

No part of the candidate's evidence in this exemplar material may be presented in an external assessment for the purpose of gaining an NZQA qualification or award.

SUPERVISOR'S USE ONLY

S

93102



931020

Draw a cross through the box (X) if you have NOT written in this booklet

☐

+

# OUTSTANDING SCHOLARSHIP EXEMPLAR



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  $250.0 \text{ mL}$  volumetric flask.

$$m(\text{Salt})_i = 27.712 - 23.920 \\ = 3.792 \text{ g}$$

$$m(\text{Salt})_f = 25.775 - 23.920 \\ = 1.855 \text{ g}$$

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

$$n = \frac{m}{Mr} \\ n(\text{H}_2\text{O}) = \frac{1.937}{18}$$

$$= 0.1076 \text{ moles H}_2\text{O}$$

$$n(\text{MgSO}_4)_f = \frac{1.855}{120.4}$$

$$= 0.01541 \text{ moles}$$

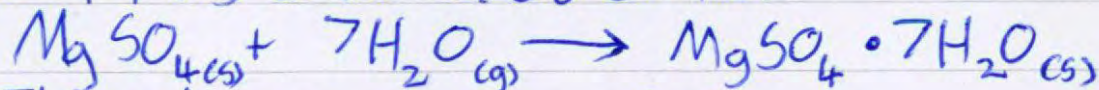
$$n = \frac{0.1076}{0.01541} = 6.9846; n \in \mathbb{N} \text{ so } n = 7$$

|                                                |                           |                          |
|------------------------------------------------|---------------------------|--------------------------|
| $M_r(\text{MgSO}_4 \cdot 7\text{H}_2\text{O})$ | $n = CV$                  | $m = nM_r$               |
| $= 120.4 + 7(18)$                              | $= 0.225 \times 0.25$     | $= 0.05625 \times 246.4$ |
| $= 246.4$                                      | $= 0.05625 \text{ moles}$ | $= 13.86 \text{ grams}$  |
|                                                | needed for solution       | of Epsom Salt            |

- (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.

During this time, the crucible is already cool. The increase in mass may come from the rehydration of  $\text{MgSO}_4$  from  $\text{H}_2\text{O}$  molecules present in the air. As the dehydration process is ~~endo~~ <sup>exo</sup>thermic (requiring heat energy in order to remove  $\text{H}_2\text{O}$ ), the rehydration is likely ~~endo~~ exothermic.



This releases energy into the surroundings, increasing the kinetic energy and random movement of the surrounding particles; entropy of the surroundings will increase. However, this process will convert 1 mole of solid and 7 moles of gas to 1 mole of solid, resulting in fewer particles in a more ordered state (fewer possible positions overall). This decreases the entropy of the system. For the rehydration process to be spontaneous, the increase in entropy of the surroundings must outweigh the decrease in entropy of the system, so  $\Delta S$  overall is positive.

- (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.

The sharp strong peak at  $\sim 1730\text{ cm}^{-1}$  could represent a carbonyl functional group ( $C=O$ ) is present, as this represents the  $C=O$  bond. ~~How~~ The slight right shoulder on this peak would also suggest it is an aldehyde, but this is difficult to confirm. The broad peak from  $3200-3600\text{ cm}^{-1}$  indicates an OH bond, and thus an alcohol group is also present. The sharp peak at  $2950\text{ cm}^{-1}$  would indicate C-H bonds are also present; ~~this cannot be~~ <sup>potentially</sup> this could be a C-H stretch, but there is no corresponding  $C=C$  <sup>medium</sup> stretch from  $1630-1490\text{ cm}^{-1}$ , making this unlikely. The functional groups could be a carboxylic acid, an aldehyde, a ketone, or an ester, all 4 with an OH group (aldehyde  $\rightarrow$

- (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. *not carbox*
  - Compound A reacted with dilute  $H_2SO_4$  under reflux to produce Compounds B and C, which were separated by distillation. *Major products? Ester*
  - Compounds B and C were both water-soluble. Compound B had a molar mass of  $118\text{ g mol}^{-1}$ , and Compound C had a molar mass of  $60\text{ g mol}^{-1}$ .
  - Compound B did not react on heating with concentrated  $H_2SO_4$ . *no OH/3°?*
  - When Compound B was reacted with  $H^+/Cr_2O_7^{2-}$ , it gave Compound D, with the molecular formula  $C_5H_8O_4$ . *aldehyde; B is carbox*
  - 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. *F is acyl, E is alcohol*

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

This space is provided for working

A is ester  $C_8H_{16}O_3$  with ~~CO<sub>2</sub>~~ or OH

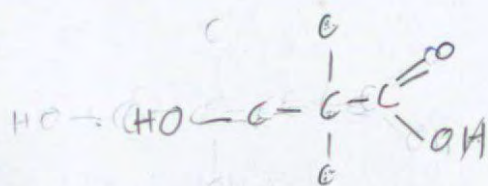
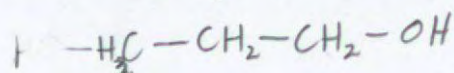
B is carboxylic

$C_5$

Cannot be eliminated?  
can be oxidised to  
dicarbox?

