Part I

Question No	Answer	Question No	Answer	Question No	Answer	Question No	Answer	Question No	Answer
01	3	11.	1	21.	1	31.	5	41.	4
02	3	12	1	22.	5	32.	5	42.	1
03	2	13.	5	23.	2	33.	4	43.	2
04	5	14.	4	24.	1	34.	5	44.	3
05	2	15	5	25.	4	35.	5	45.	4
06	3	16.	3	26.	3	36.	5	46.	4
07	4	17.	3	27.	5	37.	3	47.	4
08	2	18.	2	28.	4	38.	5	48.	2
09	5	19.	2	29.	2	39.	5	49.	3
10	1	20.	2	30.	3	40.	3	50.	4

I $\Rightarrow$ 50 x 01 = 50 marks.

Final marks:

Part I - 50%

Part II - Structure 4 x 100 = 400

Essay 4 x 150 = 600

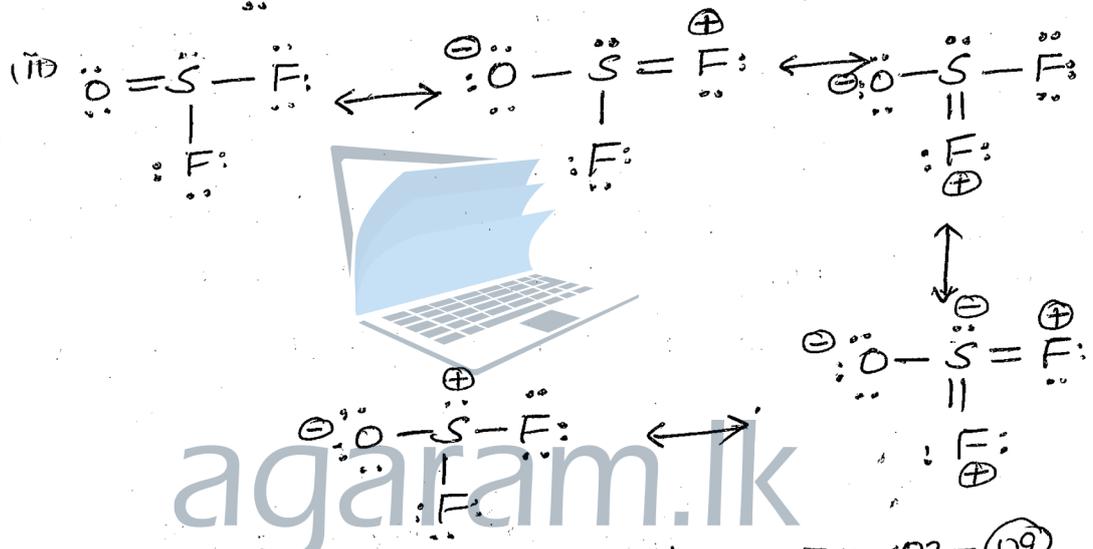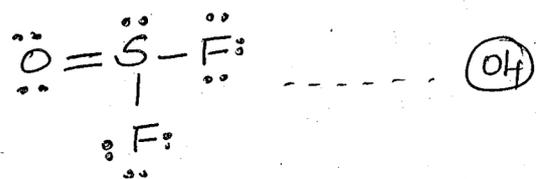$$20 \overline{\smash{\big)}\ 1000}$$

50%

Q② (a) (i) Ag_2CO_3 (ii) $(COO)_2Fe$ (iii) $AgNO_3$ (iv) $CuSO_4 \cdot 5H_2O$

(v) $MnCl_2$ (vi) $ZnCO_3$

$6 \times 05 = $ ③⓪

(b) (I) (i) J = O / oxygen , K = S / sulphur , L = F / fluorine

$3 \times 03 = $ ⓞ⑨

⓪④

(ii)

any three $3 \times 03 = $ ⓞ⑨

(iii) Electron pair geometry   <u>tetrahedral</u> } 2×03
Shape   <u>trigonal pyramidal</u> } $= $ ⓞ⑥

(II)

	N atom	O attached to N and Cl
Electron pair geometry	trigonal planar	tetrahedral
Shape	trigonal planar	angular / v-shaped
Hybridization	sp^2	sp^3

$6 \times 02 = $ ①②

(c) (i) $Be < Na < O < S$ (iv) $CH_3COO^- < OH^- < NH_2^- < CH_3^-$

(ii) $H_2CO < COCl_2 < CO < CO_2$

(iii) $NO_2^- < NO_3^- < NO_2 < NO_2^+$ (v) $CH_3COOH < CH_3CH_2OH < CH_3CHO$

$< CH_3OCH_3$

$5 \times 06 = $ ③⓪

Q② :(a) ① Let x be the mass of Mg in the alloy.

100 55

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$
$$\frac{x}{24} \qquad\qquad\qquad\qquad \frac{x}{24}$$
$$Ca + 2HCl \longrightarrow CaCl_2 + H_2$$
$$\frac{(1-x)}{40} \qquad\qquad\qquad\qquad \frac{(1-x)}{40}$$
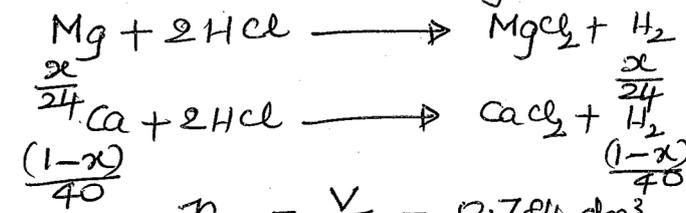
$$n_{H_2} = \frac{V}{V_m} = \frac{0.784 \, dm^3}{22.4 \, dm^3 mol^{-1}} = 0.035 \, mol \quad --- \text{⑤}$$

16

$$\frac{x}{24} + \frac{1-x}{40} = 0.035 \quad --- \text{⑤}$$

$$\Rightarrow x = 0.4 \, g \quad ----- \text{⑫}$$

mass % of Mg = 40% $\qquad 2 \times 02 = \text{⑭}$
mass % of Ca = 60%

(II) (i) $2Fe + 6H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 3SO_2 + 6H_2O$ $\Big\}$ 2×03
$\qquad Zn + 2H_2SO_4 \longrightarrow ZnSO_4 + SO_2 + 2H_2O$ $= \text{⑯}$

(ii) $H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2H^+ + 2e$ $\Big\}$ $2x$
$\qquad (\underline{or} \; SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e)$ $\Big\}$ $2 \times 03 = \text{⑯}$
$\qquad MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$

$$\Rightarrow 5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 5SO_4^{2-} + 3H_2O + 2Mn^{2+}$$
$$\qquad\qquad\qquad\qquad\qquad ------ \text{⑫}$$
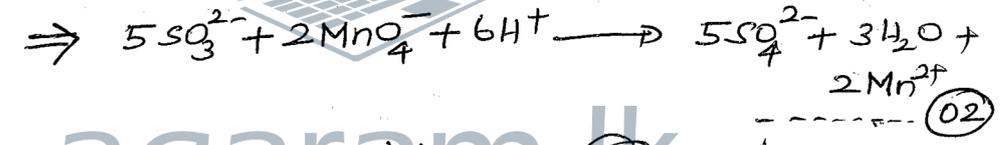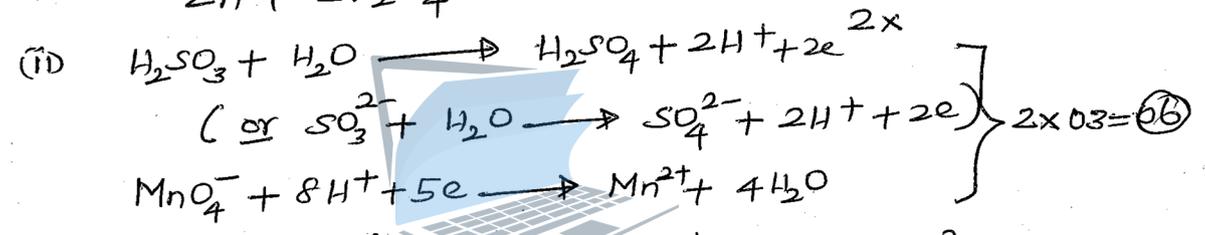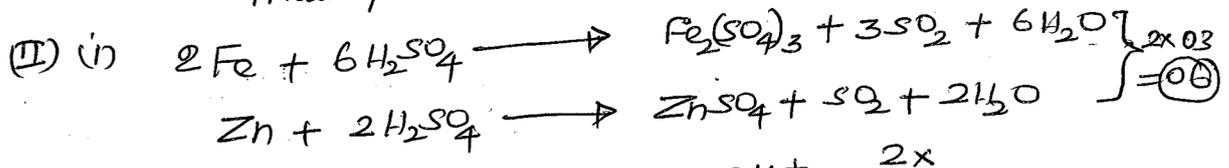
(iii) colourless $\longrightarrow$ violet --- ⑫
$\qquad$ self indicator ---- ⑫

(iv) $n_{MnO_4^-} = 0.15 \, mol \, dm^{-3} \times 40 \times 10^{-3} \, dm^3$
$$= 6 \times 10^{-3} \, mol \quad ----- \text{⑫}$$

$n_{H_2SO_3} : n_{KMnO_4} = 5 : 2 \quad --- \text{⑫}$

$\therefore n_{H_2SO_3}$ in $25 \, cm^3$ of the solution
$$= \frac{6 \times 10^{-3}}{2} \times 5 \, mol$$
$$= 15 \times 10^{-3} \, mol \quad \text{⑫}$$

$n_{H_2SO_3}$ in $200 \, cm^3$ of the sol^n = $120 \times 10^{-3} \, mol$
$$= 0.12 \, mol \quad ---- \text{⑫}$$

