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TOP SCHOLAR



Mana Tohu Mātauranga o Aotearoa
New Zealand Qualifications Authority

Scholarship 2024 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 2–24 in the correct order and that none of these pages is blank.

Do not write in any cross-hatched area (⚡). This area will be cut off when the booklet is marked.

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

QUESTION ONE

- (a) Hydrated salts contain a discrete number of molecules of water as part of their crystal structure (as opposed to anhydrous salts, which have no water as part of their crystal structure).

Epsom salts, a common health supplement, are hydrated magnesium sulfate crystals, $\text{MgSO}_4 \cdot n\text{H}_2\text{O}(s)$.

To determine the value for n in the crystal structure, a student carried out the following:

- An accurately weighed sample of the hydrated salt was heated strongly for 5 minutes in a crucible with the lid partially off.
- After heating, the lid was replaced, and the crucible with its lid was cooled and weighed.
- The heating, cooling, and weighing process was then repeated until the mass remained constant.

The results are summarised below:

Item	Mass (g)
Crucible + lid	23.920
Crucible + lid + hydrated salt	27.712
Crucible + lid + contents after first heating	26.306
Crucible + lid + contents after second heating	25.902
Crucible + lid + contents after third heating	25.775
Crucible + lid + contents after fourth heating	25.775

- (i) Use the results given to determine the whole number value for n in hydrated magnesium sulfate, $\text{MgSO}_4 \cdot n\text{H}_2\text{O}(s)$, and then calculate the mass of Epsom salts required to make a standard solution of a $0.255 \text{ mol L}^{-1} \text{ Mg}^{2+}$ ions in a 250.0 mL volumetric flask.

$$M(\text{MgSO}_4) = 24.3 + 32.1 + 64 = 120.4 \text{ g mol}^{-1}$$

$$27.712 - 23.92 = 3.792 \text{ g} = \text{mass of hydrated salt}$$

after all H_2O is removed, mass of salt is

$$(27.71 - (25.775 - 23.92)) = 1.855 \text{ g}$$

$$3.792 - 1.855 = 1.937 \text{ g } \text{H}_2\text{O}$$

$$\frac{1.937}{18} = 0.1076 \quad \frac{1.855}{120.4} = 0.01541$$

$$\frac{0.1076}{0.01541} = 6.98 = 7 \text{ mol } \text{H}_2\text{O} \text{ for every } 1 \text{ mol } \text{MgSO}_4$$

$$n = 7 \quad \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$$

$$M(\text{salt}) = M(\text{MgSO}_4 \cdot 7\text{H}_2\text{O}) = 120.4 + 7 \times 18 = 246.4 \text{ g mol}^{-1}$$

$$0.255 \times 0.25 = 0.06375 \text{ mol } \text{Mg}^{2+} \text{ required}$$

$$0.06375 \times 246.4 = 15.708 = 15.71 \text{ g Epsom salts required}$$

- (ii) After the fourth heating cycle, the contents of the crucible were left with the lid off for an hour. When the contents in the crucible were reweighed after this time, the mass had increased.

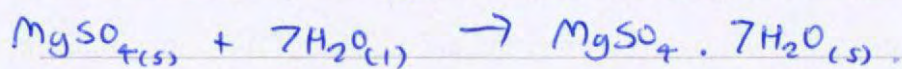
Discuss the thermodynamics of the process that has occurred over this period of time, including a balanced equation to support your answer.

After the 4th cycle, all that remains in the crucible is MgSO_4 .

Some gaseous water in the air may condense into the crucible and hydrate the MgSO_4 as the crucible is open. A process is spontaneous if $\Delta S_{\text{universe}}$

is positive ($\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$)

$\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$. When water condenses, the entropy of the surroundings ^{increases} ~~decreases~~ as this is an exothermic process as when ~~bonds~~ intermolecular forces of attraction are formed, energy is released to the surroundings. However, the entropy of the system ~~decreases~~ as the liquid water molecules are arranged with more order compared to the gaseous water molecules. The process is spontaneous, so the positive entropy change of the surroundings must outweigh the negative entropy change of the system for $\Delta S_{\text{universe}}$ to be positive.



When $\text{MgSO}_4(\text{s})$ is hydrated, the entropy of surroundings increases as when the attractive forces form between the molecules of water and ions in MgSO_4 , heat energy is released to the surroundings. The entropy of system decreases as the water molecules in the crystal structure are rigidly held and not as free as able to move compared to when in the liquid state, so the entropy of system decreases. As the process is spontaneous, $\Delta S_{\text{universe}}$ must be positive so the positive change in entropy of the surroundings must outweigh the negative change in entropy of the system.

(b) An unknown organic compound, Compound A, was produced during a multi-step reaction process. It was determined by elemental analysis to have the molecular formula $C_8H_{16}O_3$.

- (i) IR spectroscopic analysis was carried out on a sample of Compound A. The IR spectra is provided in the resource booklet.

Identify, with reasons, the possible combinations of functional groups which could be present in Compound A.

Compound A ~~must~~ could contain an OH group due to the broad stretch around $3600 - 3300\text{ cm}^{-1}$. There could also be a ~~as~~ carbon to carbon double bond because of the peak around $3100 - 3010\text{ cm}^{-1}$; there is also a strong peak around 1720 cm^{-1} so Compound A could contain a ketone or aldehyde ~~functional group~~ or an ester functional group.

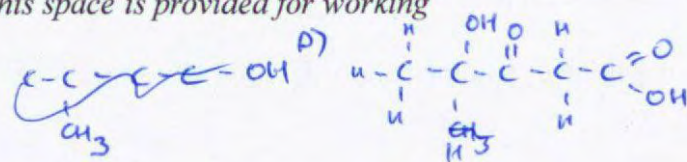
- (ii) Compound A was reacted to form a range of other compounds, which were given the labels Compounds B–F. None of A–F rotated plane-polarised light.

- Compound A was not water-soluble, and did not change the colour of damp red or blue litmus paper.
- Compound A reacted with dilute H_2SO_4 under reflux to produce Compounds B and C, which were separated by distillation.
- Compounds B and C were both water-soluble. Compound B had a molar mass of 118 g mol^{-1} , and Compound C had a molar mass of 60 g mol^{-1} .
- Compound B did not react on heating with concentrated H_2SO_4 .
- When Compound B was reacted with $H^+/Cr_2O_7^{2-}$, it gave Compound D, with the molecular formula $C_5H_8O_4$.
- Both Compounds C and D were treated separately with $SOCl_2$ to give Compounds E and F respectively. Compound F reacted violently with water, while Compound E did not.