C is alcohol

$C_3H_8O$



D:

|                                                                                                                               |                                                                                                              |
|-------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|
| <p>Compound A</p> $\text{HO} - \text{CH}_2 - \text{C}(\text{CH}_3)_2 - \text{C}(=\text{O})\text{OCH}_2\text{CH}_2\text{CH}_3$ | <p>Compound B</p> $\text{HO} - \text{CH}_2 - \text{C}(\text{CH}_3)_2 - \text{C}(=\text{O})\text{OH}$         |
| <p>Compound C</p> $\text{H}_3\text{C} - \text{CH}_2 - \text{CH}_2 - \text{OH}$                                                | <p>Compound D</p> $\text{HO} - \text{C}(=\text{O}) - \text{C}(\text{CH}_3)_2 - \text{C}(=\text{O})\text{OH}$ |
| <p>Compound E</p> $\text{H}_3\text{C} - \text{CH}_2 - \text{CH}_2 - \text{Cl}$                                                | <p>Compound F</p> $\text{Cl} - \text{C}(=\text{O}) - \text{C}(\text{CH}_3)_2 - \text{C}(=\text{O})\text{Cl}$ |

- (iii)  $^{13}\text{C}$  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:

Compound B. 4 peaks = 4 distinct carbon environments; B is the only molecule with 4 carbon environments. Peak at 185 ppm represents the COOH environment; peak at 70 ppm represents the C-OH environment. B and A are the only molecules where both are present, but A has >4 carbon environments.

Spectrum 2:

Compound ~~D~~<sup>F</sup>. 3 peaks = 3 distinct carbon environments. Peak around 175 ppm represents the COCl environment with C=O bond; slightly lower than the COOH peak in spectrum 1. Peak at 50 ppm is just outside within C-C=O range, supporting this.

\* making D an unlikely option.

Spectrum 3:

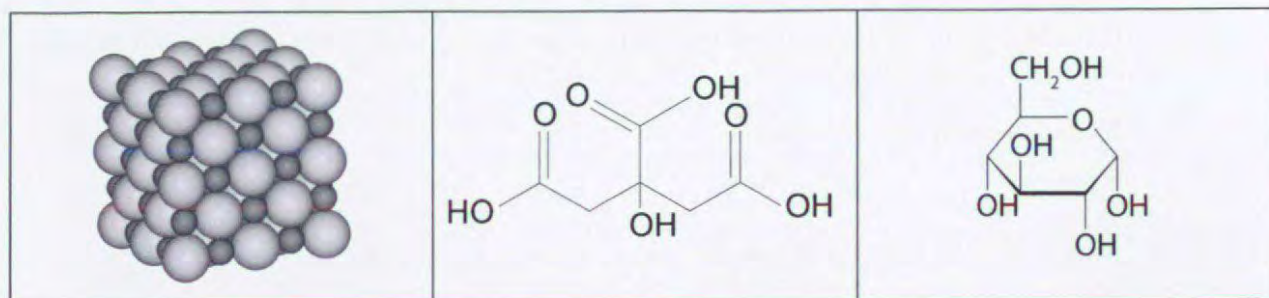
Compound C; there is no peak above 180 ppm, indicating no C=O carbon environments, so it must be C or E. The highest peak is around 65 ppm, outside of the C-Cl environment range (eliminating E as an option) but within the 55-85 ppm C-OH environment range. 3 peaks overall = 3 distinct environments = at least 3 carbon atoms.

## 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.*

Water is a polar solvent; when a solute is dissolved in it, attractive intermolecular forces occur between  $\text{H}_2\text{O}$  and solute molecules. These IMFs are stronger than those between solute particles, causing the substance to dissolve.  $\text{NaCl}$  is an ionic solid, and will be comprised of  $\text{Na}^+$  and  $\text{Cl}^-$  ions in a 3D lattice. The IMFs of attraction between  $\text{Na}^+$  and  $\delta^- \text{O}$  in  $\text{H}_2\text{O}$ , and between  $\text{Cl}^-$  and  $\delta^+ \text{H}$  in  $\text{H}_2\text{O}$ , are stronger than between  $\text{Na}^+$  and  $\text{Cl}^-$ , causing the lattice to be pulled apart and  $\text{NaCl}$  to dissolve. Citric acid and glucose are covalent molecules, so only have weak IMFs between solute molecules. Each contains many OH groups with highly polar O-H bonds (due to high EN difference between O and H), resulting in strong hydrogen bonds forming with the polar  $\text{H}_2\text{O}$  molecules (which also contain O-H bonds). These are the strongest form of IMF, and easily overcome the weak IMFs ~~between~~ between solute molecules, dissolving both glucose and citric acid.

(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:  $0.350 \text{ mol L}^{-1}$  of both  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$

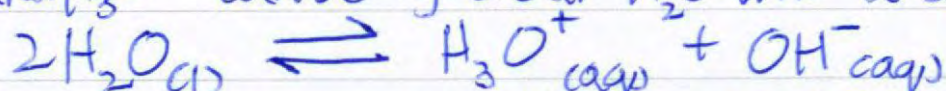
$$\text{p}K_a(\text{CH}_3\text{COOH}) = 4.76$$

(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.*

$\text{CH}_3\text{CH}_2\text{OH}$  is technically a very weak acid, but it is weak enough that its dissociation into  $\text{CH}_3\text{CH}_2\text{O}^-$  and  $\text{H}_3\text{O}^+$  can be ignored.  $\text{H}_2\text{O}$  will dissociate:



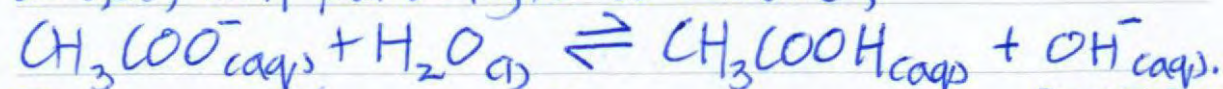
However, since the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions from this dissociation are equal, the pH will remain effectively the same as that of pure water.

