Assessment Schedule – 2021

Scholarship Chemistry (93102)

Evidence Statement

Q	Evidence	Scholarship Not Awarded	Scholarship	Outstanding Scholarship
ONE (a)	$n(\text{Ca})_{\text{initial}} = \frac{0.185 \text{g}}{40.1 \text{g mol}^{-1}} = 4.61(3466) \times 10^{-3} \text{mol}$ The colourless gas produced in the reaction was hydrogen gas. Calcium hydroxide was also formed in the solution. $\text{Ca(s)} + 2\text{H}_2\text{O}(\ell) \rightarrow \text{Ca}(\text{OH})_2(aq) + \text{H}_2(g)$ $n(\text{Ca}(\text{OH})_2) = n(\text{Ca})$ $c\left(\text{Ca}(\text{OH})_2\right)_{\text{initial}} = \frac{n\left(\text{Ca}(\text{OH})_2\right)}{0.750 \text{L}}$ $= \frac{4.61(3466) \times 10^{-3} \text{mol}}{0.750 \text{L}}$ $= 6.151(288) \times 10^{-3} \text{mol} \text{L}^{-1}$ $[\text{Ca}^{2+}] = [\text{Ca}(\text{OH})_2] = 6.151(288) \times 10^{-3} \text{mol} \text{L}^{-1}$ $[\text{OH}^-] = 2[\text{Ca}(\text{OH})_2] = 1.23(0257) \times 10^{-2} \text{mol} \text{L}^{-1}$ $Q = [\text{Ca}^{2+}][\text{OH}^-]^2$ $= 6.151(288) \times 10^{-3} \text{mol} \text{L}^{-1} \times (1.23(0257) \times 10^{-2} \text{mol} \text{L}^{-1})^2$ $= 9.31 \times 10^{-7}$ $Q < K_8(\text{Ca}(\text{OH})_2); \text{ therefore no precipitate of Ca}(\text{OH})_2 \text{ formed in the first reaction.}$ $n(\text{Ca})_{\text{additional}} = \frac{0.396 \text{g}}{40.1 \text{g mol}^{-1}} = 9.87(531) \times 10^{-3} \text{mol}$ $c\left(\text{Ca}(\text{OH})_2\right)_{\text{additional}} = \frac{n\left(\text{Ca}(\text{OH})_2\right)}{0.750 \text{L}}$ $= \frac{9.87(531) \times 10^{-3} \text{mol}}{0.750 \text{L}}$ $= \frac{9.87(531) \times 10^{-3} \text{mol}}{0.750 \text{L}}$ $= 0.0131(6708) \times 10^{-3} \text{mol} \text{L}^{-1}$	 Any of the following: [Ca²⁺] calculated correctly for either reaction one Q value calculated effect of HCl explained Cu + Cl₂ equation + E^o_{cell} Al + H⁺ equation + E^o_{cell} Al + Cu²⁺ equation + E^o_{cell} Cl⁻ + MnO₄⁻ equation + E^o_{cell} calculates initial buffer pH shows understanding of acid-base conjugate pair concentration changes with addition of HCl. 	TWO of the following: • Justifies two of the reaction observations with completion of calculations with minor errors and/or discussion of equilibrium principles. • Accounts for three of the reactions with support of E°_{cell} calculations, identification of spontaneity and balanced redox equations. • Completes calculations to determine both buffer pH values with minor error.	 Justifies all three reaction observations by correctly calculating both Q values, comparing them with K_s(Ca(OH)₂), and fully discussing equilibrium effects of addition of HCl. Accounts for all four reactions with support of E^o_{cell} calculations, identification of spontaneity, and balanced redox equations. Completes calculations to correctly determine both buffer pH values, and evaluates the final buffer in relation to the intended pH value.

$$\begin{split} [Ca^{2^+}]_{total} &= 6.151(288) \times 10^{-3} \text{ mol } L^{-1} + 0.0131(6708) \text{ mol } L^{-1} \\ &= 0.0193(1837) \text{ mol } L^{-1} \\ [OH^-]_{total} &= 1.23(0257) \times 10^{-2} \text{ mol } L^{-1} + (2 \times 0.0131(6708) \text{ mol } L^{-1}) \\ &= 0.0386(3673) \text{ mol } L^{-1} \\ Q &= [Ca^{2^+}][OH^-]^2 \\ &= 0.0193(1837) \text{ mol } L^{-1} \times (0.0386(3673) \text{ mol } L^{-1})^2 \\ &= 2.88 \times 10^{-5} \end{split}$$

 $Q > K_s(Ca(OH)_2)$; therefore a cloudy white precipitate of Ca(OH)₂ was observed.

