

SUPERVISOR'S USE ONLY

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93102



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 2023 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 (AREA DO NOT WRITE). This area may 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) The solubility constants for three compounds are given below. Lead(II) hydroxide is a white solid, whilst the two iodide compounds are both yellow in appearance.

$$K_s(\text{PbI}_2) = 8.00 \times 10^{-9} \quad K_s(\text{AgI}) = 8.30 \times 10^{-17} \quad K_s(\text{Pb(OH)}_2) = 8.00 \times 10^{-17}$$

- (i) A student pipetted 25.0 mL of 0.00167 mol L⁻¹ potassium iodide solution, KI(aq), into each of two beakers. They then added 35.0 mL of 0.0225 mol L⁻¹ lead(II) nitrate solution, Pb(NO₃)₂(aq), to one beaker and added 35.0 mL of 0.0143 mol L⁻¹ silver nitrate solution, AgNO₃(aq), to the other.

Carry out calculations to predict what the student observed in each beaker.

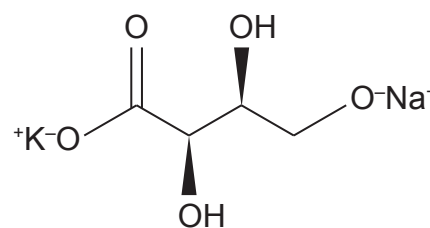
- (ii) Explain why, when preparing the lead(II) nitrate solution for the experiment described in (i), it is necessary that the measured mass of $\text{Pb}(\text{NO}_3)_2(s)$ is first dissolved in a small volume of dilute nitric acid, before dilution with distilled water.

- (b) A reaction between hydrogen peroxide solution, $\text{H}_2\text{O}_2(aq)$, and potassium sodium tartrate solution, $\text{KNaTar}(aq)$, is commonly used in schools to demonstrate the effect of reaction conditions on the rate of a reaction.

The two colourless solutions are mixed and heated to $70\text{ }^\circ\text{C}$. No obvious reaction is observed at this point. A small amount of a pale pink cobalt(II) chloride solution, $\text{CoCl}_2(aq)$, is then added, and changes begin to be observed.

First the solution turns green as the pale pink Co^{2+} ions are oxidised into green Co^{3+} ions by the hydrogen peroxide. Once the solution has changed colour, large volumes of CO_2 gas are quickly produced as the tartrate ions react with the hydrogen peroxide. The colour of the solution remains green during the reaction. Once the hydrogen peroxide is consumed, no further gas is produced.

Elaborate on the various reaction conditions required for this demonstration to work according to plan, with clear reference to particle collision theory and the role of Co^{3+} ions.



(c) Zirconium forms fluorine-containing compounds and polyatomic ions.

(i) Draw Lewis structures for the following fluorides of zirconium.

Use your existing knowledge to predict logical shapes for each ion, and give estimated bond angles.

Ion	ZrF_5^-	ZrF_6^{2-}	ZrF_7^{3-}
Lewis structure			
Shape			
Bond angles			

(ii) Explain the bond angles for one of the ions.

(a) The following is a selection of boiling points for different molecular compounds.

–2.50 °C 31.7 °C 48.5 °C 97.2 °C

(i) Match the following compounds to the boiling points provided.

propan-1-ol	1-fluoropropane	1-aminopropane	2-aminopropane

Justify your choices.

- (ii) Heptane has a boiling point of 98.4 °C.

Explain why the boiling point of heptane is higher than any of the boiling points of the compounds in (i).

- (b) (i) A complex organic reaction in a university laboratory yielded a mixture that contained two different organic compounds. Mass analysis determined that they had different molar masses. They were given the provisional labels Compound **X** and Compound **Y**.

Compounds **A**, **B**, and **C** were made from chemical treatments of the mixture of **X** and **Y** and were each subsequently isolated and analysed using spectroscopic techniques.