B contains a weak acid, which will partially dissociate:  $\text{CH}_3\text{COOH}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{CH}_3\text{COO}^-_{(aq)} + \text{H}_3\text{O}^+_{(aq)}$

Dissociation of  $\text{H}_2\text{O}$  also occurs. This creates a solution with a greater concentration of  $\text{H}_3\text{O}^+$  than  $\text{OH}^-$ , giving a  $\text{pH} < \text{pure water}$ . As this is a weak acid,  $[\text{CH}_3\text{COOH}] > [\text{H}_3\text{O}^+] > [\text{CH}_3\text{COO}^-] > [\text{OH}^-]$  as there is only partial dissociation.

C contains a basic salt, which will fully dissociate:

$\text{CH}_3\text{COONa}_{(aq)} \rightarrow \text{CH}_3\text{COO}^-_{(aq)} + \text{Na}^+_{(aq)}$ .  $\text{Na}^+$  will remain in solution, while  $\text{CH}_3\text{COO}^-$  (as a weak base), will partially react further,



This results in a solution with a greater  $[\text{OH}^-]$  than  $[\text{H}_3\text{O}^+]$ , meaning a  $\text{pH} > \text{pure water}$ .  $[\text{Na}^+]$  will be highest, followed by  $[\text{CH}_3\text{COO}^-] > [\text{OH}^-] > [\text{CH}_3\text{COOH}]$ .

then  $[H_3O^+]$  as the lowest.

Solution D is a buffer solution. The pH will depend on the relevant concentrations of ~~the~~ weak acid  $CH_3COOH$  and its conjugate base  $CH_3COO^-$ . If the two are in equal concentration ( $[CH_3COOH] = [CH_3COO^-] = [Na^+]$ ) as is implied, then the pH of the solution will be equal to the  $pK_a$  ( $pH = 4.76$ ). This is less than pure  $H_2O$ , indicating the  $[H_3O^+] > [OH^-]$ ; i.e., the solution is acidic.

- (ii) 10.0 mL of  $0.460 \text{ mol L}^{-1}$  sodium hydroxide solution,  $NaOH(aq)$ , was mixed with 45.0 mL of Solution D ( $0.350 \text{ mol L}^{-1}$  of both  $CH_3COOH$  and  $CH_3COONa$ ).

Calculate the pH of the resulting solution after mixing.

$$c(CH_3COOH) = c(CH_3COO^-) = 0.350 \text{ mol L}^{-1} \text{ initially}$$

$$n(CH_3COOH)_i = cV$$

$$= 0.35 \times 0.045$$

$$= 0.01575 \text{ moles}$$

$$n(CH_3COOH)_f = n_i - n(OH^-)$$

$$= 0.01575 - (0.46 \times 0.01)$$

$$= 0.01115$$

$$[CH_3COOH]_f = \frac{0.01115}{0.01 + 0.045}$$

$$= \frac{0.2027}{2.027} \text{ mol L}^{-1}$$

$$[CH_3COO^-]_f = \frac{0.02035}{0.01 + 0.045}$$

$$= 0.37 \text{ mol L}^{-1}$$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$= 4.76 + \log\left(\frac{0.37}{0.2027}\right)$$

$$n(CH_3COO^-) = 0.01575$$

$$n_f = n_i + n(OH^-)$$

$$= 0.02035$$

$$pH = 4.76 + 0.26$$

$$= 5.02 \text{ (3 sf)}$$

(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  $\text{AgNO}_3$  solution, a white precipitate formed.  ~~$\text{Cl}^-$~~
- 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  $\text{AgNO}_3$  solution, a white precipitate formed.  $\text{Cl}^-$
- On addition of dilute nitric acid, the precipitate remained.
- To a new 2 mL sample of Solution B, the student added 2 drops of  $\text{AgNO}_3$  solution, and a white precipitate formed.
- On addition of excess dilute  $\text{NH}_3$  solution the white precipitate dissolved.

The student concluded Solution A contained  $\text{CO}_3^{2-}$  ions, and Solution B contained  $\text{Cl}^-$  ions.

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

In solution A, the  $\text{CO}_3^{2-}$  ions in solution must have displaced the  $\text{NO}_3^-$  ions, forming an  $\text{Ag}_2\text{CO}_3$  white solid precipitate - partially soluble salt

$$2\text{Ag}^+_{\text{(aq)}} + \text{CO}_3^{2-}_{\text{(aq)}} \rightleftharpoons \text{Ag}_2\text{CO}_{3\text{(s)}} + 2\text{NO}_3^-_{\text{(aq)}}$$

When dilute  $\text{HNO}_3$  was formed, it dissociated to form  $\text{H}_3\text{O}^+$  ions:  $\text{HNO}_{3\text{(aq)}} + \text{H}_2\text{O}_{\text{(l)}} \rightarrow \text{NO}_3^-_{\text{(aq)}} + \text{H}_3\text{O}^+_{\text{(aq)}}$

These reacted with the  $\text{Ag}_2\text{CO}_3$  precipitate

$$\text{Ag}_2\text{CO}_{3\text{(s)}} + 2\text{H}_3\text{O}^+_{\text{(aq)}} \rightarrow 2\text{Ag}^+_{\text{(aq)}} + \text{CO}_{2\text{(g)}} + 3\text{H}_2\text{O}_{\text{(l)}}$$

This returns the  $\text{Ag}^+$  ions in solution (so the precipitate disappears/dissolves) and forms  $\text{CO}_2$  gas, released as bubbles/effervescence.

