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93102



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OUTSTANDING SCHOLARSHIP EXEMPLAR



NEW ZEALAND QUALIFICATIONS AUTHORITY
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QUALIFY FOR THE FUTURE WORLD
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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.

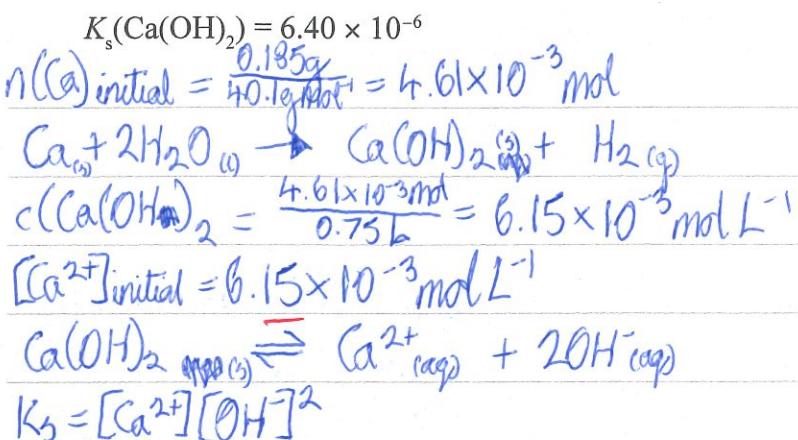
| Question | Score |
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ASSESSOR'S USE ONLY

QUESTION ONE

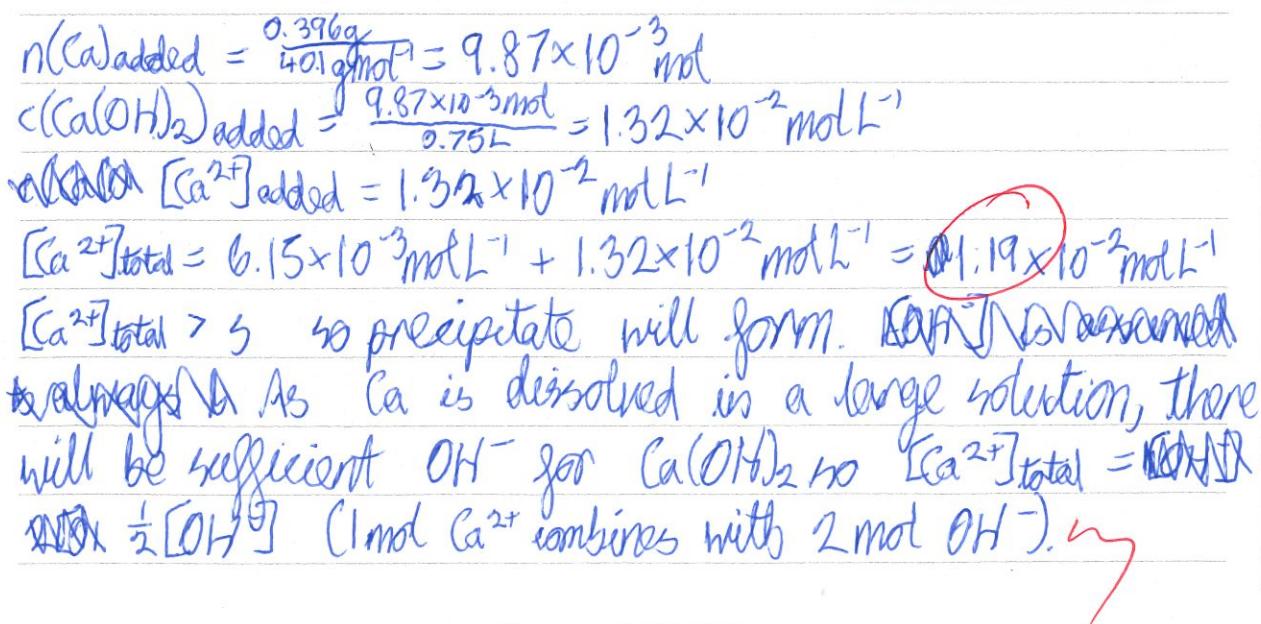
- (a) A small 0.185 g piece of calcium metal, $\text{Ca}(s)$, was dropped into a large beaker containing 750.0 mL of distilled water at 25 °C. It spontaneously reacted, producing a colourless gas and a clear, colourless solution. When a further two pieces of calcium metal, with a combined mass of 0.396 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.



$[\text{Ca}^{2+}]_{\text{initial}} < s$ so all $\text{Ca}(\text{OH})_2$ is dissolved.

Ca reacts spontaneously with H_2O to produce $\text{Ca}(\text{OH})_2$, which forms a colourless solution in water. H_2 gas is also produced.

