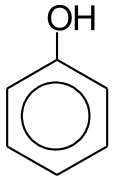
Answers to H2 Chemistry Preliminary Examinations 2009 Paper 3

1 **(a)**

- AlF_3 exists as giant ionic lattice with strong ionic bonds between the ions. Large amount of energy of energy is required to overcome the strong electrostatic attraction between oppositely charged ions and hence, a high melting point.
- $AlCl_3$ exists as a simple molecular structure. Melting involves overcoming the weak Van der Waals forces of attraction. Little energy is required to overcome the intermolecular forces of attraction and thus, $AlCl_3$ has a lower melting point as compared to $NaCl$.

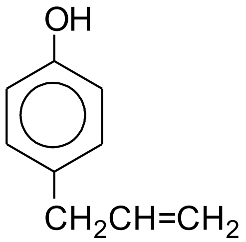
(b) **(i)**

- High C:H ratio infers that P is an aromatic compound.
- 

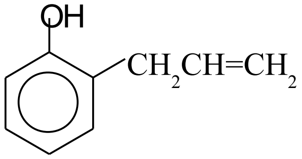
P

- With anhydrous aluminium chloride **P** undergoes electrophilic substitution reaction to form **Q. As the –OH is an activating group, the substituent will be directed to the ortho or para position.**

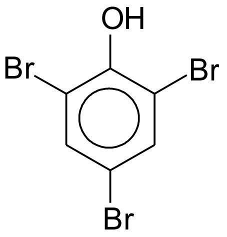
Q



OR



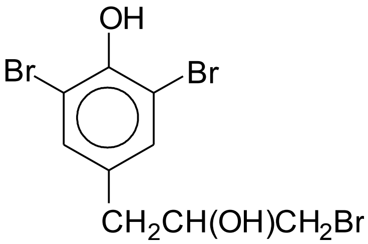
- **P** undergoes electrophilic substituition as it decolourises aqueous bromine to form white ppt **R. R** is 2,4,6-tribromophenol as -OH is a highly activating group.



- **Q** react with aqueous bromine to form white ppt **S,** with the same no of bromine atoms per molecule of **R. As Q has a C-C double bond,**

electrophilic addition takes place as well. This implies that 1 Br will be attached to one of the carbons of the C-C double bonds. Thus, only 2 Br will be attached directly to the benzene.

- **S**



S is optically active because of its chiral carbon. The mirror image of S is non-superimposable**.**

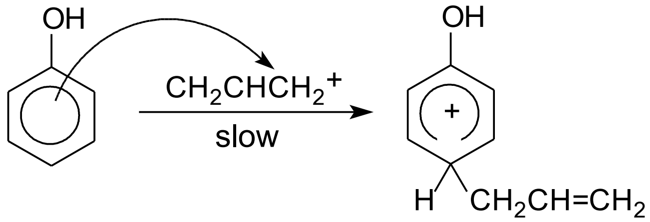
(ii)

- Electrophilic Substitution
- • Mechanism

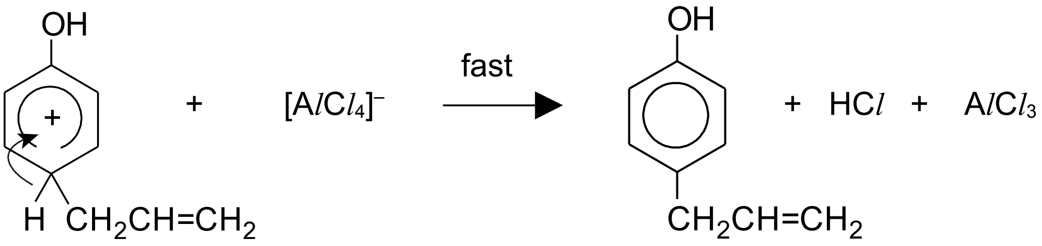
Step 1: Generation of electrophile

$$CH_2{=}CHCH_2Cl + AlCl_3 \longrightarrow CH_2{=}CHCH_2^+ + [AlCl_4]^-$$

Step 2: Electrophilic Attack



Step 3: Loss of proton



Any 2 correct steps – Max 1 mark given. 3 correct steps – 2 marks awarded.