Addition of small amounts of dilute HCl increases [H₃O⁺] in the solution. This causes equilibrium (1) to shift to the right, consuming OH⁻ ions in solution.

- (1) $H_3O^+ + OH^- \rightleftharpoons H_2O$
- (2) $Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^{-}$

As [OH⁻] in solution decreases, this causes equilibrium (2) to shift to the right to replace the OH⁻ ions consumed, causing more Ca(OH)₂ to dissolve.

Once $Q \le K_s(Ca(OH)_2)$, all the $Ca(OH)_2$ will have completely dissolved, resulting in a clear solution with no remaining solid.

(b) Any reactions with a positive E°_{cell} value will be spontaneous.

Formation of CuCl₂

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$
 $E^{\circ} = +0.34 \text{ V}$ $Cl_{2}(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$ $E^{\circ} = +1.36 \text{ V}$ $E^{\circ}_{cell} = +1.36 \text{ V} - +0.34 \text{ V} = +1.02 \text{ V}$ $Cu(s) + Cl_{2}(aq) \rightarrow Cu^{2+}(aq) + 2Cl^{-}(aq)$

Reactions with Al

$$Al^{3+}(aq) + 3e^{-} \rightarrow Al(s)$$
 $E^{\circ} = -1.68 \text{ V}$ $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $E^{\circ} = +0.34 \text{ V}$
 $E^{\circ}_{\text{cell}} = +0.34 \text{ V} - -1.68 \text{ V} = +2.02 \text{ V}$
 $2Al(s) + 3Cu^{2+}(aq) \rightarrow 3Cu(s) + 2Al^{3+}(aq)$
 $Al^{3+}(aq) + 3e^{-} \rightarrow Al(s)$ $E^{\circ} = -1.68 \text{ V}$ $2H^{+}(aq) + 2e^{-} \rightarrow H_{2}(g)$ $E^{\circ} = 0.00 \text{ V}$
 $E^{\circ}_{\text{cell}} = 0.00 \text{ V} - -1.68 \text{ V} = +1.68 \text{ V}$
 $2Al(s) + 6H^{+}(aq) \rightarrow 3H_{2}(g) + 2Al^{3+}(aq)$

Reaction with KMnO₄

$$\begin{split} & \text{MnO}_4^-(aq) + 4\text{H}^+(aq) + 3\text{e}^- \to \text{MnO}_2(s) + 2\text{H}_2\text{O}(l) \quad E^\circ = +1.69 \text{ V} \\ & \text{Cl}_2(g) + 2\text{e}^- \to 2\text{Cl}^-(aq) \quad E^\circ = +1.36 \text{ V} \\ & E^\circ_{\text{cell}} = +1.69 \text{ V} - +1.36 \text{ V} = +\textbf{0.33 V} \\ & 2\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 6\text{Cl}^-(aq) \to 2\text{MnO}_2(s) + 4\text{H}_2\text{O}(l) + 3\text{Cl}_2(g) \end{split}$$