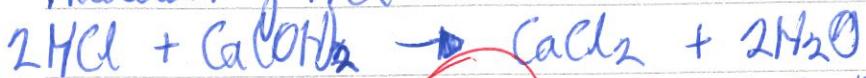


$$[\text{OH}^-]_{\text{total}} = 2[\text{Ca}^{2+}]_{\text{total}} = 3.86 \times 10^{-2} \text{ mol L}^{-1}$$

$$Q = [\text{Ca}^{2+}][\text{OH}^-]^2 = (1.93 \times 10^{-2})(3.86 \times 10^{-2})^2 \\ = 2.88 \times 10^{-5}$$

$Q > K_s$ so precipitate forms, hence a cloudy white solid was observed forming in the solution

Addition of HCl:

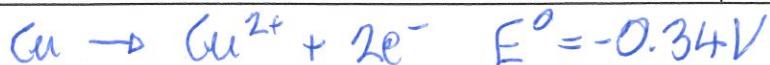


As some of the Ca^{2+} from the $\text{Ca}(\text{OH})_2$ is used up for the reaction with HCl, $[\text{Ca}^{2+}]$ from the $\text{Ca}(\text{OH})_2$ decreases. To compensate, the $\text{Ca}(\text{OH})_2$ precipitate dissolves to restore original $[\text{Ca}^{2+}]$, hence ~~as~~ the solution becomes clear.

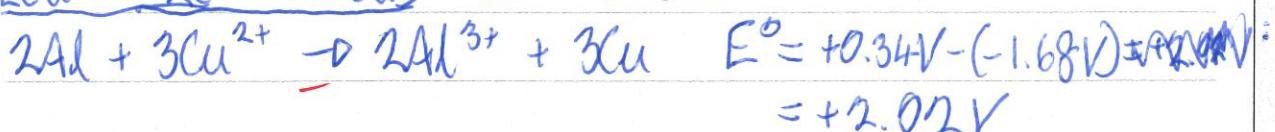
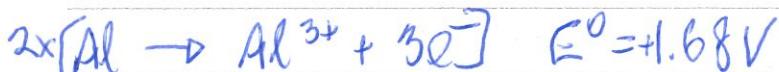
- (b) A pale-blue, weakly acidic copper(II) chloride solution, $\text{CuCl}_2(aq)$, was prepared by sitting a piece of copper metal, $\text{Cu}(s)$, in a beaker containing chlorine water, $\text{Cl}_2(aq)$. When pieces of aluminium foil, $\text{Al}(s)$, were added to a sample of the solution, the pieces 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.

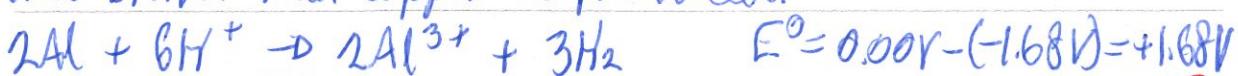
| | E° / V |
|---|----------------------|
| $2\text{H}^+(aq) + 2\text{e}^- \rightarrow \text{H}_2(g)$ | 0.00 |
| $\text{Cl}_2(g) + 2\text{e}^- \rightarrow 2\text{Cl}^-(aq)$ | +1.36 |
| $\text{Al}^{3+}(aq) + 3\text{e}^- \rightarrow \text{Al}(s)$ | -1.68 |
| $\text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(l)$ | +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 |



$E^\circ > 0$, so spontaneous.



$E^\circ > 0$, so Al spontaneously displaces the Cu^{2+} ions and brown solid copper is produced.



$E^\circ > 0$ so colourless H_2 gas is produced when Al is added to the solution.



$E^\circ = +1.69 \text{ V} - (+1.36 \text{ V}) = +0.33 \text{ V}$ $E^\circ > 0$ so MnO_4^- is spontaneously reduced to MnO_2 (brown solid) and Cl^- is oxidised to form Cl_2 gas (pale-green gas). ↗

- (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⁻¹ 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⁻¹ 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.

$$\begin{aligned} M(\text{CH}_3\text{NH}_3\text{Cl}) &= 67.5 \text{ g mol}^{-1} & pK_a(\text{CH}_3\text{NH}_3^+) &= 10.64 \\ n(\text{CH}_3\text{NH}_3\text{Cl}) &= \frac{0.1918 \text{ g}}{67.5 \text{ g mol}^{-1}} = 2.84 \times 10^{-3} \text{ mol} \\ c(\text{CH}_3\text{NH}_3\text{Cl}) &= \frac{2.84 \times 10^{-3} \text{ mol}}{0.05 \text{ L}} = 5.68 \times 10^{-2} \text{ mol L}^{-1} \\ \text{pH} &= pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \\ \text{pH} &= 10.64 + \log \left(\frac{0.0250}{5.68 \times 10^{-2}} \right) = 10.28 \rightarrow 10 \text{ is too high} \end{aligned}$$

\nwarrow pH of initial buffer solution

$$\begin{aligned} n(\text{HCl}) &= 0.0415 \text{ mol L}^{-1} \times \frac{10 \text{ mL}}{1000} = 4.15 \times 10^{-4} \text{ mol} \\ n(\text{CH}_3\text{NH}_2) &= 0.0250 \text{ mol L}^{-1} \times \frac{50 \text{ mL}}{1000} = 1.25 \times 10^{-3} \text{ mol} \\ \text{HCl} + \text{CH}_3\text{NH}_2 &\rightarrow \text{CH}_3\text{NH}_3\text{Cl} \\ n(\text{CH}_3\text{NH}_2)_{\text{remaining}} &= 1.25 \times 10^{-3} \text{ mol} - 4.15 \times 10^{-4} \text{ mol} \\ &= 8.35 \times 10^{-4} \text{ mol} \\ c(\text{CH}_3\text{NH}_2)_{\text{remaining}} &= \frac{8.35 \times 10^{-4} \text{ mol}}{0.06 \text{ L}} = 1.39 \times 10^{-2} \text{ mol L}^{-1} \\ n(\text{CH}_3\text{NH}_3\text{Cl})_{\text{total}} &= 4.15 \times 10^{-4} \text{ mol} + 2.84 \times 10^{-3} \text{ mol} \\ &= 3.26 \times 10^{-3} \text{ mol} \\ c(\text{CH}_3\text{NH}_3\text{Cl})_{\text{total}} &= \frac{3.26 \times 10^{-3} \text{ mol}}{0.06 \text{ L}} = 5.43 \times 10^{-2} \text{ mol L}^{-1} \end{aligned}$$