(c) NCl_3 (l) + $3H_2O$ (l) → $\underline{NH_3}$ (aq) + $3HOCl$ (aq)

PCl_3 (l) + $3H_2O$ (l) → $\underline{H_3PO_3}$ (aq) + $3HCl$ (aq)

- Nitrogen is in period 2 and it cannot expand its octet while phosphorus is in period 3 and can expand its octet structure.
- P is able to use its energetically accessible 3d subshell for dative bonding with H_2O in the reaction/accommodate of the lone pair of electrons from H_2O during the nucleophilic attack of H_2O on PCl_3.

(d) **(i)** $K_{sp} = [Pb^{2+}][CrO_4^{2-}]$

Let the solubility of $PbCrO_4$ be x mol dm^{-3}

$$PbCrO_4\,(s) \rightleftharpoons Pb^{2+}\,(aq) + CrO_4^{2-}\,(aq)$$

$K_{sp} = [Pb^{2+}][CrO_4^{2-}]$

$$1.69 \times 10^{-14} = x^2$$

$$x = \sqrt{K_{sp}}$$

$= 1.30 \times 10^{-7}$ **mol dm^{-3}**

The solubility of $PbCrO_4$ is 1.30×10^{-7} mol dm^{-3}.

(ii)

$$[Pb^{2+}] = \frac{K_{sp}}{[CrO_4^{2-}]} = \frac{1.69\times10^{-14}}{0.010}$$

$= 1.69 \times 10^{-12}$ mol dm^{-3}

2 **(a)** Order with respect to **E** = 1

Comparing experiment 1 and 3

$$\frac{[E]_1[NaOH]_1^x}{[E]_3[NaOH]_3^x} = \frac{(0.20)(0.30)^x}{(0.20)(0.20)^x} = \frac{0.0150}{0.0150}$$

$$\left(\frac{0.20}{0.20}\right) \times \left(\frac{0.30}{0.20}\right)^x = \frac{0.0150}{0.0150}$$

OR When [**E**] is constant but $[OH^-]$ is decreased by 1/3 the rate remains the same

- x = 0

Order with respect to **F** = 1

Comparing experiment 2 and 3

$$\frac{[F]_2[NaOH]_2^y}{[F]_3[NaOH]_3^y} = \frac{(0.10)(0.40)^y}{(0.20)(0.60)^y} = \frac{0.0080}{0.0240}$$

$$\left(\frac{0.10}{0.20}\right)\left(\frac{0.40}{0.60}\right)^y = \frac{0.0800}{0.0240}$$

- y = 1

(b) **(i)**

- When the temperature of the reaction increases (pressure remaining the same), the reactant particles gain more kinetic energy and hence move about more rapidly. There is a greater frequency of collision between reactant particles and more reactant particles have energy greater than or equal to the activation energy.
- There are more effective collisions between reactant particles giving rise to an increase in the rate of reaction.
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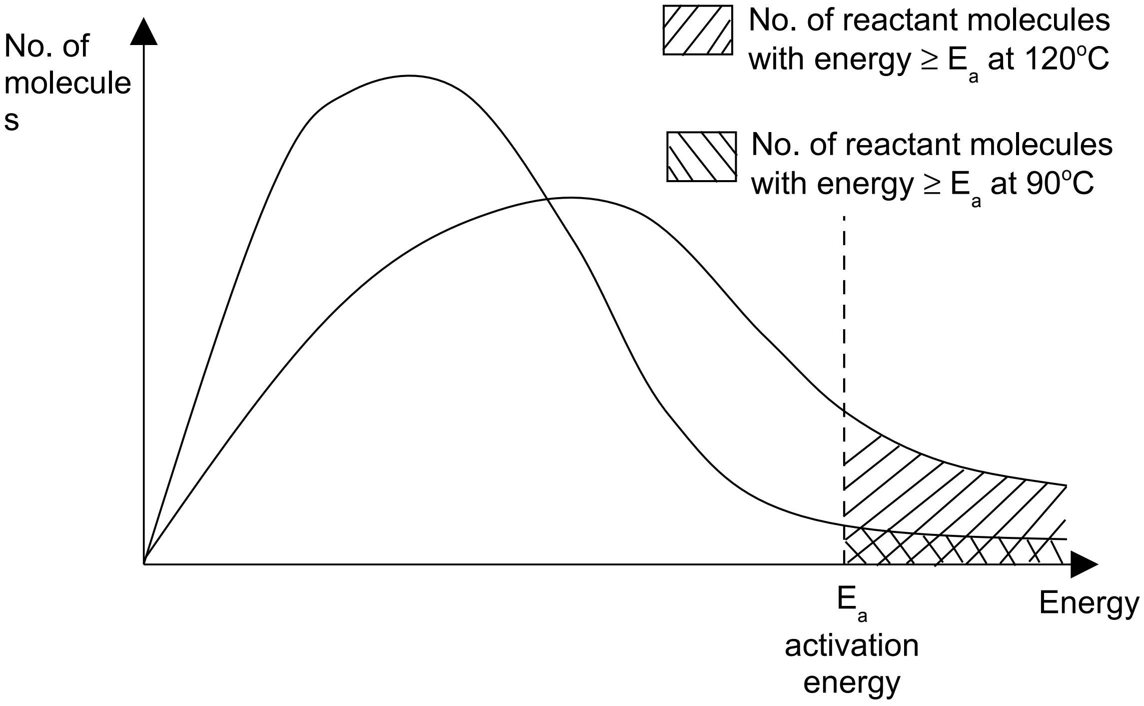