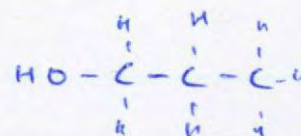
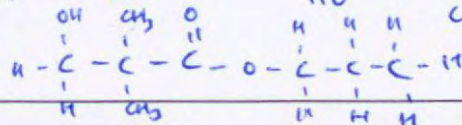
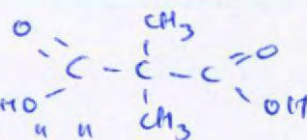
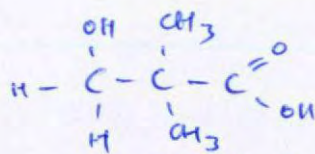
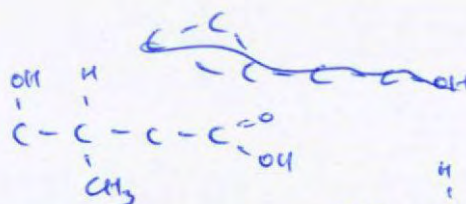
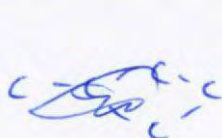
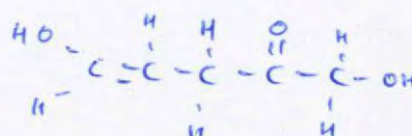
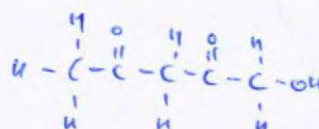
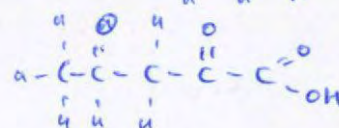
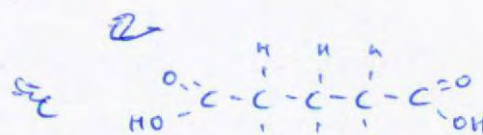
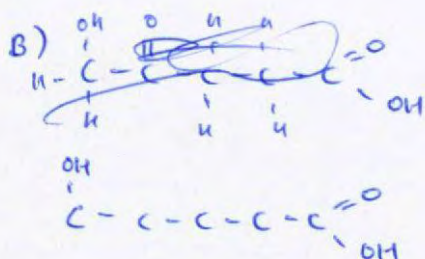
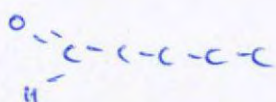
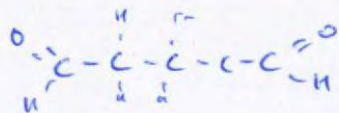
Use the information provided to identify the structures of Compounds A–F.

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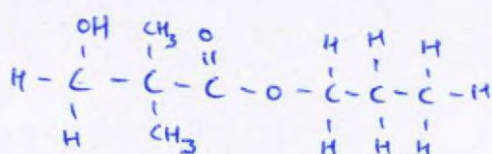
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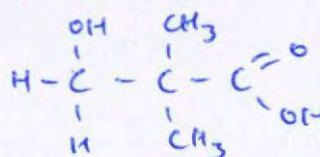
E) HO COOH



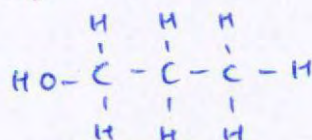
Compound A



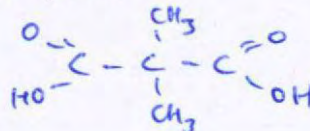
Compound B



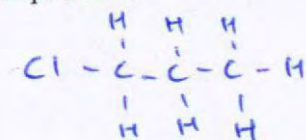
Compound C



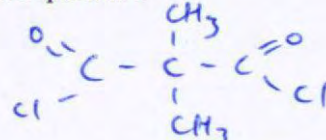
Compound D



Compound E



Compound F



(iii) ^{13}C NMR spectra for THREE of Compounds A–F are provided in the resource booklet.

Identify, with brief reasons, which of Compounds A–F could have produced the three spectra provided.

Spectrum 1:

B. There are 4 unique carbon environments indicated by the 4 peaks and B has 4 unique C environments. The peak shift around 180 ppm ^{corresponds with} represents the C in the carbonyl group and the shift around 70 ppm the C ~~in the~~ bonded to the OH group.

Spectrum 2:

D. There are 3 unique C environments in the compound corresponding with the 3 peaks in the spectrum. The peak around 170 ppm corresponds with the C in the carbonyl group while the peaks around 50 and 20 ppm represent the other 2 C environments.

Spectrum 3:

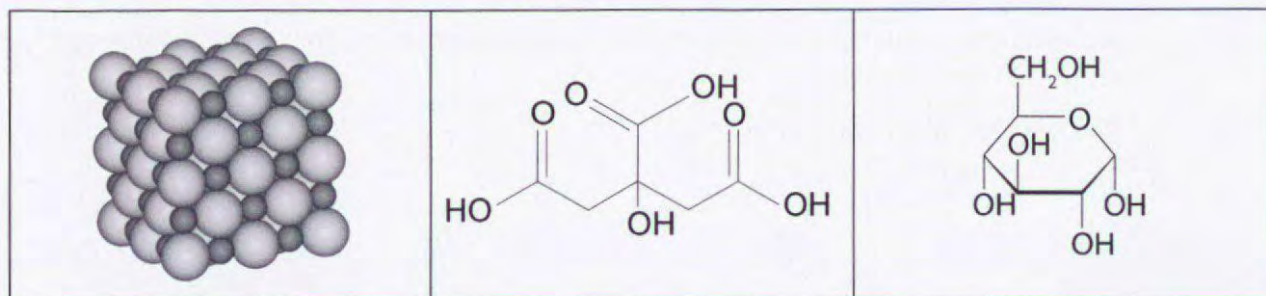
C - There are 3 unique C environments in compound C corresponding with the 3 peaks in the ^{13}C NMR spectrum. The peaks around 10 and 30 ppm correspond with C2 and C3 in compound C as they are saturated alkanes. The peak around 60 ppm corresponds with C1 as it is bonded to an OH group.

QUESTION TWO

- (a) Rehydration powders are commonly sold as medical treatments for people who are mildly dehydrated, or for use in sports drinks to help replenish water and electrolytes (salts) that have been lost through sweat.

The solution resulting from dissolving the powders in water contains a mixture of substances.

Three compounds that are present in many rehydration powders are sodium chloride, $\text{NaCl}(s)$, citric acid, $\text{C}_6\text{H}_8\text{O}_7(s)$, and glucose, $\text{C}_6\text{H}_{12}\text{O}_6(s)$.



Discuss the particle interactions which occur when these compounds are dissolved in water.

Include clear references to particles and attractive forces.

When a compound dissolves in water, the ^{solute} solute-solvent attractive forces must be greater than the solvent-solvent and solute-solute attractive forces. NaCl is an ionic compound, so when it dissolves, Na^+ ions and Cl^- ions form attractive forces with the polar H_2O molecules (shown below). These attractive forces are greater than those between Na^+ and Cl^- ions so they are soluble in water.