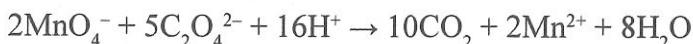
$$\begin{aligned} \text{new pH} &= 10.64 + \log \left(\frac{1.39 \times 10^{-2}}{5.43 \times 10^{-2}} \right) \\ &= 10.05 \leftarrow \text{pH of final buffer solution} \\ 10.05 \neq 10.00 &\text{ so the technician did not add a sufficient} \\ &\text{amount of HCl to achieve the intended pH.} \end{aligned}$$

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.

① 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⁻¹ and required an average titre of 18.93 mL to reach the end point.



② 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⁻¹ and required an average titre of 13.32 mL to reach the end point.

③ 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.

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

$$\text{n}(\text{MnO}_4^-) = 0.02960 \text{ mol L}^{-1} \times \frac{18.93 \text{ mL}}{2000 \text{ mL}} = 5.6 \times 10^{-4} \text{ mol}$$

$$\begin{aligned} \text{n}(\text{C}_2\text{O}_4^{2-}) \text{ in } 20 \text{ mL} &= \frac{5}{2} \text{n}(\text{MnO}_4^-) = \frac{5}{2} \times 5.6 \times 10^{-4} \text{ mol} \\ &= 1.4 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\text{n}(\text{C}_2\text{O}_4^{2-}) \text{ in } 200 \text{ mL} = 1.4 \times 10^{-3} \text{ mol} \times \frac{200 \text{ mL}}{20 \text{ mL}} = 1.4 \times 10^{-2} \text{ mol}$$

$$\text{m}(\text{H}_2\text{C}_2\text{O}_4)_{20 \text{ mL}} = 1.4 \times 10^{-3} \text{ mol} \times 90.00 \text{ g mol}^{-1} = 1.26074 \text{ g} \quad (\text{in } 20 \text{ mL})$$

$$\text{m}(\text{H}_2\text{C}_2\text{O}_4) \text{ in } 100 \text{ mL} = 5 \times 1.26074 \text{ g} = 6.30369 \text{ g}$$

(3)

7

$$n(\text{NaOH}) = 0.4790 \text{ mol L}^{-1} \times \frac{13.32 \text{ mL}}{1000} = 6.38 \times 10^{-3} \text{ mol}$$



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

~~$$n(\text{CH}_3\text{COOH}) \text{ in } 200 \text{ mL} = 6.38 \times 10^{-3} \text{ mol} \times \frac{200 \text{ mL}}{20 \text{ mL}} = 6.38 \times 10^{-2} \text{ mol}$$~~

$$m(\text{CH}_3\text{COOH}) = 6.38 \times 10^{-2} \text{ mol} \times 60.00 \text{ g mol}^{-1} = 3.82817 \text{ g (in } 20 \text{ mL)}$$

~~$$m(\text{CH}_3\text{COOH}) \text{ in } 100 \text{ mL} = 5 \times 3.82817 \text{ g} = 19.1408 \text{ g}$$~~

$$③ m(\text{solids}) \text{ in } 10 \text{ mL} = 2.130 \text{ g}$$

$$m(\text{solids}) \text{ in } 100 \text{ mL} = 10 \times 2.130 \text{ g} = 21.30 \text{ g}$$

$$m(\text{NaCl}) = m(\text{solids}) - m(\text{H}_2\text{C}_2\text{O}_4) = 21.30 \text{ g} - 6.30369 \text{ g}$$

$$m(\text{NaCl}) = 14.9963 \text{ g}$$

Final answers:

$$m(\text{H}_2\text{C}_2\text{O}_4) = 6.30 \text{ g}$$

$$m(\text{CH}_3\text{COOH}) \approx 19.14 \text{ g}$$

$$m(\text{NaCl}) \approx 14.99 \text{ g}$$

- (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 CaCO_3 and NaCl , with consideration of enthalpy and entropy changes occurring within the solute, solvent and solution.