(ii)

- When the pressure of the reaction increases (temperature remaining the same), the rate of reaction remains the same as the reactants are in the aqueous state and are not affected by pressure. Only the rate of reaction for gaseous reactants are affected by changes in pressure.

(c) **(i)**

- Compound **F** is optically active ➔ Compound **F** has at least one chiral centre, no plane of symmetry and non-superimposable mirror images.

- Compounds **E** & **F** do not react with Na metal ➔ Both Compounds **E** & **F** do not have –OH groups ➔ Compounds **E** & **F** are not alcohols

- Compounds **E** & **F** give a positive Tollens' Test ➔ Compounds **E** & **F** are both aldehydes

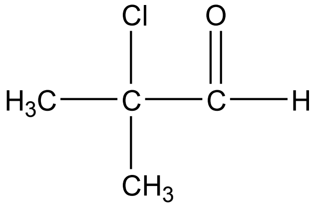
- **E** undergoes nucleophilic substitution with NaOH to form **G**. Since the reaction is first order with respect to **E** but zero order with respect to NaOH ➔ The reaction is an S_N1 reaction

- ➔ E is likely to be a tertiary halogenoalkane and **G** is a tertiary alcohol

- **F** undergoes electrophilic substitution with NaOH to form **H**. Since the reaction is first order with respect to **F** and with respect to NaOH ➔ The reaction is an S_N2 reaction

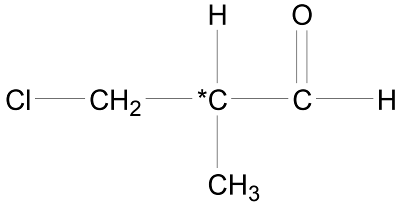
- ➔ **F** is like to be a primary halogenoalkane and **H** a primary alcohol

- **E** is



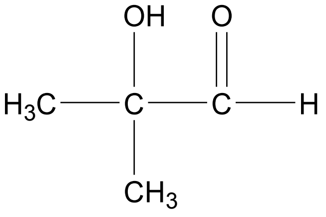
$\mathrm{H_3C-C(Cl)(CH_3)-C(=O)-H}$

- **F** is



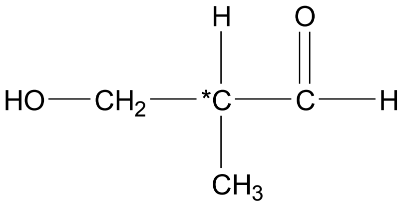
$\mathrm{Cl-CH_2-{}^{*}C(H)(CH_3)-C(=O)-H}$

