CHƯƠNG: CHUẨN ĐỘ AXIT- BAZ

III.4: Chất chỉ thị được dùng? Metyl da cam (pH= 3,3 – 4,4); metyl đỏ(4,4-6,2); p.p(8-10).

a) Chuẩn độ HCl 0,1M bằng NaOH 0,1M

$$HCl + NaOH \rightarrow NaCl + H_2O$$

C_oV_o CV => $pH_{tđ} = 7$

$$pH_1 = -\lg\frac{0,1(100-99,9)}{100+99,9} = -\lg\frac{10^{-2}}{2.10^2} = -\lg\frac{10^{-4}}{2} = 4,3$$

$$pH_2 = 14-\left(-\lg\frac{0,1(100,1-100)}{100+100,1}\right) = 9,7$$

=> Bước nhảy pH = 4,3 → 9,7

Do đó: cct= metyl da cam,metyl đỏ, p.p

b) Chuẩn độ HCOOH 0,1M bằng NaOH 0,1M, $pK_a(HCOOH) = 3,75$

$$HCOOH + NaOH \rightarrow HCOONa + H_2O$$

$$pH_{tđ} = \tfrac{1}{2}(pK_n + pK_a + \lg C_m) = \tfrac{1}{2}(14 + 3,75 + \lg 0,05)$$

$$pH_{tđ} = 8,25$$

$$pH_1 = pK_{a1} - \lg\frac{C_0V_0 - CV}{CV} = 3,75 - \lg\frac{0,1(100 - 99,9)}{0,1.99,9}$$

$$= 6,75$$

$$pH_2 = 14 - \left[- \lg\frac{CV - C_0V_0}{V_0 + V} \right] = 14 - \left[- \lg\frac{0,1(100,1 - 100)}{100 + 100,1} \right]$$

$$= 9,7$$

=> Bước nhảy pH= 6,75 → 9,7 => Chỉ dùng p.p

c)Chuẩn độ NH_3 0,1M(pK_b=4,75) bằng HCl 0,1M.

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$$

$pH_{td} = ½(pK_n - pK_b - \lg C_m) = ½(14 - 4,75 - \lg 0,05) = 5,275$

$$pH_1 = 14 - \left[pK_b - \lg \frac{C_0V_0 - CV}{CV} \right]$$

$$= 14 - \left[4,75 - \lg \frac{0,1(100 - 99,9)}{0,1.99,9} \right] = 6,25$$

$$pH_2 = - \lg \frac{CV - C_0V_0}{V_0 + V} = - \lg \frac{0,1(100,1 - 100)}{100 + 100,1} = 4,3$$

=> Bước nhảy pH = 6,25 → 4,3

=> Cct = metyl da cam, metyl đỏ

III.5:a) Chuẩn độ 25ml HCl bằng NaOH 0,05M. Tính nồng độ HCl nếu V_{NaOH}=17,5ml

b) Kết thúc chuẩn độ ở pT=4 => S%=?

c) Bước nhảy chuẩn độ nếu S%= ± 0,2%

Giải

a) $HCl + NaOH \rightarrow NaCl + H_2O$

$C_oV_o = CV \Rightarrow C_o = CV/V_o = 0,05.17,5/25 = 0,035N$

b) $pH_{td} = 7 \Rightarrow pH_c = pT = 4 < pH_{td}$:S(-);dd(HCl)

$$S\% = -\frac{10^{-pT}(C_0 + C)}{C_0.C}.10^2 = -\frac{10^{-4}(0,05 + 0,035)}{0,05.0,035}.10^2$$

S% = - 0,485%

c) $S\% = -\dfrac{10^{-pT}(0{,}05+0{,}035)}{0{,}05.0{,}035}10^2 = -0{,}2 \Rightarrow pT=4{,}38$

$S\% = +\dfrac{10^{pT-14}(0{,}05+0{,}035)}{0{,}05.0{,}035}10^2 = +0{,}2 \Rightarrow pT=9{,}62$

=> Bước nhảy pH = 4,38 → 9,62

III.6:a) Chuẩn độ 50ml CH_3COOH hết 24,25ml NaOH 0,025M. Tính nồng độ CH_3COOH.

b) Tính S% nếu pT = 10.

c) Tính pH nếu V_{NaOH} = 24,5ml

Giải

a) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

$C_oV_o = CV \Rightarrow C_o = CV/V_o = 0{,}025.24{,}25/50$

$= 0{,}012125M$

b) $pH_{td} = \frac{1}{2}(pK_n + pK_a + \lg C_m)$

$$pH_{td} = \frac{1}{2}\left(14 + 4{,}75 + \lg\frac{C_0V_0 = CV}{V_0 + V}\right)$$

$$pH_{td} = \frac{1}{2}\left(14 + 4{,}75 + \lg\frac{24{,}25.0{,}025}{50 + 24{,}25}\right) = 8{,}33$$

pT = 10 > pH_{td} => S(+): dd thừa NaOH

$$S\% = + \frac{10^{pT-14}(C_0 + C)}{C_0.C}10^2$$

$$= + \frac{10^{10-14}(0{,}012125 + 0{,}025)}{0{,}012125.0{,}025}10^2 = + 1{,}225\%$$

c) $V_c = 24,5ml > V_{tđ} = 24,25ml$

$$pH_2 = 14 - (- \lg \frac{CV - C_0V_0)}{V_0 + V})$$

$$= 14 - (- \lg \frac{0,025.24,5 - 0,012.50)}{50 + 24,5}) = 9,92$$

III.7:a) Chuẩn độ 25ml NH_3 0,05M bằng HCl 0,1M. $pH_{tđ}$? pT = 4 => V_{HCl} =?