If the no. of moles of Fe is x and the no. of moles of Zn is y, then

$$\frac{3}{2}x + y = 0.12$$
$$3x + 2y = 0.24 \quad ------ ①$$

$$56x + 64y = 2$$

ie: $7x + 8y = 0.25$ —————②

①, ② ⟹ $x = 0.142$ mol

$y = ?$

∗ Award marks if the eqⁿs are correct

Mass % Zn in the galvanized iron =

(b) (i) $A = Na_2S_2O_3$, $B = BaCl_2$, $C = Zn(NO_3)_2$

$D = MnCl_2$, $E = AgNO_3$ —— $5 × 05 = 25$

(ii) $Na_2S_2O_3 + H_2SO_4 \longrightarrow Na_2SO_4 + S\downarrow + SO_2 + H_2O$

$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow + 2HCl$

$MnCl_2 + 2NaOH \longrightarrow Mn(OH)_2 \downarrow + 2NaCl$

$2Mn(OH)_2 + O_2 \longrightarrow 2MnO_2 + 2H_2O$

$4 × 05 = 20$

Q 3 (a)(i) Initial rate: (Average) rate for a small change in time from the starting of the reaction

100 25

Average rate: The average of the individual rates measured over a time interval

06

Half life: The time taken for the concentration of a reactant to become half its initial value

$3 × 05 = 06$

(ii)(i) Expt(1) : $2.6 × 10^{-5}$ mol dm^{-3} s^{-1}

(2) : $10.4 × 10^{-5}$ mol dm^{-3} s^{-1}

(3) : $5.1 × 10^{-5}$ mol dm^{-3} s^{-1}

$3 × 02 = 06$

(ii) Rate $= k [NO]^x [H_2]^y$ —————— 02

(iii) $2.6 × 10^{-5}$ mol dm^{-3} s^{-1} $= k (6.4×10^{-3}$ mol dm$^{-3})^x (2.2×10^{-3}$ mol dm$^{-3})^y$

$10.4 × 10^{-5}$ " $= k (1.28×10^{-3}$ ")$^x (2.2×10^{-3}$ ")^y

$5.1 × 10^{-5}$ " $= k (6.4×10^{-3}$ ")$^x (4.4×10^{-3}$ ")^y

$3 × 01 = 03$

eqns. ①, ②, ③ ⟹ $x = 2$, $y = 1$ —— $2 × 01 = 02$

(iv) From (1), $k = \dfrac{2.6×10^{-5} \text{mol dm}^{-3}\text{s}^{-1}}{(6.4×10^{-3}\text{mol dm}^{-3})^2 (2.2×10^{-3}\text{mol dm}^{-3})}$ ————

$= \quad$ mol^{-2} dm^{6} s^{-1} — 02

4

(v) slowest step / $N_2O_2 + H_2 \longrightarrow N_2 + H_2O$ ④

(01)

(VI) $Rate = k_2[N_2O_2][H_2]$ ---- ⓐ

(VII) For the 1st step,

$$k_1 = \frac{[N_2O_2]}{[NO]^2} \Rightarrow [N_2O_2] = k_1[NO]^2$$

Substituting in the rate expression,

$$Rate = k_2 \cdot k_1[NO]^2[H_2] - -$$
$$= k[NO]^2[H_2] - - ⟩ ②$$

(b) (I) $Rate = k[A]^0$ or $Rate = k$ ---- ⓞ⑤

15

(II) $\dfrac{[A]_0 - [A]_t}{t} = k$ ---- ⓞ⑤

(III) $[A]_0 - [A]_t = kt$

when $t = t_{\frac{1}{2}}$, $[A]_t = \dfrac{[A]_0}{2}$ ⟩ ⓞ⑤

$\therefore [A]_0 - \dfrac{[A]_0}{2} = kt_{\frac{1}{2}} \Rightarrow t_{\frac{1}{2}} = \dfrac{[A]_0}{2k}$

(c) (I) Addition of $5 cm^3$ HCl represents half neutrali-

60
-zed point where pH = 9

$\therefore pOH = 5$ ---- ②

At this point, the resulting sol^n is a

10
buffer. --- ②

$\therefore pOH = pk_b + \log_{10}\dfrac{[salt]}{[Base]}$

Since [salt] = [Base], $pOH = pk_b$ ---- ②

$\therefore k_b = 1 \times 10^{-5} \, mol\,dm^{-3}$ ---- ④

(II) Before the addition of HCl,

initial pH of $NH_4OH = 11$

$pOH = 3$

$\therefore [OH^-] = 10^{-3} \, mol\,dm^{-3}$ -- ②

06
But $[OH^-] = \sqrt{ck_b}$ ---- ②

$\Rightarrow c = 0.1 \, mol\,dm^{-3}$ ---- ②

or (III) $\therefore$ Concentration of HCl = $0.1 \, mol\,dm^{-3}$ ---- ②

5

(iv) $[NH_4Cl] = \dfrac{0.1\ mol\,dm^{-3} \times 10\ cm^3}{20\ cm^3} = 0.05\ mol\,dm^{-3}$ ⑤ ⑮

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

pH at the equivalence point is determined by the salt (NH_4Cl) formed which undergoes hydrolysis ⑮

$$NH_{4\,(aq)}^+ + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H_{(aq)}^+$$
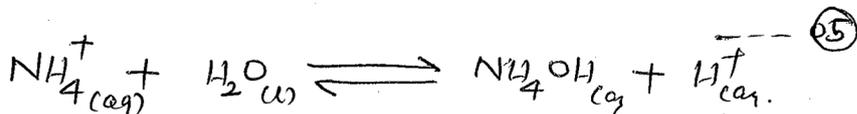
Initial : 0.05 $mol\,dm^{-3}$

at eq^m : $(0.05-x)$ x x $mol\,dm^{-3}$

$$K_{a(NH_4^+)} = \dfrac{[NH_4OH_{(aq)}]\,[H_{(aq)}^+]}{[NH_{4(aq)}^+]} \quad\text{---}\quad ⑤$$

$$= \dfrac{x^2}{0.05-x}$$

But $K_{a(NH_4^+)} = \dfrac{K_w}{k_{b(NH_4OH)}} = \dfrac{1\times10^{-14}mol^2dm^{-6}}{1\times10^{-5}mol\,dm^{-3}}$

$$= 1\times10^{-9}mol\,dm^{-3} \quad ⑮$$

$$\Rightarrow x = \sqrt{0.05 \times 1\times10^{-9}} = 5\sqrt{2}\times10^{-6} \quad\text{---}\quad ⑮$$

$$[H_{(aq)}^+] = 7.07\times10^{-6}\ mol\,dm^{-6}$$

$$\therefore pH = 6 - \log_{10}7.07 = \quad\text{---}\quad 05$$
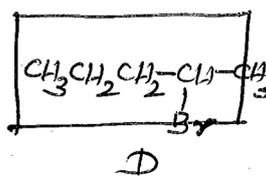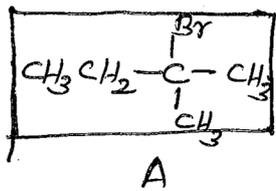
(V) For a titration to be accurate, stoichiometrically equivalent amount of <u>titrant</u> (in a burette) must be added to a solution containing the <u>analyte</u> (in a titration flask). ✱

     The volume of the titrant required to reach this stoichiometric mixture is the <u>equivalence pt</u>

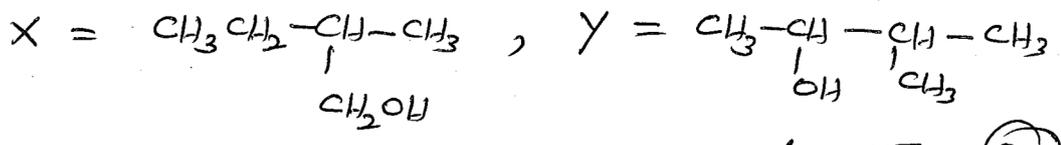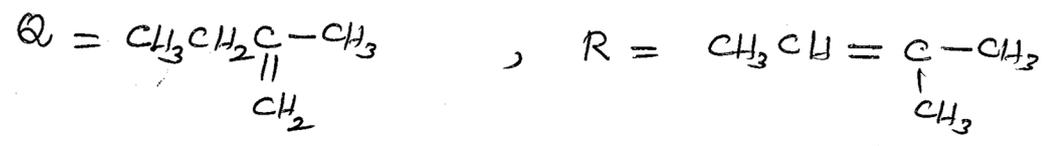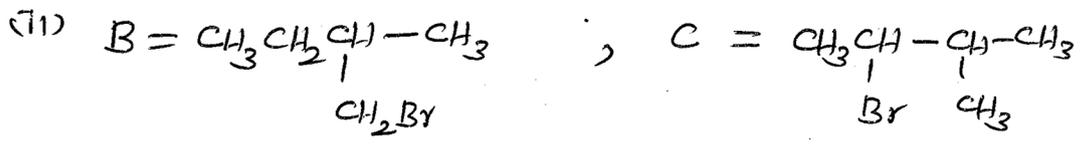   But the <u>end point</u> is that at which we stop adding the <u>titrant</u> which is <u>indicated</u> by the <u>colour change</u> of an indicator.