- **G** is



$H_3C-C(OH)(CH_3)-CHO$

- **H** is



$HO-CH_2-{}^{*}CH(CH_3)-CHO$

(ii) [

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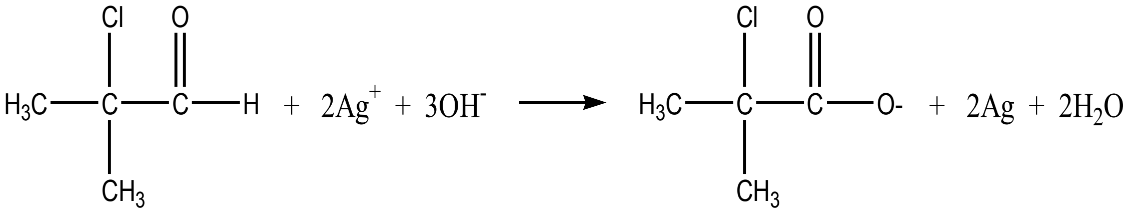
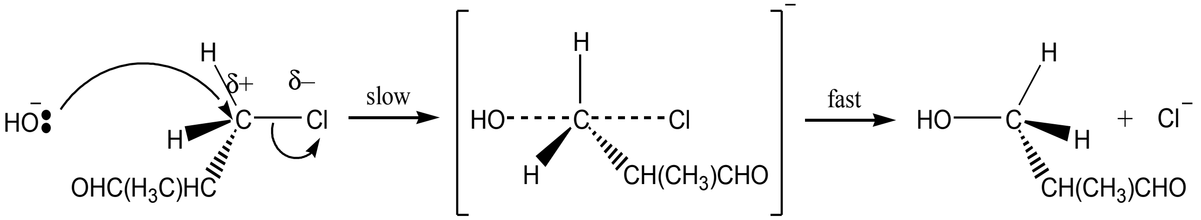


$H_3C-CCl(CH_3)-CHO + 2Ag^+ + 3OH^- \longrightarrow H_3C-CCl(CH_3)-COO^- + 2Ag + 2H_2O$

(d) Mechanism: S_N2 nucleophilic substitution

••



3 **(a)** **(i)**

- At the surface of the sea, pressure of CO_2 is 1 atm (normal atmospheric pressure)

  At 300 m below sea level, the pressure of CO_2 = $\frac{300}{10} + 1$
  = 31 atm

- Solubility of CO_2 300 m below sea level

$$= \frac{31}{1} \times 3.29 \times 10^{-2}$$

$$= 1.02 \text{ mol dm}^{-3}$$

(ii)
(I)

- $[H^+] = \sqrt{K_a \times C}$

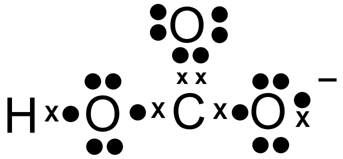
$$= \sqrt{4.5 \times 10^{-7} \times 1.02}$$

$$= 6.77 \times 10^{-4} \text{ mol dm}^{-3}$$

- $pH = -lg(6.77 \times 10^{-4})$

$$= 3.17$$

(II)

- 

(III) • Trigonal planar

(iii)
(I) • $K_{a2} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$

(II)

$$K_{a1} = \frac{[HCO_3^-][H^+]}{[CO_2]}$$

$$= 4.5 \times 10^{-7} \text{ mol dm}^{-3}$$

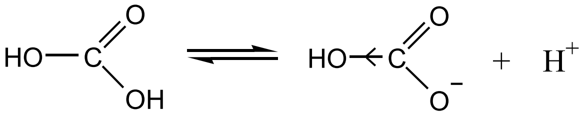
$$K_{a2} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$$

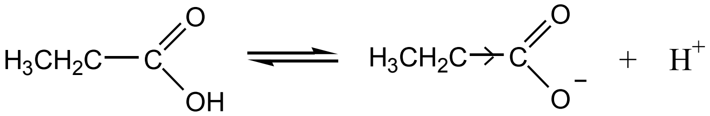
- $= \frac{[HCO_3^-][H^+]}{[CO_2]} \times \frac{[CO_2]}{[H_2CO_3]}$

$$= 4.5 \times 10^{-7} \times 400$$

- $= 1.80 \times 10^{-4} \text{ mol dm}^{-3}$

(III)



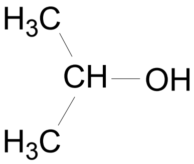


- –OH group on the HCO_3^- ion is electron withdrawing and decreases the negative charge density on the COO^- group making the ion more stable.
- However CH_3CH_2– group on the $CH_3CH_2CO_2^-$ ion is electron releasing and increases the negative charge density on the COO^- group making the ion less stable.

H_2CO_3 thus dissociates more readily to form the more stable HCO_3^- ion, causing it to be a stronger acid.