(c)
$$n(CH_3NH_5CI)_{minis} = \frac{m}{M} = \frac{0.1918 \text{ g}}{67.5 \text{ g mol}^{-1}} = 2.84(148) \times 10^3 \text{ mol}$$
 $n(CH_3NH_5)_{minis} = eV = 0.0250 \text{ mol } L^{-1} \times 0.050 \text{ L} = 1.25 \times 10^3 \text{ mol}$ $pH = pK_4 + \log \frac{m(CH_3NH_5)}{m(CH_1NH_5)}$ OR: $[CH_3NH_5] = \frac{12.5 \times 10^3 \text{ mol}}{0.05 \text{ L}} = 0.025 \text{ mol } L^{-1}$ $[CH_3NH_5] = \frac{12.5 \times 10^3 \text{ mol}}{0.05 \text{ L}} = 0.025 \text{ mol } L^{-1}$ $[CH_3NH_5] = \frac{10.64 + 0.3566(345)}{0.051} = \frac{10.64 + -0.3566(345)}{0.052} = \frac{10.0568 \text{ mol } L^{-1}}{0.0568 \text{ mol } L^{-1}}$ $[CH_3NH_5] = \frac{10.304 + 0.031 \text{ mol}}{0.054 \times 10^{-3} \text{ mol}} = \frac{10.57 \times 10^{-3} \text{ mol}}{0.058 \times 10^{-3} \text{ mol}} = 0.0568 \text{ mol } L^{-1}$ $[CH_3NH_5] = \frac{10.59 \times 10^{-3} \text{ mol}}{0.0568 \text{ mol } L^{-1}}$ $[CH_3NH_5]_{minis} = 1.25 \times 10^3 \text{ mol} + 4.15 \times 10^4 \text{ mol}} = 3.25 \times 10^4 \text{ mol}}$ $n(CH_3NH_5)_{minis} = 1.25 \times 10^3 \text{ mol} + 4.15 \times 10^4 \text{ mol}} = 3.35 \times 10^4 \text{ mol}}$ $n(CH_3NH_5)_{minis} = 2.84(148) \times 10^3 \text{ mol}} + 4.15 \times 10^4 \text{ mol}} = 3.25(648) \times 10^3 \text{ mol}}$ $n(CH_3NH_5)_{minis} = 2.84(148) \times 10^3 \text{ mol}} + 4.15 \times 10^4 \text{ mol}} = 3.25(648) \times 10^3 \text{ mol}}$ $n(CH_3NH_5)_{minis} = 2.84(148) \times 10^3 \text{ mol}} + 4.15 \times 10^4 \text{ mol}} = 3.25(648) \times 10^3 \text{ mol}}$ $n(CH_3NH_5)_{minis} = 2.84(148) \times 10^3 \text{ mol}} + 4.15 \times 10^4 \text{ mol}} = 0.0139(17) \text{ mol } L^{-1}$ $n(CH_3NH_5)_{minis} = \frac{8.35 \times 10^4 \text{ mol}}{0.064} = 0.0139(17) \text{ mol } L^{-1}$ $n(CH_3NH_5)_{minis} = \frac{8.35 \times 10^4 \text{ mol}}{0.064} = 0.0139(17) \text{ mol } L^{-1}$ $n(CH_3NH_5)_{minis} = \frac{8.35 \times 10^4 \text{ mol}}{0.064} = 0.0139(17) \text{ mol } L^{-1}$ $n(CH_3NH_5)_{minis} = \frac{8.35 \times 10^4 \text{ mol}}{0.064} = 0.0139(17) \text{ mol } L^{-1}$ $n(CH_3NH_5)_{minis} = \frac{8.35 \times 10^4 \text{ mol}}{0.064} = 0.00542(7) \text{ mol } L^{-1}$ $n(CH_3NH_5)_{minis} = \frac{8.35 \times 10^4 \text{ mol}}{0.064} = 0.00542(7) \text{ mol } L^{-1}$ $n(CH_3NH_5)_{minis} = \frac{8.35 \times 10^4 \text{ mol}}{0.064} = 0.00542(7) \text{ mol } L^{-1}$ $n(CH_3NH_5)_{minis} = \frac{8.35 \times 10^4 \text{ mol}}{0.064} = 0.00542(7) \text{ mol } L^{-1}$ $n(CH_3NH_5)_{minis} = \frac{8.35 \times 10^4 \text{ mol}}{0.064} = 0.00542(7) \text$

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• The technician did not add enough HCl(aq) to reach the intended pH value, but did get rather close.		