Citric acid deprotonates in water, so each of its COOH groups become charged carboxylate ions. The ^{attractive} attractive forces between the carboxylate ions and H_2O molecules are greater than the forces between citric acid molecules themselves, so it is soluble in water. Glucose forms intermolecular forces of attraction with water molecules, as it contains OH groups with highly polar O-H bonds, it can form hydrogen bonds with water molecules (depicted below) which make the solute-solvent ^{attractive} forces to be stronger than the solvent-solvent and solute-solute forces so glucose is soluble in water. Citric acid, when it is not deprotonated, can also form the same hydrogen bonds as hydrogen bonds.

Diagram illustrating the dissolution of sodium chloride in water:

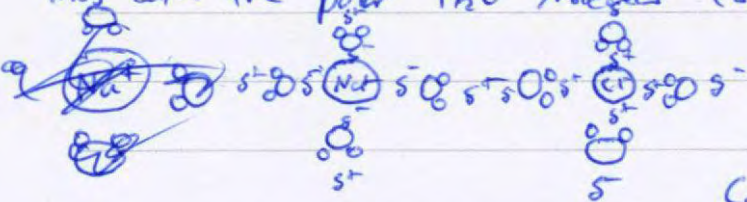
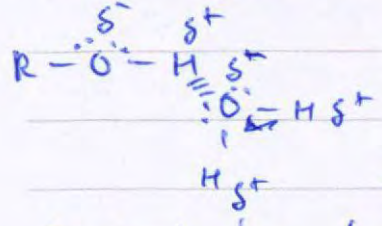


Diagram illustrating the dissolution of glucose in water:



(b) Consider the four aqueous solutions below.

Solution A: $0.350 \text{ mol L}^{-1} \text{ CH}_3\text{CH}_2\text{OH}$

Solution B: $0.350 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$

Solution C: $0.350 \text{ mol L}^{-1} \text{ CH}_3\text{COONa}$

Solution D: 0.350 mol L^{-1} of both CH_3COOH and CH_3COONa

$$\text{p}K_a(\text{CH}_3\text{COOH}) = 4.76$$

- (i) Using relevant chemical equations, compare the pH of each solution to that of pure water. Include in your answer, an outline of the relative concentrations of chemical species present in each solution.

No calculations are necessary.

pH of water = 7. $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ are equal in water.

- $\text{CH}_3\text{CH}_2\text{OH}$ is neither a proton acceptor or donor so does not dissociate to form H_3O^+ or OH^- ions in solution. Thus,

the pH of solution A is the same as in water.

- CH_3COOH is a weak acid. It dissociates partially to form H_3O^+ ions.



Hence, $[\text{H}_3\text{O}^+]$ is greater in solution B than in water.

The pH of solution B is lower than in water.

- CH_3COO^- is a weak base. It partially dissociates, forming OH^- ions.

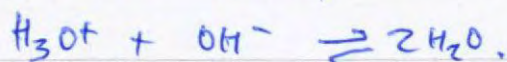


$[\text{OH}^-]$ is greater in C than in water so the pH of C is greater than in water.

- $K_a(\text{CH}_3\text{COOH}) = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$ Because ^{the} $\text{p}K_a$ of CH_3COOH is below 7, CH_3COOH is a

stronger acid than CH_3COO^- is a base so a greater proportion of CH_3COOH will dissociate in solution to form H_3O^+ ions. This means that when added in equal concentrations, $[\text{H}_3\text{O}^+]$ will be greater than $[\text{OH}^-]$ so the pH of D is lesser than in water.

- For all solutions,



where $10^{-7} = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$. Where $[\text{H}_3\text{O}^+]$ is

then 10^{-7}
 greater, $[\text{OH}^-]$ will be lower, than $[\text{H}_3\text{O}^+]$. The same
 is true for the inverse, such that when $[\text{H}_3\text{O}^+]$ is lower, $[\text{OH}^-]$ is greater than $[\text{H}_3\text{O}^+]$

- (ii) 10.0 mL of 0.460 mol L⁻¹ sodium hydroxide solution, NaOH(aq), was mixed with 45.0 mL of Solution D (0.350 mol L⁻¹ of both CH₃COOH and CH₃COONa).

Calculate the pH of the resulting solution after mixing.

$$\begin{aligned}
 & \text{Reaction: } \text{OH}^- + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \\
 & 0.045 \times 0.35 = 0.01575 \text{ mol CH}_3\text{COO}^- \\
 & 0.46 \times 0.01 = 4.6 \times 10^{-3} \text{ mol OH}^- \text{ added} \\
 & 0.01575 - 4.6 \times 10^{-3} = 0.01115 \text{ mol CH}_3\text{COOH remaining} \\
 & 0.01575 + 4.6 \times 10^{-3} = 0.02035 \text{ mol CH}_3\text{COO}^- \text{ in solution} \\
 & K_a(\text{CH}_3\text{COOH}) = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \\
 & [\text{CH}_3\text{COOH}] = \frac{0.01115}{0.055} = 0.2027 \text{ mol L}^{-1} \\
 & \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{0.02035}{0.055} = 0.37 \text{ mol L}^{-1} \\
 & 10^{-4.76} = \frac{[0.37][\text{H}_3\text{O}^+]}{[0.2027]} \quad [\text{H}_3\text{O}^+] = 9.52 \times 10^{-6} \text{ mol L}^{-1} \\
 & \text{pH} = -\log(9.52 \times 10^{-6}) = 5.02
 \end{aligned}$$

(c) A student was tasked with determining the anions and cations present in two aqueous solutions using qualitative analysis.

(i) To determine the anions, they carried out the following tests.

Solution A

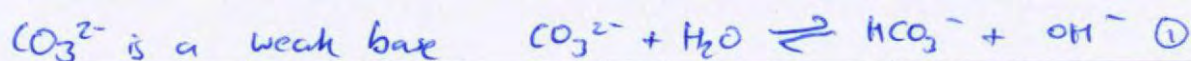
- The student started with 2 mL of Solution A in a clean test tube.
- On addition of 2 drops of AgNO_3 solution, a white precipitate formed.
- On addition of dilute nitric acid, the precipitate dissolved, and gas was produced.

Solution B

- The student started with 2 mL of Solution B in a clean test tube.
- On addition of 2 drops of AgNO_3 solution, a white precipitate formed.
- On addition of dilute nitric acid, the precipitate remained.
- To a new 2 mL sample of Solution B, the student added 2 drops of AgNO_3 solution, and a white precipitate formed.
- On addition of excess dilute NH_3 solution the white precipitate dissolved.

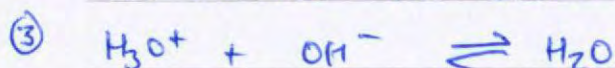
The student concluded Solution A contained CO_3^{2-} ions, and Solution B contained Cl^- ions.