(b) **(i)** •• dilute HCl or dilute H_2SO_4 , reflux
NaOH(aq) , reflux

(ii) ••
In acid hydrolysis



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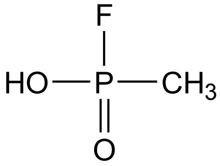
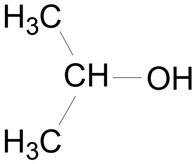


$HO-P(=O)(F)-CH_3$

OR

In alkaline hydrolysis



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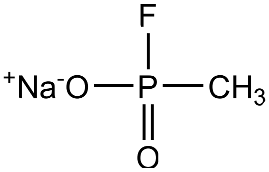


$^{+}Na^{-}O-P(=O)(F)-CH_3$

(iii)
- Less resistant
- P-O bond length is longer than C-O, lower bond energy and easier to break **OR**
  P is more susceptible to nucleophilic attack due to the highly electronegative F.

(iv)

- Carbon, being a period 2 element does not have energetically accessible vacant d-orbitals to allow it to expand its octet structure and accommodate the electrons from fluorine.

(v) •• Any 2 of the following structures

$(CH_3O)PCl_2$ OR
$(CH_3O)_2PCl$ OR
$(CH_3O)P(Cl)(OH)$ OR
$(CH_3O)P(OH)_2$ OR
$(CH_3O)_3P$ OR
$P(Cl_2)(OH)$ OR
$P(OH)_3$

4 (a) (i)

$MgO\ (s) + 2HNO_3\ (aq) \rightarrow Mg(NO_3)_2\ (aq) + H_2O\ (l)$

Amount of MgO = $\frac{0.500}{24.3 + 16.0} = 0.0124$ mol

- Amount of HNO_3 = $\frac{50}{1000} \times 0.100 = 0.00500$ mol (limiting reagent)
- Amount of $Mg(NO_3)_2$ produced = $\frac{0.005}{2} = 0.00250$ mol

(ii)

$Mg(OH)_2 + 2NH_4NO_3 \rightarrow Mg(NO_3)_2 + 2NH_3 + 2H_2O$

- Amount of $Mg(NO_3)_2$ = $\frac{1.5}{24.3 + 28.0 + 96.0} = 0.0101$ mol
- Volume of NH_3 produced = $0.0101 \times 2 \times 24 = 0.485\ dm^3$

(iii)

- $2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$

  Brown gas of NO_2 will be observed.

(iv)

- $Ba(NO_3)_2$ is <u>more thermally stable</u> than $Mg(NO_3)_2$, hence <u>it will not decompose at 330°C.</u>
- Ba^{2+} is <u>less polarizing / lower charge density</u> than Mg^{2+} as it has a <u>larger size</u>, hence the NO_3^- is polarised to a smaller extent in $Ba(NO_3)_2$.

(b) (i)

$\Delta G = \Delta H - T\Delta S$

$\Delta H = \Delta G + T\Delta S$

$= (-473) + 298(-180/1000)$

- $= -526.6$ kJ mol^{-1}

$\Delta H_r = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$

$-526.6 = 3(+85) + 7(-286) + 2(-124) - \Delta H_f(\text{reactants})$

$\Delta H_r(\text{reactants}) = -1468.4$ kJ mol^{-1}

- $y = -1468.4 / 4 = -367.1$

(ii)

- At high temperature, the positive $-T\Delta S$ eventually outweighs negative ΔH, and so $\Delta G = \Delta H - T\Delta S$ becomes positive. (At high temperature, the reaction will be not spontaneous/feasible)

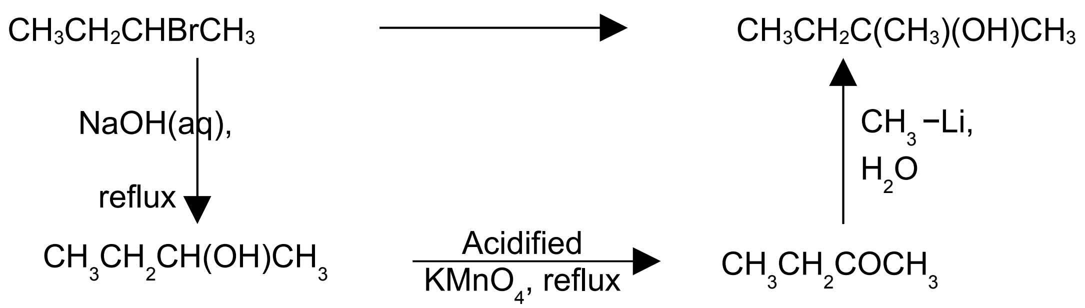
(c) (i)

- Li^+ cation is small in size and highly polarising in nature / has high charge density / has similar charge density to Mg^{2+}. It polarises the CO_3^{2-} anion to a greater extent than other Group I metals allowing it to be decomposed into the oxide and CO_2 like the Group II metals.

