SUPERVISOR'S USE ONLY

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

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NZQA | Mana Tohu Mātauranga o Aotearoa
New Zealand Qualifications Authority

Scholarship 2025
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 2–28 in the correct order and that none of these pages is blank.

Do not write in the margin ( ). 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

QUESTION ONE

(a) Sodium hydrogen carbonate, $NaHCO_3(s)$, and citric acid, $H_3Cit(s)$, are used in fizzy vitamin tablets. Once a tablet is dropped into a glass of water, a spontaneous reaction is observed, resulting in the formation of bubbles of gas which mix the contents of the tablet throughout the solution, and there is a decrease in the temperature of the solution.

(i) Discuss the entropy changes occurring during this reaction.

Include a balanced chemical equation in your answer.

(ii) Explain why a reaction is only observed once the tablet is dissolved in water.

(b) Pure bromine trifluoride, BrF_3, can conduct electricity in the liquid form, owing to its ability to undergo autoionisation. This involves the reaction of two BrF_3 molecules to form ions.

Two proposed reactions for the autoionisation are:

(1) $2BrF_3 \rightarrow BrF_2^- + BrF_4^+$ **OR** (2) $2BrF_3 \rightarrow BrF_2^+ + BrF_4^-$

(i) Predict, with support of Lewis diagrams, the shapes and F–Br–F bond angles for the four different ions which could be produced during autoionisation.

BrF_2^- *Lewis diagram:*	BrF_4^+ *Lewis diagram:*
Shape/bond angle:	*Shape/bond angle:*
BrF_2^+ *Lewis diagram:*	BrF_4^- *Lewis diagram:*
Shape/bond angle:	*Shape/bond angle:*

(ii) Each reaction involves the transfer of a fluorine ion.

Justify which reaction, (1) or (2), is more likely to give the ions responsible for the conductivity.

(iii) The two possible shapes for BrF_3 molecules are T-shaped or trigonal planar.

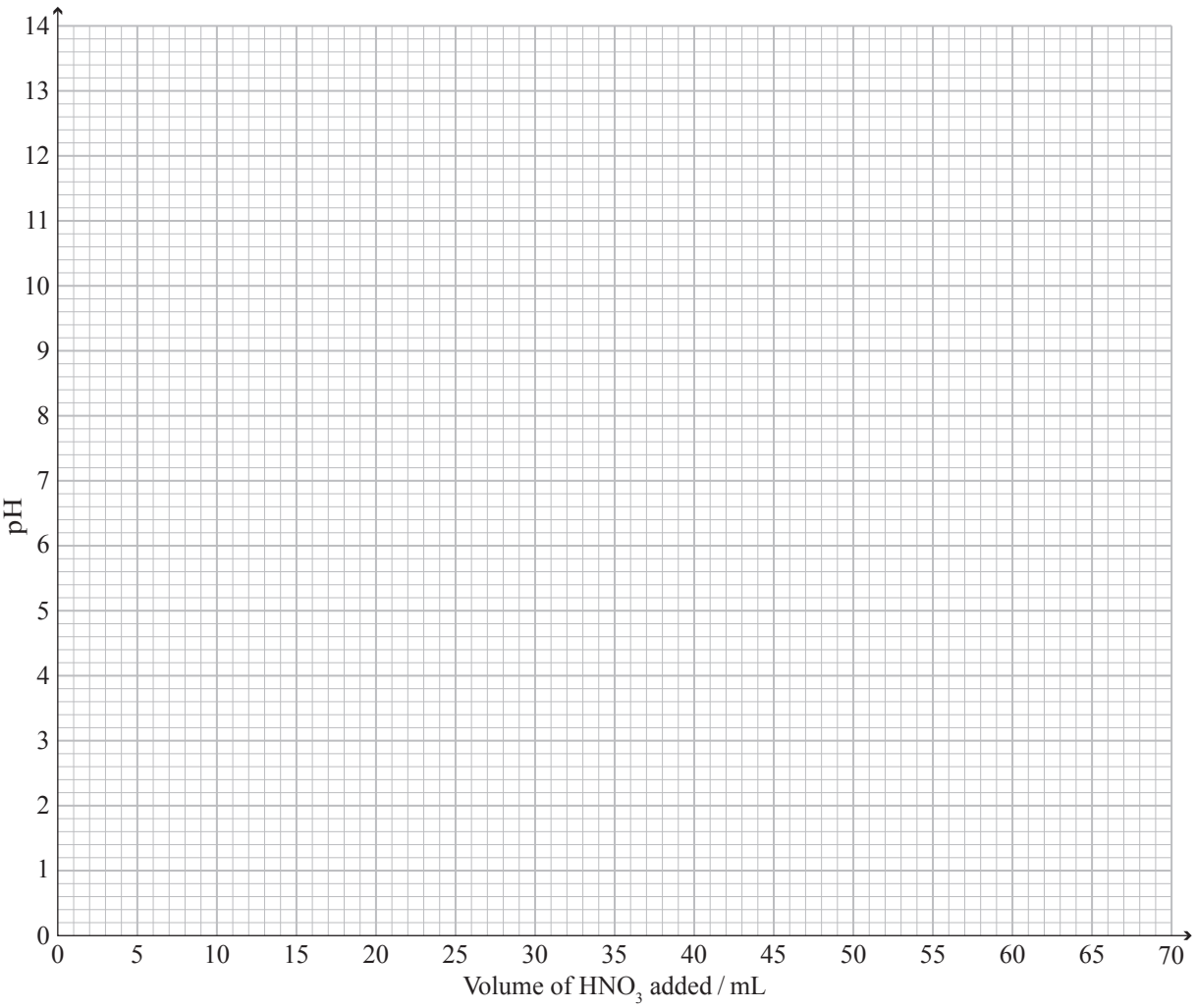
Explain which of the two shapes is correct, and justify whether the BrF_3 molecules will be polar or non-polar.