     End point is a little excess compared to the equivalence pt, the difference being called the titration error ($\pm 0.05\ cm^3$) ---
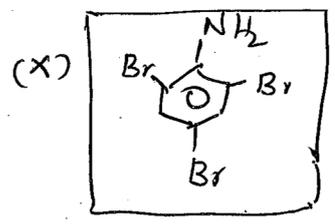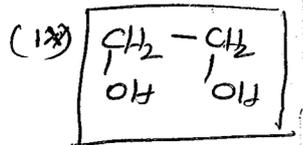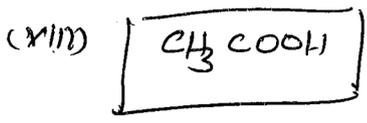
35

12

④ (a)
(i)

100   40

A: $CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_3$

D: $CH_3CH_2CH_2-\underset{\underset{Br}{|}}{CH}-CH_3$

P: $CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$

S: $CH_3CH_2CH=CH-CH_3$

$4 \times 03 = \boxed{12}$

(ii) $B = CH_3CH_2\underset{\underset{CH_2Br}{|}}{CH}-CH_3$, $C = CH_3\underset{\underset{Br}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

$Q = CH_3CH_2\underset{\underset{CH_2}{||}}{C}-CH_3$, $R = CH_3CH=\underset{\underset{CH_3}{|}}{C}-CH_3$

$X = CH_3CH_2-\underset{\underset{CH_2OH}{|}}{CH}-CH_3$, $Y = CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$
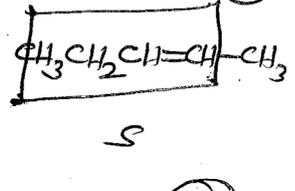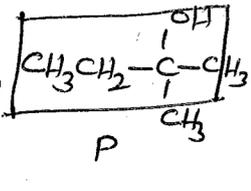
$6 \times 03 = \cancel{20} \boxed{18}$

(iii) Any suitable test —————— ⑤

(iv) Nucleophilic substitution ——— ⑤

$A \xrightarrow{NaOH} P$ ————— ⑤

(b) (i) $CH_3C \equiv C-CH_2CH_3$ (ii) benzene–$CH=CH-CH_3$

40

(iii) benzene–$\underset{\underset{CH_2}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$, CH_3OH

(iv) $CH_3\underset{\underset{OH}{|}}{CH}-CH_2-\underset{\underset{CH_2NH_2}{|}}{CH}-CH_3$

(v) $C_2H_5CONH-CH_3$

(vi) benzene–COOH, benzene–$CH_2\underset{\underset{OH}{|}}{CH}-CH_3$

(vii) benzene ring with COONa, NH_2, CH_2OH

(viii) CH_3COOH

(ix) $\underset{\underset{OH}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH_2}$

(x) benzene ring with NH_2, Br, Br, Br

$10 \times 04 = \boxed{40}$

7

(c)

15.
$$CH_3 \overset{CH_3}{\underset{CH_3}{C}}=N-NH-\!\!\!\bigcirc\!\!-NO_2 \qquad NO_2 \qquad ---\quad \text{(05)}$$

$$CH_3 \overset{CH_3}{\underset{CH_3}{C}}=O \quad \overset{..}{H_2N}-\overset{..}{NH}\!\!\!\bigcirc \qquad \longrightarrow \qquad CH_3-\overset{OH}{\underset{CH_3}{C}}-\overset{H}{N}-NH-\!\!\!\bigcirc\!\!-NO_2 \qquad NO_2$$

(02) (02) (08)

$$\downarrow -H_2O$$

$$CH_3-\overset{C}{\underset{CH_3}{C}}=N-NH-\!\!\!\bigcirc\!\!-NO_2 \qquad NO_2$$

(03)

Essay

(5) 60. (a) (i) $\quad 3A_{(g)} \rightleftharpoons 2B_{(g)}$
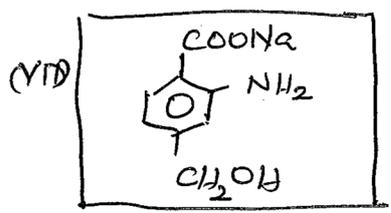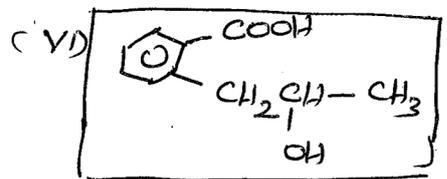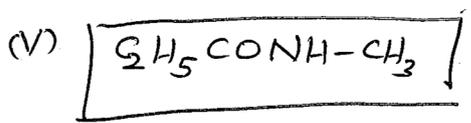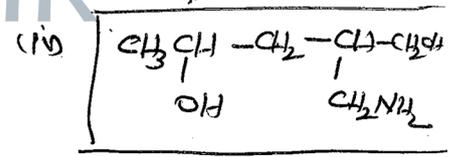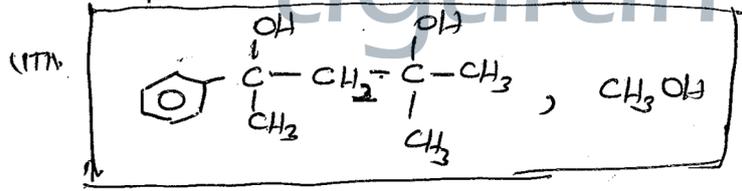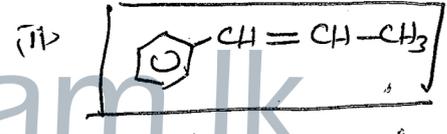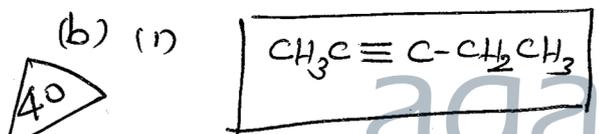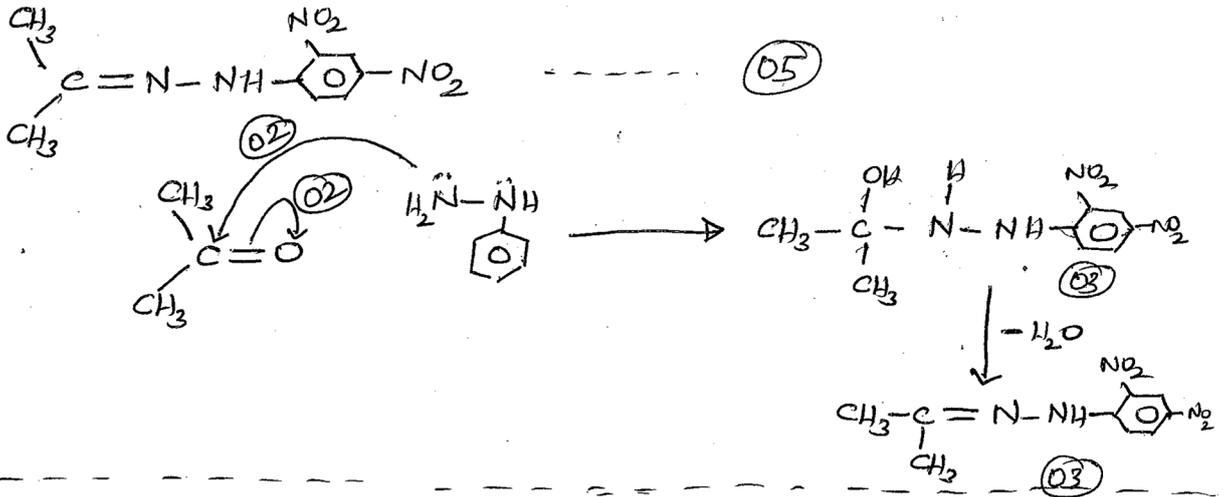
Initially: a mol

At eq^m: $a-0.6a \qquad 0.4a$
$\qquad = 0.4a$

(05)

$X_A = X_B = \frac{1}{2}$ --- (05)

$P_A = \frac{1}{2}P$, $P_B = \frac{1}{2}P$

$K_p = \dfrac{P_B^2}{P_A^3}$ --- (05)

$\qquad = \dfrac{\left(\frac{1}{2}P\right)^2}{\left(\frac{1}{2}P\right)^3} = \dfrac{2}{P}$ (05)

$\therefore K_p = 2\times10^{-5} \ N^{-1}m^2$ ---

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(ii) At 2T:

$$3A_{(g)} \rightleftharpoons 2B_{(g)}$$
$$\searrow\!\!\nwarrow$$
$$C_{(g)} + 2D_{(g)}$$
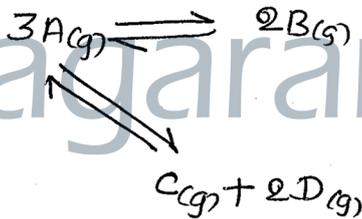
Amt. of A converted to C and D is $0.3a$

$\therefore n_C = 0.1a$, $n_D = 0.2a$ --- $2\times03=$(06)

Remaining $n_A = 0.4a$ (given)

$\therefore$ Amt. of $A_{(g)}$ converted to $B_{(g)}$ is $0.3a$ ---

$\qquad n_B = 0.2a$ ------ (02)

$n_{Tot.} = n_A + n_B + n_C + n_D = 0.9a$ ---

$X_A = \frac{4}{9}$, $X_B = \frac{2}{9}$, $X_C = \frac{1}{9}$, $X_D = \frac{2}{9}$

------ $4\times02=$(08)

Let P be the total pressure of the system at 2T

Using $P \propto nT$,

$\qquad \dfrac{2\times10^5 \ Nm^{-2}}{P} = \dfrac{0.8a \times T}{0.9a \times 2T}$ ---- (02)

$\Rightarrow P = 4.5\times10^5 \ Nm^{-2}$ ---- (02)

For the first equilibrium:

$$K_p = \frac{P_B^2}{P_A^3} = \frac{\left(\frac{2}{9} \times 4.5 \times 10^5 \, Nm^{-2}\right)^2}{\left(\frac{4}{9} \times 4.5 \times 10^5 \, Nm^{-2}\right)^3}$$ (05)
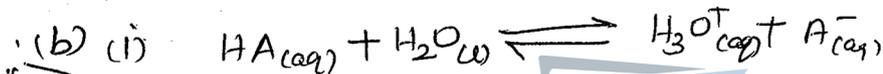
$$= \frac{1}{8} \times 10^{-5} \, N^{-1}m^2$$

For the second equilibrium:

$$K_p = \frac{P_C \times P_D^2}{P_A^3}$$ (05)

$$= \frac{\left(\frac{1}{9} \times 4.5 \times 10^5 \, Nm^{-2}\right)\left(\frac{2}{9} \times 4.5 \times 10^5 \, Nm^{-2}\right)^2}{\left(\frac{4}{9} \times 4.5 \times 10^5 \, Nm^{-2}\right)^3}$$ (05)

$$= \frac{1}{16}$$

(b) (i) $HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$

$$K_c = \frac{[H_3O^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}][H_2O_{(l)}]}$$

Since H_2O is in large excess $[H_2O] = const.$ } (05)

$$\therefore K_c[H_2O_{(l)}] = \frac{[H_3O^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]} = const = K_a$$

