

SUPERVISOR'S USE ONLY

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93102



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

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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	Score
ONE	
TWO	
THREE	
FOUR	
TOTAL	

ASSESSOR'S USE ONLY

(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).

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

- 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.

- (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.

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

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

This space is provided for working

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.

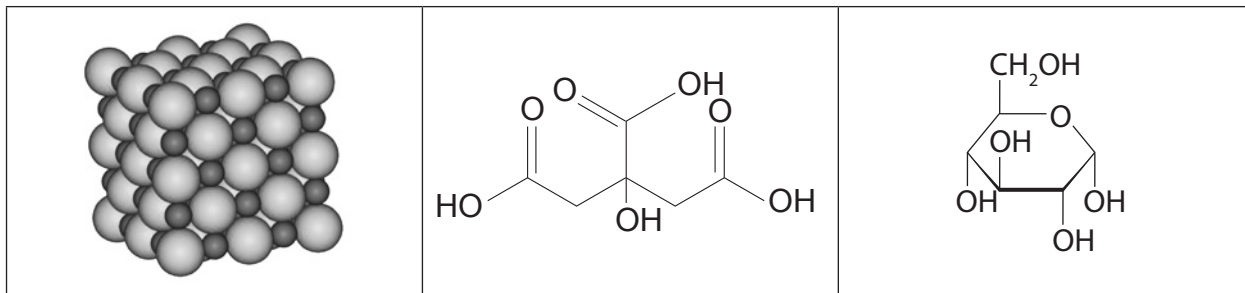
Spectrum 1:

Spectrum 2:

Spectrum 3:

- 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.

- (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
- $\text{p}K_{\text{a}}(\text{CH}_3\text{COOH}) = 4.76$
- (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.*

Solution D: 0.350 mol L⁻¹ of both CH₃COOH and CH₃COONa

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

- (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.

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

Calculate the pH of the resulting solution after mixing.

- ### Solution A

- ### Solution B

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

- (ii) To determine the cations, the student added sodium hydroxide solution, $\text{NaOH}(aq)$, 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.

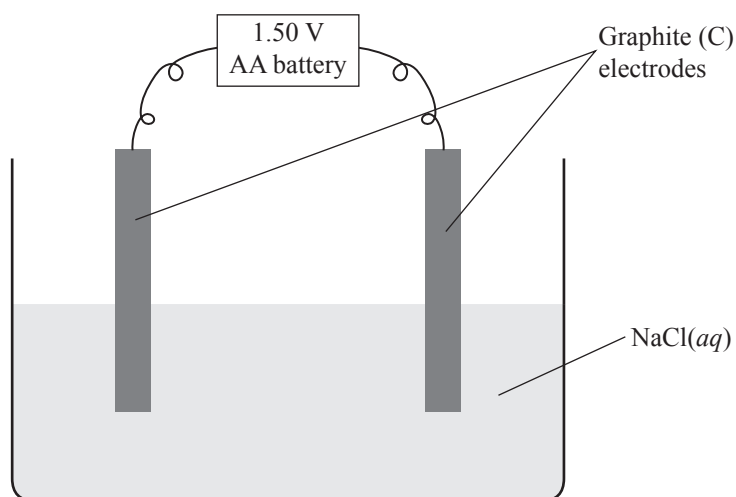
Use calculations to determine the cation and show why no precipitate was formed in Solution **B**.

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

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 NaOCl in the bottle.

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

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

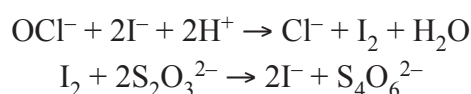
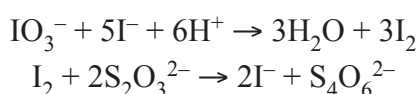
0.533 g of potassium iodate, $\text{KIO}_3(s)$, was dissolved in distilled water in a 100.0 mL volumetric flask. 10.0 mL aliquots of this solution were mixed in conical flasks with excess potassium iodide solution, $\text{KI}(aq)$, and 10 mL of dilute sulfuric acid, $\text{H}_2\text{SO}_4(aq)$. This 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} .

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

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

- 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.

$$\left(\begin{array}{ccccccc} \text{H} & & \text{H} & \text{O} & & & \text{O} \\ | & & | & || & & & || \\ -\text{N}-(\text{CH}_2)_6- & \text{N}- & \text{C}- & (\text{CH}_2)_8- & \text{C}- & & \\ & & & & & & || \end{array} \right)_n$$

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

- (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.