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$$

$C_oV_o = CV \Rightarrow V_{tđ} = C_oV_o/C = 0,05.25/0,1 = 12,5ml$

$$pH_{tđ} = \frac{1}{2}(pK_n - pK_b - \lg \frac{C_0V_0}{V_0 + V})$$

$$pH_{tđ} = \frac{1}{2}(14 - 4,75 - \lg \frac{0,05.25}{25 + 12,5}) = 5,296$$

*pT = 4 < pH_{td} => F>1: dd thừa HCl

$$pH = pT = -\lg\frac{CV - C_0V_0}{V_0 + V} = 4 \Rightarrow \frac{CV - C_0V_0}{V_0 + V} = 10^{-4}$$

$$CV - C_0V_0 = (V_0 + V)10^{-4} \Rightarrow V(C - 10^{-4}) = V_0(C_0 + 10^{-4})$$

$$V = \frac{V_0(C_0 + 10^{-4})}{C - 10^{-4}} = \frac{25(0{,}05 + 10^{-4})}{0{,}1 - 10^{-4}} = 12{,}5249\text{ml}$$

b) pH khi thêm 12,3ml HCl : $V_c < V_{td}$ => dd NH_3

$$pH = 14 - \frac{1}{2}(pK_b - \lg\frac{C_0V_0 - CV}{V_0 + V})$$

$$= 14 - \frac{1}{2}(4{,}75 - \lg\frac{0{,}05.25 - 0{,}1.12{,}3}{25 + 12{,}3}) = 9{,}99$$

c) pT=5 <pH_{td} => S(+):dd HCl

$$S\% = \frac{10^{-pT}(Co + C)}{Co.C}.10^2 = \frac{10^{-5}(0{,}05 + 0{,}1)}{0{,}05.0{,}1}.10^2 = +0{,}03\%$$

III.8: $50ml \begin{cases} HCl\ 0,1M \\ HA 0,1M (pK_a=6) \end{cases} + NaOH\ 0,2M$

a) pH khi F = 0

$pH_o = -lgC_o(HCl) = -lg0,1 = 1$

b) pH khi chuẩn độ 99,9% HCl

:HCl chuẩn độ trước

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Xem như HCl đã chuẩn độ hết(dd chỉ còn HA)

$C_{01}.V_0 = C.V_1 \Rightarrow V_1 = C_{01}.V_0/C = 0,1.50/0,2 = 25ml$

$$pH_1 = \tfrac{1}{2}[pK_a - lgC_o(HA)] = \tfrac{1}{2}\left(6 - lg\frac{C_{01}V_0}{V_0 + V_1}\right)$$

$$= \tfrac{1}{2}\left(6 - lg\frac{0,1.50}{50 + 25}\right) = 3,59$$

c) pH khi 2 axit đã trung hòa hết

$$HA + NaOH \rightarrow NaA + H_2O$$

$C_{02}.V_o = CV_2 \Rightarrow V_2 = C_{02}.V_o/C = 0,1.50/0,2 = 25ml$

$pH_2 = ½[pK_n + pK_a + lgC_{NaA}]$

$$C_{NaA} = \frac{C_{02}.V_0}{V_0 + V_1 + V_2} = \frac{0,1.50}{50 + 25 + 25} = 0,05M$$

$pH_2 = ½(14+6+lg0,05) = 9,35$

III.9: 50ml { HA 0,05M(pK_{a1}=3,75 ; HB 0,1M(pK_{a2}=7,5 } +NaOH 0,1M

a) $pH_{tđ1}$

:$pK_{a2} - pK_{a1} = 7,5-3,75 = 3,75 \Rightarrow$ ch.độ riêng từng axit(xem HA và HB như 1 axit yếu 2 chức: H_2X)

=> Tại điểm tương đương (1):

$HA + NaOH \rightarrow NaA + H_2O$

Hoặc: $H_2X + NaOH \rightarrow NaHX + H_2O$

$C_{01}.V_0 = C.V_1 \Rightarrow V_1 = C_{01}.V_0/C = 0,05.50/0,1 = 25ml$

$pH_{tđ1} = ½(pK_{a1} + pK_{a2}) = ½(3,75 + 7,5) = 5,625$

b) $pH_{tđ2}$: $HB + NaOH \rightarrow NaB + H_2O$

$C_{02}.V_0 = CV_2 \Rightarrow V_2 = C_{02}.V_0/C = 0,1.50/0,1 = 50ml$

$pH_{tđ2} = ½(pK_n + pK_{a2} + \lg C_{NaB})$

$$C_{NaB} = \frac{C_{02}.V_0}{V_0 + V_1 + V_2} = \frac{0,1.50}{50 + 25 + 50} = 0,04M$$

$pH_{tđ2} = ½(14 + 7,5 + \lg 0,04) = 10,05$

c) pT=4 $< pH_{tđ1}$ => S(-):dd (HA)

$$S\% = -\frac{10^{-pT}}{K_{a1} + 10^{-pT}} 10^2 = -\frac{10^{-4}}{10^{-3,5} + 10^{-4}} 10^2 = -24\%$$

d): pT = 10 $< pH_{tđ2}$ => S(-): dd (HB)

$$S\% = -\frac{10^{-pT}}{K_{a2} + 10^{-pT}} 10^2 = -\frac{10^{-10}}{10^{-7,2} + 10^{-10}} 10^2 = -0,16\%$$