(ii) $HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$

Initially: c   --- $mol\,dm^{-3}$

at eq^m: c-x   x   x -- $mol\,dm^{-3}$

$$K_a = \frac{[H_3O^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]} \quad \cdots \; "$$

$$= \frac{x^2}{c-x}$$

Since ionization of weak acid is very small,

$$c - x \doteq c$$

$$\therefore K_a = \frac{x^2}{c} \Rightarrow x = \sqrt{cK_a} = [H_3O^+_{(aq)}]$$ (05)

$$pH = -\log_{10}[H_3O^+_{(aq)}]$$

$$= -\log_{10}(cK_a)^{1/2}$$ (05)

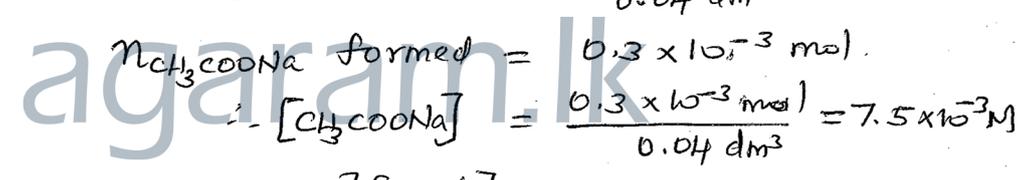$$\alpha \qquad pH = -\frac{1}{2}\log_{10}c - \frac{1}{2}\log_{10}K_a$$

9

(iii) After dilution, concentration of $HA = \frac{c}{100}$ ⑨

$\therefore$ pH of the final sol^n = $-\frac{1}{2}\log_{10}K_a - \frac{1}{2}\log_{10}\frac{c}{100}$ ⑤

final pH $-$ initial pH $= -\frac{1}{2}\log_{10}K_a - \frac{1}{2}\log_{10}\frac{c}{100}$

$$- \left(-\frac{1}{2}\log_{10}K_a - \frac{1}{2}\log_{10}c\right)$$

$$= \frac{1}{2}\left[\log_{10}c - \log\frac{c}{100}\right]$$

$$= 1 \quad \text{------} \quad ⑤$$

(iv) $[H_3O^+_{(aq)}] = \sqrt{cK_a} = \sqrt{0.02 \times 1.8 \times 10^{-5}}$ mol dm^{-3}

$$= 6 \times 10^{-4} \text{ mol dm}^{-3} \quad \text{-----} \quad ⑤$$

$$\therefore pH = -\log_{10}(6 \times 10^{-4}) = 4 - \log_{10}6 = 3.2219 \quad \text{----} ⑤$$

(V) (i) $CH_3COOH_{(aq)} + NaOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$

Initial $n_{CH_3COOH} = 0.02 \text{ mol dm}^{-3} \times 25 \times 10^{-3} \text{ dm}^3$

$$= 0.5 \times 10^{-3} \text{ mol} \quad ⑤$$

Added $n_{NaOH} = 0.02 \text{ mol dm}^{-3} \times 15 \times 10^{-3} \text{ dm}^3$

$$= 0.3 \times 10^{-3} \text{ mol} \quad \text{--} ⑤$$

$\therefore$ Remaining moles of $CH_3COOH = 0.2 \times 10^{-3}$ mol

$$[CH_3COOH] = \frac{0.2 \times 10^{-3} \text{ mol}}{0.04 \text{ dm}^3} = 5 \times 10^{-3} M.$$

n_{CH_3COONa} formed $= 0.3 \times 10^{-3}$ mol

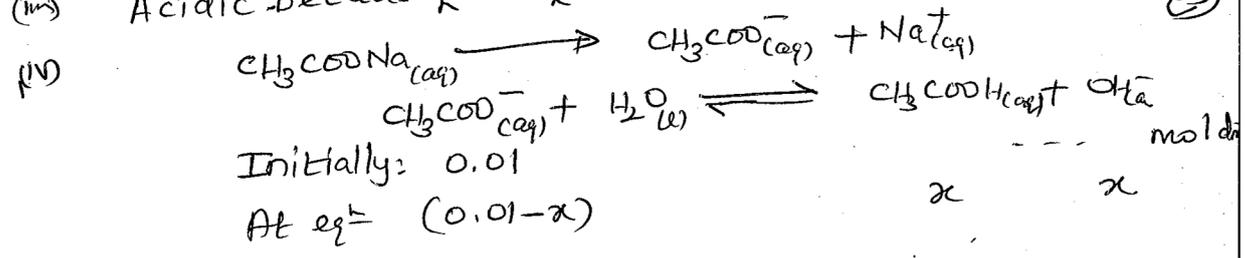$$\therefore [CH_3COONa] = \frac{0.3 \times 10^{-3} \text{ mol}}{0.04 \text{ dm}^3} = 7.5 \times 10^{-3} M$$
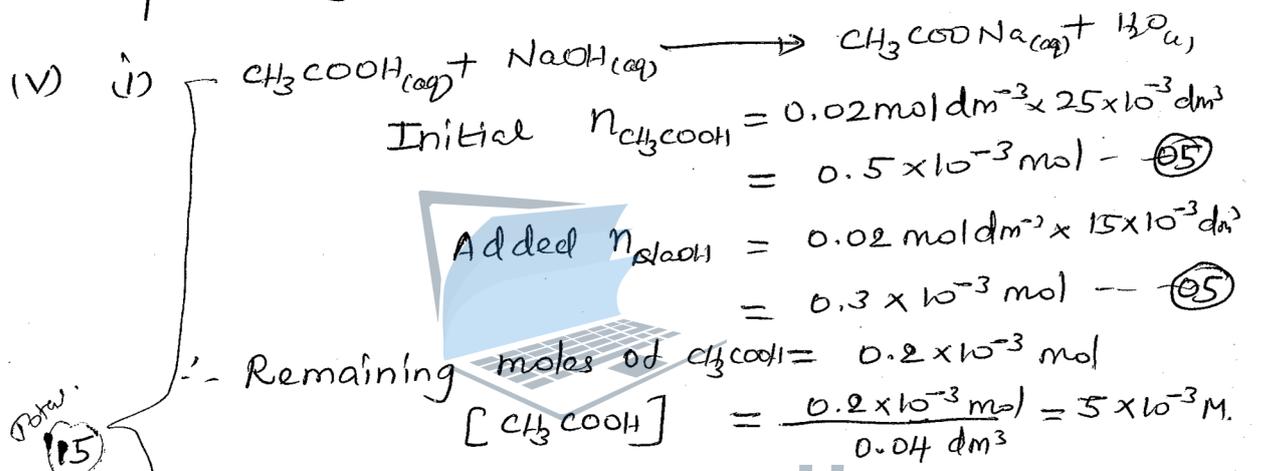
$$K_a = \frac{[CH_3COO^-_{(aq)}][H_3O^+_{(aq)}]}{[CH_3COOH_{(aq)}]}$$

$$[H_3O^+_{(aq)}] = \frac{K_a[CH_3COOH]}{[CH_3COO^-_{(aq)}]} = \frac{1.8 \times 10^{-5} \text{ mol dm}^{-3} \times 5 \times 10^{-3} \text{ mol dm}^{-3}}{7.5 \times 10^{-3} \text{ mol dm}^{-3}}$$

$$= 1.2 \times 10^{-5} \text{ mol dm}^{-3} \quad \text{---} \quad ⑤$$

$$pH = -\log(1.8 \times 10^{-5}) = 5 - \log_{10}1.2 =$$

(ii) $V_{NaOH} = 25 \text{ cm}^3$ ⑩

(iii) Acidic because of the hydrolysis of the salt formed (CH_3COONa)   ⑤

(iv) $CH_3COONa_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)} \quad \text{---} \text{ mol dm}$$

Initially: 0.01 x x

At eq^m $(0.01-x)$

Total 15

$$K_{b(CH_3COO^-)} = \frac{[CH_3COOH_{(aq)}][OH^-_{(aq)}]}{[CH_3COO^-_{(aq)}]} = \frac{x^2}{0.01-x} \quad \text{⑩}$$

$$0.01 - x \simeq 0.01$$

$$\therefore \frac{x^2}{0.01} = \frac{K_w}{K_{a(CH_3COOH)}} = \frac{1\times10^{-14} \, mol^2 \, dm^{-6}}{1.8\times10^{-5} \, mol\,dm^{-3}} = 5.6\times10^{-10}$$

$$x = \sqrt{5.56\times10^{-12}} \, mol\,dm^{-3} \quad \text{⑤}$$

$$\Rightarrow pH = 14 - (6 - \tfrac{1}{2}\log 5.56) = 8 + \tfrac{1}{2}\log 5.56$$

⑩ (Ⅰ)

(i) The N atom of the NO molecule should collide with the terminal O atom of the O_3 molecule

The colliding molecules NO and O_3 should possess energy greater than the activation energy for the re^n. $\quad 2\times 05 = \text{⑩}$

(ii) rate $\propto [NO][O_3]$ — — — — ⓐⓢ ⓪④

(Ⅱ)(i) A $\to$ Reactants, X $\to$ 1st activated complex,

I $\to$ Intermediate, Y $\to$ 2nd activated complex,

E $\to$ Products $\quad 5\times 02 = \text{⑩}$

I enthalpy of re^n = $-(b-a)$ $\Big\}$ $3\times 01 = \text{③}$

Ⅱ) $E_{a_1} = e-c$, $E_{a_2} = d-c$

(iii) X $\Rightarrow$ $CH_3-\overset{\underset{CH_3}{|}}{C}{}^{\delta+}\cdots Br^{\delta-}$, I $\Rightarrow$ $CH_3-\overset{\underset{CH_3}{|}}{C}{}^{+}$, Y $\Rightarrow$ $CH_3-\overset{\underset{CH_3}{|}}{\overset{|}{\underset{|}{C}}}\cdots OH$