Use equilibrium principles and balanced chemical equations to justify the observations made during the qualitative analysis.



when AgNO_3 is added, the $2\text{Ag}^+ + \text{CO}_3^{2-} \rightarrow \text{Ag}_2\text{CO}_3(s)$

② $2\text{Ag}^+_{(aq)} + \text{CO}_3^{2-}_{(aq)} \rightleftharpoons \text{Ag}_2\text{CO}_3(s)$ a precipitate of Ag_2CO_3 forms. However, when HNO_3 is added, H_3O^+ ions are added to solution.



From equation 3, increasing $[\text{H}_3\text{O}^+]$ will decrease $[\text{OH}^-]$. This will cause the equilibrium in equation 1 to shift to favor the products to replace the OH^- ions, decreasing $[\text{CO}_3^{2-}]$. When $[\text{CO}_3^{2-}]$ decreases, from equation 2, the equilibrium will shift to favor the left side to replace the CO_3^{2-} , therefore causing the precipitate to dissolve as its solubility increases.

$\text{Ag}_2\text{CO}_3(s) + 2\text{HNO}_3(aq) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l) + 2\text{AgNO}_3(aq)$

acid reacts with a metal carbonate to form CO_2 gas, which was the gas produced in A.

For B, when AgNO_3 is added, $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)}$ ④

a precipitate of AgCl forms, when HNO_3 is added, the Cl^- and Ag^+ are exchanged. However, when NH_3 is added,

2 $\text{Ag}^+_{\text{aq}} + \text{NH}_3_{\text{(aq)}} + 4\text{NH}_3_{\text{(aq)}} \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+_{\text{(aq)}}$ a complex ion is formed, which is soluble in water. This decreases $[\text{Ag}^+]_{\text{aq}}$ thus in equilibrium 4, the equilibrium shifts to favor the right side to replace Ag^+_{aq} by increasing solubility.

- (ii) To determine the cations, the student added sodium hydroxide solution, NaOH(aq) , to samples of **A** and **B**, but neither produced a precipitate. The student concluded that the cation in each solution must be sodium ions, Na^+ .

Their teacher noted this was the incorrect result for Solution **B**, and they told the student that it contains either Mg^{2+} or Ba^{2+} ions, and should have formed a hydroxide precipitate.

The student had placed 2 mL of Solution **B** in a test tube and slowly added up to 5 mL of $0.0875 \text{ mol L}^{-1} \text{ NaOH(aq)}$ without getting any precipitate. The teacher repeated the procedure, and the result was the same.

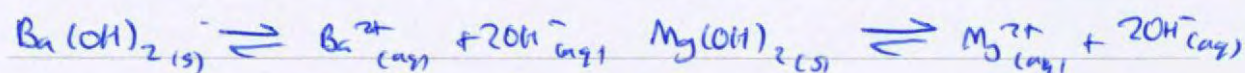
Solution **B** had been prepared by taking 30.0 mL of a 0.100 mol L^{-1} stock solution, diluting it to 150.0 mL using distilled water, before placing it into dropper bottles.

Use calculations to determine the cation and show why no precipitate was formed in Solution **B**.

$$K_s(\text{Ba}(\text{OH})_2) = 3.00 \times 10^{-4} \quad K_s(\text{Mg}(\text{OH})_2) = 7.10 \times 10^{-12}$$

$$\frac{0.1 \times 0.03}{0.15} = 0.02 \text{ mol L}^{-1} = [\text{salt metal chloride}]$$

$$\frac{0.02 \times 0.002}{0.007} = 5.71 \times 10^{-3} \text{ mol L}^{-1} = [\text{metal ion}]$$



$$K_s(\text{Ba}(\text{OH})_2) = [\text{Ba}^{2+}][\text{OH}^-]^2 \quad K_s(\text{Mg}(\text{OH})_2) = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$Q_s = 5.71 \times 10^{-3} \times [\text{OH}^-] = \frac{0.0875 \times 0.005}{0.007} = 0.0625 \text{ mol L}^{-1}$$

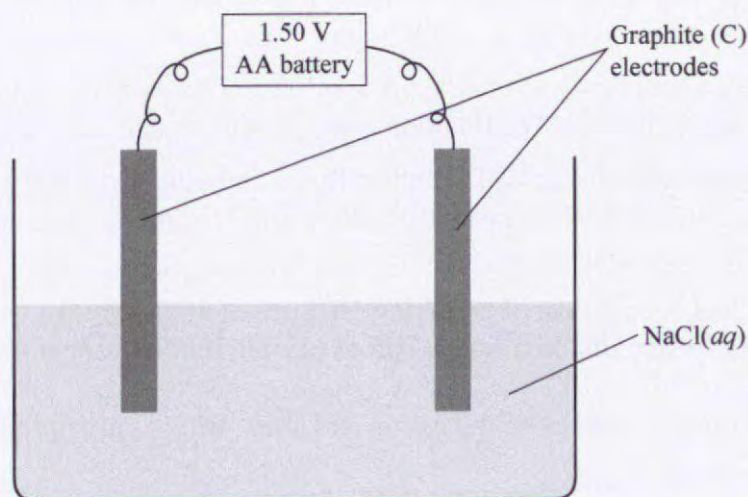
$$Q_s = [5.71 \times 10^{-3}][0.0625]^2 = 2.23 \times 10^{-5}$$

As $Q_s > K_s$ for $\text{Mg}(\text{OH})_2$ but no precipitate formed, this means the solution contains Ba^{2+} . No precipitate forms as $Q_s < K_s(\text{Ba}(\text{OH})_2)$.

QUESTION THREE

- (a) Saltwater chlorination, a process involving electrolysis, is an alternative to directly adding chlorine-based chemicals to swimming pool water. In standard electrolysis conditions, the strongest oxidant reacts at one electrode, and the strongest reductant reacts at the other. However in high salt concentrations, electrolysis of salt water, $NaCl(aq)$, results in the production of aqueous chlorine $Cl_2(aq)$ instead. This then provides protection to the water.

To replicate this process for a science fair project, a student set up the equipment shown in the diagram below, to demonstrate the chlorination of salt water. Their apparatus included two graphite electrodes, a 1.50 V AA battery, conductive wires, and a concentrated solution of sodium chloride. Once set up, however, no reaction was observed.



Outline modifications the student would need to make to their demonstration to enable the production of chlorine in the solution.

In your answer you should clearly explain all aspects of the electrolytic process, including an outline of the changes occurring at the cathode, the anode, and to the solution, during chlorine production, with support of relevant calculations and equations.