III.10: Ch.d 50ml H_3PO_4 hết 100ml NaOH 0,05M

a) $C_{H_3PO_4}$ (Dùng chỉ thị p,p)

$$H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O$$

C_oV_o $\quad CV = 2C_oV_o$

$$C_0 = \frac{CV}{2V_0} = \frac{0,05.100}{2.50} = 0,05M$$

b) Đường cong chuẩn độ

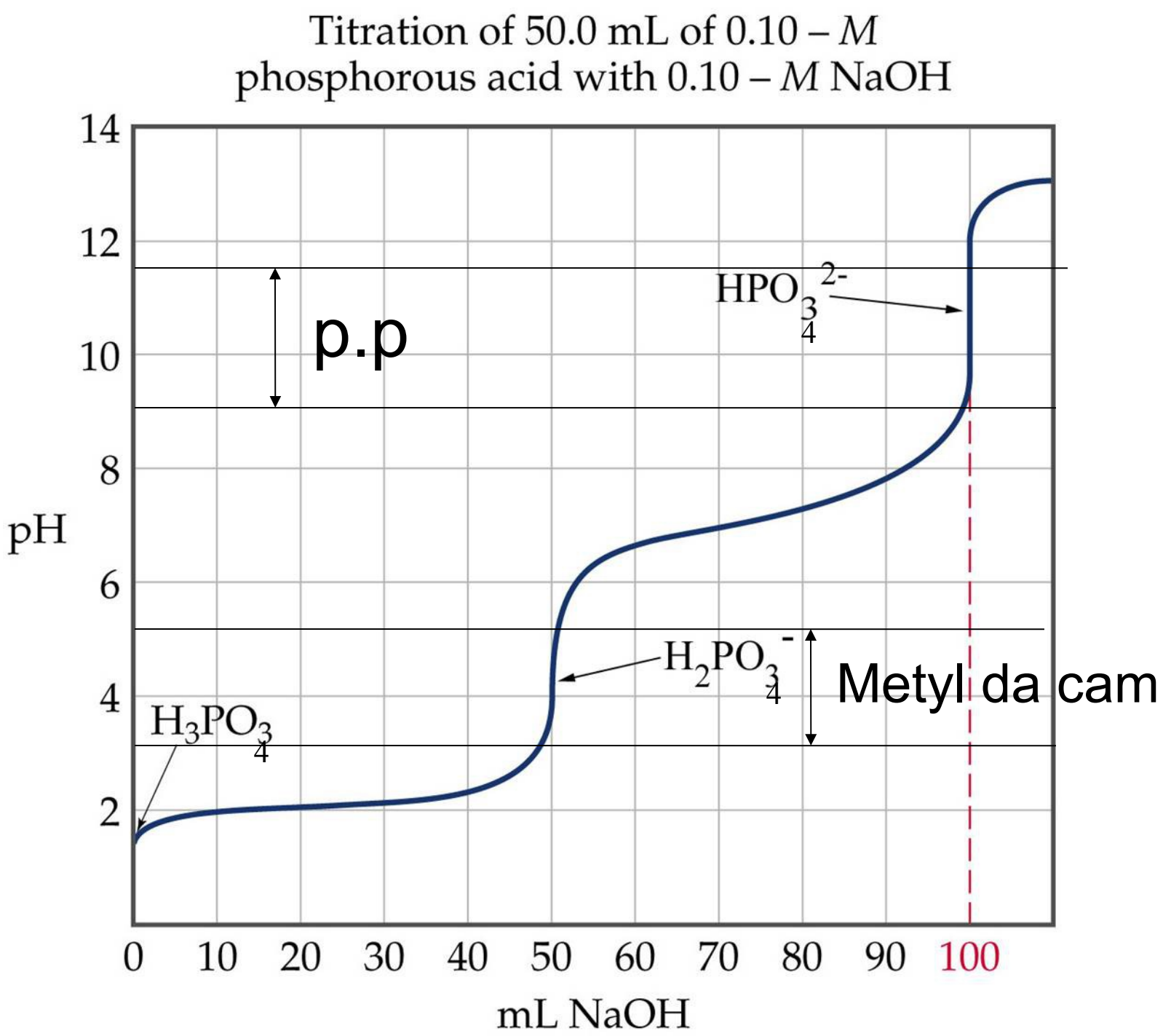
$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$

$pH_o = ½(pK_{a1} - \lg C_o) = ½(2,15 - \lg 0,05) = 1,725$

$pH_{tđ1} = ½(pK_{a1} + pK_{a2}) = ½(2,15 + 7,2) = 4.675$

$NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O$

$pH_{tđ2} = ½(pK_{a2} + pK_{a3}) = ½(7,2 + 12,35) = 9,775$


Titration of 50.0 mL of 0.10 – M
phosphorous acid with 0.10 – M NaOH
pH
mL NaOH
14
12
10
8
6
4
2
0
10
20
30
40
50
60
70
80
90
100
p.p
HPO3 2-
4
H2PO3 -
4
H3PO3
4
Metyl da cam

III.11: chuẩn độ 50ml Na_2CO_3 0,05M bằng HCl 0,1M.(H_2CO_3 có:pK_{a1}=6,35; pK_{a2}=10,33)

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$$

$$pH_o = ½(pK_n + pK_{a2} + lgC_o)$$

$$= ½(14 + 10,33 + lg0,05) = 11,51$$

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

$$pH_{tđ1} = ½(pK_{a1} + pK_{a2}) = ½(6,35+10,33) = 8,34$$

$$NaHCO_3 + HCl \rightarrow CO_2 + H_2O + NaCl$$

$$pH_{tđ2} = 4$$

p.p ← đtđ1

Metyl da cam ← đtđ2

III.12: 50ml(H_2SO_4 + H_3PO_4) $\xrightarrow{NaOH\,(0,05M)}$

* ct(metyl da cam): V_{NaOH} = 36,5ml
* ct(p.p): V_{NaOH} = 45,95ml

} C_o ?

