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93102



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# TOP SCHOLAR



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## Scholarship 2021 Chemistry

Time allowed: Three hours  
Total score: 32

Check that the National Student Number (NSN) on your admission slip is the same as the number at the top of this page.

You should answer ALL the questions in this booklet.

Pull out Resource Booklet 93102R from the centre of this booklet.

Show ALL working.

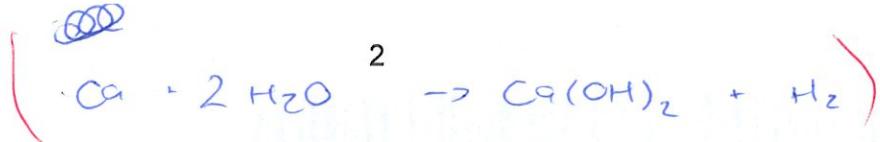
If you need more room for any answer, use the extra space provided at the back of this booklet.

Check that this booklet has pages 2–20 in the correct order and that none of these pages is blank.

**YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.**

Question	Score
ONE	
TWO	
THREE	
FOUR	
<b>TOTAL</b>	

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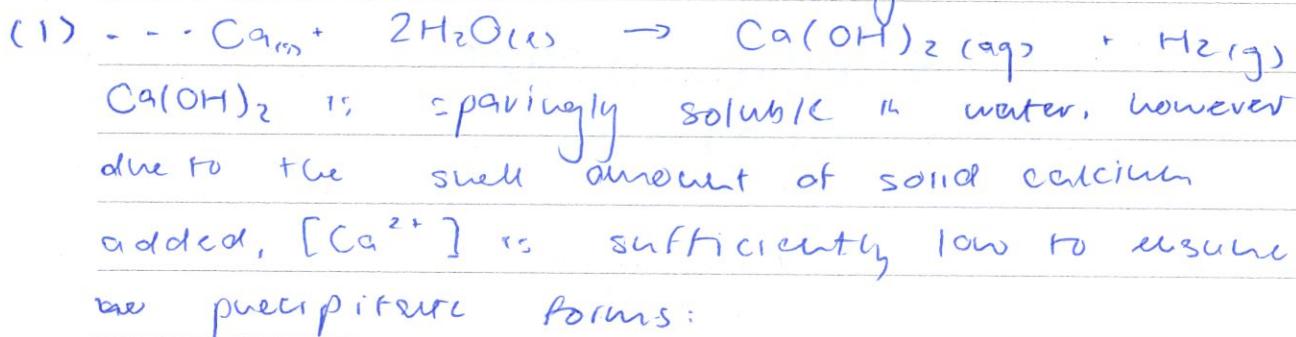
## QUESTION ONE

- (a) A small 0.185 g piece of calcium metal,  $\text{Ca}(s)$ , was dropped into a large beaker containing 750.0 mL of distilled water at 25 °C. It spontaneously reacted, producing a colourless gas and a clear, colourless solution. When a further two pieces of calcium metal, with a combined mass of 0.396 g, were then added to the same beaker, they also spontaneously reacted to produce a colourless gas, but a cloudy white solid was observed forming in the solution as the metal pieces reacted. Addition of a small volume of dilute hydrochloric acid solution,  $\text{HCl}(aq)$ , caused the solution to become clear.

Justify these observations with use of calculations, balanced chemical equations, and equilibrium principles.

$$K_s(\text{Ca(OH)}_2) = 6.40 \times 10^{-6}$$

Initially, calcium reacted to form a clear  $\text{Ca(OH)}_2$  solution and colourless  $\text{H}_2$  gas:



$$n(\text{Ca}) = 0.185 \text{ g} / 40.1 \text{ g mol}^{-1} = 4.613 \times 10^{-3} \text{ mol}$$

$$[\text{Ca}^{2+}] = 4.613 \times 10^{-3} \text{ mol} / 0.75 \text{ L} = 6.151 \times 10^{-3} \text{ mol L}^{-1}$$

$$[\text{OH}^-] = 10^{-7} + 2 \times 6.151 \times 10^{-3} = 0.01230 \text{ mol L}^{-1}$$

$$Q_s(\text{Ca(OH)}_2) = [\text{Ca}^{2+}][\text{OH}^-]^2 = 6.151 \times 10^{-3} \times (0.0123)^2 \\ = 9.31 \times 10^{-7} \quad | < 6.4 \times 10^{-6}$$

As  $Q_s < K_s$ , no  $\text{Ca(OH)}_2$  precipitate will form, so solution remains colourless.

As more Ca is added, the same reaction (1), occurs, however the increase in both  $[\text{Ca}^{2+}]$  and  $[\text{OH}^-]$  as a result sees the with  $\text{Ca(OH)}_{(s)}$  precipitate form and the solution turn cloudy:

$$n(\text{Ca})_{\text{tot}} = 0.531 \text{ g} / 40.1 \text{ g mol}^{-1} = 0.01327 \text{ mol}$$

$$[\text{Ca}^{2+}] = 0.01327 \text{ mol} / 0.75 \text{ L} = 0.0177 \text{ mol L}^{-1}$$

$$[\text{OH}^-] = 2 \times 0.01932 = 0.03864 \text{ mol L}^{-1}$$

$$Q_s(\text{Ca(OH)}_2) = 0.01932 \times 0.03864^2 = 2.384 \times 10^{-5}$$

As  $Q_s > K_s$ , solution is over saturated, ~~so the~~  
solvability equilibrium.



~~This is the right~~, will favour the reactants)

precipitation of  $\text{Ca}^{2+}$  and  $\text{OH}^-$  out of solution  
to form  $\text{Ca(OH)}_2$  to return the system to  
equilibrium.

