

Paper 3

1 (a) Aluminium has a <u>giant metallic lattice structure</u> [1] and <u>metallic bonding</u> <u>between Al³⁺ ions and a sea of delocalised electrons</u>. [1]



[1] Number of electrons should be 3 times that of Al^{3+} ions

(b) (i) Oxidising agent [1]

(ii) $n(S_2O_3^{2-}) = 17.5 \times 0.1 / 1000 = 0.00175 \text{ mol}$

 $n(I_2)$ in 25.0 cm³ = 0.00175 / 2 = 0.000875 mol [1]

 $n(I_2)$ in 250.0 cm³ = 0.000875 × 10 = 0.00875 mol [1] ecf

 $n(Cu^{2+}) = 0.00875 \times 2 = 0.0175 \text{ mol}$

mass of Cu in alloy = $0.0175 \times 63.5 = 1.11g$

percentage of mass of Cu in alloy = $1.11 / 1.20 \times 100 = 92.6\%$ [1] ecf

(iii) The titre value would be higher. [1]

Without step 3, $\underline{Fe^{3+}}$ ion in the solution will <u>undergo reaction with I⁻</u>, causing <u>more iodine to be produced</u>. [1]

- (c) (i) $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ $\frac{101 \times 1500}{30 + 273} = \frac{81 \times V_2}{23 + 273}$ $V_2 = 1830 \text{ cm}^3$ [1]
 - (ii) The volume will be <u>smaller</u> as CO₂ has <u>significant dispersion forces</u> between molecules. [1]



Note: DO NOT allow hydrogenation and DO NOT allow substitution



- (g) (i) Olympicene is <u>not a planar molecule</u> since it contains a <u>sp³ carbon</u> which has a <u>tetrahedral</u> geometry around this carbon. [1]
 - (ii) 18π electrons [1]
 - (iii) Olympicene has a <u>larger electron cloud size</u> which causes <u>dispersion</u> <u>forces</u> to be much <u>stronger</u> than those in benzene, hence requiring <u>more</u> <u>energy</u> to overcome. [2]
- (h) disproportionation [1]
- **3 (a) (i)** Let the solubility of MgCO₃ and Mg(OH)₂ be x and y respectively in mol dm⁻³.

For MgCO₃ $K_{sp} = [Mg^{2+}][CO_3^{2-}]$ $1.0 \times 10^{-5} = (x)(x)$ $x = 3.16 \times 10^{-3} \text{ mol dm}^{-3}$ [1]

For Mg(OH)₂ $K_{sp} = [Mg^{2+}][OH^{-}]^{2}$ $1.1 \times 10^{-11} = (y)(2y)^{2}$ $y = 1.40 \times 10^{-4} \text{ mol dm}^{-3}$ [1]

- (ii) $[Mg^{2+}][OH^{-}]^2 = 1.1 \times 10^{-11}$ $(3.0 \times 10^{-5})[OH^{-}]^2 = 1.1 \times 10^{-11}$ $[OH^{-}] = 6.06 \times 10^{-4} \text{ mol dm}^{-3}$ [1]
- (iii) CO₃²⁻ ions are added first to precipitate Ca²⁺ as CaCO₃ such that the filtrate contains mainly Mg²⁺ and very little Ca²⁺.[1]

The addition of CO_3^{2-} must be controlled to prevent precipitation of Mg^{2+} as $MgCO_3$ [1]

- (iv) Heat [½] solid Mg(OH)₂ strongly. Mg(OH)₂(s) \rightarrow MgO(s) + H₂O(g) [½]
- (b) (i) $Al : 1s^2 2s^2 2p^6 3s^2 3p^1 [1/_2]$ Mg: $1s^2 2s^2 2p^6 3s^2 [1/_2]$

The <u>3p</u> subshell of Al is <u>further away from the nucleus</u> than the <u>3s</u> subshell. There is weaker attraction between the nucleus and the outermost electron of Al. Hence less energy is needed to remove the 3p electron, resulting in lower ionisation energy. **[1]**

(ii) MgCl₂ dissolves and dissociates in aqueous solution. Mg²⁺ has <u>slightly high</u> <u>charge density</u>. <u>Slight hydrolysis occurs</u>, [½] forming a slightly acidic solution of pH 6.5 [½]

 $MgCl_{2}(s) + 6H_{2}O(l) \rightarrow [Mg(H_{2}O)_{6}]^{2+}(aq) + 2Cl^{-}(aq)$ $[Mg(H_{2}O)_{6}]^{2+}(aq) + H_{2}O(l) \stackrel{\checkmark}{Y} [Mg(H_{2}O)_{5}(OH)]^{+}(aq) + H_{3}O^{+}(aq) [\frac{1}{2}]$

AlCl₃ dissolves in water to form aqueous ions.