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

$$K_s(\text{NaCl}) > 1.00$$

$$\Delta_{\text{sol}}H = \Delta_{\text{lat}}H + \Delta_{\text{hydr}}H$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

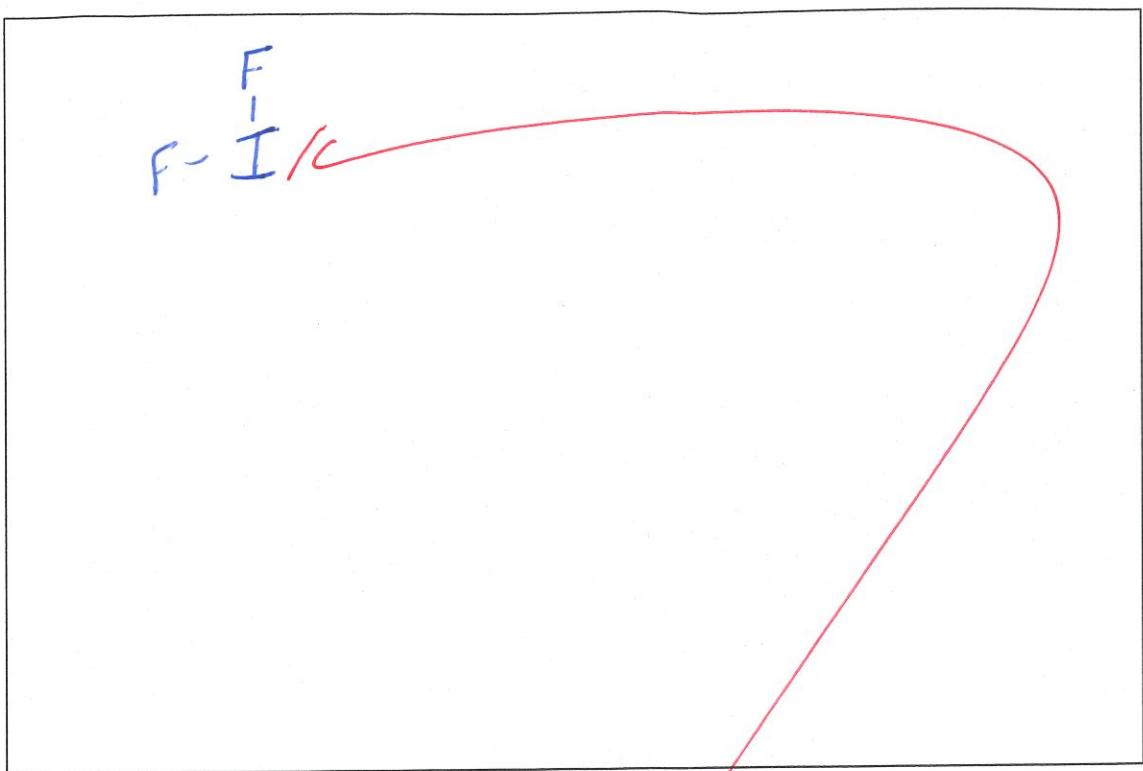
Factors that affect the solubilities of ionic compounds are the size of the charges on the ions, and the ionic radii of the metal ions. A larger ionic charge means so more energy is needed to dissociate the ionic compound, so $\Delta_{\text{lat}}H$ increases. A smaller ionic radii means *a stronger force of attraction between the cations and anions so more energy is needed to dissociate the ionic compound so $\Delta_{\text{lat}}H$ increases.

While the dissolution of both NaCl and CaCO_3 will lead to an increase in the entropy of the system as the ions dissociate and become mobile in water, the $\Delta_{\text{sol}}H$ for NaCl is positive, so entropy of the surroundings decreases due to the dissolution reaction being endothermic. ~~so $\Delta S_{\text{sur}} < 0$~~ NaCl dissolves readily in water however, so the increase in the entropy of the system must therefore outweigh the decrease in the entropy of the surroundings.

Although $\Delta_{\text{sol}}H$ of CaCO_3 is negative (exothermic), CaCO_3 does not dissolve readily in water ($K_s = 3.3 \times 10^{-9}$). This can be attributed to the larger charge (Ca^{2+} vs Na^+), which has more effect than the larger ionic radii ($\text{Ca}^{2+} > \text{Na}^+$). This means that a lot more energy is needed to dissociate the CaCO_3 compared to NaCl

SEE EXTRA SPACE ↗

- (c) (i) Draw all potential 3-dimensional structures for the IF_2O_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 IF_2O_2^- ion.

A large red curved arrow is drawn on a set of horizontal lined paper, starting from the top line and extending downwards and to the right, ending near the bottom line. This arrow likely indicates the direction of electron movement or repulsion in the molecule.

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 CO_2 and 4.410 g of H_2O .



$$M(X) = 90 \text{ g mol}^{-1}$$



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

$$n(\text{H}) = 2n(\text{H}_2\text{O})$$

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

$$n(\text{H}) = 0.49 \text{ mol}$$

$$\text{mM(O)} = 4.388 \text{ g} - 0.19525 \text{ mol} \times 12 \text{ g mol}^{-1} - 0.49 \text{ mol} \times 1 \text{ g mol}^{-1} \\ = 1.555 \text{ g}$$

$$n(\text{O}) = \frac{1.555 \text{ g}}{16 \text{ g mol}^{-1}} = 9.72 \times 10^{-2} \text{ mol}$$