HCl reacts with  $\text{OH}^-$  in solution to form  $\text{H}_2\text{O}$ :



Hence,  $[\text{OH}^-]$  will decrease. In the solvability equilibrium (2), this will cause the reaction  
to favour the products / the dissolution of  
 $\text{Ca(OH)}_{2(\text{aq})}$  to replace the rest  $\text{OH}^-$ . Hence  
the white  $\text{Ca(OH)}_{2(s)}$  precipitate will dissolve,  
causing the cloudy white solution to turn  
clear //

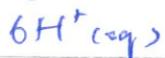
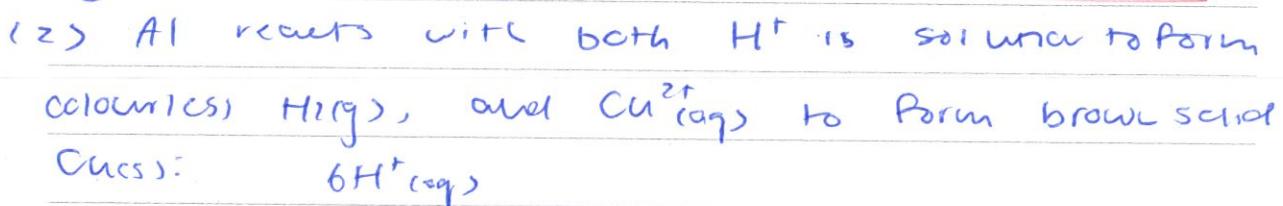
- (b) A pale-blue, weakly acidic copper(II) chloride solution,  $\text{CuCl}_2(aq)$ , was prepared by sitting a piece of copper metal,  $\text{Cu}(s)$ , in a beaker containing chlorine water,  $\text{Cl}_2(aq)$ . When pieces of aluminium foil,  $\text{Al}(s)$ , were added to a sample of the solution, the pieces of foil slowly disappeared as a colourless gas and brown solid were produced. When potassium permanganate,  $\text{KMnO}_4(s)$ , was added to a separate sample of the solution, a brown solid and pale-green gas were produced.

Using the standard electrode potentials provided in the table below, justify the reactions described above with use of balanced chemical equations and cell potential calculations.

	$E^\circ / \text{V}$
$2\text{H}^+(aq) + 2\text{e}^- \rightarrow \text{H}_2(g)$	0.00
$\text{Cl}_2(g) + 2\text{e}^- \rightarrow 2\text{Cl}^-(aq)$	+1.36
$\text{Al}^{3+}(aq) + 3\text{e}^- \rightarrow \text{Al}(s)$	-1.68
$\text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(l)$	+1.23
$\text{MnO}_4^-(aq) + 4\text{H}^+(aq) + 3\text{e}^- \rightarrow \text{MnO}_2(s) + 2\text{H}_2\text{O}(l)$	+1.69
$\text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu}(s)$	+0.34



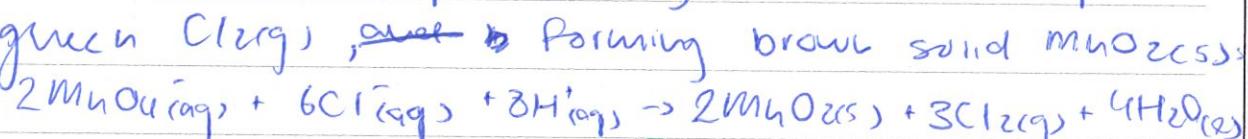
$$\text{E}_{\text{cu}} = +1.36 - 0.34 = +1.02 \text{ V} > 0, \text{ so the reduction of Cu with respect to blue } \text{Cu}^{2+} \text{ solution by } \text{Cl}_2 \text{ is spontaneous.}$$



$$\text{E}_{\text{cu}} = 0 - (-1.68) = +1.68 \text{ V} > 0, \text{ so reaction is spontaneous.}$$



$$\text{E}_{\text{cu}} = +0.34 - (-1.68) = +2.02 \text{ V} > 0, \text{ so reaction is spontaneous.}$$



- (c) A buffer solution with pH = 10.00 was required for an experiment. The following procedure was used to prepare this solution.

A technician began by dissolving 0.1918 g of methylammonium chloride,  $\text{CH}_3\text{NH}_3\text{Cl}(s)$ , into 50.0 mL of 0.0250 mol L<sup>-1</sup> methylamine solution,  $\text{CH}_3\text{NH}_2(aq)$ . However, when the pH of the solution was measured, it was found to be too high. To lower the pH, 10.0 mL of 0.0415 mol L<sup>-1</sup> hydrochloric acid solution,  $\text{HCl}(aq)$ , was added.

Calculate the pH of the initial and final buffer solutions, and decide whether the technician added a sufficient amount of hydrochloric acid to achieve the intended pH.

$$M(\text{CH}_3\text{NH}_3\text{Cl}) = 67.5 \text{ g mol}^{-1} \quad pK_a(\text{CH}_3\text{NH}_3^+) = 10.64$$

Initial:

$$[\text{CH}_3\text{NH}_3^+] = \frac{0.1918 \text{ g}}{67.5 \text{ g mol}^{-1}} \times \frac{1}{0.05 \text{ L}} = 0.05683 \text{ mol L}^{-1}$$

$$[\text{CH}_3\text{NH}_2] = 0.025 \text{ mol L}^{-1}$$

$$K_a = \frac{[\text{CH}_3\text{NH}_2^*][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]}, [\text{H}_3\text{O}^+] = K_a \times \frac{[\text{CH}_3\text{NH}_3^+]}{[\text{CH}_3\text{NH}_2^*]}$$

$$[\text{H}_3\text{O}^+] = 10^{-10.64} \times \left( \frac{0.025}{0.05683} \right)^{-1} = 5.208 \times 10^{-11} \text{ mol L}^{-1}$$

$$\text{pH} = -\log 5.208 \times 10^{-11} \approx 10.28$$

Final:

$$n(\text{HCl})_{\text{add}} = 0.0415 \text{ mol L}^{-1} \times 0.01 \text{ L} = 4.15 \times 10^{-4} \text{ mol}$$

$$n(\text{CH}_3\text{NH}_2) = 0.025 \text{ mol L}^{-1} \times 0.05 \text{ L} = 1.25 \times 10^{-3} \text{ mol}$$

~~$$n(\text{CH}_3\text{NH}_2) - n(\text{CH}_3\text{NH}_3^+) = 0.025 \times 10^{-3} / 67.5 \text{ g mol}^{-1} = 2.841 \times 10^{-5} \text{ mol}$$~~



$$n(\text{CH}_3\text{NH}_2)_{\text{final}} = 1.25 \times 10^{-3} - 4.15 \times 10^{-4} = 8.35 \times 10^{-4} \text{ mol}$$

$$n(\text{CH}_3\text{NH}_3^+)_{\text{final}} = 2.841 \times 10^{-5} + 4.15 \times 10^{-4} = 3.265 \times 10^{-4} \text{ mol}$$



$$[\text{H}_3\text{O}^+] = 10^{-10.64} \times \frac{3.265 \times 10^{-4}}{0.06 \text{ L}}$$

$$= 8.96 \times 10^{-11} \text{ mol L}^{-1}$$

$$\text{pH} = -\log 8.96 \times 10^{-11} \approx$$

$$= 10.05$$

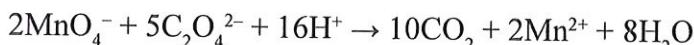
So we will quite enough HCl was added to reach pH exactly 10. //

## QUESTION TWO

- (a) A solution was prepared for a competition by mixing varying amounts of three compounds; ethanoic acid,  $\text{CH}_3\text{COOH}(l)$ , sodium chloride,  $\text{NaCl}(s)$ , and oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4(s)$ , in a volume of water,  $\text{H}_2\text{O}(l)$ . There was no solid remaining in the final solution. Groups of students were each given 100.0 mL of the solution and were tasked with determining the mass of each of the three compounds in the sample provided.