In solution B, the first test tube has  $\text{Ag}^+$  react with  $\text{Cl}^-$  to form a white  $\text{AgCl}$  precipitate



This  $\text{AgCl}$  does not react with  $\text{H}_3\text{O}^+$ , so no reaction

$$\text{Ag}^+_{\text{(aq)}} + \text{Cl}^-_{\text{(aq)}} \rightleftharpoons \text{AgCl}_{\text{(s)}} \quad \text{- partially soluble salt.}$$

is observed; the higher  $[NO_3^-]$  does not impact the solubility. In the 2nd test tube, again an  $AgCl$  ppt forms. When  $NH_3(aq)$  is added, it ~~displaces Cl from~~ <sup>reacts with</sup>  $Ag^+$ , forming a complex ion soluble in water; ~~the precipitate dissolves~~

$$Ag^+_{(aq)} + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+_{(aq)} \quad \rightarrow$$

- (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  $0.0875 \text{ mol L}^{-1} NaOH(aq)$  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  $0.100 \text{ mol L}^{-1}$  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**.

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

$$c(B)_i = \frac{c_i V_i}{V_f}$$

$$= \frac{0.1 \times 30}{150}$$

$$= 0.02 \text{ mol L}^{-1}$$

$$c(B)_f = \frac{c_i V_i}{V_f}$$

$$= \frac{0.02 \times 2}{2+5}$$

$$= 0.005714 \text{ mol L}^{-1}$$

$$IP = [B][OH^-]^2$$

$$= 0.005714 \times 0.0875^2$$

$$= 4.375 \times 10^{-5}$$

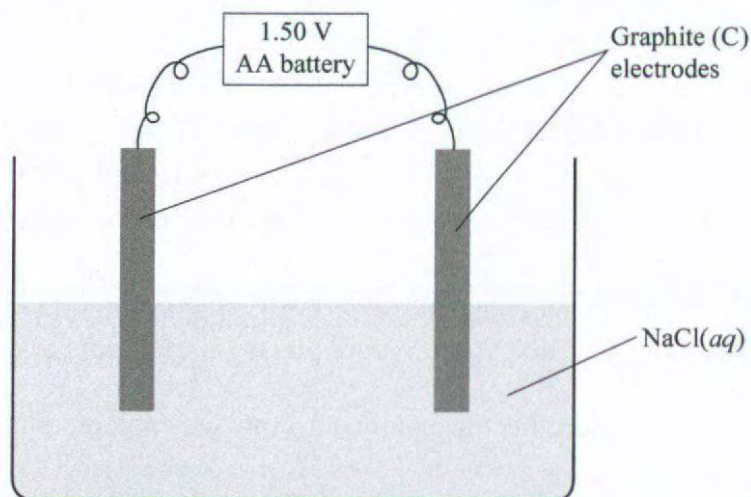
$IP > K_s(Mg(OH)_2)$ , so an  $Mg(OH)_2$  ppt would have formed if  $Mg^{2+}$  was present

As  $IP < K_s(Ba(OH)_2)$ , no  $Ba(OH)_2$  ppt would have formed; the concentrations of  $Ba^{2+}$  and  $OH^-$  are too low.

$Ba^{2+}$  is the cation, as no ppt formed.

### 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,  $\text{NaCl}(aq)$ , results in the production of aqueous chlorine  $\text{Cl}_2(aq)$  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.

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

$$E^\circ(\text{H}_2\text{O}/\text{H}_2) = -0.83 \text{ V}$$

$$E^\circ(\text{Cl}_2/\text{Cl}^-) = +1.36 \text{ V}$$

$$E^\circ(\text{O}_2/\text{H}_2\text{O}) = +0.82 \text{ V}$$



- (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  $\text{NaOCl}$  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

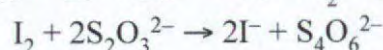
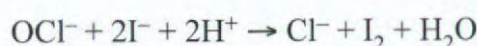
5.00 mL of the pool chlorine solution was pipetted into a 250.0 mL volumetric flask, and filled to the mark. 25.0 mL aliquots of the dilute solution were mixed in conical flasks with excess potassium iodide solution,  $\text{KI}(aq)$ , and 10 mL of dilute sulfuric acid,  $\text{H}_2\text{SO}_4(aq)$ . 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                                             |

Avg =



| 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,  $\text{NaOCl}$ , in the pool chlorine bottle, in  $\text{g L}^{-1}$ .

$$\begin{aligned}
 M(\text{KIO}_3) &= 214 \text{ g mol}^{-1} \\
 n(\text{KIO}_3) &= \frac{0.533}{214} \\
 &= 0.002491 \text{ moles} \\
 c &= \frac{n}{V} = \frac{0.002491}{0.1} \\
 &= 0.02491 \text{ mol L}^{-1} \\
 n &= 0.02491 \times 0.01 \\
 &= 2.491 \times 10^{-4} \text{ moles in} \\
 &\text{each aliquot}
 \end{aligned}$$

$$\begin{aligned}
 M(\text{NaOCl}) &= 74.4 \text{ g mol}^{-1} \\
 &= 7.472 \times 10^{-4} \text{ moles } \text{I}_2 \\
 &= 1.494 \times 10^{-3} \text{ moles of} \\
 &\text{S}_2\text{O}_3^{2-} \text{ needed}
 \end{aligned}$$