~~1.9525 : 0.49 : 9.72 × 10⁻²~~

$$\underline{0.19525 : 0.49 : 9.72 \times 10^{-2}} \quad \underline{9.72 \times 10^{-2}} \quad \underline{9.72 \times 10^{-2}}$$



$$M(\text{C}_2\text{H}_5\text{O}) = 45 \text{ g mol}^{-1}$$

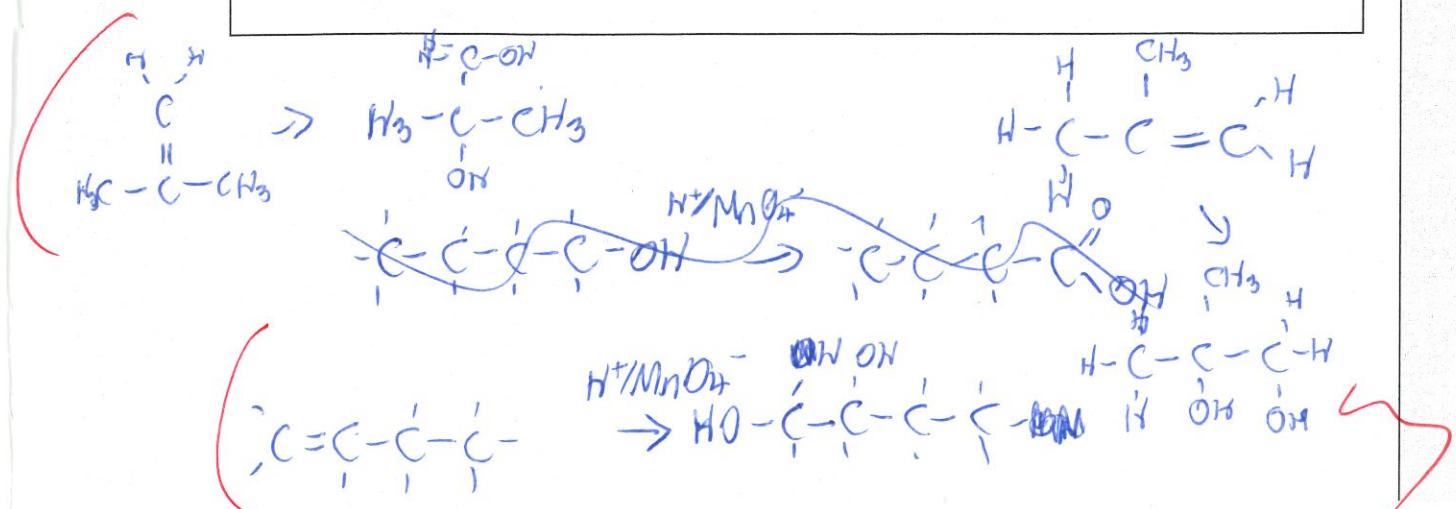
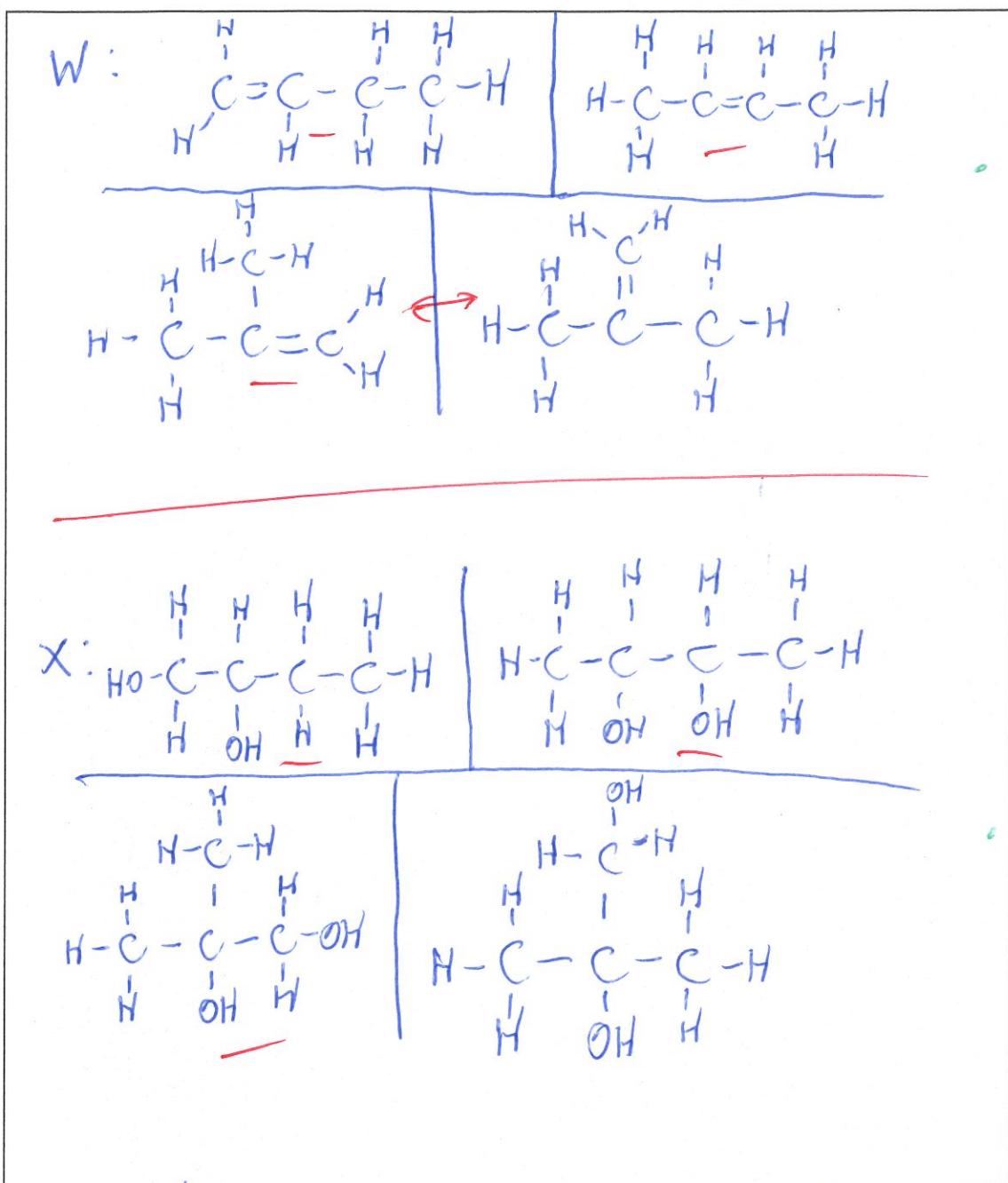
$$\frac{90 \text{ g mol}^{-1}}{45 \text{ g mol}^{-1}} = 2$$