One group of students carried out the following procedures in the laboratory.

First, the students diluted the solution by pipetting 20.00 mL into a 200.0 mL volumetric flask, and filling it to the mark with distilled water. The students then titrated 20.00 mL samples of the diluted solution with a standardised potassium permanganate solution,  $\text{KMnO}_4(aq)$ . The potassium permanganate solution had a concentration of 0.02960 mol L<sup>-1</sup> and required an average titre of 18.93 mL to reach the end point.



Next, the students titrated further 20.00 mL samples of the diluted solution with a standardised sodium hydroxide solution,  $\text{NaOH}(aq)$ , using phenolphthalein as the indicator. The sodium hydroxide solution had a concentration of 0.4790 mol L<sup>-1</sup> and required an average titre of 13.32 mL to reach the end point.

Finally, each student in the group pipetted 10.00 mL of the original undiluted solution into pre-weighed beakers. Each beaker was heated to evaporate all liquids, then the beakers and any solids remaining were weighed. The average mass of solids remaining was 2.130 g.

From these measurements, determine the final answers that the group should have submitted in the competition.

$$M(\text{NaCl}) = 58.50 \text{ g mol}^{-1} \quad M(\text{H}_2\text{C}_2\text{O}_4) = 90.00 \text{ g mol}^{-1} \quad M(\text{CH}_3\text{COOH}) = 60.00 \text{ g mol}^{-1}$$

Titration One:

$$\begin{aligned} n(\text{MnO}_4^-) &= 0.0296 \text{ mol L}^{-1} \times 0.01893 \text{ L} \\ &= 5.603 \times 10^{-5} \text{ mol.} \end{aligned}$$

$$\begin{aligned} n(\text{C}_2\text{O}_4^{2-}) &= \frac{5}{2} \times n(\text{MnO}_4^-) = \frac{5}{2} \times 5.603 \times 10^{-5} \\ &= 1.4008 \times 10^{-4} \text{ mol} \quad \text{in 20mL dilute} \end{aligned}$$

$$\begin{aligned} n(\text{C}_2\text{O}_4^{2-}) \text{ in } 20\text{mL undiluted} &= 0.014008 \text{ mol} \\ n(\text{C}_2\text{O}_4^{2-}) \text{ in } 100\text{mL} &= 0.07004 \text{ mol} \\ n(\text{H}_2\text{C}_2\text{O}_4) &= 0.07004 \text{ mol} \times 90 \text{ g mol}^{-1} \end{aligned}$$

$$[\text{C}_2\text{O}_4^{2-}] = 1.4008 \times 10^{-4} \text{ mol} / 0.02 \text{ L} = 0.07004 \text{ mol L}^{-1}$$

$$n(\text{C}_2\text{O}_4^{2-})_{200\text{mL}} = 0.07004 \text{ mol L}^{-1} \times 0.2 \text{ L} = 0.014008 \text{ mol}$$

$$n(\text{C}_2\text{O}_4^{2-})_{100\text{mL undiluted}} = 0.014008 \times 5 = 0.07004 \text{ mol}$$

$$m(\text{C}_2\text{O}_4^{2-}) = 0.07004 \text{ mol} \times 90 \text{ g mol}^{-1} = 6.304 \text{ g.}$$

Titration Two:

$$n(\text{OH}^-) = 0.479 \text{ mol L}^{-1} \times 0.01332 \text{ L}$$



$$n(\text{OH}^-) = 6.38 \times 10^{-3} \text{ mol} = 0.16$$

$$n(\text{CH}_3\text{COOH}) + 2 \times n(\text{H}_2\text{C}_2\text{O}_4) = 6.38 \times 10^{-3} \text{ mol}$$

$$n(\text{H}_2\text{C}_2\text{O}_4) = 1.4008 \times 10^{-3} \text{ mol}$$

$$n(\text{CH}_3\text{COOH}) = 6.38 \times 10^{-3} - 2 \times 1.4008 \times 10^{-3}$$

$$= 3.579 \times 10^{-3} \text{ mol} \quad \text{in 20mL dilute.}$$

$$n(\text{CH}_3\text{COOH})_{\text{in 10mL}} \text{ undiluted} = 0.1789 \text{ mol}$$

$$m(\text{CH}_3\text{COOH}) = 0.1789 \text{ mol} \times 60 \text{ g/mol}^{-1} = 10.73 \text{ g}$$

mass analysis:

in 10mL:

$$m(\text{CH}_3\text{COOH}) = 1.073 \text{ g}, \quad m(\text{H}_2\text{C}_2\text{O}_4) = 0.6304 \text{ g}$$

$$m(\text{NaCl}) = 2.13 - 1.073 - 0.6304 \\ = 0.4262 \text{ g}$$

∴ in 100mL:

$$m(\text{NaCl}) = 4.262 \text{ g}$$

$$m(\text{CH}_3\text{COOH}) = 10.73 \text{ g}$$

$$m(\text{H}_2\text{C}_2\text{O}_4) = 6.304 \text{ g}$$

- (b) The enthalpy of solution,  $\Delta_{\text{sol}}H$ , is the enthalpy change that occurs when one mol of a solid dissolves to produce a solution. The  $\Delta_{\text{sol}}H$  for calcium carbonate,  $\text{CaCO}_3(s)$ , in water is negative, while the  $\Delta_{\text{sol}}H$  for sodium chloride,  $\text{NaCl}(s)$ , in water is positive.