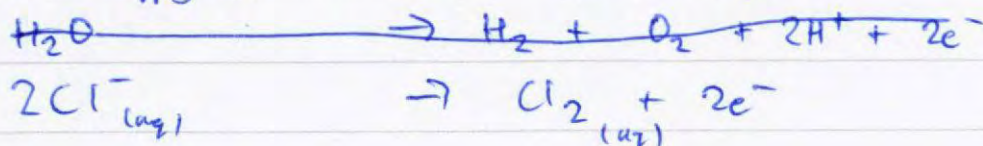
$$E^\circ(Na^+/Na) = -2.71 \text{ V}$$

$$E^\circ(Cl_2/Cl^-) = +1.36 \text{ V}$$

$$E^\circ(H_2O/H_2) = -0.83 \text{ V}$$

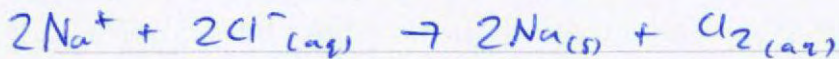
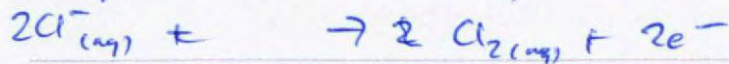
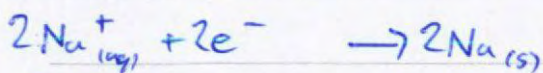
$$E^\circ(O_2/H_2O) = +0.82 \text{ V}$$

~~The strongest oxidant has the most positive E° value, which is H_2O in this case. The strongest reductant has the least positive E° value, which is Na .~~ For Cl_2 to form, $E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox}$
 ~~$= -0.83 - (+1.36) = -2.19 \text{ V}$~~ The strongest oxidant is H_2O .
 $E^\circ_{cell} = -0.83 - (1.36) = -2.19 \text{ V}$. ^{at least} 2.19 V is required to force the reaction to occur. 1.50 V is not sufficient, so a supply of at least 2.19 V is required.





this cannot occur in reduced conditions,



$$E^\circ_{\text{cell}} = -2.71 - 1.36 = -4.07\text{V}$$

at least 4.07V must be supplied to drive this reaction.

At the cathode, a deposit of white solid sodium metal forms.

At the anode, ^{colorless} ~~colorless~~ $\text{Cl}_{2(g)}$ colorless aqueous chlorine is formed.

Oxidation occurs at the anode and reduction occurs at the cathode.

~~Electrons will flow from the anode to the cathode~~

In the solution, $[\text{Na}^+]$ and $[\text{Cl}^-]$ will decrease.

~~The anode must be~~

~~The electrodes are inert so they do not participate~~

- (b) An alternative to saltwater chlorination is to directly add sodium hypochlorite, $\text{NaOCl}(aq)$, to swimming pools.

As part of an investigation into chemical products, a student brought a bottle of pool chlorine into school from home. The pool chlorine was a solution of sodium hypochlorite, $\text{NaOCl}(aq)$; however the label stating the concentration had deteriorated and fallen off the bottle.

The student was tasked with determining the concentration of NaOCl in the bottle.

To analyse the solution, the following method was followed by the student:

Standardisation of $\text{Na}_2\text{S}_2\text{O}_3$

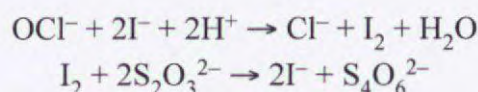
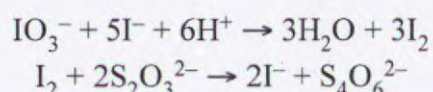
0.533 g of potassium iodate, $\text{KIO}_3(s)$, was dissolved in distilled water in a 100.0 mL volumetric flask. 10.0 mL aliquots of this solution were mixed in conical flasks with excess potassium iodide solution, $\text{KI}(aq)$, and 10 mL of dilute sulfuric acid, $\text{H}_2\text{SO}_4(aq)$. This was then titrated with sodium thiosulfate solution, $\text{Na}_2\text{S}_2\text{O}_3(aq)$, using a starch indicator. The student recorded their data in the first table below.

Pool chlorine analysis

5.00 mL of the pool chlorine solution was pipetted into a 250.0 mL volumetric flask, and filled to the mark. 25.0 mL aliquots of the dilute solution were mixed in conical flasks with excess potassium iodide solution, $\text{KI}(aq)$, and 10 mL of dilute sulfuric acid, $\text{H}_2\text{SO}_4(aq)$. This was then titrated with the same sodium thiosulfate solution, $\text{Na}_2\text{S}_2\text{O}_3(aq)$, using the starch indicator. The student recorded their data in the second table below.

Standardisation of $\text{Na}_2\text{S}_2\text{O}_3$	
Titre	Volume $\text{Na}_2\text{S}_2\text{O}_3(aq)$ (mL)
1	16.50
2	16.45
3	17.10
4	17.45
5	16.40

Pool chlorine analysis	
Titre	Volume $\text{Na}_2\text{S}_2\text{O}_3(aq)$ (mL)
1	18.75
2	18.15
3	18.10
4	17.95
5	18.55



Use the student data provided to determine the concentration of sodium hypochlorite, NaOCl , in the pool chlorine bottle, in g L^{-1} .

$$M(\text{KIO}_3) = 214 \text{ g mol}^{-1}$$

$$M(\text{NaOCl}) = 74.4 \text{ g mol}^{-1}$$

$$\frac{0.533}{214} / 0.1 = 2.49 \times 10^{-3} \text{ mol L}^{-1} = [\text{KIO}_3]$$

$$2.49 \times 10^{-3} \times 0.01 = 2.49 \times 10^{-5} \text{ mol} = n(\text{IO}_3^-)$$

$$2.49 \times 10^{-5} \times 3 = 7.47 \times 10^{-5} \text{ mol} = n(\text{I}_2) \text{ each}$$

$$7.47 \times 10^{-5} \times 2 = 1.49 \times 10^{-4} \text{ mol} = n(\text{S}_2\text{O}_3^{2-}) \text{ added}$$

Average ~~the~~ of ~~one~~ value added of $\text{S}_2\text{O}_3^{2-}$ (average value 2)

$$(16.5 + 16.45 + 16.7) / 3 = 16.45 \text{ mL}$$

$$(1.49 \times 10^{-4}) / 0.01645 = 9.08 \times 10^{-3} \text{ mol L}^{-1} = [\text{S}_2\text{O}_3^{2-}]$$

average volume for iod chloride analysis = $(18.15 + 18.1 + 17.95)/3$

$$= 18.07 = 18.1 \text{ mL} = 0.0181 \text{ L}$$

$$(9.08 \times 10^{-3}) / 0.0181 = \cancel{5.03 \times 10^{-4} \text{ mol}} \times 0.0181 = 1.64 \times 10^{-4} \text{ mol}$$

of $\text{S}_2\text{O}_3^{2-}$ added

$$1.64 \times 10^{-4} / 2 = 8.22 \times 10^{-5} \text{ mol} = n(\text{I}_2)_{\text{formed}} = n(\text{OCl}^-) \text{ in aliquot}$$

$$8.22 \times 10^{-5} \times 100 / 0.025 = \cancel{2.06 \times 10^{-6}} \quad 3.29 \times 10^{-3} \text{ mol L}^{-1} = [\text{OCl}^-]$$