$$\begin{aligned}
 V_{\text{avg}}(\text{Na}_2\text{S}_2\text{O}_3) &= \frac{16.5 + 16.45 + 16.4}{3} \\
 &= 16.45 \text{ mL}
 \end{aligned}$$

$$C = \frac{n}{V}$$

$$C(S_2O_3^{2-}) = \frac{1.494 \times 10^{-3}}{0.01645}$$

$$= 0.09084 \text{ mol/L}$$

Chlorination analysis

$$V_{\text{avg}}(S_2O_3^{2-}) = \frac{18.15 + 18.1 + 17.95}{3}$$

$$= 18.07 \text{ mL}$$

$$n(S_2O_3^{2-}) = CV$$

$$= 0.09084 \times 0.01807$$

$$= 0.001641 \text{ moles } S_2O_3^{2-}$$

$$= 8.206 \times 10^{-4} \text{ moles } I_2$$

$$= 8.206 \times 10^{-4} \text{ moles } OCl^-$$

$$C_f(OCl^-) = \frac{8.206 \times 10^{-4}}{0.025}$$

$$= 0.03283 \text{ mol/L } OCl^- \text{ dilute}$$

$$C_1 = \frac{C_2 V_2}{V_1}$$

$$= \frac{0.03283 \times 250}{5}$$

$$= 1.64 \text{ moles L}^{-1} OCl^- \text{ in initial solution}$$

$$n = \frac{m}{M_r}$$

$$m = n M_r$$

$$C_m = C_n M_r$$

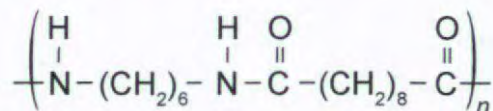
$$= 1.64 \times 74.4$$

$$= 122.1 \text{ g L}^{-1} OCl^-$$

- (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:



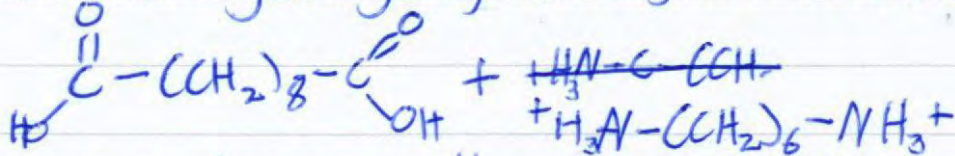
- (i) Nylon-6,10 fabrics may degrade if they are exposed to other chemical substances.

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

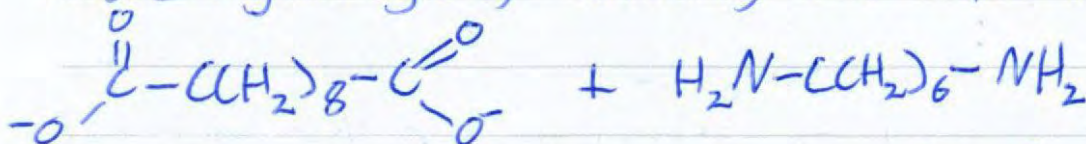
*Include structural equations where relevant.*

Nylons are polyamides, with each monomer being joined to those adjacent by an amide bond (C-N-C=O). These bonds can be broken through acidic or basic hydrolysis; thus, dilute acids and bases will be able to break down this polymer into its monomers, causing damage to the fabrics.

Dilute acids will cause this polymer to undergo acidic hydrolysis, forming the following monomers:



A weak base will cause it to undergo basic hydrolysis, forming the following monomers:



In both processes, an  $\text{H}_2\text{O}$  molecule is added to each amide bond, breaking it apart. Other small inorganic molecules such as  $\text{HCl}$  may cause similar hydrolysis reactions.

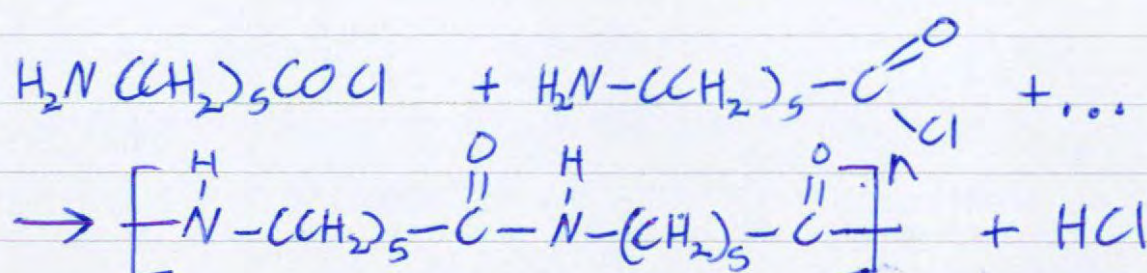
- (ii) Nylon-6,6 and nylon-6 are produced from some of the compounds given in the table.