Discuss the thermodynamic factors that affect the relative solubilities of  $\text{CaCO}_3$  and  $\text{NaCl}$ , with consideration of enthalpy and entropy changes occurring within the solute, solvent and solution.

$$K_s(\text{CaCO}_3) = 3.3 \times 10^{-9} \quad K_s(\text{NaCl}) > 1.00$$

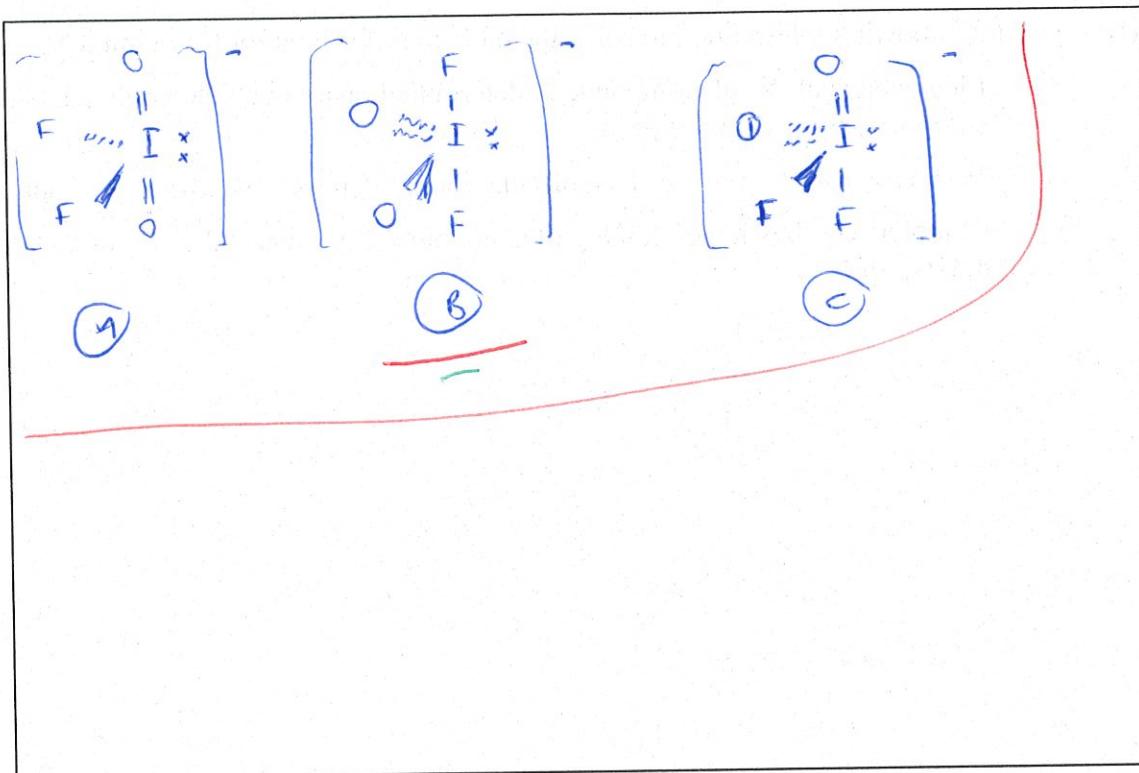


Dissolution of  $\text{CaCO}_3$  is exothermic, so heat energy is released into the solution meaning ~~that~~ the kinetic energy and hence amount of random motion / disorder of the solution increases i.e. entropy of the ~~solutions~~<sup>solvent</sup> increases. However, the low value of solubility implies the total entropy will decrease / the total entropy is only slightly positive so the entropy of the solute,  $\text{CaCO}_3$ , likely increases as solid  $\text{CaCO}_3$  particles dissolve in solution, leaving greater degree of random motion. The entropy of the solvent,  $\text{H}_2\text{O}$ , must therefore decrease significantly as  $\text{H}_2\text{O}$  molecules surrounding dissolved  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions are more ordered than  $\text{H}_2\text{O}$  molecules in pure solution. The decrease in entropy of the solvent ( $\text{H}_2\text{O}$ ) will therefore outweigh the increase in both solute and solution, making total entropy change slightly positive, and so the solubility of  $\text{CaCO}_3(s)$  relatively low (hence low  $K_s$ ). e.

- $\text{NaCl}$  is, however, readily soluble in water (hence  $K_s > 1$ ). The entropy of solution is positive / endothermic, meaning heat energy →



- (c) (i) Draw all potential 3-dimensional structures for the  $\text{IF}_2\text{O}_2^-$  ion.



- (ii) In VSEPR theory, it is observed that a bond from the central atom to an atom of lower electronegativity occupies more space than the bond from the central atom to an atom of higher electronegativity. Double bonds have greater electron density and, thus, greater repulsion than single bonds.

Justify the most probable positional arrangement of atoms in the  $\text{IF}_2\text{O}_2^-$  ion.

O has lower electronegativity than F, and O atoms are double bonded to the central I atom while Fs are only single bonded. As I has 5 ~~regions of~~ e<sup>-</sup> domains around it, it exists as a trigonal bipyramidal arrangement. In this arrangement, the equatorial positions are those of minimal repulsion as they are located further from the other bonds than the axial positions. Hence, to minimize repulsion, the lone e<sup>-</sup> pair and =O will occupy the equatorial positions, so the most probable arrangement will be (B).

## QUESTION THREE

(a) (i) Use the following information to solve the molecular formula for Compound X.

- Elemental analysis of Compound X determined that it contained only the elements carbon, hydrogen, and oxygen.
- Mass spectrometry produced a molecular ion ( $M^+$ ) peak at 90 m/z for Compound X.
- Complete combustion of 4.388 g of Compound X produced 8.591 g of  $\text{CO}_2$  and 4.410 g of  $\text{H}_2\text{O}$ .

$$n(\text{CO}_2) = 8.591 \text{ g} / 44 \text{ g mol}^{-1} = 0.19525 \text{ mol.}$$

$$n(\text{H}_2\text{O}) = 4.410 \text{ g} / 18 \text{ g mol}^{-1} = 0.245 \text{ mol.}$$

$$n(X) = 4.388 \text{ g} / 70 \text{ g mol}^{-1} = 0.06276 \text{ mol.}$$

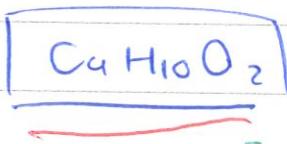
$$n(C)_{\text{atoms}} = 0.19525 / 0.06276 = 4 \text{ C atoms.}$$

$$n(H) = 2 \times 0.245 / 0.06276 = 10 \text{ H atoms}$$

$$\cancel{n(O)} = (2 \times 0.19525),$$

$$n(O) = (90 - 4 \times 82 - 10) / 16 = 2 \text{ O atoms}$$

$\therefore$  X has formula:

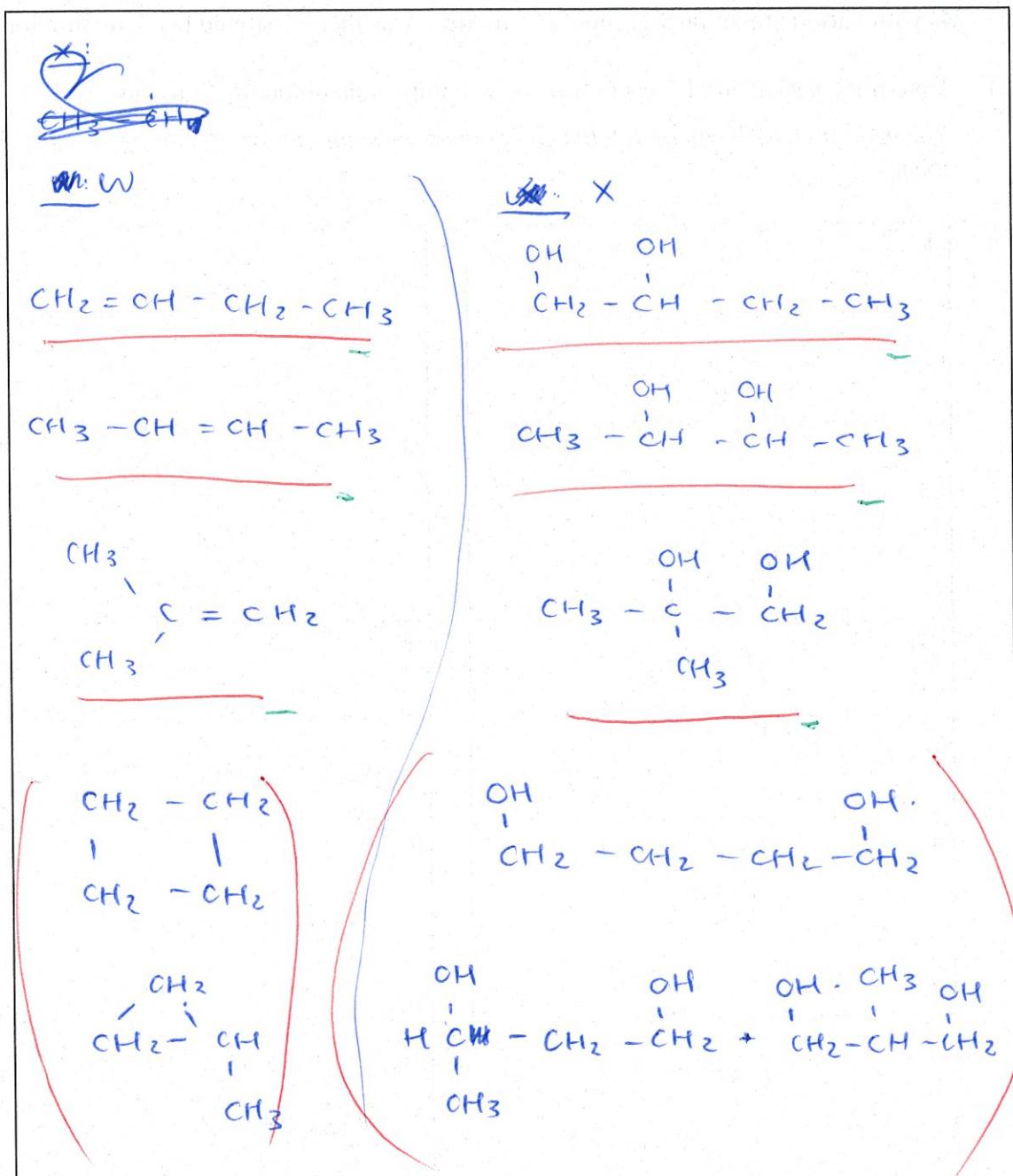


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- (ii) Compound X was produced following reaction of Compound W with  $\text{H}^+/\text{MnO}_4^-$ .

Draw all possible structures for Compounds X and W.

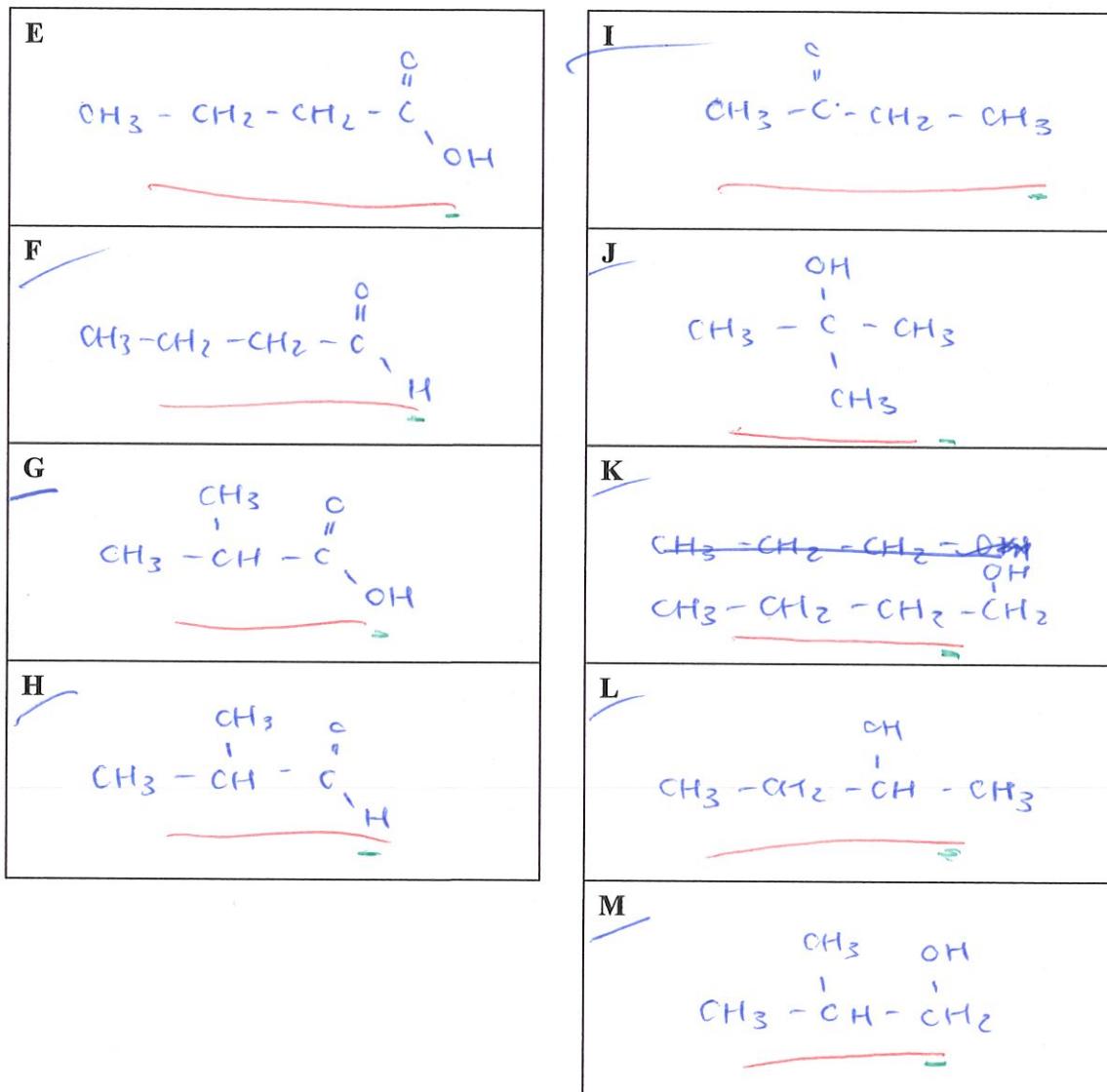
You do not need to name any of the structures.