Use the mass analysis data provided below, and the IR and ^{13}C NMR spectra provided in the resource booklet, to determine the structures and names of Compounds **A**, **B**, and **C**.

$$M(\text{A}) = 59 \text{ g mol}^{-1} \quad M(\text{B}) = 72 \text{ g mol}^{-1} \quad M(\text{C}) = 88 \text{ g mol}^{-1}$$

Compound A	Compound B	Compound C
Name:	Name:	Name:
Structure:	Structure:	Structure:

- (ii) Compounds **A**, **B**, and **C** were isolated after the following chemical treatments:

A sample of the mixture of **X** and **Y** was heated with dilute NaOH solution, forming three products. TWO of these could be distilled from the reaction mixture and separated, and they were labelled Compounds **A** and **B**.

A second sample of the mixture of **X** and **Y** was heated with dilute HCl solution, and three products were formed. TWO of these could be distilled from the reaction mixture and separated. One was identified as Compound **B**, but the other product was new, and was subsequently labelled Compound **C**.

Use the mass analysis data provided below, and your knowledge of Compounds **A**, **B**, and **C**, to determine the structures of Compounds **X** and **Y**.

$$M(\text{X}) = 142 \text{ g mol}^{-1} \quad M(\text{Y}) = 129 \text{ g mol}^{-1}$$

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Compound X	Compound Y
Structure:	Structure:

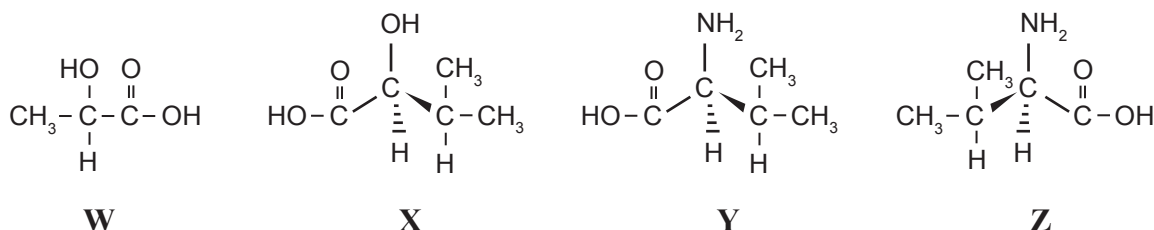
(iii) Why could only two of the three products from each treatment process be distilled from the reaction mixtures?

- $$\text{Ba(OH)}_2(s) + 2\text{NH}_4\text{Cl}(s) \rightarrow \text{BaCl}_2(aq) + 2\text{NH}_3(g) + 2\text{H}_2\text{O}(\ell) \quad \Delta_r H = +90.66 \text{ kJ mol}^{-1}$$
- $$c(\text{glass}) = 0.753 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$$

- (ii) Briefly outline thermodynamic factors that contribute to the overall spontaneity of the reaction occurring in the beaker.

QUESTION THREE

- (a) Valinomycin is an antibiotic which can be obtained from several different bacteria of the *Streptomyces* genus. Four molecules are the building blocks for the structure of valinomycin, and they are given the labels Compounds **W**, **X**, **Y**, and **Z**. Their structures are as follows:



These four molecules can all be synthesised from two other organic molecules, Compounds **F** and **G**.

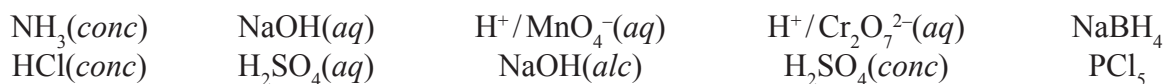
- Compound **F** has the molecular formula $\text{C}_3\text{H}_5\text{OCl}$. It does not produce steamy fumes when added to water, it does not form a silver mirror when added to Tollens' reagent, and it does not decolourise $\text{Br}_2(\text{aq})$.
- Compound **G** has the molecular formula $\text{C}_5\text{H}_{10}\text{O}$. It has a branched chain structure, and it exists as a pair of geometric isomers.

Use the information provided above to determine the structures of Compounds **F** and **G** and use these to produce logical reaction schemes for the synthesis of Compounds **W**, **X**, **Y**, and **Z**.

You may only select from the reagents provided below.

You can assume you would be able to separate and isolate specific compounds or isomers as required for successive steps.

Reagents available:



This space is provided for working.