Q	Evidence		Scholarship Not Awarded	Scholarship	Outstanding Scholarship
TWO (a)	n(H ₂ C ₂ O ₄) _{flask} n(H ₂ C ₂ O ₄) _{solution} m(H ₂ C ₂ O ₄) _{solution} Determination of Cl n(NaOH) n(H ₃ O ⁺) _{aliquot} n(H ₃ O ⁺) _{flask} n(CH ₃ COOH) _{flask} n(CH ₃ COOH) _{solution} m(CH ₃ COOH) _{solution}	= $0.0296 \text{ mol } L^{-1} \times 0.01893 \text{ L}$ = $5.603(28) \times 10^{-4} \text{ mol}$ = $5.603(28) \times 10^{-4} \text{ mol} \times \frac{5}{2}$ = $1.400(82) \times 10^{-3} \text{ mol}$ = $1.400(82) \times 10^{-3} \text{ mol} \times 10$ = $0.01400(82) \text{ mol} \times 5$ = $0.0700(41) \text{ mol} \times 90.0 \text{ g mol}^{-1}$ = $6.303(69) \text{ g}$ H ₃ COOH = $0.4790 \text{ mol } L^{-1} \times 0.01332 \text{ L}$ = $6.380(28) \times 10^{-3} \text{ mol}$ = $6.380(28) \times 10^{-3} \text{ mol}$ = $6.380(28) \times 10^{-3} \text{ mol} \times 10$ = $0.06380(28) \text{ mol}$ = $n(\text{CH}_3\text{COOH})_{\text{flask}} + 2 \times n(\text{H}_2\text{C}_2\text{O}_4)_{\text{flask}}$ = $n(\text{H}_3\text{O}^+)_{\text{flask}} - 2 \times n(\text{H}_2\text{C}_2\text{O}_4)_{\text{flask}}$ = $0.06380(28) \text{ mol} - 2 \times 0.01400(82) (41) \times 10^{-3} \text{ mol}$ = $0.03578(64) \text{ mol} \times 5$ = $0.1789(32) \text{ mol} \times 60.0 \text{ g mol}^{-1}$ = $10.73(592) \text{ g}$ aCl = 2.13 g	Any of the following: • [H ₂ C ₂ O ₄] in diluted sample • [CH ₃ COOH] in diluted sample • correct mass for any of the three substances in the original sample • enthalpy changes explained for either compound • entropy changes to the solute, solvent, or solution explained for either compound • logical reason provided for variation in solubilities of NaCl and CaCO ₃ , with links to K _s values • correct Lewis diagram and/or identification of lone pair of electrons on I atom • see-saw shape drawn, based on trigonal bipyramidal electron cloud arrangements • explanation given using VSEPR theory to justify a 3D structure.	 TWO of the following: Calculates masses for two of the substances present in the original sample, with minor errors. Explanation given for the comparative solubilities of NaCl and CaCO₃ with consideration of the enthalpy and entropy changes occurring when the compounds dissolve. A number of 3D shapes for the arrangement of atoms in IF₂O₂⁻ ions are drawn, and one arrangement logically justified based on correct VSEPR theory. 	 TWO of the following: Correctly calculates the masses of H₂C₂O₄, CH₃COOH, and NaCl in the original sample. Comprehensively justifies the comparative solubilities of NaCl and CaCO₃ by discussing the enthalpy and entropy changes occurring in the dissolution of the ionic compounds, with links to the charges on the ions. All possible 3D shapes for the arrangement of atoms in IF₂O₂⁻ ions are drawn, including acknowledgement of I=O double bonds and justification of the correct bonding arrangement based on VSEPR theory.