- (b) Compounds E–H are a group of alcohols that naturally occur in a mixture together. They are isomers with the molecular formula  $C_4H_{10}O$ . Addition of acidified potassium dichromate solution,  $H^+/K_2Cr_2O_7(aq)$ , to a sample of the mixture, followed by gentle heating, resulted in the formation of a variety of new organic compounds. In the conditions used, not all the compounds fully reacted, and the final mixture contained nine different organic compounds (E–M) with various functional groups. The mixture was then separated using distillation.

- (i) Determine a structure for each of the nine compounds in the final mixture.

*The order in which you assign the compounds does not matter. You do not need to name them.*



- (ii) Using the labels given to your compounds above, discuss the chemistry involved in the separation of Compounds E–M.

You should explain the predicted order in which they would separate during distillation.

*Distillation separates substances based on their boiling points, with the substance with lowest boiling point evaporating and being collected first. The boiling point is, in turn,*

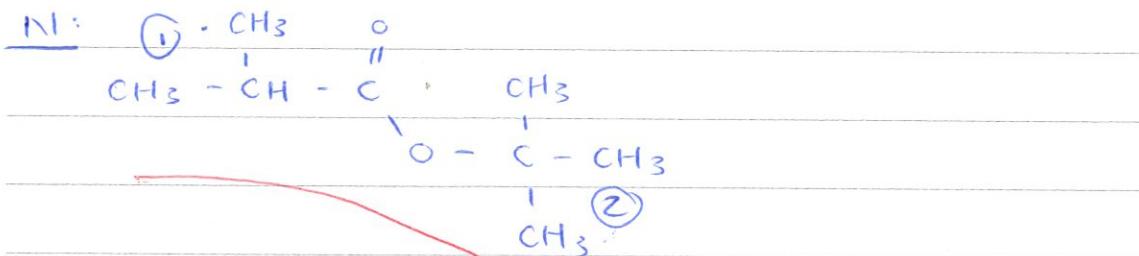
determined by the strength of intermolecular forces - stronger forces require more heat energy to overcome and correspond to higher boiling points. The molar mass of the compounds are identical, so the ~~strength~~<sup>degree</sup> of temporary-induced dipole forces will be the same. So, boiling points depend on ~~the~~ whether H-bonding occurs, and the efficiency of molecule packing. The first to distill off will be any aldehydes / ketones as (unlike alcohols / amines), they cannot form strong H-bonds, leaving only the much weaker permanent dipole forces due to the  $\text{C}=\text{O}$  bond. Between these compounds the ~~the~~ differences in b.p. will be due to efficiency of molecule packing. H, due to the added methyl chain will have best efficient packing, followed by I and then F. More efficient packing allows molecules to pack closer, the more points of contact and greater closeness of molecules increasing the strength of temporary dipole forces. Hence, order of these are H first, then I then F.

Next to distill off are the alcohols, which have higher boiling points than aldehydes / ketones due to H bonding occurring due to hydroxy ( $\text{OH}$ ) groups. The highly electronegative O draws  $e^-$  density from the H atom, allowing the  $\text{S}^+$  ..

(iii) Compound N can be synthesised using two of compounds E–M from part (i).

When analysed using  $^{13}\text{C}$  NMR, only five peaks are detected in the spectra for this compound.

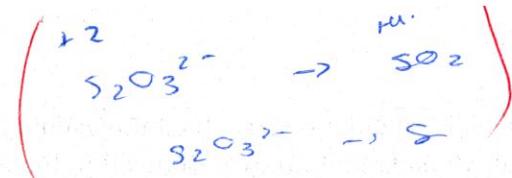
Determine the structure of Compound N, give the conditions required for the synthesis to occur, and explain the resulting  $^{13}\text{C}$  NMR peaks of the product.



N is formed via an esterification reaction.

A solution containing compounds G and J must be heated under reflux with a concentrated sulfuric acid catalyst.

- N has 3 C atoms, but only 5  $^{13}\text{C}$  NMR peaks, and hence only 5 unique carbon environments. This indicates some symmetry in the compound. In N, this is due to the methyl ( $-\text{CH}_3$ ) branches on the "acid" part and "alcohol" part - due to symmetry / being bonded to identical atoms,  $^{13}\text{C}$  NMR cannot distinguish between them (i.e. count as the same C environment) and so the  $^2_{\text{CH}_3}$ 's marked (1) count as 1 peak, and the  $^3_{-\text{CH}_3}$ 's marked (2) also count as one (different) peak //.



## QUESTION FOUR

- (a) Solid sodium thiosulfate,  $Na_2S_2O_3$ , can react with both dilute hydrochloric acid,  $HCl(aq)$ , and concentrated nitric acid,  $HNO_3(conc)$ .

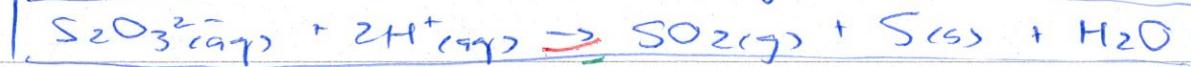
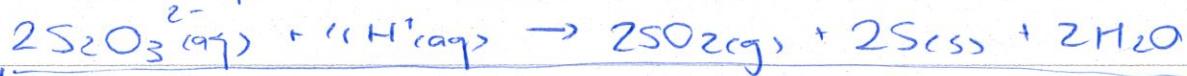
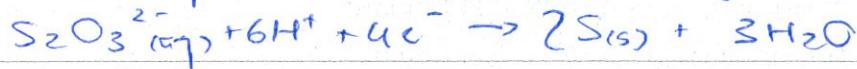
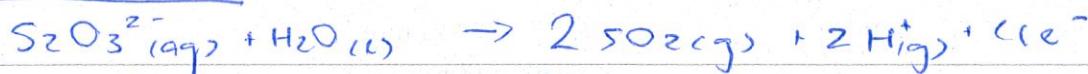
When it is reacted with dilute hydrochloric acid,  $HCl(aq)$ , colourless sulfur dioxide gas,  $SO_2(g)$ , is released from the mixture, and a yellow solid is slowly formed in the solution.