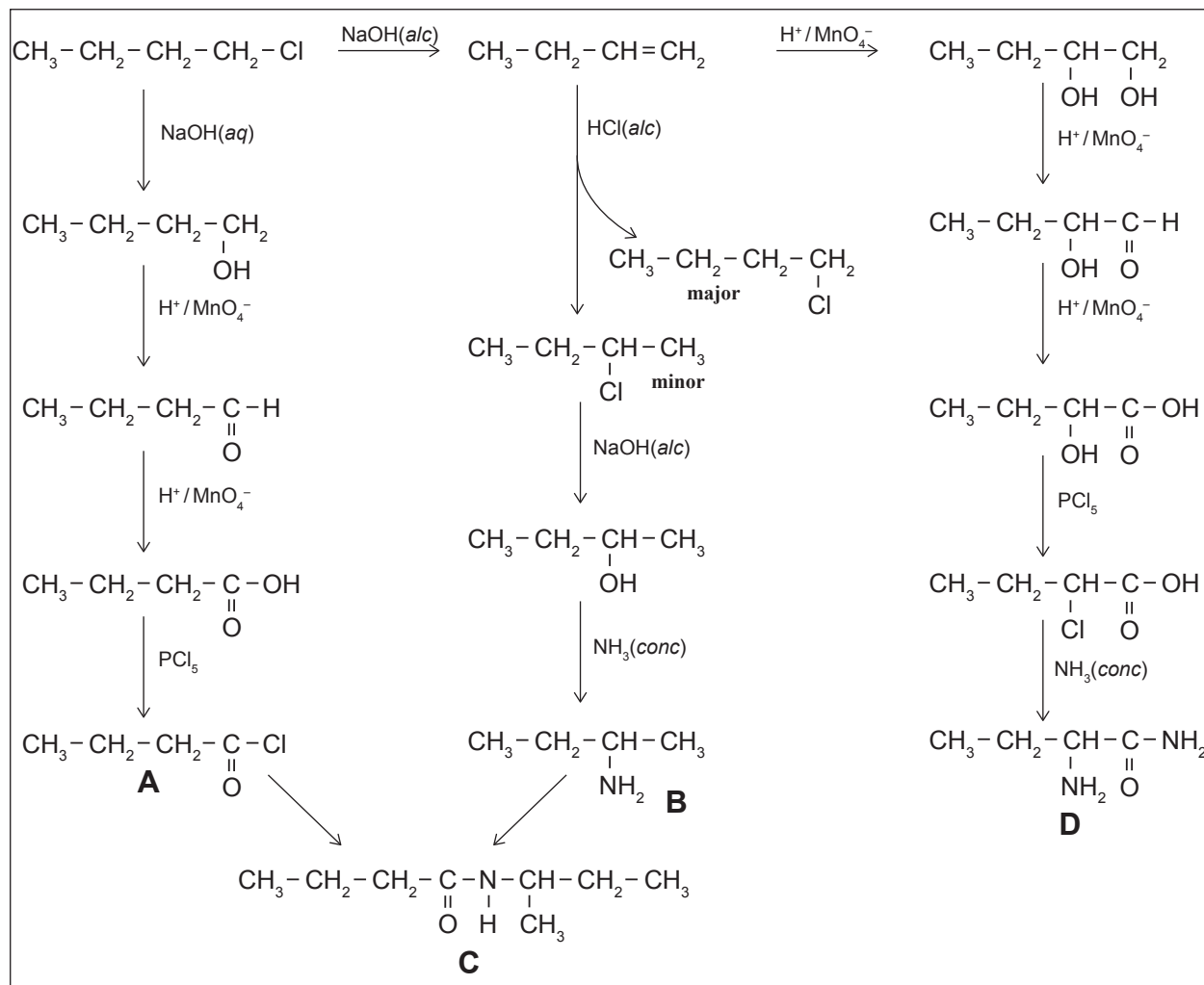
Include a structural equation for the formation of one nylon.

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.

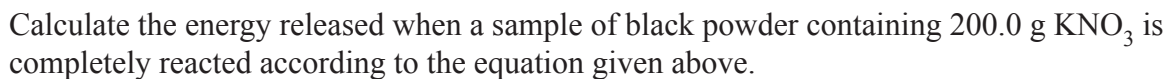
Their teacher has identified that there are errors in their scheme.



- (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.

- $$10\text{KNO}_3(s) + 8\text{C}(s) + 3\text{S}(s) \rightarrow 2\text{K}_2\text{CO}_3(s) + 3\text{K}_2\text{SO}_4(s) + 6\text{CO}_2(g) + 5\text{N}_2(g)$$



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

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

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

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

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

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

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

$$\text{SO}_3(\text{g}) + \text{K}_2\text{O}(\text{s}) \rightarrow \text{K}_2\text{SO}_4(\text{s}) \quad \Delta_r H^\circ = -635.3 \text{ kJ mol}^{-1}$$

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

Question Four continues
on the following page.

- The chemicals were: silicon dioxide, SiO₂
ethanamide, CH₃CONH₂
methylammonium chloride, CH₃NH₃Cl
phosphorus trichloride, PCl₃

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

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

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QUESTION
NUMBER

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