Molecular formula: $\text{C}_2\text{H}_{10}\text{O}_2$ ↗

- (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.

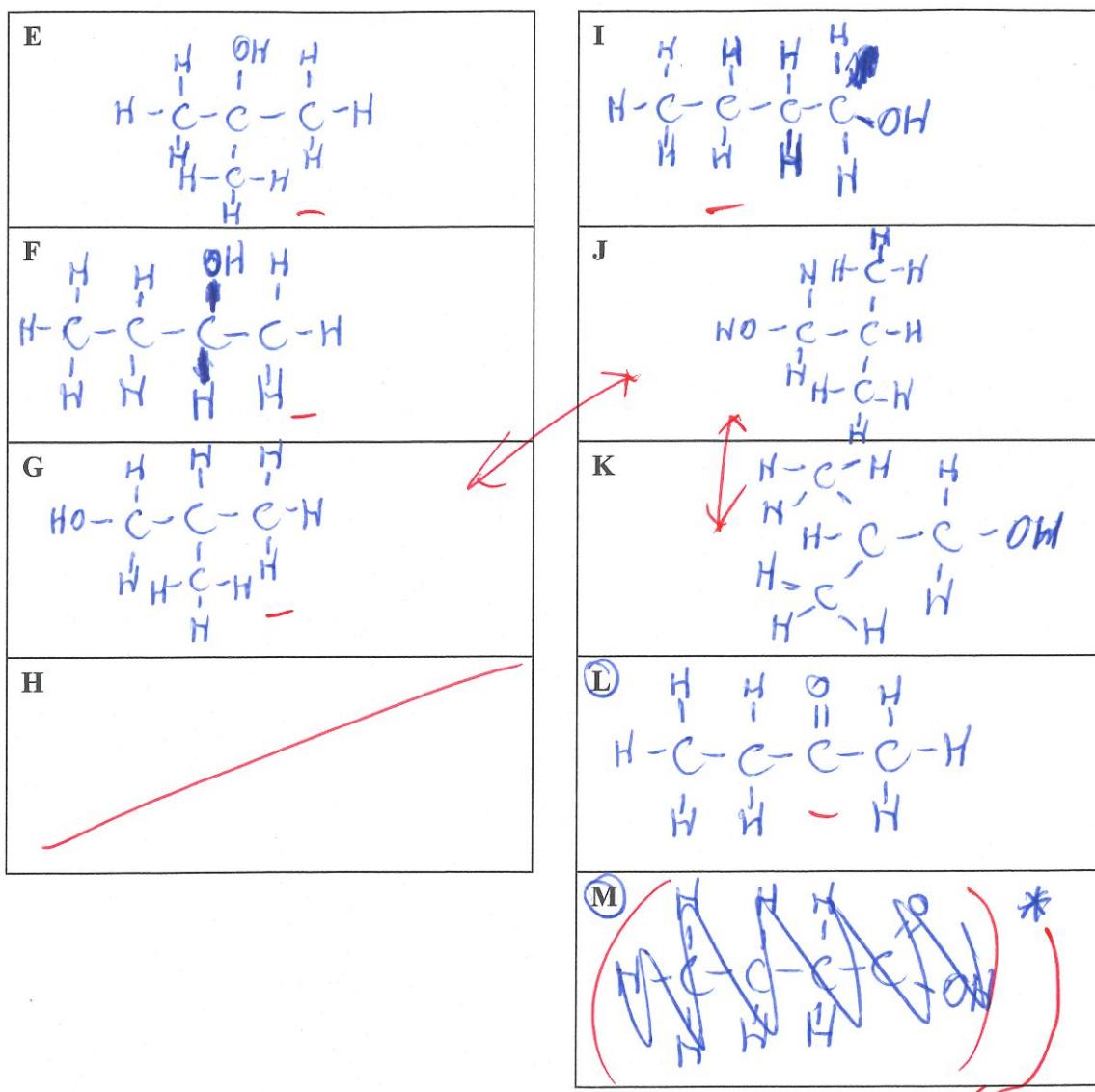
You do not need to name any of the structures.



- (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.