When it is reacted with concentrated nitric acid,  $HNO_3(conc)$ , brown nitrogen dioxide gas,  $NO_2(g)$ , is released from the mixture and the same yellow solid is again observed in the solution. This second solution additionally tests positive for the presence of sulfate ions,  $SO_4^{2-}(aq)$ .

Account for the oxidation and reduction processes occurring in the reactions with  $HCl(aq)$  and  $HNO_3(conc)$ .

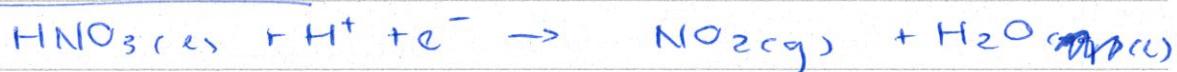
You should write balanced equations, and use changes in oxidation numbers to justify the oxidant(s) and reductant(s) in the reactions.

Dilute HCl:



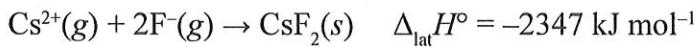
- this is a <sup>spontaneous</sup> disproportionation reaction, with  $S_2O_3^{2-}$  acting as both oxidant (as the number of S decreases from +2 in  $S_2O_3^{2-} \rightarrow 0$  in  $S(s)$ ) and reducing agent (O.N increases from +2 in  $S_2O_3^{2-}$  to +4 in  $SO_2(g)$ ).  $HCl(aq)$  provides the acidic conditions required for the disproportionation reaction (products  $H^+$  /  $Cl^-$  are byproducts).

conc.  $HNO_3$ :



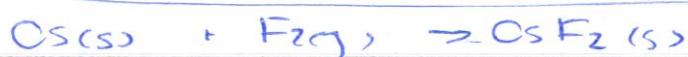
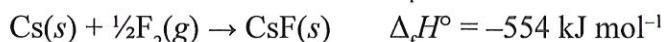
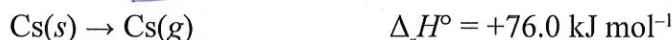
Here,  $S_2O_3^{2-}$  is the reductant (O.N of S increases from +2 in  $S_2O_3^{2-} \rightarrow +6$  in  $SO_4^{2-}$ ), while  $HNO_3$  is the oxidant (O.N. of N decreases from +5 in  $HNO_3 \rightarrow +4$  in  $NO_2(g)$ ), ...

- (b) Hess's law calculations use the known enthalpy changes of various reactions to calculate the enthalpy change for an overall reaction for which the enthalpy changes cannot be measured. For example, Hess's law can be used to determine lattice formation enthalpies. These are a measure of the enthalpy change when one mole of an ionic solid is formed from its ions in the gaseous state. Caesium(II) fluoride,  $\text{CsF}_2(s)$ , is an example of an ionic salt that does not exist, but the theoretical lattice formation enthalpy can be calculated using Hess's law and depicted as:



- (i) Using the thermochemical information provided, calculate the theoretical enthalpy of formation,  $\Delta_fH^\circ$ , for  $\text{CsF}_2(s)$ , and then justify why  $\text{CsF}_2$  does not exist, but  $\text{CsF}$  does.

Consider the position of these elements in the periodic table in your answer.



$$\Delta_fH(\text{CsF}) = +31 \text{ kJ mol}^{-1}$$

~~hence the entropy of formation is positive,  
heat energy is absorbed from surroundings/  
process is not thermodynamically favoured.~~

F is the most electronegative element  
(so it will strongly attract bonding  $e^-$ ) while

Cs is one of the least electronegative elements  
(so it will very easily lose its valence  $e^-$ ).

The enthalpy of formation of  $\text{CsF}_2$  is  
positive, while that of  $\text{CsF}$  is negative –  
meaning the formation of  $\text{CsF}_2$  is not +ve/-

dynamically favoured. This is primarily due to the  $\text{Cs}^{2+}$  ion - the removal of the dual valence  $e^-$  from Cs requires considerably more energy ~~the~~ ( $+2430 \text{ kJ mol}^{-1}$ ) than to remove the first ( $+382 \text{ kJ mol}^{-1}$ ), primarily because removal of this dual  $e^-$  is from a lower energy level ion, which experiences decreased shielding and therefore a much greater electrostatic attraction to the positive nucleus. So, despite the ~~more~~<sup>extra</sup> energy released when the ionic bonds in  $\text{CsF}_2$  form, it is far more favourable to remove... below →

- (ii) Justify the differences in the lattice formation enthalpies for  $\text{CsF}$  and  $\text{CsF}_2$ .

$$\Delta_{\text{lat}}H^\circ(\text{CsF}(s)) = -757 \text{ kJ mol}^{-1}$$

The lattice formation enthalpy depends only on the strength of the ionic bonds formed (as no bonds are being broken). For  $\text{CsF}_2$ , not only are we forming twice the number of ionic bonds, but due to the larger charge on the  $\text{Cs}^{2+}$  ion (vs. the  $\text{Cs}^+$  ion), the resulting ionic bonds which form are stronger than the ionic bond in  $\text{CsF}$ . The stronger and more numerous ionic bonds in  $\text{CsF}_2$  will hence release more energy when it forms from its gaseous ions, and so the lattice enthalpy is more negative than that of  $\text{CsF}$  //

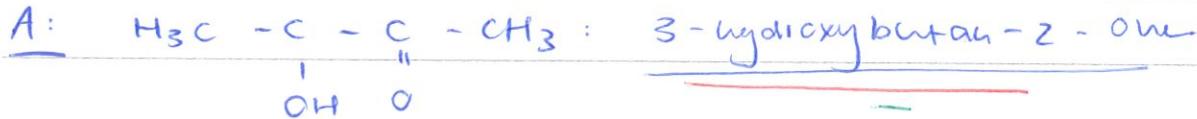
Question Four continues  
on the next page.

(c) Compounds A–D are constitutional isomers with a molar mass less than  $100 \text{ g mol}^{-1}$ .

$^{13}\text{C}$  NMR and IR spectra for Compounds A–D are provided in the resource booklet.