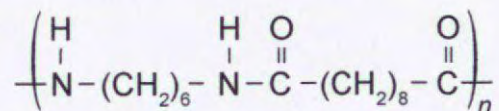
$$\frac{250}{5} \times 3.29 \times 10^{-3} = 0.164 \text{ mol L}^{-1} = [\text{OCl}^-] \text{ in 5 mL sample}$$

$$\cancel{24.4} \quad 0.164 \times 74.4 = 12.2 \text{ g} = 12.2 \text{ g L}^{-1} = [\text{OCl}^-]$$

- (c) Nylons are a family of synthetic polymers. Some types of nylon are combined with other polymers and used in textiles such as clothing and swimwear.

Nylons may be designated nylon-X,Y, where the X and Y are derived from carbon chain lengths in the monomers. An example is nylon-6,10. Nylons designated as nylon-Z, are produced from single monomers with carbon chain length Z.

This diagram shows a section of the nylon-6,10 polymer:

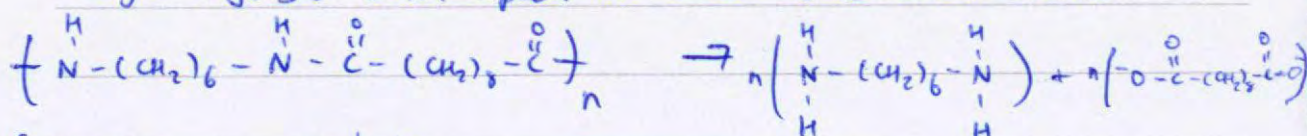


- (i) Nylon-6,10 fabrics may degrade if they are exposed to other chemical substances.

Considering the type of functional groups present in nylon-6,10, discuss which chemical substances may cause damage to such fabrics.

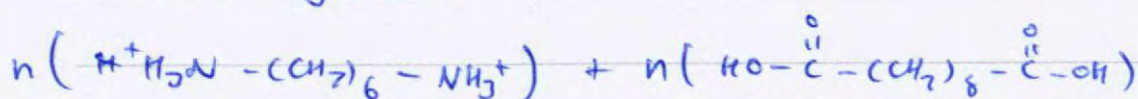
Include structural equations where relevant.

nylon-6,10 contains multiple amide links. This means that it can undergo hydrolysis when exposed to dilute base or acid.



forming products
forming the above products in the basic hydrolysis basic hydrolysis.

In acidic hydrolysis,



is formed. Therefore, such fabrics should be kept away from dilute acid or base, or else they may break and form the above products.

- (ii) Nylon-6,6 and nylon-6 are produced from some of the compounds given in the table.

Compound U $\text{HO}(\text{CH}_2)_6\text{OH}$	Compound V $\text{ClOC}(\text{CH}_2)_4\text{COCl}$
Compound W $\text{H}_2\text{N}(\text{CH}_2)_5\text{COCl}$	Compound X $\text{H}_2\text{NOC}(\text{CH}_2)_4\text{CONH}_2$
Compound Y $\text{HOOC}(\text{CH}_2)_4\text{COOH}$	Compound Z $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$

Choose monomer(s) which could be used to manufacture these two nylons and justify your decision.

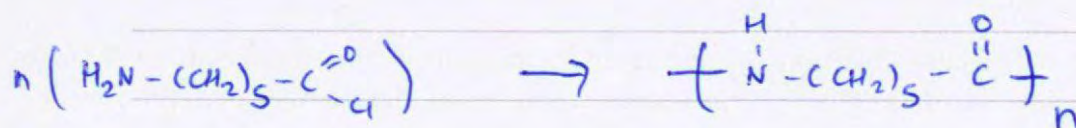
Include a structural equation for the formation of one nylon.

Nylon-6,6 would be derived from 2 monomers with 6 C atoms.
This could be compounds V and ~~W~~^Z as they will react in a condensation polymerisation reaction to form nylon-6,6.

Both compounds have 6 C atoms and will form 1 amide link between the monomers at each end.

Nylon-6 is derived from a single monomer with length 6.

This could be compound W, because at 1 end it contains a COCl group and at the other end a NH_2 group, which can react to form an amide link, forming a long chain polymer, and ejecting a smaller HCl molecule for each amide link formed.