* Mdc: $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ (1)

$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$ (2)

(1)=> $C.V_1 = 2C_{o1}.V_o$;(2)=> $C.V_2 = C_{o2}.V_o$

=> $C(V_1 + V_2) = (2C_{o1} + C_{o2}).V_o$

=> $2C_{o1} + C_{o2} = 0,05.36,5/50 = 0,0365M$ (a)

* p,p :$H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + H_2O$ (3)

(3)=>$C.V_3=2C_{o2}.V_o$ => $C(V_1+V_3)=2(C_{o1}+C_{o2})/V_o$

$C_{o1}+ C_{o2}= 0,05.45,95/2.50= 0,022975M$ (b)

(a) và (b) => C_{o1}=0,013525M và C_{o2}=$9,45.10^{-3}$M

III.13:

25ml { Na_2CO_3 0,05M, NaOH 0,05M } + HCl 0,1M { a) p.p: V_{HCl}? b mdc: V_{HCl}? }

a) p.p $NaOH + HCl \rightarrow NaCl + H_2O$ (1)

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$ (2)

(1) và (2)=> $CV_1 = (C_{o1} + C_{o2})V_o$

=> $V_1 = (0,05+0,05).25/0,1 = 25ml$

b) mdc:

$Na_2CO_3 + 2HCl \rightarrow CO_2 + H_2O + 2NaCl$ (3)

(1) và (3)=> $CV_2 = (C_{o1} + 2C_{o2})V_o$

=> $V_2 = (0,05 + 2.0,05).25/0,1 = 37,5ml$

III.14: 4,0g $CH_3COOH \xrightarrow{H_2O}$ 200ml

50ml $\xrightarrow[32,7ml]{NaOH\ 0,5M}$ => $\%CH_3COOH$ trên thị trường?

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

$C_oV_o = CV \Rightarrow C_o = 0,5.32,7/50 = 0,327M$

$\Rightarrow n_{CH3COOH} = 0,327.0,2 = 0,0654mol$

$m_{CH3COOH} = 60.0,0654 = 3,924g$

$\%CH_3COOH = 3,924.100/4 = 98,1\%$

III.15: 1,1526g(A) $\xrightarrow{H_2SO_4đđ}$ $\xrightarrow{H_2O}$ 100ml

5ml $\xrightarrow[\text{Chưng cất}]{\text{NaOHđđ}}$ $NH_3\uparrow$ $\xrightarrow{\text{20ml HCl 0,1M}}$

HCl(thừa) $\xrightarrow[\text{8,35ml}]{\text{NaOH 0,1M}}$

a) pư: $A + H_2SO_4đđ \rightarrow (NH_4)_2SO_4$ (1)

$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3\uparrow + Na_2SO_4 + 2H_2O$ (2)

$NH_3 + HCl \rightarrow NH_4Cl$ (3)

$HCl + NaOH \rightarrow NaCl + H_2O$ (4)

b) %N: (4) => n_{HCl}(thừa)= 0,1.8,35= 0,835mmol

(3) => $n_{NH3} = n_{HCl}$(pư)=0,1.20 – 0,835=1,165mmol

=> m_N=14.1,165.100/5=326,2mg

%N = 0,3262.100/1,1526= 28,3%

$NH_3 + HCl \rightarrow NH_4Cl$ (3)

C_0V_0 $C'V'_1$

$HCl + NaOH \rightarrow NaCl + H_2O$ (4)

$C'V'_2$ CV

$C'V' = C_0V_0 + CV \Rightarrow n_{NH_3} = C_0V_0 = C'V' - CV$

$= 0,1.20 - 0,1.8,35$

$= 1,165$ mmol

CHƯƠNG IV: CHUẨN ĐỘ PHỨC CHẤT

IV.1: 3gmẫu(MgO+ CaO)[tạp chất] $\xrightarrow{HCl}$ 500ml(A)

* 25ml(A) $\xrightarrow{NaOH\ 2N}$ $\xrightarrow[pH=10,\ NET]{5ml\ đệm\ NH_3/NH_4^+}$ $\xrightarrow[28,75ml]{Trilon\ B\ 0,1M}$

* 25ml(A) $\xrightarrow[pH = 12;\ murexit]{25ml\ NaOH\ 2N}$ $\xrightarrow[5,17ml]{Trilon\ B\ 0,1M}$

a) Phương trình pư:

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O \quad (1)$$

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \quad (2)$$

$$HCl + NaOH \rightarrow NaCl + H_2O \quad (3)$$

$$MgCl_2 + H_2Y^{2-} \rightleftarrows MgY^{2-} + 2HCl \quad (4)$$

$$CaCl_2 + H_2Y^{2-} \rightleftarrows CaY^{2-} + 2HCl \quad (5)$$

} Pư ch.độ

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2\downarrow + 2NaCl \quad (6)$$

b) % mỗi chất trong mẫu

$MgCl_2 + H_2Y^{2-} \rightleftarrows MgY^{2-} + 2HCl$ (4)

$C_{01}.V_0 \quad CV_1$

$CaCl_2 + H_2Y^{2-} \rightleftarrows CaY^{2-} + 2HCl$ (5)

$C_{02}.V_0 \quad CV_2$

(4),(5)=> $(C_{01}+C_{02})V_0 = C(V_1+V_2)$ (a)

=> $C_{01}+C_{02}$=0,1.28,75/25= 0,115M

$CaCl_2 + H_2Y^{2-} \rightleftarrows CaY^{2-} + 2HCl$ (5)

$C_{02}.V_0 = C.V_3$ => C_{02}= 0,1.5,17/25= 0,02068M

=> C_{01}= 0,115-0,02068=0,09432M

m_{MgO}= 40.0,09432.0,5= 1,8864g=> %= 62,88%

m_{CaO}= 56.0,02068.0,5=0,57904g=>%= 19,3%

IV.2:

25ml dd A:(Mg^{2+},Ca^{2+}) $\xrightarrow[\text{pH = 12; murexit}]{\text{25ml NaOH 2N}}$ $\xrightarrow[\text{5,17ml}]{\text{Trilon B 0,1M}}$