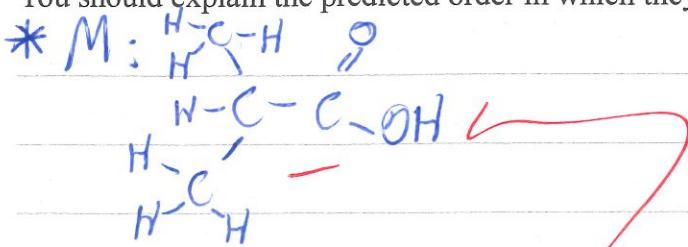
- (i) Determine a structure for each of the nine compounds in the final mixture.

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.



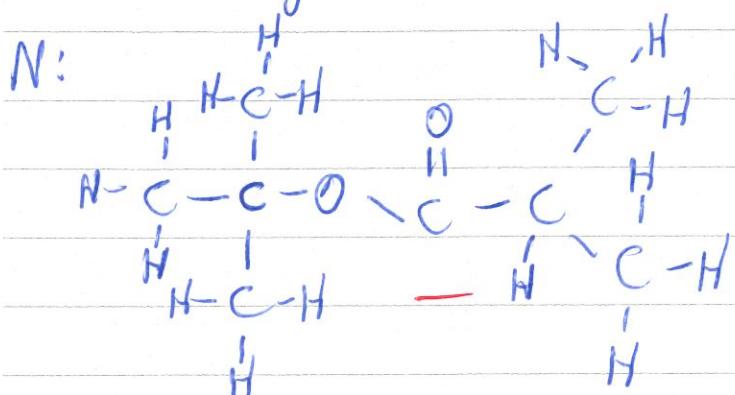
Compound L is a ketone formed from the oxidation of secondary alcohols such as compound F. All other compounds except for the ketone have hydroxyl groups, which can form strong hydrogen bonds with other compounds possessing either a $\text{C}=\text{O}$ group (carbonyl), a -OH group (hydroxyl) or -COOH group (carboxyl). These hydrogen bonds are stronger than permanent dipole-dipole bonds, such as those between $\text{C}=\text{O}$ groups on different compounds. Hence, the ketone (compound L) will have the lowest ~~with~~ boiling point so is expected to be the first compound extracted via distillation.

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

When analysed using ^{13}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}C NMR peaks of the product.

N is an ester formed in a condensation reaction between an alcohol and a carboxylic acid. The conditions required are heat with ~~sulfuric acid catalyst~~.



Since compounds E–M have 4 carbons, to produce a compound that combines two of compounds from E–M, one compound must have 2 carbon environments. Compound E satisfies this, and is also an alcohol, which is required for the condensation reaction.

Compound M must therefore be a carboxylic acid and have 3 carbon environments, so the ester will have a total of 5 carbon environments. Compound M satisfies this.

QUESTION FOUR

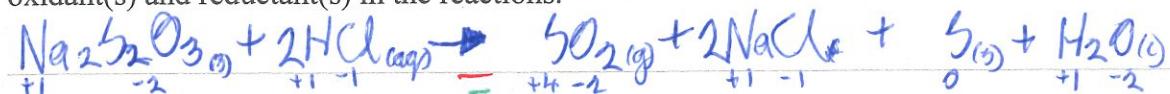
- (a) Solid sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, can react with both dilute hydrochloric acid, $\text{HCl}(aq)$, and concentrated nitric acid, $\text{HNO}_3(\text{conc})$.

When it is reacted with dilute hydrochloric acid, $\text{HCl}(aq)$, colourless sulfur dioxide gas, $\text{SO}_2(g)$, is released from the mixture, and a yellow solid is slowly formed in the solution.

When it is reacted with concentrated nitric acid, $\text{HNO}_3(\text{conc})$, brown nitrogen dioxide gas, $\text{NO}_2(g)$, 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, $\text{SO}_4^{2-}(aq)$.

Account for the oxidation and reduction processes occurring in the reactions with $\text{HCl}(aq)$ and $\text{HNO}_3(\text{conc})$.

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

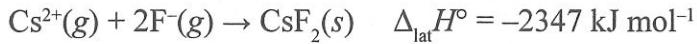


$\text{S}_2\text{O}_3^{2-}$ When $\text{Na}_2\text{S}_2\text{O}_3$ reacts with HCl , the changes in oxidation states occurs to the S ~~which~~ in $\text{S}_2\text{O}_3^{2-}$, which is both oxidized and reduced (disproportionation reaction). S has an oxidation state of +2 in $\text{S}_2\text{O}_3^{2-}$, but is oxidized and its oxidation state increases from +2 to +4 in SO_2 . It is reduced in the formation of elemental sulfur, whereby its oxidation state is decreased from +2 to 0.



Both the N in NO_3^- and the S in $\text{S}_2\text{O}_3^{2-}$ are involved in the redox processes in this reaction. The N in NO_3^- has an oxidation state of +5, and is reduced when it forms NO_2 , with its oxidation state decreasing from +5 to +4. The S in $\text{S}_2\text{O}_3^{2-}$ has an oxidation state of +2 and is both oxidized and reduced to form SO_4^{2-} and S, respectively. Its oxidation state increases from +2 to +6 in the formation of SO_4^{2-} , and its oxidation state decreases from +2 to 0.

- (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, Δ_fH° , for $\text{CsF}_2(s)$, and then justify why CsF_2 does not exist, but CsF does.