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

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 will be formed from monomer W



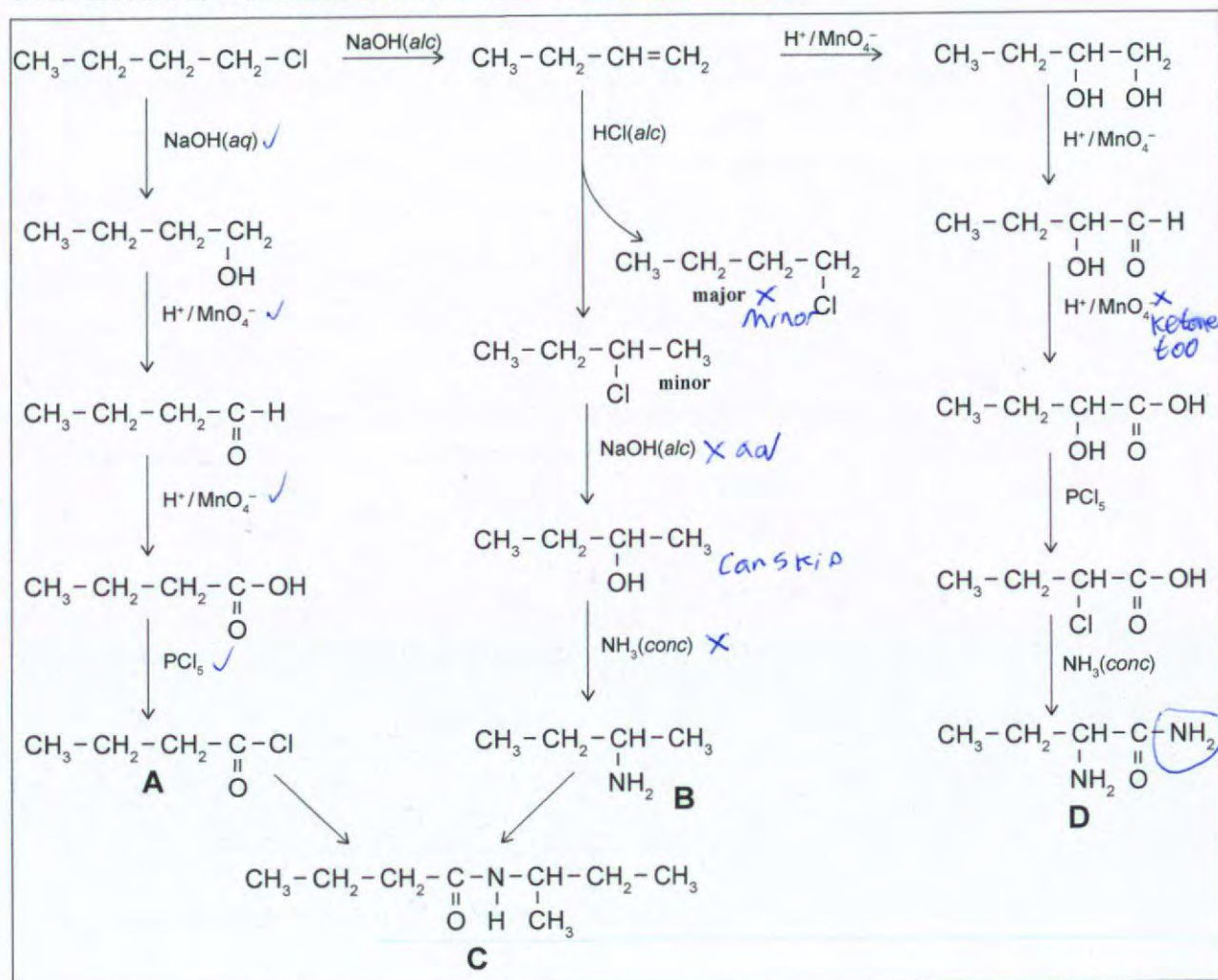
This is a single monomer, with a chain length of 6, and an  $\text{NH}_2$  group on one end and a  $\text{COCl}$  group on the other, allowing it to form amide bonds and construct a polyamide from just one monomer. Nylon 6,6 will be formed from monomers V and Z, or Y and Z in acidic conditions. Both pairs of monomers contain only monomers of carbon chain length 6, hence nylon-6,6. Z has an  $\text{NH}_2$  group on both ends; V has a  $\text{COCl}$  group on both ends, while Y has a  $\text{COOH}$  group. This allows both monomers in either pair to form a continuous chain by alternating monomers, with each joined together by an amide bond.

# 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.



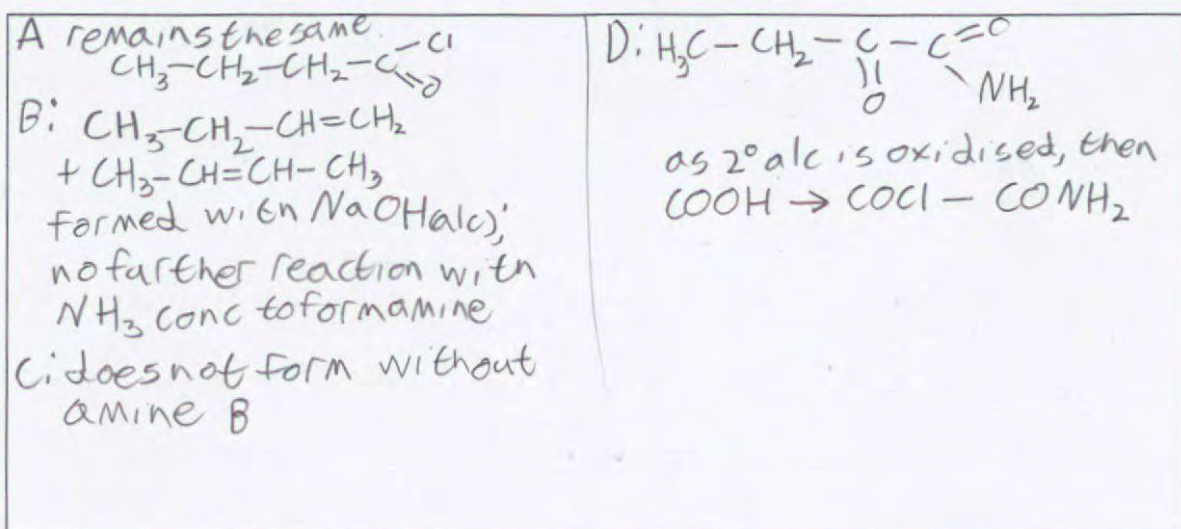
- (i) Identify and discuss any errors in the reagents or structures in the scheme above. Propose suitable alternative reagents or steps necessary to produce the intended final products.