Reaction schemes:

- (b) Vitamin C ($\text{C}_6\text{H}_8\text{O}_6$) is known to degrade over time in aqueous solutions due to reaction with oxygen that is also dissolved in the water. Dry powders are less prone to degradation and can be used to prepare drinks with more reliable and consistent levels of the vitamin.

To investigate the extent of degradation of Vitamin C due to oxygen exposure, an 80.0 g sachet of an orange drink powder was emptied into a 1.00 L volumetric flask, filled to the mark using distilled water, and briefly mixed until all the solids had dissolved. The nutritional information on the drink powder packaging stated that the sachet should contain 130 mg of Vitamin C.

Two halves of the solution, and a blank control, were analysed using an iodometric titration procedure. The primary standard used in the titration was a potassium iodate solution, $\text{KIO}_3(\text{aq})$. This solution was prepared by dissolving 0.132 g into 1.00 L of distilled water in a volumetric flask.

The first half of the drink was analysed immediately. The second half of the drink was stirred in the open air then left uncovered for 24 hours, before being analysed. The control solution also analysed contained only water.

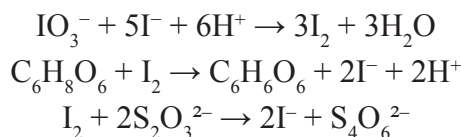
In each titration, a 20.0 mL aliquot of the solution being analysed was pipetted into a conical flask. This was followed by addition of 150 mL of distilled water, 5 mL of 1 mol L^{-1} hydrochloric acid, $\text{HCl}(\text{aq})$, 5 mL of 1% potassium iodide solution, $\text{KI}(\text{aq})$, and 20.0 mL of the potassium iodate standard solution. This resulted in the formation of iodine in the flask, which then reacted with any Vitamin C present.

The remaining iodine in the flask was then titrated with a sodium thiosulfate solution, $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$, and the titration was repeated with further 20.0 mL aliquots until average titres could be determined.

Solution	Average titre/ mL
Control	27.20
Drink (fresh)	16.10
Drink (24 hours)	18.35

- (i) Carry out calculations to determine the concentration of the sodium thiosulfate solution used, whether the nutritional information on the sachet was accurate, and the percentage of Vitamin C remaining in the drink after 24 hours of atmospheric exposure.

$$M(\text{Vitamin C}) = 176.1 \text{ g mol}^{-1} \quad M(\text{KIO}_3) = 214 \text{ g mol}^{-1}$$





www.woolworths.
com.au/shop/
productdetails/264554/
raro-sweet-navel-orange-
flavoured-beverage-mix

(a) There are various periodic trends observed between elements in the periodic table. These trends are fundamentally due to the protons and electrons within the different atoms.

- Give a clear definition for the term, and include references to electron arrangements where appropriate.

N³⁻ O²⁻ Ne



VO₂⁺ VO²⁺ V³⁺ V²⁺



Use cell potential calculations to identify the **final** colour and oxidation number for vanadium in each experiment, following addition of the powdered metal.

$$\begin{array}{lll} E^\circ(\text{VO}_2^+/\text{VO}^{2+}) = +1.00 \text{ V} & E^\circ(\text{VO}^{2+}/\text{V}^{3+}) = +0.34 \text{ V} & E^\circ(\text{V}^{3+}/\text{V}^{2+}) = -0.26 \text{ V} \\ E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V} & E^\circ(\text{Sn}^{2+}/\text{Sn}) = -0.14 \text{ V} & E^\circ(\text{Ag}^+/\text{Ag}) = +0.80 \text{ V} \end{array}$$

(c) Two acid-base titrations were carried out in a school chemistry laboratory.