* 25ml(A) $\xrightarrow[\text{pH=10, NET}]{\text{5ml đệm } NH_3/NH_4^+}$ $\xrightarrow[\text{10,34ml}]{\text{Trilon B 0,1M}}$

=> Nồng độ Ca^{2+} và Mg^{2+}

pH = 12

$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2\downarrow +$ (1)

$Ca^{2+} + H_2Y^{2-} \rightleftarrows CaY^{2-} + 2H^+$ (2)

$C_{02}V_0 = CV_1 \Rightarrow C_{02} = 0,1.5,17/25 = 0,02068M$

pH = 10 => $Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-$

$Mg^{2+} + H_2Y^{2-} \rightleftarrows MgY^{2-} + 2H^+$ (3)

$C_{01}V_0 = CV_2 \Rightarrow C_{01} = 0,1.10,34/25 = 0,04136M$

IV.3:

$50ml \begin{cases} Fe^{3+} \\ Al^{3+} \end{cases}$ Trilon B 0,04M, pH = 2; 29,61ml → 50ml Trilon B, pH = 5 → Fe^{3+} 0,03228M, 19,03ml →

=> Nồng độ mỗi chất

$Fe^{3+} + H_2Y^{2-} \rightleftarrows FeY^- + 2H^+$ (1)

$C_{01}V_0 = CV_1$ => $C_{01} = 0,04.29,61/50 = 0,0237M$

$Al^{3+} + H_2Y^{2-} \rightarrow AlY^- + 2H^+$ (2)

$C_{02}V_0 \quad C'V'_1$

$H_2Y^{2-} + Fe^{3+} \rightleftarrows FeY^- + 2H^+$ (3)

$C'V'_2 \quad CV$

(2) Và (3) =>$C_{02}V_0 + CV = C'V'$

$C_{02} = (0,04.50 - 0,03228.19,03)/50 = 0,0277M$

IV.4:

25ml dd X(Pb^{2+} và Ni^{2+}) $\xrightarrow[pH=10;\ 21,4ml]{Trilon\ B\ 0,02M}$ Nồng độ Ni^{2+}, Pb^{2+}

25ml X $\xrightarrow[12,05ml\ Trilon\ B]{KCN(che\ Ni^{2+})}$

$Pb^{2+} + H_2Y^{2-} \rightleftarrows PbY^{2-} + 2H^+$ (1)

$Ni^{2+} + H_2Y^{2-} \rightleftarrows NiY^{2-} + 2H^+$ (2)

$(C_{01} + C_{02})V_0 = CV_1$

$\Rightarrow C_{01}+C_{02} = 0,02.21,4/25 = 0,01712M$

$Ni^{2+} + 4CN^- \rightleftarrows [Ni(CN)_4]^{2-}$ (3)

(1) $\Rightarrow C_{01} = 0,02.12,05/25 = 0,00964M$

$\Rightarrow C_{02} = 0,01712 - 0,00964 = 0,00748M$

IV.5: $0,65g(Al\ldots) \xrightarrow{H_2O} 250ml(A)$

$20ml(A) \xrightarrow{MgY^{2-}(dư)} \xrightarrow[pH=9;\ 7,6ml]{Trilon\ B\ 0,1M} => \%Al$

$Al^{3+} + MgY^{2-} \rightarrow AlY^{-} + Mg^{2+}$ (1)

$C_0.V_0 \qquad\qquad\qquad\qquad C_0.V_0$

$Mg^{2+} + H_2Y^{2-} \rightleftarrows MgY^{2-} + 2H^{+}$ (2)

$C_0.V_0 \quad CV$

(1) Và (2) => $C_0V_0 = CV$

=> $C_0 = 0,1.7,6/20 = 0,038M$

=> $n_{Al} = 0,038.0,25 = 0,0095mol$

$m_{Al} = 27.0,0095 = 0,2565g$

$\%Al = 0,2565.100/0,65 = 39,5\%$

Chuẩn độ oxy hóa khử

V.1: [KIO_3+KI(dư)] $\xrightarrow[100ml]{HCl}$ I_2 $\xrightarrow[10,5ml]{Na_2S_2O_3\ 0,01M}$

=> C_{HCl}= ?

$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$ (1)

x x/2

$I_2 + 2S_2O_3^{2-} \rightleftarrows 2I^- + S_4O_6^{2-}$ (2)

x/2 x

(1) và (2)=> n_{HCl}= x =0,01.0,0105=0,000105mol

=> C_{HCl} = 0,000105/0,1= 0,00105M

V.2: Tính E_{dd} khi đã thêm:

a)90ml $KMnO_4$ 0,01M+ 100mlFe^{2+}0,05M(pH=0)

$C_N(MnO_4^-)=5.0,01=0,05N$

$C_N(Fe^{2+}) =1.0,05=0,05N$

$5Fe^{2+} + MnO_4^- + 8H^+ \rightleftarrows 5Fe^{3+} + Mn^{2+} + 4H_2O$

$F =1 \Rightarrow C_0V_0=CV \Rightarrow V_{td} = 100.0,05/0,05=100ml$

$* V_1=90ml < V_{td}$; $F_1=CV/C_0V_0= 0,05.90/0,05.100$

$= 0,9$

$$E_1 = E^0_{Fe3+/Fe2+} + \frac{0,059}{1} \lg \frac{F}{1-F}$$

$$E_1 = 0,77 + \frac{0,059}{1} \lg \frac{0,9}{1-0,9} = 0,826V$$

b) 110ml MnO_4^- + 100ml Fe^{2+}

$V_2 = 110ml > V_{tđ}$ =>F= 110.0,05/100.0,05=1,1

$$E_2 = E^0_{MnO_4^-/Mn^{2+}} + \frac{0,059}{5}\lg(F-1)$$

$$E_2 = 1,51 + \frac{0,059}{5}\lg(1,1-1) = 1,498V$$

V.3:Chuẩn độ 25ml Fe^{2+} 0,01M bằng Ce^{4+} 0,02M

Tính thế của dd khi thêm:

a) 12,5ml Ce^{4+}

$Fe^{2+} + Ce^{4+} \rightleftarrows Fe^{3+} + Ce^{3+}$

$C_N(Fe^{2+}) = C_M$; $C_N(Ce^{4+}) = C_M$

F=1:$V_{tđ}$= 0,01.25/0,02= 12,5ml

$E_{tđ}$=(0,77 + 1,44)/2 = 1,105V

b) 12,48ml Ce^{4+}

$V_1 < V_{td} \Rightarrow \quad F_1 = 12{,}48.0{,}02/0{,}01.25 = 0{,}9984$

$$E_1 = E^0_{Fe^{3+}/Fe^{2+}} + \frac{0{,}059}{1} \lg \frac{F}{1-F}$$

$$E_1 = 0{,}77 + \frac{0{,}059}{1} \lg \frac{0{,}9984}{1 - 0{,}9984} = 0{,}935V$$

c) 12,52ml Ce^{4+}

$V_2 > V_{td} \Rightarrow \quad F_2 = 12{,}52.0{,}02/0{,}01.25 = 1{,}0016$

$$E_2 = E^0_{Ce^{4+}/Ce^{3+}} + \frac{0{,}059}{5} \lg(F - 1)$$

$$E_2 = 1{,}44 + \frac{0{,}059}{1} \lg(1{,}0016 - 1) = 1{,}275V$$

V.4: Tính thế dd khi chuẩn độ thiếu và thừa 0,2% so với điểm tương đương

a) Chuẩn độ Mo^{3+} bằng MnO_4^- (pH=0)

$$5Mo^{3+} + 3MnO_4^- + 4H^+ \rightleftarrows 5MoO_2^{2+} + 3Mn^{2+} + 2H_2O$$

* -0,2% => $(F-1).10^2 = -0,2$ => $F = 0,998$

$$E_1 = E^0_{MoO_2^{2+}/Mo^{3+}} + \frac{0,059}{3} \lg \frac{F}{1-F}$$

$$E_1 = 0,16 + \frac{0,059}{3} \lg \frac{0,998}{1-0,998} = 0,213V$$

* +0,2% => $(F-1).10^2 = 0,2$ => $F = 1,002$

$$E_2 = E^0_{MnO_4^-/Mn^{2+}} + \frac{0,059}{5} \lg(F-1)$$

$$E_2 = 1,51 + \frac{0,059}{5} \lg(1,002-1) = 1,478V$$

b) Chuẩn độ Ti^{3+} bằng MnO_4^-(pH=0)

$$5Ti^{3+} + MnO_4^- + 2H^+ \rightleftarrows 5TiO^{2+} + Mn^{2+} + H_2O$$

* -0,2% => $(F-1).10^2 = -0,2 \Rightarrow F = 0,998$

$$E_1 = E^0_{TiO^{2+}/Ti^{3+}} + \frac{0,059}{1}\lg\frac{F}{1-F}$$

$$E_1 = 0,4 + \frac{0,059}{1}\lg\frac{0,998}{1-0,998} = 0,559V$$

* +0,2% => $(F-1).10^2 = 0,2 \Rightarrow F = 1,002$

$$E_2 = E^0_{MnO_4^-/Mn^{2+}} + \frac{0,059}{5}\lg(F-1)$$

$$E_2 = 1,51 + \frac{0,059}{5}\lg(1,002-1) = 1,478V$$

V.5: $Pb^{2+} \rightarrow PbCrO_4\downarrow \xrightarrow[KI(dư)]{H^+} I_2 \xrightarrow[23,5ml]{Na_2S_2O_3\ 0,1M}$

=> mg Pb?

$Pb^{2+} + CrO_4^{2-} \rightarrow PbCrO_4\downarrow$ (1)

x x

$2PbCrO_4 + 2H^+ \rightarrow 2Pb^{2+} + Cr_2O_7^{2-} + H_2O$ (2)

x x/2

$6I^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$ (3)

x/2 3x/2

$I_2 + 2S_2O_3^{2-} \rightleftarrows 2I^- + S_4O_6^{2-}$ (4)

3x/2 $3x = 0,1.23,5 = 2,35mmol$

(1),(2),(3),(4)=> $n_{Pb} = x = 2,35/3 = 0,78mmol$

$m_{Pb} = 207.0,78 = 161,46mg$

V.6: 1,048g(Ca..) → 250ml(A) $\xrightarrow{C_2O_4^{2-}}$ ↓ $\xrightarrow[0,25N,10,25ml]{H^+,MnO_4^-}$

a) Phương trình pư:

$Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4\downarrow$ (1)

x x

$CaC_2O_4 + 2H^+ \rightarrow Ca^{2+} + H_2C_2O_4$ (2)

x x

$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightleftarrows 10CO_2 + 2Mn^{2+} + 8H_2O$ (3)

$C_0V_0 = CV = 0,25.10,25 = 2,5625 mđlg$

(1),(2),(3) => $n_{Ca} = 2,5625/2 = 1,28125 mmol$

$m_{Ca} = 40.1,28125 = 51,25mg = 0,05125g$

%Ca = 0,05125.100/1,048 = 4,89%

V.7: 0,935g(Cr_2O_3) $\xrightarrow[50ml\ Fe^{2+}\ 0,08M]{H^+}$ $\xrightarrow[14,85ml]{MnO_4^-\ 0,004M}$

a) Phương trình pư $Cr_2O_3 \xrightarrow{[O]} 2CrO_4^{2-}$ (1)

x 2x

$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$ (2)

2x x

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$ (3)

$N'V_1$ N_0V_0

$5Fe^{2+} + MnO_4^- + 8H^+ \rightleftarrows 5Fe^{3+} + Mn^{2+} + 4H_2O$ (4)