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

The first mistake is in the formation of the major and minor products; 1-chlorobutane (labelled as the major product) is the minor product, and should not be used. 2-chlorobutane is labelled the minor product, yet is actually the major product. This is easy to remedy by swapping the

label on the reaction pathway, second is the use of  $\text{NaOH}_{(\text{alc})}$  in the substitution reaction between 2-chlorobutane and 2-butanol; this will instead produce but-1-ene (<sup>minor</sup>~~major~~) and but-2-ene (major) products.  $\text{NaOH}_{(\text{aq})}$  is the correct reagent for this step, and will produce the desired alcohol. The third mistake is producing this alcohol (2-butanol) in order to form ~~but-2-amine~~ but-2-amine by substitution with  $\text{NH}_3(\text{conc})$ . This would actually require  $\text{NH}_3(\text{conc})$  (or  $\text{NH}_3(\text{alc})$ ) to be reacted with the previous product, 2-chlorobutane; the production of butan-2-ol is unnecessary. The fourth mistake is in the ~~re~~oxidation of ~~1,2-butandiol~~ ~~1,2~~-butandiol;  $\text{H}^+/\text{MnO}_4^-$  will also oxidise the 2° alcohol to form a ketone. This can be fixed by reacting ~~the~~ with a reducing agent  $\text{NaBH}_4$  after the  $\text{COOH}$  group has been formed, but before chlorination with  $\text{PCl}_5$ , in order to return the 2nd° alcohol but leave the carboxylic acid, as  $\text{NaBH}_4$  cannot reduce ~~the~~  $\text{COOH}$   $\rightarrow$

- (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.



- (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  $\text{KNO}_3$  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 ( $\text{kJ mol}^{-1}$ )

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

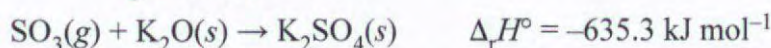
$$\Delta_f H^\circ (\text{K}_2\text{CO}_3(\text{s})) = -1146$$

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

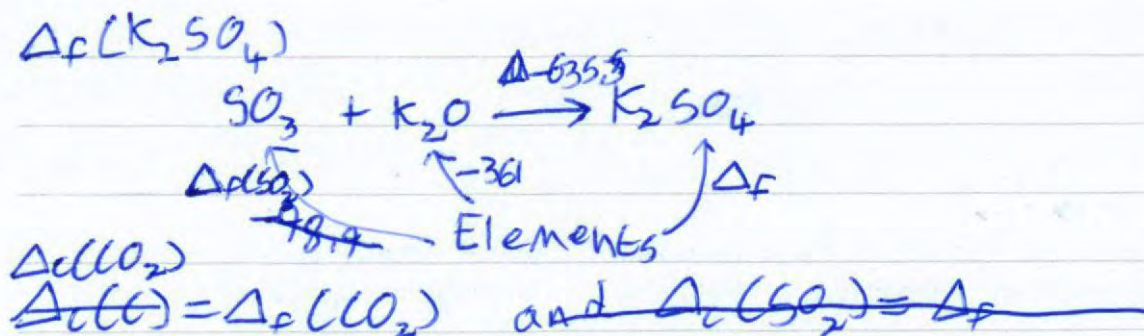
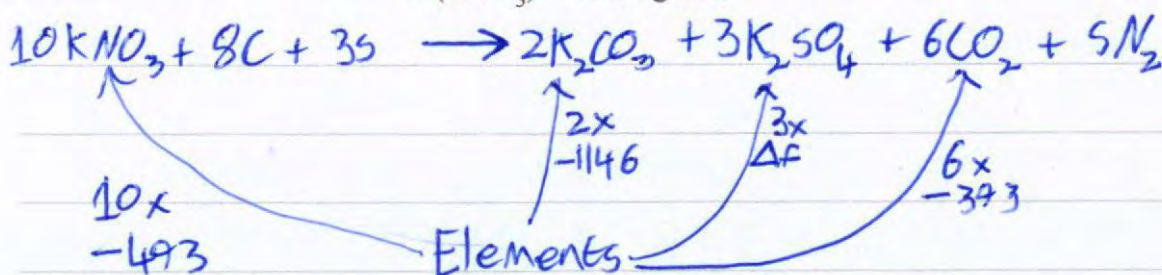
$$\Delta_f H^\circ (\text{SO}_2(\text{g})) = -296.8$$

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

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



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



$$\Delta_f(\text{SO}_3) = \Delta_c(\text{SO}_2)$$

$$\Delta_f(\text{K}_2\text{SO}_4) = -635.3 + -361 + -98.9$$

$$= -1095.2$$

$$\Delta_r + 10(-493) = 2(-1146) + 3(-1095.2) + 6(-393)$$

$$\Delta_r - 4930 = -2292 - 3285.6 - 2358$$

$$\Delta_r = -3005.6 = -3006 \text{ kJ mol}^{-1}$$

$$\Delta_r H = \frac{-q}{n}$$

W -

$$q = \Delta_r H \times n$$

$$n = \frac{m}{M_r}$$

$$= \frac{200}{101.1}$$

$$= 1.978 \text{ moles of } \text{KNO}_3$$

$$q = \frac{1.978}{10} \times 3006$$

$$= 594.6 \text{ kJ released}$$

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,  $\text{SiO}_2$   
 ethanamide,  $\text{CH}_3\text{CONH}_2$   
 methylammonium chloride,  $\text{CH}_3\text{NH}_3\text{Cl}$   
 phosphorus trichloride,  $\text{PCl}_3$