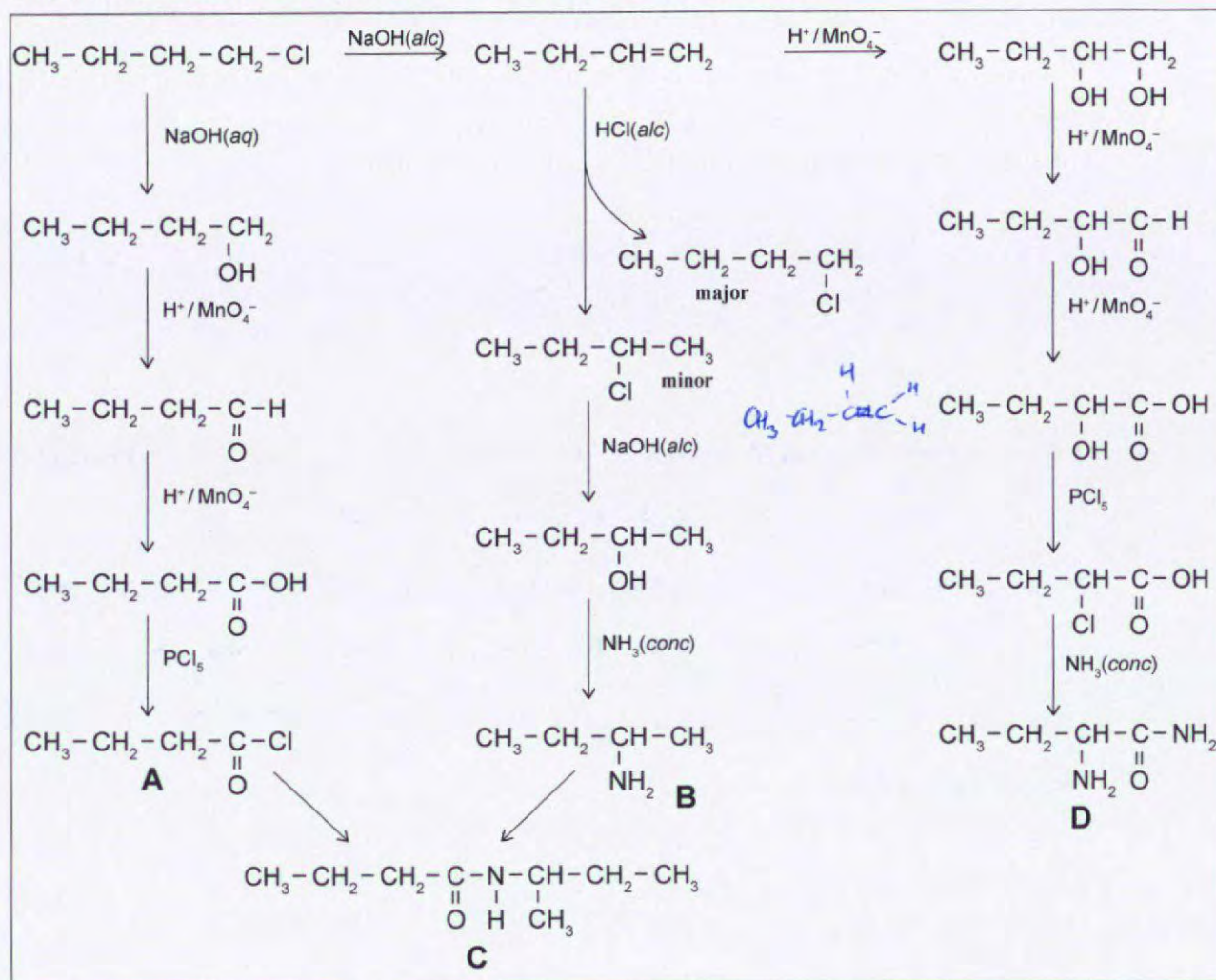


QUESTION FOUR

- (a) Organic chemists apply their knowledge to the development of new reaction pathways for the synthesis of organic compounds.

A student studying organic chemistry has attempted to construct reaction pathways from 1-chlorobutane to a primary and secondary amide, and has described these in the scheme shown below.

Their teacher has identified that there are errors in their scheme.



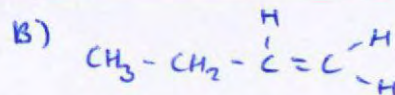
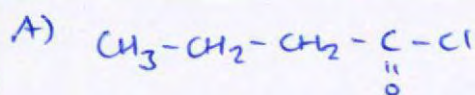
- (i) Identify and discuss any errors in the reagents or structures in the scheme above. Propose suitable alternative reagents or steps necessary to produce the intended final products.

Four products, **A–D**, have been labelled to assist in your discussion.

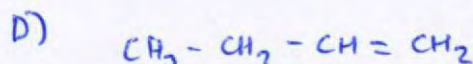
- From 1-butanol to product B, the student used $\text{NH}_3(\text{conc})$ to substitute the OH group with an NH_2 group which cannot occur. Instead, the student should first substitute the OH group with a Cl atom using PCl_5 , then use $\text{NH}_3(\text{conc})$ to substitute the Cl atom with an NH_2 group.
- The major and minor products of the addition reaction of

- but-1-ene with $\text{HCl}_{(\text{aq})}$ are swapped around. The major product shall be 2-chlorobutane and the minor product 1-chlorobutane.
- From 2-chlorobutane to butan-2-ol, $\text{NaOH}_{(\text{aq})}$ is used to substitute the Cl group, however this would result in an elimination reaction. $\text{NaOH}_{(\text{aq})}$ shall be used instead.
 - From but-1-ene to the ~~but-1,2-diol~~ ^{butan-1,2-diol}, $\text{H}^+/\text{MnO}_4^-$ is used but MnO_4^- in ~~neutral conditions~~ ^{neutral conditions} shall be used instead to form the diol.
 - ~~From~~ ^{when} the butan-1,2-diol ~~to the~~ is oxidised, the OH group bonded to C2 shall also be oxidised to a ketone. To fix this, after the aldehyde is ~~oxidised~~ ^{oxidised} to a carboxylic acid, NaBH_4 shall be used, ~~rather than~~ ^{reducing the butanoic acid} so an OH group is ~~still~~ ^{still} bonded to C2 and it can be substituted with a Cl atom.
 - $\text{NH}_3_{(\text{conc})}$ will not substitute the OH group in the carboxylic acid with an NH_2 group when forming D. Instead, ~~the~~ ^{SO} SOCl_2 shall first be added, forming an acyl chloride and then $\text{NH}_3_{(\text{conc})}$ shall be added.

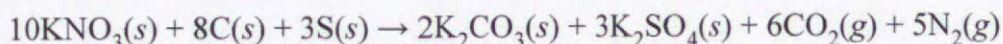
- (ii) Give the structures for the products which would be formed if the synthesis process was carried out using the reagents that the student has proposed in their reaction scheme.



C) would not form



- (b) Black powder, a key component in many fireworks, is a mixture of chemicals that react together to release a large amount of heat and gaseous products. Manufacturers of black powder follow recipes that require a careful ratio of reactants to ensure good fireworks displays. A simplified equation representing the reaction of black powder is shown below.



Calculate the energy released when a sample of black powder containing 200.0 g KNO_3 is completely reacted according to the equation given above.

You can assume all other reactants are present in the correct amounts for a complete reaction.

Enthalpy changes (kJ mol^{-1})

$$\Delta_f H^\circ (\text{KNO}_3(s)) = -493.0 \quad \checkmark$$

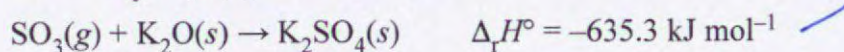
$$\Delta_f H^\circ (\text{K}_2\text{CO}_3(s)) = -1146 \quad \checkmark$$