$3\times 01 = \text{③}$

- -

⑥(a)(i) Stating Raoult's law — — — ⑩

⑥⑩(ii) Consider the binary sol^n of two completely miscible liquids A and B which is in equilibrium with its vapour
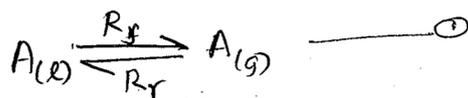
$$A_{(\ell)} \underset{R_r}{\overset{R_f}{\rightleftharpoons}} A_{(g)} \quad\text{——①}$$

$$B_{(\ell)} \rightleftharpoons B_{(g)} \quad\text{——②}$$

If the rate of A molecules going into vapour phase from liquid
R_1, then $\quad R_1 = k'[A_{(\ell)}]$

$[A_{(\ell)}] \propto X_A$, mole fraction in the liquid

$$\therefore R_1 = k_1 \times X_A \quad \text{——} \quad ③$$

If the rate of A molecules going from vapour phase into liquid phase is R_2, then

$$R_2 = k''[A_{(g)}]$$

$[A_{(g)}] \propto P_A$, partial pressure of A

$$\therefore R_2 = k_2 \times P_A \quad \text{——} \quad ⑩$$

When eqm is etablished, $R_1 = R_2$

From eqns ③, ⑩ $\Rightarrow$ $k_1 X_A = k_2 P_A$
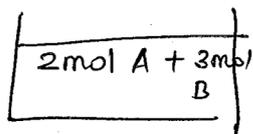
$$P_A = \frac{k_1}{k_2} X_A$$

$$P_A = k X_A$$

when $\alpha_A = 1$, $P_A = P_A^\circ \Rightarrow k = P_A^\circ$

Hence, $P_A = X_A P_A^\circ$

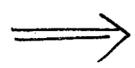$P_A, \alpha_A, P_A^\circ \rightarrow 3 \times 02 = ⑥$ $\quad$ $ ^{III}{}^{ly}$ $P_B = X_B P_B^\circ$

$$\text{——} \quad ⑩$$

(iii)

2mol A + 3mol B	$\Rightarrow$

Initially
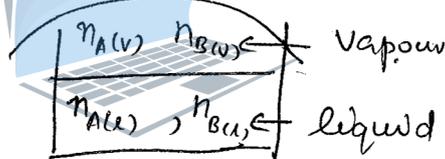
At equilibrium

$$n_{A(V)} = \frac{10}{100} \times 2 \, mol = 0.2 \, mol$$

$$n_{B(V)} = \frac{20}{100} \times 3 \, mol = 0.6 \, mol \quad \Big\} \, 2 \times 02 = ④$$

$$n_{A(\ell)} = 2 - 0.2 = 1.8 \, mol \quad \Big\} \, 2 \times 02 = ④$$

$$n_{B(\ell)} = 2.4 \, mol.$$

<u>In the vapour phase,</u>

$$X_{A(vap.)} = \frac{0.2}{0.8} = \frac{1}{4} \quad \Big\} \, 2 \times 02 = ④$$

$$X_{B(vap)} = \frac{0.6}{0.8} = \frac{3}{4}$$

$$P_A = X_{A(vap.)} \times P_{Tot} = \frac{1}{4} \times 4.8 \times 10^5 \, Nm^{-2}$$

$$= 1.2 \times 10^5 \, Nm^{-2} \quad \text{——} \quad ④$$

$$P_B = X_{B(vap)} \times P_{Tot} = \frac{3}{4} \times 4.8 \times 10^5 \, Nm^{-2}$$

$$= 3.6 \times 10^5 \, Nm^{-2} \quad ④$$

In the liquid phase

$$x_{A(liq)} = \frac{1\cdot8}{4\cdot2} = \frac{3}{7}$$

$$x_{B(liq)} = \frac{2\cdot4}{4\cdot2} = \frac{4}{7}$$

$\Big\}$ $2 \times 02 = 04$

Applying Raoult's law,

$$P_A = x_A P_A^{\circ} \implies P_A^{\circ} = \frac{P_A}{x_A}$$

$$= \frac{1\cdot2 \times 10^5 \, Nm^{-2}}{3/7}$$

$$\doteq 2\cdot8 \times 10^5 \, Nm^{-2} \quad ⑤$$

$$P_B^{\circ} = \frac{P_B}{x_B}$$

$$= \frac{3\cdot6 \times 10^5 \, Nm^{-2}}{4/7} = 6\cdot3 \times 10^5 \, Nm^{-2} \quad ⑤$$

(b) ④⁰

← butanol layer
← water layer
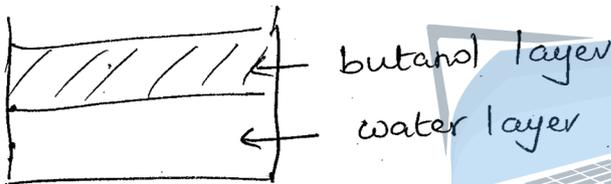
Let c mol dm^{-3} be the concentration of NaOH used

Water layer :

$N^{\underline{o}}$ of moles of NaOH required.
$$= c \, mol\,dm^{-3} \times 5 \times 10^{-3} \, dm^3$$
$$= 5c \times 10^{-3} \, mol \quad ③$$

$$CH_3COOH_{(aq)} + NaOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$$

$\therefore$ $N^{\underline{o}}$ of moles of $CH_3COOH = 5c \times 10^{-3} \, mol$

$$[CH_3COOH]_{aq.} = \frac{5c \times 10^{-3} \, mol}{25 \times 10^{-3} \, dm^3} \quad ③$$

$$= \frac{c}{5} \, mol\,dm^{-3} \quad ③$$

Butanol layer :

$N^{\underline{o}}$ of moles of NaOH required
$$= c \, mol\,dm^{-3} \times 40 \times 10^{-3} \, dm^3$$
$$= 40c \times 10^{-3} \, mol \quad ③$$

$N^{\underline{o}}$ of moles of $CH_3COOH = 40c \times 10^{-3} \, mol$

$\therefore$ $[CH_3COOH]_{butanol} = \frac{40c \times 10^{-3} \, mol}{10 \times 10^{-3} \, dm^3}$

$$= 4c \, mol\,dm^{-3} \quad ③$$

$$K_D = \frac{[CH_3COOH]_{aq}}{[CH_3COOH]_{butanol}}$$

$$= \frac{\frac{c}{5} \, mol \, dm^{-3}}{4c \, mol \, dm^{-3}} = \frac{1}{20} \quad \text{——— (05)}$$

(iii)

butanol, $25 cm^3$

$0.05 \, mol \, dm^{-3}$
$CH_3COOH_{(aq)}$, $50 cm^3$
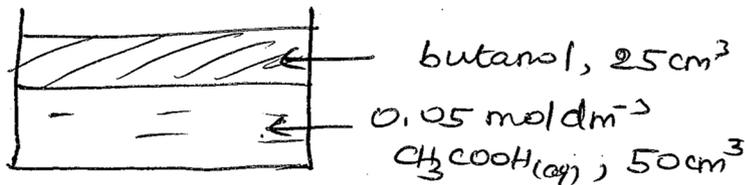
Initially , n_{CH_3COOH} in aqueous layer

$$= 0.05 \, mol \, dm^{-3} \times 50 \times 10^{-3} \, dm^3$$

$$= 2.5 \times 10^{-3} \, mol \quad \text{——— (05)}$$

At equilibrium, if the amt. in moles of CH_3COOH gone into butanol layer is x,

the remaining n_{CH_3COOH} in aqueous layer

$$= (2.5 \times 10^{-3} - x) \quad \text{—— (02)}$$

$$[CH_3COOH]_{butanol} = \frac{x}{25} \times 1000 = 40x \, mol \, dm^{-3} \quad \text{——(02)}$$

$$[CH_3COOH]_{aq.} = \frac{(2.5 \times 10^{-3} - x)}{50} \times 1000$$

$$= 20(2.5 \times 10^{-3} - x) \, mol \, dm^{-3} \quad \text{(02)}$$

$$K_D = \frac{1}{20} = \frac{20(2.5 \times 10^{-3} - x)}{40x}$$

$$x = 2.22 \times 10^{-3} \, mol \quad \text{——— (02)}$$

n_{CH_3COOH} in aqueous layer $= 2.5 \times 10^{-3} - 2.22 \times 10^{-3}$

$$= 0.28 \times 10^{-3} \, mol \quad \text{——(02)}$$

n_{CH_3COOH} in $20 cm^3 = \frac{0.28 \times 10^{-3} \times 20}{50}$

$$= 0.112 \, mol \quad \text{—— (02)}$$

n_{NaOH} required $= 0.112 \, mol$
Volume of it $= \frac{0.112 \, mol}{0.2 \, mol \, dm^{-3}}$

$$= 0.56 \, dm^3 \quad \text{——— (03)}$$

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(c)(i) $NaHSO_{4(aq)} + NaOH_{(aq)} \rightleftharpoons Na_2SO_{4(aq)} + H_2O_{(l)}$

50

Nᵒ of moles of $NaHSO_4$ = $2 \, mol \, dm^{-3} \times 25 \times 10^{-3} \, dm^3$

$= 0.05 \, mol$ --- (05)

Volume of NaOH required = $25 \, cm^3$

When $50 \, cm^3$ of $1 \, M \, Mg(NO_3)_2$ is added

$Mg^{2+}_{(aq)}$ ion concentration = SO_4^{2-} concentration

$= 0.5 \, mol \, dm^{-3}$ --- (05)

$$Mg^{2+}_{(aq)} + SO^{2-}_{4(aq)} \rightleftharpoons MgSO_{4(s)}$$

Concentration at eqᵐ: $(0.5-x)$ $(0.5-x)$

$$[Mg^{2+}_{(aq)}][SO^{2-}_{4(aq)}] = K_{sp}$$ ———

$$(0.5-x)^2 = 8.1 \times 10^{-5} \, mol^2 \, dm^{-6}$$ --- (05)

$$x = 491 \times 10^{-3} \, mol \, dm^{-3}$$ ——— (05)