 $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^{-}(aq)$



(c) (i) $Q = I x t = n_e x F$

200 x 3 x 3600 = n_e x 96500

ne = (200 x 3 x 3600)/96500 = 22.4 mol [½]

$$Ca^{2+} + 2e^- \rightarrow Ca^-$$

Mass of Ca formed = $\frac{22.4 \times 40.1}{2}$ = 449 g [½]

(ii) From Data Booklet,

 $2H_2O + 2e^- = 2H_2 + 2OH^ E^{\ominus} = -0.83V$ $Ca^{2+} + 2e^- = Ca$ $E^{\ominus} = -2.87 V$ [1]

Since $E^{\ominus}(H_2O/H_2)$ is <u>less negative</u> than $E^{\ominus}(Ca^{2+}/Ca)$, H₂O will be <u>preferentially</u> reduced at the cathode instead of Ca²⁺. No Ca metal will be obtained. [1]

(iv) Possible simple chemical tests to distinguish compounds J and L where J is ethanol (C₂H₅OH) and L has two functional groups (carboxylic acid and ketone):

[3] KMnO₄(aq) with H₂SO₄(aq), heat Purple KMnO₄ decolourised for **J**. Purple colour remains for **L**.





M, **N** or **Q** has a <u>high C:H ratio</u> \Rightarrow contains a <u>benzene</u> ring [0.5]

(d)

Since **M** is <u>neutral</u> and contains N atom, the other functional group present in **A** is likely to be an <u>amide</u> **[0.5]**

M undergoes <u>alkaline hydrolysis</u> **[0.5]** with NaOH(aq) to form salt of **N** and **P** \Rightarrow **M** contains an <u>amide</u>

M undergoes <u>nucleophilic substitution</u> **[0.5]** with NaOH(aq) to form **N** \Rightarrow <u>alcohol</u> is also present in **N** / <u>alkyl chloride</u> present in **M [0.5]**

The <u>alcohol and carboxylic acid</u> [0.5] group in N undergoes <u>condensation</u> (accept esterification) [0.5] when heated with concentrated H_2SO_4 to give a cyclic <u>ester Q</u>. [0.5]

P undergoes <u>oxidative cleavage</u> **[0.5]** with acidified potassium manganate(VII) to form $^+H_3NCH_2CO_2H$ and (CH₃)₂CO. \Rightarrow **Q** contains an <u>alkene</u> **[0.5]**



(ii) Mn can exhibit variable oxidation states due to the <u>close similarity in energy of</u> <u>the 3d and 4s electrons</u>. Hence, once the 4s electrons are removed, some or all the 3d electrons may also be removed without requiring much more energy. [1]

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(accept Br on C-2)



[1] for each correct structure, maximum 4 marks

Accept other possible side-chains for X: –COCOCH₃, –COCH(OH)CH₃

[0.5] for any of these six underlined explanations, maximum 3 marks for explanation]

Maximum total: 6 marks

- U undergoes <u>electrophilic addition</u> of HBr to V; so U contains <u>C=C double</u> bond / is an alkene.
- **U** undergoes <u>mild oxidation</u> with cold alkaline KMnO₄ to form a <u>diol</u> **W**.
- W is further oxidised on warming to form X. As X gives a positive CHI₃ test, it must be a <u>methyl ketone, RCOCH₃, or CH₃CH(OH)R</u>.
- The <u>side-chain oxidation</u> of W and X by hot KMnO₄ gives benzene-1,2dicarboxylic acid.
- (ii) During the electrophilic addition of HBr to the double bond in U, a <u>carbocation</u> is formed (as a reaction intermediate). The geometry about the <u>positively</u> charged carbon is (trigonal) planar, hence it has <u>equal chances of being</u> attacked from the top or bottom by the bromide ion (the nucleophile) in the subsequent step, forming a <u>racemic mixture/equal amounts of both</u> enantiomers, which is optically inactive (since the optical activity of each enantiomer cancels off that of the other). [4 x 0.5]