$$\Delta_f H^\circ (\text{K}_2\text{O}(s)) = -361.0 \quad \checkmark$$

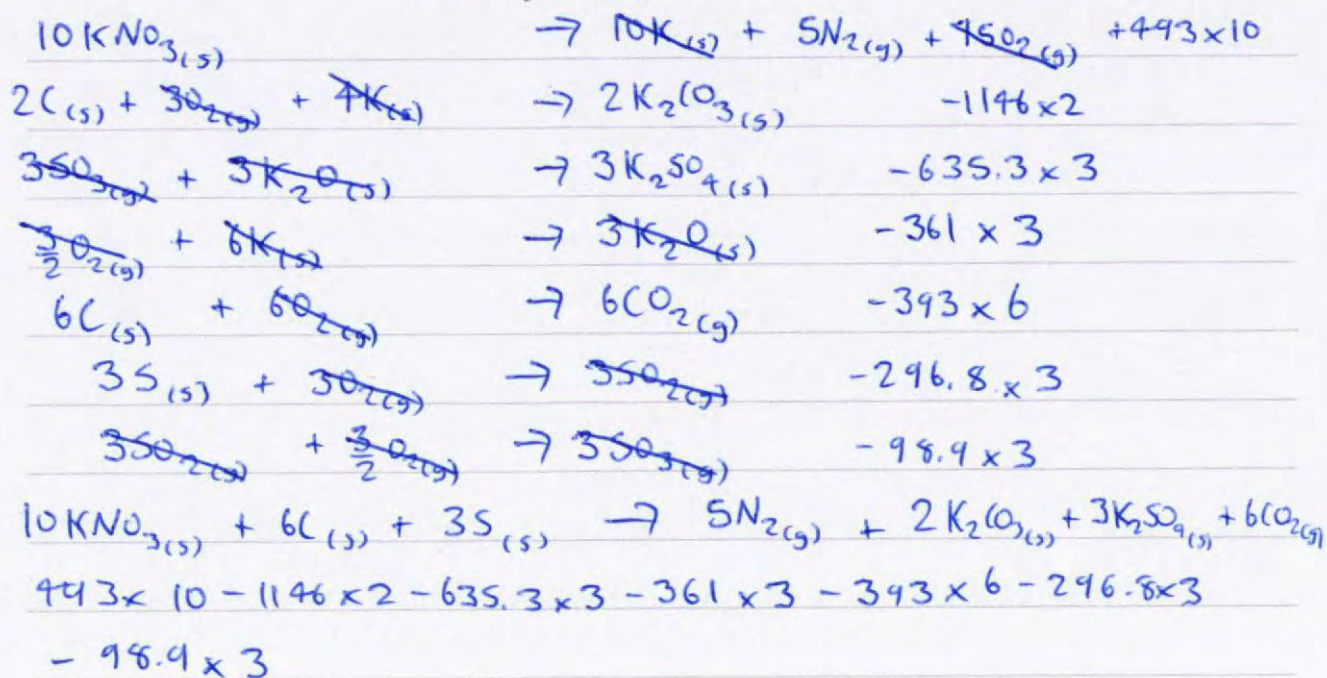
$$\Delta_f H^\circ (\text{SO}_2(g)) = -296.8 \quad \checkmark$$

$$\Delta_c H^\circ (\text{SO}_2(g)) = -98.9$$

$$\Delta_c H^\circ (\text{C}(s)) = -393.0 \quad \checkmark$$



$$M(\text{KNO}_3) = 101.1 \text{ g mol}^{-1}$$



$$= -3896 \text{ kJ mol}^{-1} = \Delta_r H^\circ$$

$$\frac{200}{101.1} = 1.978 \text{ mol KNO}_3$$

$$\frac{1.978}{10} \times 3896 = 770.7 \text{ kJ} \quad \text{energy is released.}$$

Question Four continues
on the following page.

- (c) Samples of four chemicals were lined up on a laboratory bench at room temperature. Three of the chemicals were white solids, and one was a colourless liquid.

The chemicals were: silicon dioxide, SiO_2
 ethanamide, CH_3CONH_2
 methylammonium chloride, $\text{CH}_3\text{NH}_3\text{Cl}$
 phosphorus trichloride, PCl_3

Use your understanding of structure and bonding to account for the states of each chemical at room temperature.

- The melting points of a compound depend on the strength of attractive forces ^{between} the particles in the compound. The stronger the attractive forces, the more heat energy is required to overcome these forces thus the greater the melting point.
- SiO_2 is a giant 3D covalent network molecule. It is made up of Si ^{atoms} covalently bonded to O atoms in a giant lattice. The strength of these covalent bonds is very high therefore significant amounts of heat energy are required to overcome these covalent bonds and SiO_2 is a solid at room temperature.
 - CH_3CONH_2 is a molecular substance so is made up of ~~discrete~~ ^{discrete} molecules of CH_3CONH_2 attracted to each other by ~~the~~ ^{intermolecular} forces of attraction. PCl_3 is also a molecular substance so ^{also} experiences ~~the~~ ^{intermolecular} forces of attraction. However, both ~~CH₃CONH₂~~ ^{CH_3CONH_2} experience permanent dipole-dipole attractions as both molecules ~~are~~ ^{have} an overall molecular dipole. ~~This is~~ However, only CH_3CONH_2 can form hydrogen bonds because of the highly polar N-H bond. A hydrogen bond is depicted in Fig. 1 below. While PCl_3 cannot, therefore, the intermolecular forces of attraction are stronger in CH_3CONH_2 than in PCl_3 hence CH_3CONH_2 is ~~a~~ likely to be a solid while PCl_3 is a ~~liquid~~ colourless liquid. This is despite the stronger instantaneous dipole-induced dipole attractions in PCl_3 as it has a larger molar mass thus larger electron cloud. $M(\text{PCl}_3) \approx 137.5 \text{ g mol}^{-1}$ while $M(\text{CH}_3\text{CONH}_2) \approx 59 \text{ g mol}^{-1}$ so the effect of the hydrogen

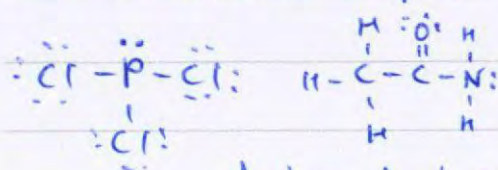
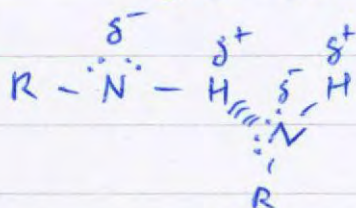


Fig. 1



in PCl_3 hence CH_3CONH_2 is a likely to be

a solid while PCl_3 is a ~~liquid~~ colourless liquid. This is despite the stronger instantaneous dipole-induced dipole attractions in PCl_3 as it has a larger molar mass thus larger electron cloud. $M(\text{PCl}_3) \approx 137.5 \text{ g mol}^{-1}$ while $M(\text{CH}_3\text{CONH}_2) \approx 59 \text{ g mol}^{-1}$ so the effect of the hydrogen

Extra space if required.

Write the question number(s) if applicable.

QUESTION
NUMBER

Q4)c) ~~but~~ not outweigh the ~~st~~ effect of the strong - intermolecular - dipole ~~induced dipole - dipole~~ induced dipole attractions, as hydrogen bonds are very strong.

• $\text{CH}_3\text{NH}_3\text{Cl}$ must be a solid at room temperature as it is an ionic substance. It is made up of ^{alternating} positively charged CH_3NH_3^+ ions and negatively charged Cl^- ions held together by strong ionic bonds in a 3D lattice. These ionic bonds require significant amounts of heat energy to overcome so $\text{CH}_3\text{NH}_3\text{Cl}$ has a high melting point and is a solid at room temperature.

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

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