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

$\text{PCl}_3$  is the liquid; the other 3 substances are solids at RT.  $\text{PCl}_3$  is a covalent molecule, with only weak IMFs between each  $\text{PCl}_3$  molecule. These IMFs consist of ID-ID attraction and PD-PD attractions, as the  $\text{PCl}_3$  molecule is asymmetric and thus polar ( $\text{P}^{\delta+}-\text{Cl}^{\delta-}$  dipoles do not cancel). ~~It is not~~  $\text{SiO}_2$  is a ~~an~~ covalent macromolecule network, comprised of a 3D lattice of Si and O atoms joined by covalent bonds. These bonds require a large amount of heat energy to overcome, giving  $\text{SiO}_2$  a high MP and making it solid at RT.  $\text{CH}_3\text{NH}_3\text{Cl}$  is an ionic salt comprised of a 3D lattice of alternating  $\text{CH}_3\text{NH}_3^+$  and  $\text{Cl}^-$  ions held together by ionic bonds. These ionic bonds are very strong, again requiring a large amount of heat energy to overcome, giving an MP far above RT.  $\text{CH}_3\text{CONH}_2$  is a covalent molecule, like  $\text{PCl}_3$ . It has a molar mass of  $59\text{ g mol}^{-1}$ , compared to  $\text{PCl}_3$ 's Mr of  $137.5\text{ g mol}^{-1}$ , meaning it has weaker ID-ID attractive forces than  $\text{PCl}_3$ . ~~It~~ Both are also polar, so have PD-PD attractive IMFs as well. However,  $\text{CH}_3\text{CONH}_2$  contains highly polar N-H bonds (due to the large difference in electronegativity between N and H), creating strong dipoles. This allows hydrogen bonds to form between the  $\delta^+ \text{H}$  of  $\text{H}-\text{N}$

Extra space if required.

Write the question number(s) if applicable.

QUESTION  
NUMBER

- 16i and ketone may have 2 OH groups if there is only one C=O group, due to there being 3 O atoms).
- 2c This decreases the  $[Ag^+]$  in solution, shifting the  $Ag^+/Cl^-$  equilibrium left. This favours the backwards dissolution reaction, causing the AgCl ppt to dissolve.
- 4c the  $NH_2$  group of one molecule, and the lone electron pair on the N of another. Hydrogen bonds are the strongest form of IMF; their presence in  $CH_3CONH_2$  outweighs its <sup>weaker</sup> ~~lower~~ ID-ID attraction, giving it stronger IMFs overall. These require more energy to overcome, giving  $CH_3CONH_2$  an MP above RT, making it a solid. As  $PCl_3$  has the weakest IMFs overall, it has the least energy needed to overcome them, and so its MP is below RT; it is a liquid.
- 4ai A fifth mistake occurs where  $PCl_5$  is used to substitute OH for Cl in the preparation of D, but does not substitute the OH of the COOH group to form an acid chloride. In reality, this would form 2-chlorobutanoyl chloride. However, the next step (reacting with  $NH_3$  (conc)) would still produce the same product, as the  $NH_3$  would

Extra space if required.

Write the question number(s) if applicable.

QUESTION  
NUMBER

both Cl groups to form 2-aminobutanamide (V)  
Thus the student may need to fix their reaction  
scheme, but no ~~chem~~ changes to the reagents  
will be needed.

93102

## Outstanding Scholarship

**Subject:** Chemistry

**Standard:** 93102

**Total score:** 26

| Q | Score | Marker commentary                                                                                                                                                                                                                                                                                                                                                                      |
|---|-------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1 | 7     | <p>a) Determined the formula of <math>\text{MgSO}_4 \cdot 7\text{H}_2\text{O}</math> but calculated incorrect mass. Discusses thermodynamic principles accurately. Six structures drawn correctly.</p> <p>b) Links peaks on ir spectrum to bond and possible functional groups to given molecular formula. Signal in <math>^{13}\text{C}</math> nmr linked to carbon environments.</p> |
| 2 | 6     | <p>a) Discusses interactions between NaCl and water. Identifies hydrogen bonding between citric acid and glucose and water. Justifies the pH of four solutions using equations and calculates the pH of a mixture.</p> <p>b) Describes observation for both reactions.</p> <p>c) Uses an incorrect Q value to justify the solution contains <math>\text{Ba}^{2+}</math>.</p>           |
| 3 | 6     | <p>a) No response.</p> <p>b) Calculates the concentration of sodium hypochlorite (<math>122.1 \text{ gL}^{-1}</math>).</p> <p>c) Explains acidic and basic hydrolysis with all four products drawn and discusses suitable monomers with a structural equation.</p>                                                                                                                     |
| 4 | 7     | <p>a) Identifies five errors in the scheme and gives some alternative steps. Draws all four products for the scheme given.</p> <p>b) Uses Hess's Law to calculate energy releases but has several errors.</p> <p>c) Discusses the particle interactions the determine the state at room temperature of four different substances.</p>                                                  |