For a process to be spontaneous there must be an overall increase in the total entropy of the system and the surroundings ($\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$). The enthalpy of solution for NaCl is positive and not favourable, as it results in a decrease in surroundings entropy. For NaCl to have a relatively high solubility there must be a favourable (positive) change in system entropy. The enthalpy of solution for CaCO₃ is negative and favourable as it results in an increase in surroundings entropy. For CaCO₃ to have a relatively low solubility there must be either only a small increase, or a decrease in the system entropy. The dissolving of both **solutes** will contribute towards an **increase** in system entropy, as in each case two mols of aqueous ions are released in the dissociation, and there is a greater degree of randomness in the arrangement of the ions in solution versus the ions in a fixed solid lattice. There will be a **decrease** in system entropy for the **solvent** in each case, as when the **solution** is formed, the randomness of H₂O molecules decreases with the formation of more ordered complex ions/hydration shells around the positive and negative ions. For NaCl, the Na⁺ and Cl⁻ ions are small and have low charge, so will attract only a small number of H₂O molecules, resulting in a relatively small reduction in the solvent entropy, and thus the system entropy. The entropy increase due to the dissolving of the solute will not be offset much, giving an overall large system **entropy change** (sufficient enough to offset the decrease in surroundings entropy) giving a large ΔS_{total} , and **high** solubility. For CaCO₃, the stronger attractive forces between the larger and more highly charged Ca²⁺ and CO₃²⁻ ions and H₂O molecules result in a greater number of H₂O molecules being arranged around the ions, and a larger reduction in solvent entropy. The solute entropy increase will be offset to a greater extent, leading to an overall lower system entropy change, smaller ΔS_{total} , and lower solubility for CaCO₃.

(c)(i)	F	0_	0	_	_
	F O : O : O) 		0=ï	0=ï
	[`O	∥ `F	`F	0- - -	[,O

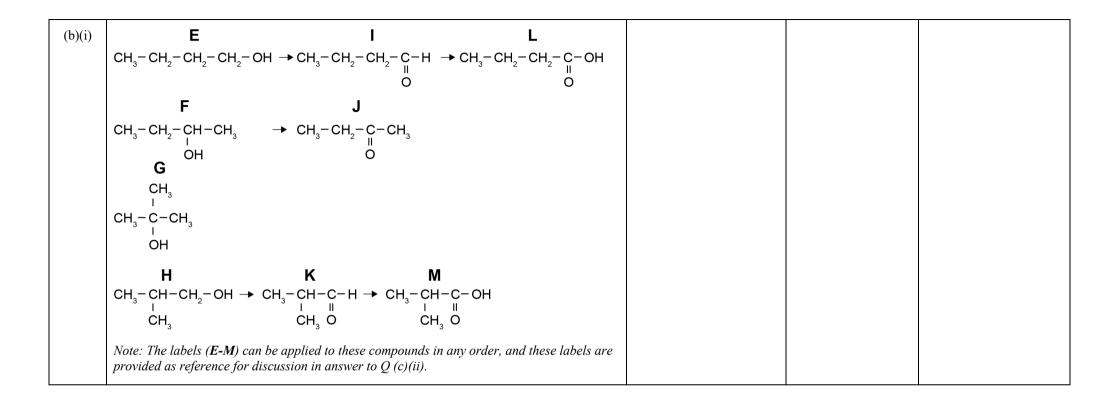
(ii) The lone electron pairs have the greatest repulsion and therefore will occupy equatorial positions to achieve the greatest bond angle with bonding electron pairs, leading to a see-saw shaped molecule.

The I=O double bonds have greater electron-electron repulsion than the I-F single bonds, so will also occupy equatorial positions with bond angles of 120°.

The first structure above will be the most probable molecular geometry.

Q Evi	ridence	Scholarship Not Awarded	Scholarship	Outstanding Scholarship
n(C) n(C) n(C) n(C) n(C) n(C) n(C) n(C)	$\begin{aligned} \text{(C)} &= 0.1952 \times 12 \text{ g mol}^{-1} = 2.343 \text{ g} \\ \text{(H2O)} &= \frac{m}{M} = \frac{4.410 \text{ g}}{18 \text{ g mol}^{-1}} \\ &= 0.2450 \text{ mol} \\ \text{(H)} &= 2 \times n(\text{H2O}) = 2 \times 0.245 \text{ mol} = 0.4900 \text{ mol} \\ \text{(H)} &= 0.4900 \text{ mol} \times 1 \text{ g mol}^{-1} = 0.4900 \text{ g} \\ \text{(O)} &= 4.388 \text{ g} - (2.343 \text{ g} + 0.4900 \text{ g}) = 1.555 \text{ g} \\ 1.555 \text{ g} \end{aligned}$	 Any of the following: calculates an incorrect molecular formula but aspects of calculations are correct draws some potential diol and alkene, or alcohol and carboxylic acid structures for Compounds X and W identifies the correct structures for alcohols E-H identifies the structures of three oxidation products I-M explains distillation fractions in relation to intermolecular attractions explains variation in H-bonding between molecules determines an ester structure for Compound M explains reaction conditions for ester synthesis. explains ¹³C NMR peaks and/or bonding environments. 	TWO of the following: • Determines the correct molecular formula for Compound X (C4H10O2), and draws an alkene and diol structure for Compounds W and X. • Draws the structural formulae for most of Compounds E-M, and justifies the order that different compounds will separate under distillation with reference to H-bonding or molecular packing. • Determines an ester structure for Compound M, with explanation of reaction conditions and ¹³ C NMR peaks, with minor omissions.	 Determines the correct molecular formula for Compound X (C₄H₁₀O₂) with clearly detailed working, and draws all potential structures for Compounds W and X. Draws the structural formulae for all of Compounds E-M, and comprehensively justifies the order in which the compounds will separate under distillation, with clear links to H-bonding and molecular packing. Determines the correct ester structure for Compound M, explains the reaction conditions required, and clearly justifies the ¹³C NMR peaks with links to equivalent carbon bonding environments.