(ii)

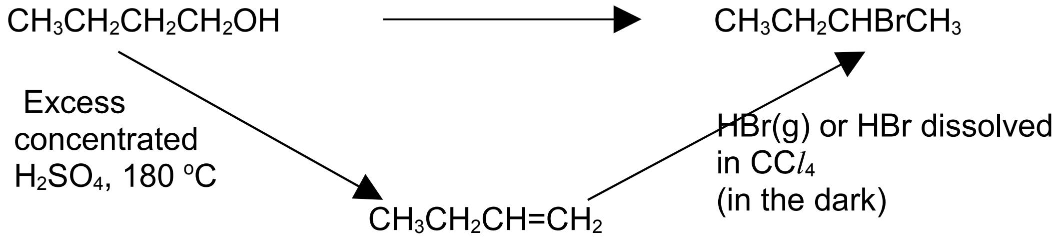
- Nucleophilic addition

(iii)



3m for reagents and conditions, 2m for intermediates.

(iv)



2m for reagents and conditions, 1m for intermediate.

5 **(a)** **(i)**

- Mn is a transition element which forms Mn^{2+} in which the d subshell is partially filled with 5 electrons.
- Water molecule is a ligand and has a lone pair of electrons on O atom that can form a dative bond with the central metal ion Mn^{2+}.

(ii)

- When the ligands approach the central metal ion, splitting of the d-orbitals occur. The energy gap, ΔE between the non-degenerate orbitals corresponds to the wavelength of light in the visible region of the electromagnetic spectrum.
- When d-d transition of electrons takes place, radiation in the visible region of the electromagnetic spectrum corresponding to ΔE is absorbed.
- The light energy not absorbed will be seen as the colour of the complex.

(b) **(i)**

- Empirical formula of **A** = MnO_2

(ii)

- **B = MnO_4^-**
- It is a **disproportionation** reaction
- **$3\ MnO_4^{2-} + 2H_2O \rightarrow 2\ MnO_4^- + MnO_2 + 4OH^-$**

(c) **(i)**

- $5Fe^{2+} \equiv MnO_4^-$
- no. of moles of MnO_4^- = $\frac{1}{5} \times \frac{15}{1000} \times 0.250 = 7.50 \times 10^{-4}$ mol

(ii)

- $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

(iii)

- no. of moles of MnO_4^- reacted with H_2O_2 = $3.00 \times 10^{-3} - 7.50 \times 10^{-4}$
  = 2.25×10^{-3} mol

$5H_2O_2 \equiv 2MnO_4^-$

- no. of moles of H_2O_2 = $\frac{5}{2} \times 2.25 \times 10^{-3} = 5.63 \times 10^{-3}$ mol

  mass of H_2O_2 = $5.63 \times 10^{-3} \times [2(1.0)+2(16.0)] = 0.191\text{g}$

- percentage by mass of H_2O_2 in sample = $\frac{0.191}{5.75} \times 100 = 3.32\%$

(iv)

- no. of moles of O_2 produced = 5.63×10^{-3} mol
- volume of O_2 produced = $5.63 \times 10^{-3} \times 24 = 0.135$ dm^3

(v)

- Number of moles of silver produced = 1.08 / 108 = 1.00×10^{-2} mol
  Since Ag ≡ e, number of moles of electrons transferred = 1.00×10^{-2} mol

- Q = I × time = n × F
  $10 \times (\mathbf{t} \times 60) = 1.00 \times 10^{-2} \times 96500$
  t = 1.61 min

  Number of moles of **manganese** produced = 0.183 / 54.9
  = 0.00333 mol

  $Mn^{x+} + xe \rightarrow Mn$

1.00×10^{-2} mol of electrons liberated 0.00333 moles of Mn
x mol of electrons liberated one mole of Mn.

- therefore x = 1.00×10^{-2} / 0.00333
  = 3