$N'V_2$ NV :(3),(4)=> $N_0V_0 = (N'V' - NV)$

$N_0V_0 = 0,08.50 - 0,004.5.14,85 = 3,703 mđlg$

(1),(2)=> $m_{Cr} = 2.52.3,703/6 = 64,18mg$

%Cr = 0,06418.100/0,935= 6,86%

CHƯƠNG VI: Chuẩn độ kết tủa

VI.1: a) Tính pAgkhi thêm:

*19,8ml dd $AgNO_3$ 0,1N vào 20ml dd NaBr 0,1N

$$NaBr + AgNO_3 \rightleftarrows AgBr + NaNO_3$$

$C_0V_0 = CV \Rightarrow V_{tđ} = 0,1.20/0,1 = 20ml$

$V_1 = 19,8ml < V_{tđ}$

$$pBr = -\lg\frac{CoVo - CV}{Vo + V} = -\lg\frac{0,1.20 - 0,1.19,8}{20 + 19,8} = 3,3$$

$\Rightarrow pAg_1 = pT_{AgBr} - pBr = -\lg 10^{-12} - 3,3 = 8,7$

* $V_2 = 20ml = V_{tđ} \Rightarrow pAg_{tđ} = pBr_{tđ} = ½\ pT = 6$

* $V_3 = 20{,}2ml > V_{td}$

$$pAg = -\lg\frac{CV - CoVo}{Vo + V} = -\lg\frac{0{,}1.20{,}2 - 0{,}1.20}{20 + 20{,}2} = 3{,}3$$

b) Bước nhảy : 8,7→ 3,3

c) * S%= -0,2% => F<1: dd thừa NaBr

$$S\% = -\frac{[Br^-](Co + C)}{Co.C}.10^2 = -0{,}2$$

$$[Br^-] = \frac{0{,}2.Co.C}{(Co + C).10^2} = \frac{0{,}2.0{,}1.0{,}1}{(0{,}1 + 0{,}1).10^2} = 10^{-4}M$$

=> $[Ag^+] = 10^{-12}/10^{-4} = 10^{-8}M$

=> pAg = 8

* S%= + 0,2% => F>1: dd thừa Ag^+

$$S\% = + \frac{[Ag^+](Co+C)}{Co.C}.10^2 = +0,2$$

$$[Ag^+] = \frac{0,2.Co.C}{(Co+ C).10^2} = \frac{0,2.0,1.0,1}{(0,1+ 0,1).10^2} = 10^{-4} M$$

=> pAg = 4

VI.2: a) C_{K2CrO4} = ? Để kết tủa Ag_2CrO_4 ở đtđ

$$Br^- + Ag^+ \rightleftarrows AgBr\downarrow$$

$$CrO_4^{2-} + 2Ag^+ \rightarrow Ag_2CrO_4\downarrow$$

Đtđ: $$[Ag^+] = \sqrt{T_{AgBr}} = \sqrt{10^{-12,28}} = 10^{-6,14}\ M$$

$$T_{Ag_2CrO_4} = [Ag^+]^2 [CrO_4^{2-}]$$

$$\Rightarrow [CrO_4^{2-}] = \frac{T_{Ag_2CrO_4}}{[Ag^+]^2}$$

$$[CrO_4^{2-}] = \frac{10^{-11,95}}{[10^{-6,14}]^2} = 10^{0,33} = 2,13M$$

b) Chuẩn độ NaBr 0,01M bằng $AgNO_3$ 0,01M với $C_{K2CrO4} = 2.10^{-3}M \Rightarrow pAg = ?$

$$T_{Ag_2CrO_4} = [Ag^+]^2 [CrO_4^{2-}]$$

$$[Ag^+] = \sqrt{\frac{T_{Ag_2CrO_4}}{[CrO_4^{2-}]}}$$

$$[Ag^+] = \sqrt{\frac{10^{-11,95}}{10^{-3}}} = 10^{-4,475} M \Rightarrow pAg = 4,475$$

VI.3: 0,74g(Cl^-…) $\xrightarrow{H_2O}$ 250ml dd(A)

50ml(A) $\xrightarrow{40ml\ Ag^+(0,1M)}$ $\xrightarrow[19,35ml]{SCN^-(0,058M)}$ =>%Cl

$Cl^- + Ag^+ \rightarrow AgCl\downarrow$ (1)

C_0V_0 $C'V_1$

$Ag^+ + SCN^- \rightleftarrows AgSCN$ (2)

$C'V_2$ CV

(1),(2) => $C_0=(C'V'- CV)/V_0$

$C_0 = (0,1.40-0,058.19,35)/50 = 0,0575M$

$m_{Cl} = 35,5.0,0575.0,25=0,51g$

%Cl = 0,51.100/0,74 = 69,03%

VI.4: 1,7450g(Ag…) → 200ml dd(A)

10ml(A) $\xrightarrow[11,75ml]{SCN^-(0,0467N)}$ =>%Ag ?