(ii)	Compound \mathbf{X} (C ₄ H ₁₀ O ₂) can only be a diol molecule. This will be formed from reaction of an alkene (Compound \mathbf{W}) with H ⁺ /MnO ₄ ⁻ . Possible isomers for \mathbf{X} and \mathbf{W} are:		
	$CH_3 - CH_2 - CH = CH_2 \xrightarrow{H^+/MnO_4^-} CH_3 - CH_2 - CH - CH_2$ $OH OH$		
	$CH_{3}-CH=CH-CH_{3}\xrightarrow{H^{+}/MnO_{4}^{-}}CH_{3}-CH-CH-CH_{3}$ $OH OH$		
	$ \begin{array}{ccc} CH_{3} & CH_{3} \\ CH_{3}-C=CH_{2} & \xrightarrow{H^{+}/MnO_{4}^{-}} & CH_{3}-C-CH_{2} \\ & & & & & & & & & & & \\ CH_{3}-C=CH_{2} & \xrightarrow{H^{+}/MnO_{4}^{-}} & CH_{3}-C-CH_{2} \\ & & & & & & & & & & & \\ & & & & & & &$		



(ii) **Distillation**

The temperature that each compound will boil at is dependent on the strength of the attractive forces between the compounds. This is affected by the functional groups present, the ability for those functional groups to form hydrogen bonds with other molecules, and whether the molecules are straight-chain or branched-chain molecules. Branched-chain molecules sit further apart from each other (do not pack as well) and, as a result, have weaker attractive forces that require less energy to overcome.

Compounds **I**, **J**, **K**: The aldehyde and ketone compounds do not form hydrogen-bonds between molecules, so will boil off first. Compound **K** with the branched chain will have the lowest boiling point of the three. Compounds **I** and **J** will have very similar boiling points, and boil off next.

Compounds \mathbf{E} , \mathbf{F} , \mathbf{G} , \mathbf{H} : The alcohol compounds will boil off next, due to the hydrogen-bonds that form between molecules with the presence of the $-\mathrm{OH}$ functional group. Compound \mathbf{G} is a tertiary alcohol with the most branched structure, so will have the lowest boiling point due to the weakest intermolecular attractions. Compound \mathbf{F} is a secondary alcohol and will boil next, due to weaker hydrogen-bonding between molecules. Compound \mathbf{H} and Compound \mathbf{E} are both primary alcohols so will separate last. Compound \mathbf{H} is a branched chain molecule that cannot pack as close as Compound \mathbf{E} , so will boil next. Compound \mathbf{E} will have the highest boiling point of the alcohols, due to having the least branched structure and, therefore, the strongest intermolecular attractions.

Compounds \mathbf{L} , \mathbf{M} : The carboxylic acid compounds will boil off last, due to increased hydrogen-bonding and dimerisation of carboxylic acid molecules with the presence of the carboxylic acid functional groups. Compound \mathbf{M} will have a lower boiling point than Compound \mathbf{L} , due to the branched-chain molecules not packing as closely together, therefore having weaker attractions.