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

| | |
|---|---|
| $\text{Cs}(s) \rightarrow \text{Cs}(g)$ | $\Delta_fH^\circ = +76.0 \text{ kJ mol}^{-1}$ |
| $\text{Cs}(g) \rightarrow \text{Cs}^+(g) + \text{e}^-$ | $\Delta_fH^\circ = +382 \text{ kJ mol}^{-1}$ |
| $\text{Cs}^+(g) \rightarrow \text{Cs}^{2+}(g) + \text{e}^-$ | $\Delta_fH^\circ = +2430 \text{ kJ mol}^{-1}$ |
| $\text{F}_2(g) \rightarrow 2\text{F}(g)$ | $\Delta_fH^\circ = +158 \text{ kJ mol}^{-1}$ |
| $\text{F}(g) + \text{e}^- \rightarrow \text{F}^-(g)$ | $\Delta_fH^\circ = -334 \text{ kJ mol}^{-1}$ |
| $\text{Cs}(s) + \frac{1}{2}\text{F}_2(g) \rightarrow \text{CsF}(s)$ | $\Delta_fH^\circ = -554 \text{ kJ mol}^{-1}$ |

$$\Delta_fH^\circ = 4725 \text{ kJ mol}^{-1}$$

$$76 + 382 + 2430 + 158 - 2 \times 334 + 2347 = 4725 \text{ kJ mol}^{-1}$$

- (ii) Justify the differences in the lattice formation enthalpies for CsF and CsF₂.

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

Cs^{2+} has a larger charge* than Cs^+ , so will form stronger forces of attraction between with anions. Hence, a lot more energy is released upon the formation of CsF₂ (as Cs^{2+} is forming ionic bonds with F⁻) compared to CsF (Cs^+ is forming ionic bonds with F⁻).

The lattice enthalpy of formation of CsF₂ is therefore more exothermic than the lattice enthalpy of formation of CsF (as $\Delta_{\text{lat}}H^\circ = -2347 \text{ kJ mol}^{-1}$ as $\Delta_{\text{lat}}H^\circ = -757 \text{ kJ mol}^{-1}$).

*and smaller ionic radius.

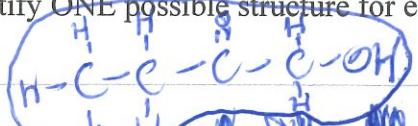
Question Four continues
on the next page.

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

^{13}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.

$M < 100 \text{ g mol}^{-1}$

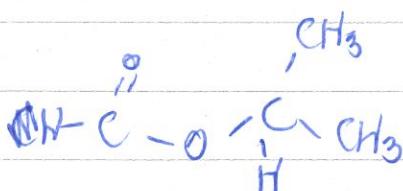


1-hydroxybutanal

A:

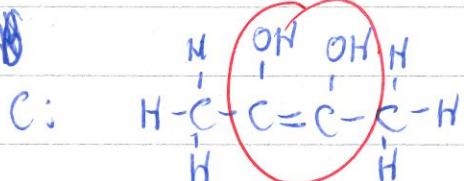


B:



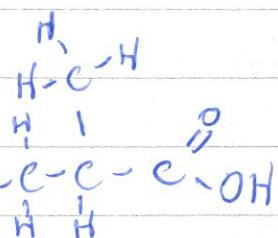
3-propyl methanate

C:



but-2-ene-2,3-diol

D:



2,2-dimethylpropanoic acid

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

peaks

A: Has 4 C environments, with ^{13}C NMR peaks at around 220 and 60, implying a ketone and alcohol respectively. No peak at around 180 confirms this as there is no carboxyl group present.

B: Has 3 C environments, so two C are in the same environment. No O-H band at $3600-3300 \text{ cm}^{-1}$ on IR spectra so no hydroxyl group present. C=O band at $1750-1735 \text{ cm}^{-1}$ so implies ester. Confirmed ester with ^{13}C NMR peak at 160.

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

seen

2.

b) therefore it is less thermodynamically favorable and hence its relative solubility is much lower than NaCl. The $\Delta_{\text{hyd}}H$ of Ca^{2+} and CO_3^{2-} will be very large due to the strong force of attraction between the ~~the~~ polar H_2O molecules and the ions, and this compensates for the large $\Delta_{\text{sol}}H$. However, hydration shells form and can be considered a decrease in entropy of the system. This makes it thermodynamically unfavorable for the CaCO_3 to dissolve.

NaCl has a much lower $\Delta_{\text{lat}}H$ and its ions have a much lower $\Delta_{\text{hyd}}H$ due to the smaller ionic charge, so much less energy is needed to split the lattice, and much less energy is released from the hydration of the Na^+ and Cl^- ions. Although $\Delta_{\text{sol}}H$ is positive, it is very small and the small increase in entropy from the dissociation of NaCl compensates for it so the dissolution of NaCl is thermodynamically favourable ($K_s > 1$).

4.

a) Hence, in the reaction between $\text{Na}_2\text{S}_2\text{O}_3$ and HCl, the ~~$\text{S}_2\text{O}_3^{2-}$~~ is both the oxidant and the ~~reductant~~ reductant.

In the reaction between $\text{Na}_2\text{S}_2\text{O}_3$ and HNO_3 , the NO_3^- is the oxidant, and the $\text{S}_2\text{O}_3^{2-}$ is ~~both~~ both the reductant and the oxidant. seen

QUESTION
NUMBER

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

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