$Ag^+ + SCN^- \rightleftarrows AgSCN\downarrow$

$C_0V_0 = CV \Rightarrow C_0 = 0,0467.11,75/10 = 0,055M$

$m_{Ag} = 108.0,055.0,2 = 1,185g$

%Ag = 1,185.100/1,745= 67,92%

VI.5: Chuẩn độ 25ml Ag^+ (0,1M) = Cl^-(0,1M)

a) $V_{Cl^-} = 24ml$ $Ag^+ + Cl^- \rightleftarrows AgCl\downarrow$

$V_{tđ} = 0,1.25/0,1 = 25ml$: $V_1 = 24ml < V_{tđ}$

$$pAg = -\lg\frac{CoVo - CV}{Vo + V} = -\lg\frac{0,1.25 - 0,1.24}{25 + 24} = 2,69$$

$\Rightarrow$ pCl = pT_{AgCl} - pAg = $-\lg10^{-10} - 2,69 = 7,31$

b) $V_2 = 25ml = V_{td}$ => pAg=pCl= 5

c) $V_3 = 26ml > V_{td}$:dd thừa Cl^-

$$pCl = -\lg \frac{CV - CoVo}{Vo + V} = -\lg \frac{0,1.26 - 0,1.25}{25 + 26} = 2,7$$

=> pAg = 10-2,7 = 7,3

VI.6: Tính bước nhảy:

a) Chuẩn độ Cl^-(0,1M)= Ag^+(0,1M):%S= ± 0,1%

$$X^- + Ag^+ \rightleftarrows AgCl\downarrow$$

* S= -0,1% :dd thừa Cl^-

$$\%S = - \frac{[Cl^-](Co+C)}{Co.C}10^2 = -0,1$$

$$[Cl^-] = \frac{0,1.0,1.0,1}{(0,1+0,1).10^2} = 0,5.10^{-4}\,M \Rightarrow pCl = 4,3$$

* S = + 0,1% => Dd thừa Ag^+

$$\%S = + \frac{[Ag^+](Co+C)}{Co.C}10^2 = +0,1$$

$$[Ag^+] = \frac{0,1.0,1.0,1}{(0,1+0,1).10^2} = 0,5.10^{-4}\,M$$

=> pAg= 4,3

pCl = 10 - 4,3 = 5,7

=> Bước nhảy: 4,3→ 5,7

b) Chuẩn độ Br^- (0,1M) = Ag^+ (0,1M)

* S = -0,1% => Dd thừa Br^-

$$\%S = - \frac{[Br^-](Co+C)}{Co.C}10^2 = -0,1$$

$$[Br^-] = \frac{0,1.0,1.0,1}{(0,1+0,1).10^2} = 0,5.10^{-4} M \Rightarrow pBr = 4,3$$

* S = + 0,1% => Dd thừa Ag^+

$$\%S = + \frac{[Ag^+](Co+C)}{Co.C}10^2 = +0,1$$

$$[Ag^+] = \frac{0,1.0,1.0,1}{(0,1+0,1).10^2} = 0,5.10^{-4} M \Rightarrow pAg = 4,3$$

$pBr = -\lg 10^{-12} - 4,3 = 7,7$ =>Bước nhảy: 4,3→7,7

c) Chuẩn độ I^-(0,1M) = Ag^+(0,1M)

* S = - 0,1% => Dd thừa I^-

$$\%S = -\frac{[I^-](Co+C)}{Co.C}10^2 = -0,1$$

$$[I^-] = \frac{0,1.0,1.0,1}{(0,1+0,1).10^2} = 0,5.10^{-4}\,M \Rightarrow pI = 4,3$$

* S = + 0,1% => Dd thừa Ag^+

$$\%S = +\frac{[Ag^+](Co+C)}{Co.C}10^2 = +0,1$$

$$[Ag^+] = \frac{0,1.0,1.0,1}{(0,1+0,1).10^2} = 0,5.10^{-4}\,M \Rightarrow pAg = 4,3$$

$pI = -\lg 10^{-16} - 4,3 = 11,7$ =>Bước nhảy: 4,3→11,7

VI.7: 25ml Ag^+ $\xrightarrow{Cl^-(dư)}$ 0,4306g↓

50ml Ag^+ $\xrightarrow{SCN^-}$ 32,58ml

} C_{Ag+} và C_{SCN-}?

$Ag^+ + Cl^- \rightarrow AgCl\downarrow$ (1)

$Ag^+ + SCN^- \rightleftarrows AgSCN\downarrow$ (2)

(1) => $n_{Ag+} = 0,4306/143,5 = 3.10^{-3}$mol

=> $C_{Ag+} = 3.10^{-3}/0,025 = 0,12M$

(2) => $C_{SCN-} = 0,12.50/32,58 = 0,184M$

VI.8: 0,3074g $\begin{cases} NaCl(80\%) \\ NaBr \end{cases} \xrightarrow[V_{Ag+} = ?]{Ag^+(0,1M)}$

$NaCl + AgNO_3 \rightleftarrows AgCl\downarrow$ (1)

$NaBr + AgNO_3 \rightleftarrows AgBr\downarrow$ (2)

m_{NaCl}=0,3074.80/100 = 0,24592g

m_{NaBr} = 0,3074- 0,24592 =0,06148g

(1) => $V_1(Ag^+)$ = 0,24592/58,5/0,1=0,042 lit

(2) => $V_2(Ag^+)$ = 0,06148/103/0,1=0,006 lit

=> V_{Ag+} = 42 + 6 = 48ml

VI.9:

$1{,}988g \begin{cases} KBr \\ KI \end{cases} \rightarrow 500ml(A) : 25ml(A) \xrightarrow[11{,}52ml]{Ag^+(0{,}0568M)}$

$50ml(A) \xrightarrow{[O]} I_2 \xrightarrow{\text{tách } I_2} \text{Dd còn lại} \xrightarrow[7{,}1ml]{Ag^+(0{,}0568M)}$

$KBr + AgNO_3 \rightleftarrows AgBr\downarrow + KNO_3$ (1)

$KI + AgNO_3 \rightleftarrows AgI\downarrow + KNO_3$ (2)

(1),(2) => $C_{01} + C_{02} = 0{,}0568.11{,}52/25 = 0{,}02617M$

(2) => $C_{01} = 0{,}0568.7{,}1/50 = 0{,}008M$

=> $C_{02} = 0{,}02617 - 0{,}008 = 0{,}018M$

%KBr = 119.0,008.0,5.100/1,988= 23,94%

%KI = 166.0,018.0,5.100/1,988= 75,15%