(iii) Compound N can be synthesised from Compounds G and M.

Compound N is an ester that can be synthesised from either the carboxylic acid and alcohol directly, using concentrated sulfuric acid, $H_2SO_4(conc)$ and heat to catalyse the reaction, or by first reacting the carboxylic acid into an acyl chloride, then reacting it with the alcohol compound without the use of a catalyst or heat.

Due to some carbons being bonded to the same group, only five unique carbon environments exist in the final compound. At one end of the molecule, three CH₃ groups are in identical bonding environments. At the other end of the molecule, two CH₃ groups are in identical bonding environments. The remaining carbon atoms in the molecule are each in unique bonding environments.

Q	Evidence	Scholarship Not Awarded	Scholarship	Outstanding Scholarship
FOUR (a)	Reaction with HCl(aq): $S_2O_3^{2-} + 6H^+ + 4e^- \rightarrow 2S + 3H_2O$ $S_2O_3^{2-} + H_2O \rightarrow 2SO_2 + 2H^+ + 4e^-$ $2S_2O_3^{2-} + 4H^+ \rightarrow 2SO_2 + 2S + 2H_2O$ $S_2O_3^{2-} + 2H^+ \rightarrow SO_2 + S + H_2O$ The oxidation state of S both increases and decreases in this reaction, and thus $S_2O_3^{2-}$ is acting as both the oxidant and reductant (disproportionation). The oxidation number of S increased from +2 in $S_2O_3^{2-}$ to +4 in SO_2 , indicating a loss of electrons and oxidation. The oxidation number of S decreased from +2 in $S_2O_3^{2-}$ to 0 in S, indicating a gain of electrons and reduction. Reaction with HNO3(conc): $S_2O_3^{2-} + 6H^+ + 4e^- \rightarrow 2S + 3H_2O$ $S_2O_3^{2-} + 6H^+ + 4e^- \rightarrow 2S + 3H_2O$ $S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8e^-$ $2S_2O_3^{2-} + 2H_2O \rightarrow 2SO_4^{2-} + 2S + 4H^+ + 4e^-$ $HNO_3 + H^+ + e^- \rightarrow NO_2 + H_2O$ $4HNO_3 + S_2O_3^{2-} \rightarrow 4NO_2 + 2SO_4^{2-} + 2S + 2H_2O$ $2HNO_3 + S_2O_3^{2-} \rightarrow 2NO_2 + SO_4^{2-} + S + H_2O$ (simplified) The oxidation state of S both increases and decreases in this reaction (disproportionation), so $S_2O_3^{2-}$ is acting as both an oxidant and reductant, while the oxidation state of N is also decreasing, making it also an oxidant in the reaction. The oxidation number of S increased from +2 in $S_2O_3^{2-}$ to +6 in SO_4^{2-} , indicating a loss of electrons and oxidation. The oxidation number of S decreased from +2 in $S_2O_3^{2-}$ to 40 in S, indicating a gain of electrons and reduction. The oxidation number of N decreased from +5 in HNO ₃ to +4 in NO ₂ , indicating a gain of electrons and reduction.	 Any of the following: correct balanced equation for H⁺ + S₂O₃²⁻ reaction correct balanced equation for HNO₃ + S₂O₃²⁻ reaction oxidant(s) and reductant(s) for one reaction correct with links to oxidation number changes Δ_tH^o calculated for CsF₂ with minor error variation in Δ_{lat}H^o values explained structures determined for two of Compounds A-D explanation given for one structure with links to spectroscopic data. 	 Fully accounts for either of the redox reactions with correct balanced equation, identification of oxidant(s) and reductant(s), and justification using changes in oxidation numbers. Calculates Δ_tH^o for CsF₂ with minor error, and discusses reasons for variation in either the Δ_tH^o or Δ_{lat}H^o values for CsF and CsF₂. Determines a structure and name for three of Compounds A-D, with some justification of spectroscopic data. 	 TWO of the following: Fully accounts for both redox reactions including correct balanced equations, identification of oxidant(s) and reductant(s), and justification using changes in oxidation numbers. Calculates Δ_tH^o for CsF₂ and discusses reasons for variation in Δ_tH^o and Δ_{lat}H^o values for CsF and CsF₂. Determines a structure and name for each of Compounds A-D, with detailed justification of spectroscopic data.