Therefore, amt. of $MgSO_4$ precipitated

in $100 \, cm^3 = 0.0491 \, mol$ --- (05)

mass of $MgSO_4$ ppt. $= 0.0491 \, mol \times 112 \, g \, mol^{-1}$

$= 5.5 \, g$ ——— (05)

(ii) $NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^+_{(aq)}$

$- mol \, dm^{-3}$

Initially: 0.5

at eqᵐ : 0.5-x $\qquad x \qquad x$

$$K_{a(NH_4^+)} = \frac{[NH_4OH_{(aq)}][H^+_{(aq)}]}{[NH^+_{4(aq)}]} = \frac{K_w}{K_b}$$ --- (05)

$$\frac{x^2}{0.5-x} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$$0.5 - x \simeq 0.5$$

$$x^2 = 0.5 \times 5.56 \times 10^{-10} \, mol^2 \, dm^{-6}$$ --- (05)

$$[H^+_{(aq)}] = x = 1.67 \times 10^{-5} \, mol \, dm^{-3}$$ --- (05)

$$pH = -\log_{10}[H_3O^+]/mol \, dm^{-3}$$

$$= 5 - \log_{10} 1.67 = 4.78$$ --- (03)

To have $pH = 6$, $[H^+_{(aq)}] = 10^{-6}$ mol dm^{-3}

$$[NH^+_{4(aq)}] = \frac{[H^+_{(aq)}]^2}{K_a} = \frac{1 \times 10^{-12} \text{ mol}^2\text{dm}^{-6}}{5.56 \times 10^{-10} \text{ mol dm}^{-3}} \quad \text{(05)}$$

Dilution factor $= \dfrac{0.5}{1.8 \times 10^{-3}} = 277.8$. ___ (02)

(7) (i) Faraday's laws

(I) The mass of a chemical substance deposited at an electrode during electrolysis is directly proportional to the quantity of electricity (expressed in coulombs) passed through the cell.

(II) The masses of different substances produced by the same quantity of electricity are proportional to the equivalence mass of the substances.

$2 \times 05 = \boxed{10}$

(ii) (i) $E^\ominus_{cell} = E^\ominus_{Ag^+_{(aq)}/Ag_{(s)}} - E^\ominus_{M^{n+}_{(aq)}/M_{(s)}}$

$1.56\,V = 0.80\,V - E^\ominus_{M^{n+}_{(aq)}/M_{(s)}}$

$\Rightarrow E^\ominus_{M^{n+}_{(aq)}/M_{(s)}} = 0.80\,V - 1.56\,V$

$= -0.76\,V$ ___ (05)

(ii) Anode: $M_{(s)}/M^{n+}_{(aq)}$, Cathode: $Ag_{(s)}/Ag^+_{(aq)}$ $2 \times [03 + 02]$
        $(-)$ $(+)$

(iii) Anode: $M_{(s)} \longrightarrow M^{n+}_{(aq)} + ne$ $\Big\}$ $2 \times 05 = \boxed{10}$
     Cathode: $Ag^+_{(aq)} + e \longrightarrow Ag_{(s)}$

(iv) Cell re^n $M_{(s)} + nAg^+_{(aq)} \longrightarrow M^{n+}_{(aq)} + nAg_{(s)}$ ___ (05)
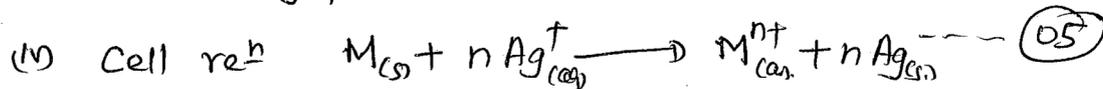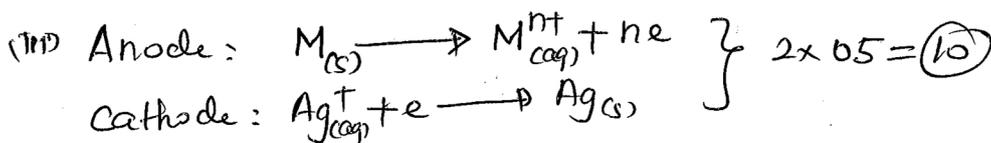
(v) To facilitate the migration of ions / $\Big\}$ (05)
    to maintain electrical neutrality.

    NH_4Cl / NH_4NO_3 ___ ___ any one. (05)

(vi) (i) $Ag^+_{(aq)} + e \longrightarrow Ag_{(s)}$
     for 108 g of Ag $\rightarrow$ 1 mol electron = 96500 C
     ∴ for 54 mg of Ag $\rightarrow$ $\dfrac{96,500 \times 54 \times 10^{-3}}{108}$

     $= 48.25$ C ___ (05)

16
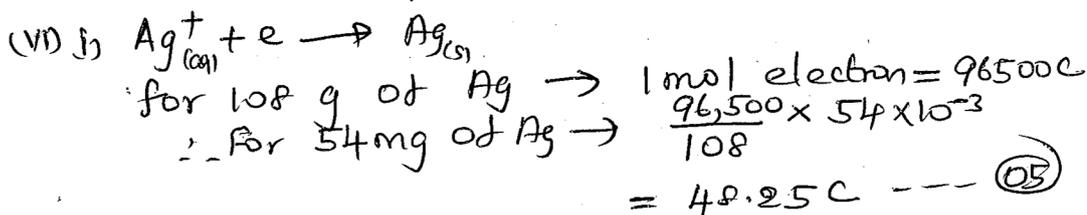
(II) $\dfrac{48.25\,C}{96500\,C\,mol^{-1}} = 0.5 \times 10^{-3}\,mol$ ———— ⑤   ⑯

(III) For 16.35 mg of M → $0.5 \times 10^{-3}\,mol$ e^{-}

∴ For 65.4 g of M → $\dfrac{0.5 \times 10^{-3}}{16.35} \times 65.4 \times 10^{3}$

$= 2\,mol.\ e^{-}$ —— ⑤

(IV) $M^{n+}_{(aq)} + ne \longrightarrow M_{(s)}$

∴ $n = 2$ ———— ⑤
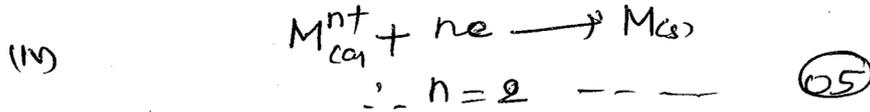
(b) (I) Oxidation state of Cr = +3 ——— ⑤

(II) $Cr^{3+} = 1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}3d^{3}$ ——— ⑤
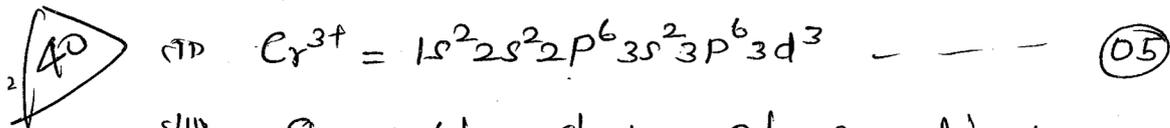
(III) Since the shape of coordination sphere is octahedral, there must be 6 (unidentate) ligands ——— ⑤

H atoms exist only as NH_3 and therefore there must be four NH_3 ligands ⑤

The other ligands can be NO_2^- or Cl^-

Since cpd. A gives white ppt with $AgNO_3$, it must have Cl^- ion ——— ⑤

A ⟹ $[Cr(NH_3)_4(NO_2)Cl]\,Cl$ ——— ⑤
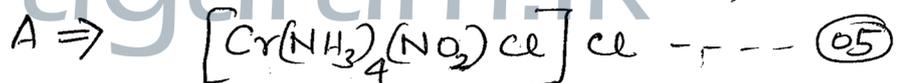
As B does not give ppt. with $AgNO_3$, the two Cl^- must be ligands and anion is NO_2^- ———— ⑤

B ⟹ $[Cr(NH_3)_4Cl_2]\,NO_2$ ———— ⑤

(c) (I) $2MnO_4^{-}{}_{(aq)} + 10\,I^{-}_{(aq)} + 16H^{+}_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5I_{2(aq)} + 8H_2O_{(l)}$

$x\,mol$

$MnO_{2(s)} + 4H^{+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + I_{2(aq)} + 2H_2O_{(l)}$

$y\,mol$

$I_{2(aq)} + 2S_2O_3^{2-}{}_{(aq)} \longrightarrow 2I^{-}_{(aq)} + S_4O_6^{2-}{}_{(aq)}$
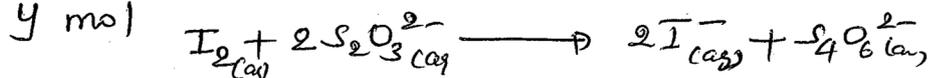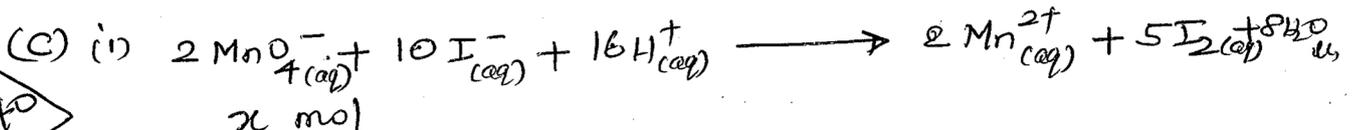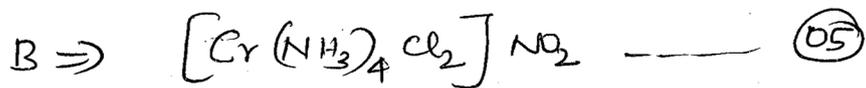
eqns. $3 \times 05 =$ ⑮

$$\frac{5x}{2} + y = \frac{1}{2} \times 2 \, mol \, dm^{-3} \times 45 \times 10^{-3} dm^3$$

$$5x + 2y = 0.09 \quad —————— \text{①} \quad \Big\} \, 2 \times 05 = \boxed{10}$$