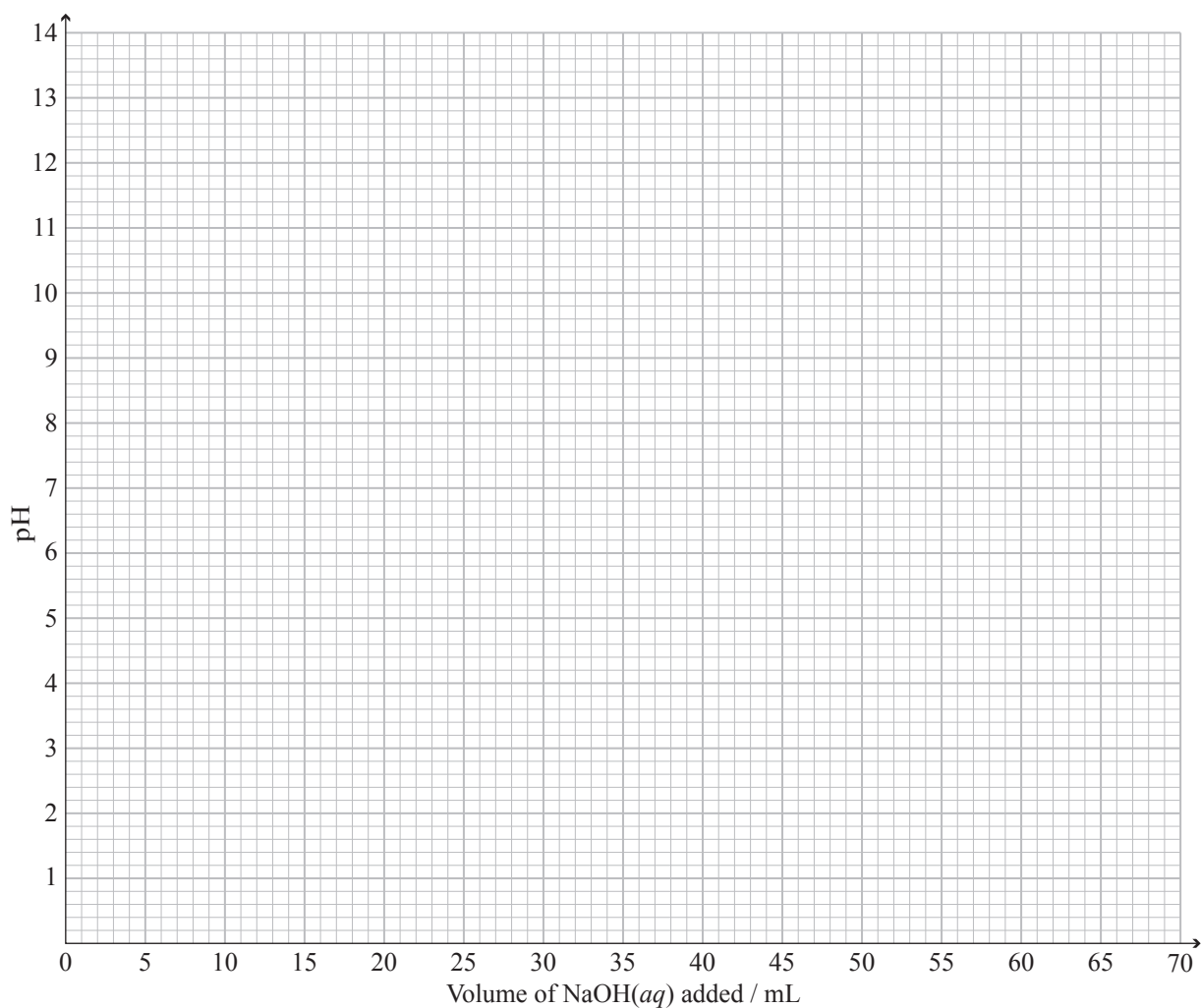
- In the first titration, 0.0886 mol L⁻¹ sodium hydroxide solution, NaOH(aq), was added to 30.0 mL of hydrochloric acid, HCl(aq), which had an initial pH of 1.04.
- In the second titration, 0.0886 mol L⁻¹ sodium hydroxide solution, NaOH(aq) was added to a 30.0 mL solution of hypochlorous acid, HOCl(aq), which had an initial pH of 4.16.

(i) Carry out calculations to determine key points on the titration curve for each experiment.

Use these points to draw the two predicted curves on the graph space provided.

Key values may include: the initial concentrations of the two acids, the volume and pH at the equivalence point, the pH at halfway to the equivalence point, and the pH after 10 mL of excess base has been added.

$$\text{p}K_{\text{a}}(\text{HOCl}) = 7.53$$



Question Four continues
on the following page.

(ii) Calculate the pH at the point where the two curves intersect.

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

QUESTION
NUMBER

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

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