(b)(i)	$\Delta_{f}H^{\circ}(CsF_{2}) = \Delta_{at}H^{\circ}(Cs) + \Delta_{BE}H^{\circ}(F_{2}) + \Delta_{IE}H^{\circ}(Cs) + \Delta_{IE}H^{\circ}(Cs^{+}) + 2 \times \Delta_{EA}H^{\circ}(F) - 2\Delta_{lat}H^{\circ}(CsF_{2})$ $= 76.0 + 158 + 382 + 2430 + 2 \times -334 + -2347$ $= +31 \text{ kJ mol}^{-1}$		
	The enthalpy of formation for CsF is exothermic and more favourable than the enthalpy of formation for CsF ₂ , which is endothermic. This will be due to Cs being located in Group 1 of the periodic table, with only one valence electron. The first ionisation energy for Cs (+383 kJ mol ⁻¹) is considerably less than the second ionisation energy for Cs (+2430 kJ mol ⁻¹), based on removal of electrons from the 6s versus 5p orbitals. Therefore, the second ionisation enthalpy value makes the energy requirements prohibitive towards the formation of CsF ₂ .		
(ii)	The lattice enthalpy value for CsF_2 is more negative (exothermic) due to the greater electrostatic attraction between the F^- ions and Cs^{2+} ions compared with Cs^+ ions. The increased charge density in the Cs^{2+} ions attracts the F^- ions better and, therefore, the ionic bonds formed are stronger. Cs^{2+} ion is smaller than Cs^+ ion which increases the strength of the bond formed.		

(c) Molecular Formula: C₄H₈O₂

Compound A

IR data: O-H bond stretch above 3000 cm⁻¹ (indicates alcohol / acid), C=O bond stretch around 1700 cm⁻¹ (indicates ketone / aldehyde / acid / ester).

¹³C NMR data: 4 peaks, four unique C-environments, one above 200 ppm (indicates C=O from ketone), one at around 60 ppm (indicates C=OH from alcohol).

Key summary points: Evidence indicates separate –OH and C=O functional groups, four distinct carbon environments.

Possible structure(s): 1-hydroxybutan-2-one, 4-hydroxybutan-2-one, 2-hydroxybutanal, 3-hydroxybutanal, 4-hydroxybutanal, 3-hydroxybutan-2-one

Compound B

IR data: C=O bond stretch around 1700 cm⁻¹ (indicates acid / aldehyde / ketone / ester), no O–H stretch present (indicates not alcohol / acid).

¹³C NMR data: 3 peaks, three unique C-environments, one at 160 ppm (indicating C=O from ester / acid) and another at around 60 ppm (indicating C-O from alcohol / ester).

Key summary points: Evidence indicates an ester molecule with two equivalent carbons to give three carbon environments.

Possible structure(s): methylethyl methanoate

Compound C

IR data: O-H stretch above 3000 cm⁻¹ (indicates alcohol), no C=O stretch present in spectra (eliminates aldehyde / acid / ester / ketone).

¹³C NMR data: 2 peaks, two unique C-environments, one at 60 ppm (indicates alcohol), and one at 130 ppm (indicates C=C from alkene).

Key summary points: Evidence indicates the molecule has two pairs of identical carbons, with alkene and alcohol functional groups, likely diol to give molecular formula and symmetry.

Possible structure(s): **but-2-en-1,4-diol**

Compound D

IR data: O-H stretch around 3000 cm⁻¹, very wide (indicates -OH from carboxylic acid), C=O stretch around 1700 cm⁻¹ (indicating acid / aldehyde / ketone / ester).

¹³C NMR data: 3 peaks, three unique C-environments, with one around 180 ppm (indicating carboxylic acid).

Key summary points: Evidence indicates two eqivalent carbons in the molecule to fit molecular formula, and the presence of a carboxylic acid functional group. Molecule must be a branched-chain carboxylic acid.

Possible structure(s): methylpropanoic acid

Cut Scores

Scholarship	Outstanding Scholarship
17 – 24	25 – 32