$$158x + 87y = 3.32 \quad ——————\text{②}$$
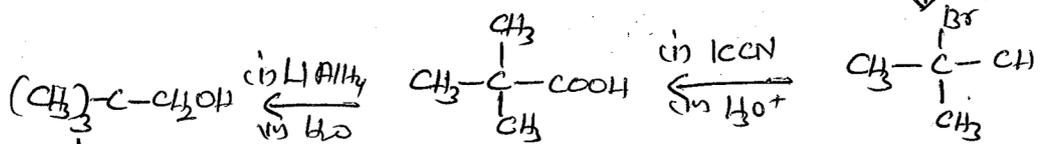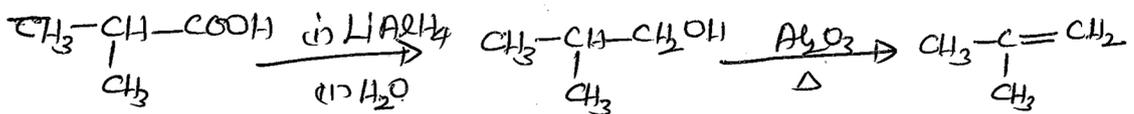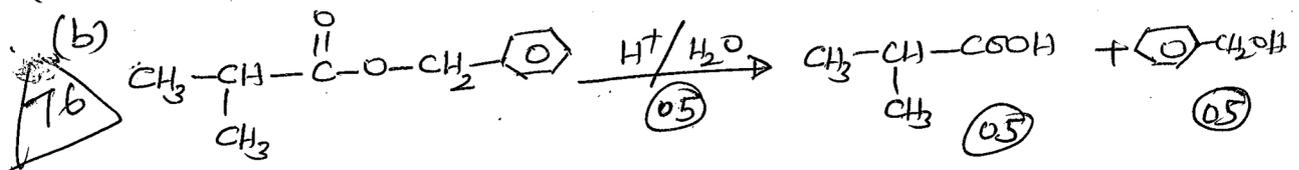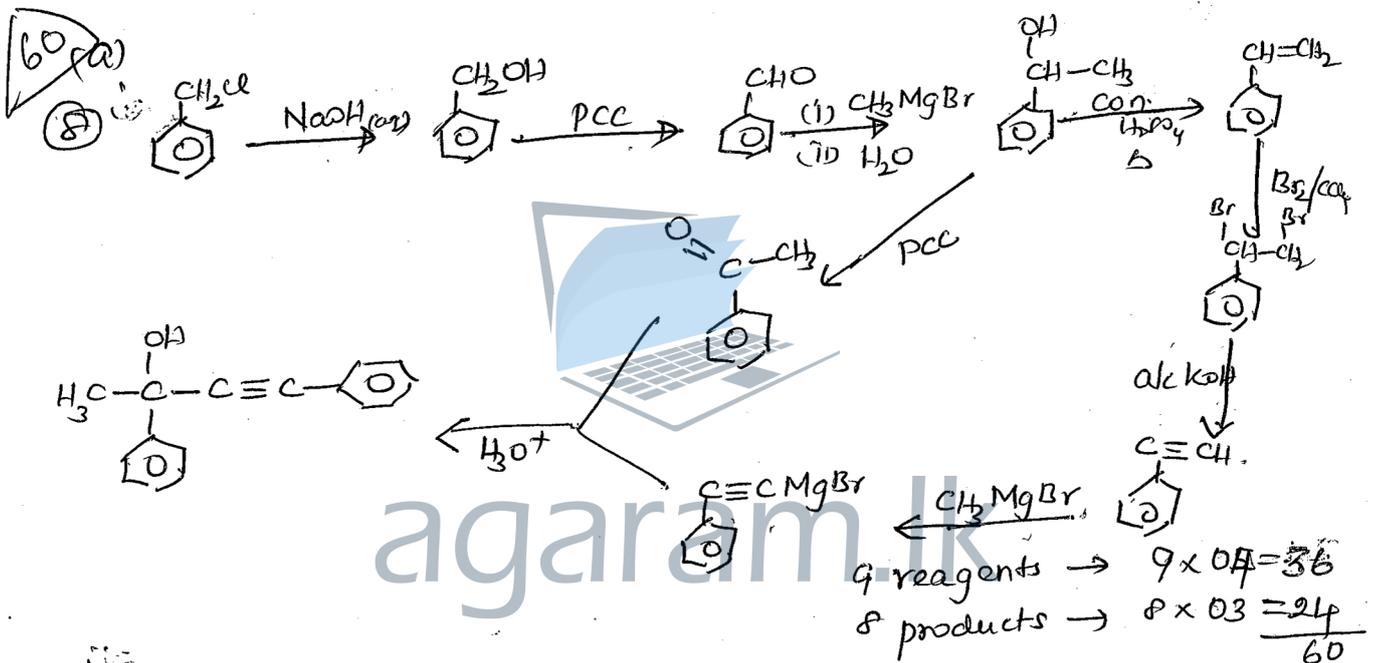
$$\text{①} \times 87 - \text{②} \times 2 \Rightarrow 435x - 316x = 7.83 - 6.64$$

$$119x = 1.19$$

$$x = 0.01 \, mol \quad ——— \boxed{05}$$

Percentage purity of $KMnO_4 = \frac{1.58}{3.32} \times 100\%$

$$= 47.6\% \quad —— \boxed{10}$$

60 (a)

G reagents → $9 \times 04 = \cancel{36}$
8 products → $8 \times 03 = 24$
$\overline{\quad\quad 60 \quad}$

(b)
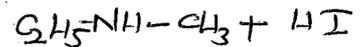

reagents $6 \times 04 = 24$
products $6 \times 04 = 24$

18

$$\text{C}_6\text{H}_5\text{—CH}_2\text{OH} \xrightarrow[\text{(03)}]{PBr_3} \text{C}_6\text{H}_5\text{—CH}_2Br \xrightarrow[\text{(03)}]{Mg/Dry\ ether} \text{C}_6\text{H}_5\text{—CH}_2MgBr$$

$$(CH_3)_3C - \overset{O}{\overset{\|}{C}} - H \underset{\text{(02)}}{} + \text{C}_6\text{H}_5\text{—CH}_2MgBr \xrightarrow{H_3O^+} \underset{\text{(02)}}{} \overset{OH}{\underset{|}{(CH_3)_3C - CH - CH_2 - C_6H_5}}$$

(03) $\Big\downarrow$ Conc. H_2SO_4, $\triangle$
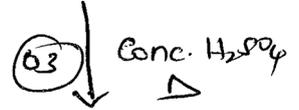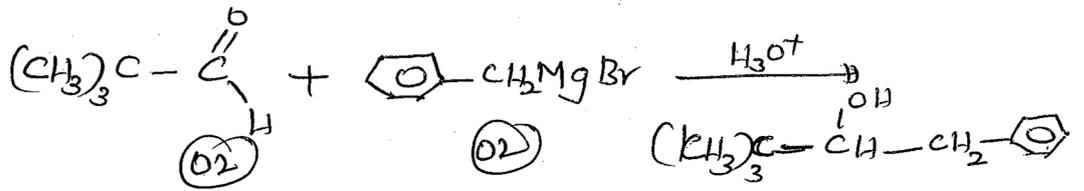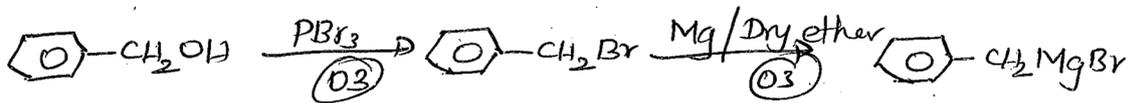
Required product

Total for (b) (76)

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(14) (c) (i) Nucleophilic substitution (followed by elimination)

(ii)
$$C_2H_5 - \overset{..}{N}H_2 \underset{\text{(02)}}{\curvearrowright} CH_3 \overset{\frown}{\underset{\text{(02)}}{I}} \longrightarrow \Big[C_2H_5 \overset{H}{\underset{H}{\overset{|}{N^+}}} - CH_3 + :\overset{-}{I} \Big]\ \text{(03)}$$
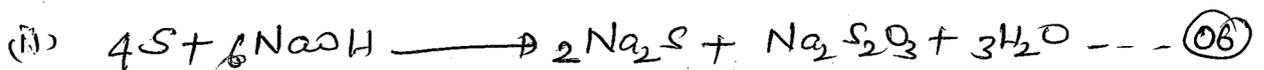
(02)

$\Big\downarrow$

$$C_2H_5 - NH - CH_3 + HI$$
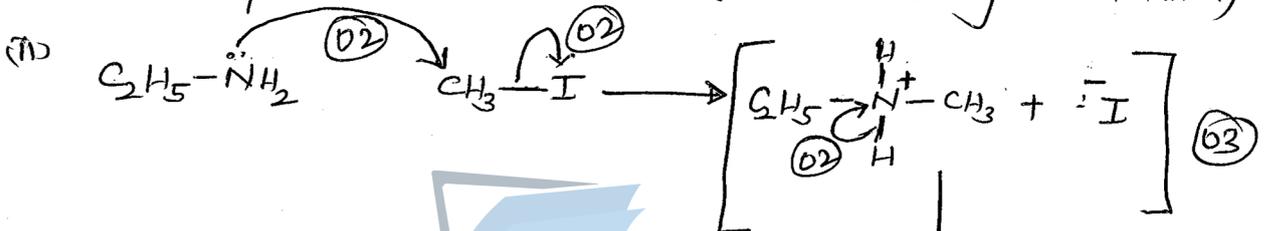
(iii) The lone pair on N in propionamide is less available to take part in a nucleophilic reaction.