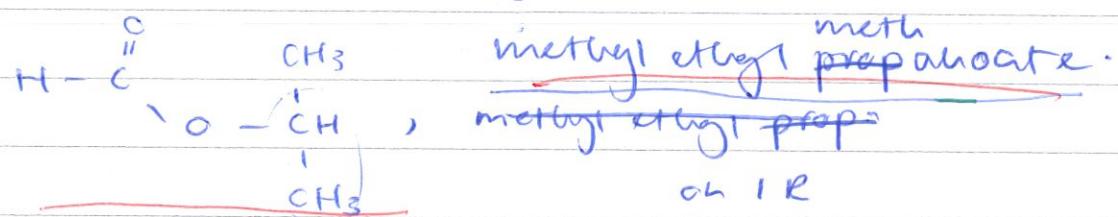
Use the spectral data provided to determine the molecular formula for the isomers A–D, then determine, name, and justify ONE possible structure for each compound.

molecular formula:  $\text{C}_4\text{H}_8\text{O}_2$ .

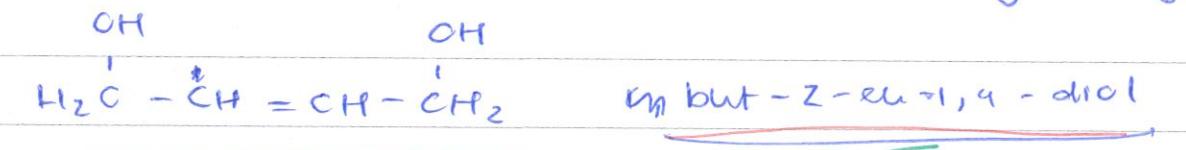


$\Rightarrow$  strong peak at  $\sim 3400 \text{ cm}^{-1}$  on IR due to O-H stretch, peak at  $\sim 1700 \text{ cm}^{-1}$  on IR due to Ketone C=O stretch. 4 unique environments indicates degree of symmetry, the downfield peak at  $\sim 200 \text{ ppm}$  on NMR spectrum due either to aldehyde or ketone.

B: No peak at  $3600 - 3300 \text{ cm}^{-1}$  on IR suggests no -OH group. Peak at  $160 \text{ ppm}$  on NMR suggests ester group (cannot be alkene as the molecular formula  $\text{C}_4\text{H}_8\text{O}_2$  demands only alkene has 2 OHs), and only 3 peaks on NMR suggest 3 C environments, i.e. 2 identical C atoms so, B is:



C: Peak at  $\sim 3400 \text{ cm}^{-1}$  indicates -OH, ~~peak~~ (as does peak at  $\sim 1000 \text{ cm}^{-1}$ ), lack of peak at  $\sim 1700 \text{ cm}^{-1}$  shows no C=O present, so we must have a diol. Peak at  $\sim 130 \text{ ppm}$  on NMR suggests  $\text{R}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{C}-\text{R}$  group, and having only 2 peaks shows C must have some symmetry:



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Extra space if required.  
Write the question number(s) if applicable.

1)b)  $E_{cell} = +0.69 - 1.36 = +0.33V > 0$ , so reaction is spontaneous //

2)b) is absorbed from the surrounding solution, causing the kinetic energy / degree of random motion of particles in solution to decrease, so the entropy of the solution decreases. Similar to  $\text{CaCO}_3$ , the entropy of solvent,  $\text{H}_2\text{O}$ , will decrease as  $\text{H}_2\text{O}$  molecules surrounding dissolved ions are more ordered. However, this entropy decrease in  $\text{NaCl}$  is not as large as  $\text{CaCO}_3$  as the ions dissolved are much smaller. Also as with  $\text{CaCO}_3$ , the entropy of solute,  $\text{NaCl}$ , increases. However, for  $\text{NaCl}$  this increase is not large as the regular crystal lattice  $\text{NaCl}$  exists in is more ordered than that of  $\text{CaCO}_3$  (here  $\text{NaCl}$  exists as crystals in solid form, while  $\text{CaCO}_3$  is a powder), so the increase in entropy of  $\text{Na}^+$  and  $\text{Cl}^-$  ions are removed from this lattice is significantly larger. This increase in entropy of the solute,  $\text{NaCl}$ , is enough to compensate of decreases in entropy of solution and solvent - so the process is overall thermodynamically favourable to greater extent the dissolution of  $\text{CaCO}_3$ , making  $\text{NaCl}$  much more soluble. //

Extra space if required.

Write the question number(s) if applicable.

See

3(b)ii) H to form strong electrostatic attractions with lone  $e^-$  pairs on O atoms on adjacent molecules. As with before, molecular shape and efficiency of packing determines the order of the alcohols, with M first (i.e. lowest b.p. due to least efficient packing), then J (slightly more efficient due to symmetry of molecule), then L, and K.

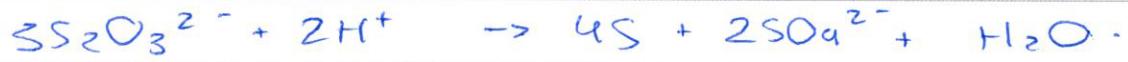
The carboxylic acids come the final to distill off, having higher b.p. / strongest intermolecular forces due to greater capacity to form H-bonds  $H_2^+$ . These alcohols (both C=O and -OH groups present), and the ability to form dimers (which will effectively increase strength of temporary dipole forces by increasing size of molecules).

E will have the higher boiling point due to the linear shape allowing for more efficient packing. Hence, C distils first, and E last so the order of distillation is:

H, I, F, M, J, L, K, C, E //

4(b)ii) ~~and the 1st  $e^-$  from another Cs atom then~~ <sup>to</sup> form  $CsF$  then the 2nd  $e^-$  from a  $Cs^+$  ion to form  $CsF_2$  - where  $CsF_2$  will not exist //

4) a) Meanwhile, the acidic conditions supplied by the acid allow for the disproportionation of  $S_2O_3^{2-}$ , thus like forming  $SO_4^{2-}$  and  $S(s)$ :



$S_2O_3^{2-}$  again acts as both oxidant ( $\Delta O.N.$  of S decreases from +2 in  $S_2O_3^{2-}$  to 0 in S) and reducent ( $\Delta O.N.$  of S increases from +2 in  $S_2O_3^{2-}$  to +6 in  $SO_4^{2-}$ ).

4) c) D:  $\begin{array}{c} CH_3 \\ | \\ CH_3 - C - C(OH) \\ || \\ OH \end{array}$ , 2-methyl propanoic acid.  
Peak at Downfield peak at  $\approx 180$  ppm on NMR spectra suggest acidic group, 3 peaks suggests some symmetry (i.e. the methyl groups). Peak at  $\approx 170$   $cm^{-1}$  on IR due to  $C=O$ , and slight peak  $> 3000$   $cm^{-1}$  due to  $-OH$ .

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