow$  dilution factor  
 (initial volume of  $Mn^{2+}$ )      (Total volume of solution)

$$[Mn^{2+}] = 6.67 \times 10^{-3} M$$

$$\therefore pMn^{2+} = -\log [Mn^{2+}] = -\log (6.67 \times 10^{-3})$$

$$pMn^{2+} = 2.18$$

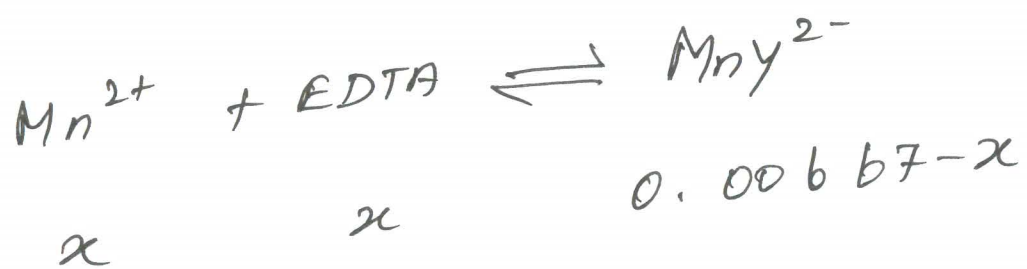
(16)

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

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

$\downarrow$  Initial volume of  $Mn^{2+}$   
 $\downarrow$  Initial concentration of  $Mn^{2+}$   
 $\downarrow$  Dilution factor  
 $\rightarrow$  Total volume of  $Mn^{2+}$

$$[MnY^{2-}] = 0.00667M.$$



$$\frac{0.00667 - x}{x^2} = \alpha_{Y^{4-}} \cdot K_f$$

$$\frac{0.00667 - x}{x^2} = 4.1 \times 10^{11}$$

$$\therefore x = 1.28 \times 10^{-7}$$

$$\therefore x = [Mn^{2+}] = 1.28 \times 10^{-7} M.$$

$$K' = 4.1 \times 10^{11}$$

(17)

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

$$= -\log (1.28 \times 10^{-7})$$

$$p^{Mn^{2+}} = 6.89$$

$$[Mn^{2+}] = 1.28 \times 10^{-7}$$

60.0 mL: There are 10.0 mL of excess EDTA.

$$\therefore [EDTA] = (0.0100 M) \left( \frac{10.0 mL}{85.0 mL} \right)$$

$\downarrow$  original concentration of EDTA

$\downarrow$  volume of excess EDTA  
 $\uparrow$  total volume of solution.

$$= 1.176 \times 10^{-3} M$$

$$[MnY^{2-}] = \left( \frac{25.0 mL}{85.0 mL} \right) (0.0200 M)$$

$\downarrow$  original volume of  $Mn^{2+}$   
 $\uparrow$  total volume of solution

$\uparrow$  original concentration of  $Mn^{2+}$

$$[MnY^{2-}] = 5.88 \times 10^{-3} M$$

$$[Mn^{2+}] = \frac{[MnY^{2-}]}{[EDTA] K_f}$$

$$= \frac{(5.88 \times 10^{-3} M)}{(1.176 \times 10^{-3}) (4.1 \times 10^{11})}$$

$$[Mn^{2+}] = 1.22 \times 10^{-11} M$$

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

$$= -\log (1.22 \times 10^{-11})$$

$$p^{Mn^{2+}} = 10.91$$

$$\begin{aligned} \therefore [MnY^{2-}] &= 5.88 \times 10^{-3} M \\ [EDTA] &= 1.176 \times 10^{-3} M \\ K_f &= 4.1 \times 10^{11} \end{aligned}$$