(05)

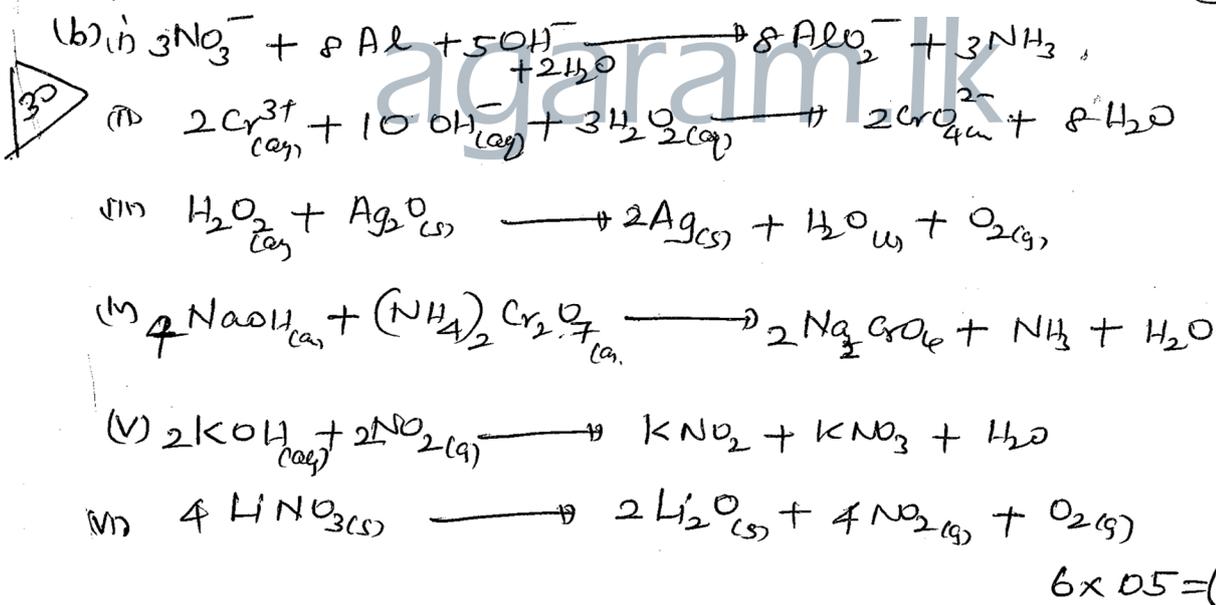Reason: It is delocalized on to the $\rangle C=O$ group.

or due to resonance $$CH_3CH_2 - \overset{O}{\overset{\|}{C}} - \overset{..}{N}H_2 \longleftrightarrow CH_3 - CH_2 - \overset{O^-}{\underset{NH_2}{\overset{|}{C}}}$$

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(9) (a)(i) $A = CuS$, $B = [CuCl_4]^{2-}$, $C = H_2S$, $D = Cu(OH)_2$,

(120) $E = [Cu(NH_3)_4]^{2+}$, $F = S$, $G = Na_2S$, $H = Na_2S_2O_3$

$I = SO_2$

$9 \times 06 = $ (54)

(ii) $4S + 6NaOH \longrightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O$ --- (06)
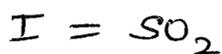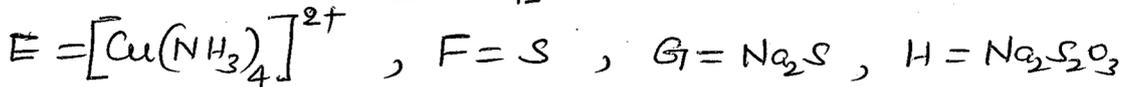
(iii) Formation of white precipitate first is due to $Ag_2S_2O_3$ --- (10)

$$2AgNO_{3(aq)} + Na_2S_2O_{3(aq)} \longrightarrow Ag_2S_2O_3\downarrow + 2NaNO_3$$
(s) (10)
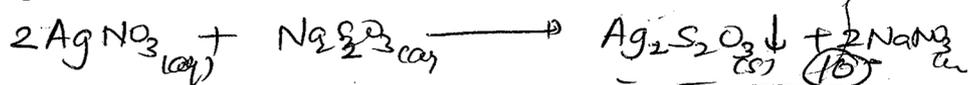
The white precipitate turns black due to the formation of Ag_2S.

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S\downarrow + H_2SO_4 \quad -\}- ⑩$$

$$(or \quad Ag_2S_2O_3 \longrightarrow Ag_2S + SO_3)$$

(III) $2H_2S + SO_2 \longrightarrow 3S + 2H_2O$ —————— ⑩

(±)
oxidizing agent SO_2 ⎫
reducing agent H_2S ⎭ $2×05 = ⑩$

(b) (i) Ag^+ , Cr^{3+} ———— $2×05 = ⑩$

(II) Formation of yellow coloured solution — ⑩

$$2Cr(OH)_{3(s)} + 4OH^-_{(aq)} + 3H_2O_{2(aq)} \longrightarrow 2CrO_4^{2-}_{(aq)} + 8H_2O_{(l)} \quad ⑩$$

(a)

⑩ (i) $X \Rightarrow Zn^{2+}$, $Y \Rightarrow Ni^{2+}$, $Z \Rightarrow Fe^{3+}$ ——— $3×05 = ⑮$

(II) $ZnCl_4^{2-}$ — colourless , $NiCl_4^{2-}$ — yellow , $FeCl_4^-$ —

——— $3×(03+02)$
$= ⑮$

(b)(i) $3NO_3^- + 8Al + 5OH^- \xrightarrow{+2H_2O} 8AlO_2^- + 3NH_3$

(II) $2Cr^{3+}_{(aq)} + 10OH^-_{(aq)} + 3H_2O_{2(aq)} \longrightarrow 2CrO_4^{2-}_{(l)} + 8H_2O$

(III) $H_2O_{2(aq)} + Ag_2O_{(s)} \longrightarrow 2Ag_{(s)} + H_2O_{(l)} + O_{2(g)}$

(IV) $4NaOH_{(aq)} + (NH_4)_2Cr_2O_{7(aq)} \longrightarrow 2Na_2CrO_4 + NH_3 + H_2O$

(V) $2KOH_{(aq)} + 2NO_{2(g)} \longrightarrow KNO_2 + KNO_3 + H_2O$

(VI) $4LiNO_{3(s)} \longrightarrow 2Li_2O_{(s)} + 4NO_{2(g)} + O_{2(g)}$

$6×05 = ㉚$

(C) (A) Determination of Cl^- concentration

$$n_{AgCl} = \frac{0.287 g}{143.5 g mol^+} - - - -$$

$$= 0.002 \, mol \quad - - - ⑤$$

$\therefore$ Concentration of $Cl^- = 0.08 \, mol dm^{-3}$ —— ⑤

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(B)

$$2Fe^{3+}_{(aq)} + 3H_2S_{(g)} \longrightarrow 2FeS_{(s)} + S_{(s)} + 6H^+_{(aq)}$$

$$4FeS + 7O_2 \longrightarrow 2Fe_2O_3 + 4SO_2$$

$$S + O_2 \longrightarrow SO_2$$

$$2MnO_4^- + 5SO_2 + H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$$

$$2MnO_4^- + 5SO_4^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$
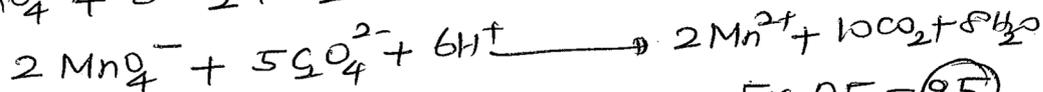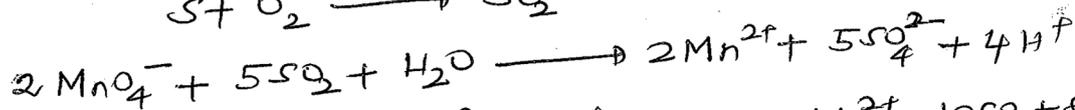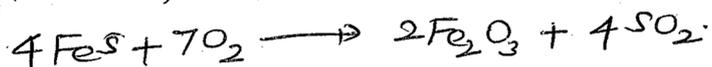
$$5 \times 05 = \boxed{25}$$

$$n_{C_2O_4^{2-}} = 0.12\ mol\,dm^{-3} \times 25 \times 10^{-3}\,dm^3 \text{ - - - - -}$$

$$= 3 \times 10^{-3}\ mol \text{ - - - - - } \boxed{05}$$

$$\therefore n_{MnO_4^-} \text{ remaining} = \frac{2}{5} \times 3 \times 10^{-3} = 1.2 \times 10^{-3}\ mol \text{ - - - } \boxed{05}$$

$$MnO_4^- \text{ moles reacted with } SO_2 = \frac{0.048}{1000} \times 50 - 1.2 \times 10^{-3}$$

$$= 1.2 \times 10^{-3}\ mol - \boxed{05}$$

$$Fe^{3+}\ mol = FeS\ mol = SO_2\ mol \text{ - - -}$$

$$= 1.2 \times 10^{-3}\ mol \times \frac{5}{2} \times \frac{2}{3}$$

$$= 2 \times 10^{-3}\ mol \quad \boxed{05}$$

$$\therefore Fe^{3+} \text{ concentration} = \frac{2 \times 10^{-3}}{25} \times 1000\ mol\,dm^{-3}$$

$$= 0.08\ mol\,dm^{-3} \text{ - - } \boxed{05}$$

(C) Determination of the concentration of H^+ :

$$NaOH\ mol = \text{overall } H^+ \text{ mol in the filtrate (B)}$$

$$= \frac{0.6 \times 20}{1000} = 12 \times 10^{-3}\ mol \\ - \boxed{05} -$$

$$H^+ \text{ mol from } H_2S = 3 \times Fe^{3+}\ mol \text{ - - } \boxed{05}$$

$$= 3 \times 2 \times 10^{-3}\ mol$$

$$= 6 \times 10^{-3}\ mol \text{ - - - } \boxed{05}$$

$$H^+ \text{ mol in the initial } sol^n = (12 \times 10^{-3} - 6 \times 10^{-3})\ mol \\ - \boxed{05}$$

$$= 6 \times 10^{-3}\ mol$$

$$\therefore \text{ Concentration of } H^+ \text{ in the initial } sol^n = \frac{6 \times 10^{-3}}{25} \times 1000$$

$$= 0.24\ mol\,dm^{-3} \text{ - - } \boxed{10}$$