(c) A titration was carried out using 25.00 mL of ethylamine solution, $CH_3CH_2NH_2(aq)$, to which 0.1300 mol L^{-1} nitric acid, $HNO_3(aq)$, was added. The volume of $HNO_3(aq)$ at the equivalence point was 34.98 mL.

(i) Carry out sufficient calculations to draw the predicted curve for this titration on the grid on the opposite page.

Key values may include: The initial concentration and pH of the base, the pH at the equivalence point, the pH at halfway to the equivalence point, and the pH after 20.00 mL of excess acid has been added.

$pK_a(CH_3CH_2NH_3^+) = 10.64$



(ii) For the solutions formed after 18 mL and 28 mL of HNO_3 have been added, evaluate their buffering capacity against strong acid and strong base.

Calculations are not required.

QUESTION TWO

(a) A common equilibrium demonstration in classrooms utilises a solution made when cobalt(II) chloride, $CoCl_2(s)$, has been dissolved in hydrochloric acid, $HCl(aq)$. This solution is purple in colour when it contains an equimolar mixture of two coloured complex ions, $[CoCl_4]^{2-}(aq)$ which is blue, and $[Co(H_2O)_6]^{2+}(aq)$ which is pink.

(i) Write a balanced chemical equation for this equilibrium system, and use it to explain what would be observed if either of the following chemicals were added to a sample of the purple solution:

- concentrated $HCl(conc)$
- solid $AgNO_3(s)$.

(ii) Cobalt chloride paper is prepared by soaking pieces of filter paper in a pink-coloured cobalt(II) chloride solution, and then drying the paper. The paper becomes dark blue in appearance once it is dry, and it can be used as a chemical indicator.

Predict which chemical the paper can be used to test for, and justify your prediction.

(b) Compound A, $C_5H_{11}Cl$, rotates plane-polarised light, and produces a ^{13}C NMR spectrum with four peaks.

(i) Four reactions were carried out in sequence in a round-bottomed flask, starting with a sample of Compound A. After each reaction was complete, all inorganic substances were removed, and any organic compounds remaining were left unseparated in the flask to be used as reactants in the next reaction.

The reagent used in the first reaction was NaOH(*alc*). The reagent in the second reaction was dilute H_2SO_4. The reagent in the third reaction was acidified potassium dichromate solution, $H^+/Cr_2O_7^{2-}$, and the reagent in the fourth reaction was HCl(*conc*).

Determine the structure of Compound A, and construct a reaction scheme which shows all possible organic products formed during these reactions. Label any major and minor products formed.

(ii) Explain how ^{13}C NMR and IR spectroscopy could be used to distinguish the final reaction products from each other.

You may apply labels to these compounds in your scheme and refer to these in your answer below.

(c) The table below lists five descriptions that each identify a particular element.

(i) Place the symbol for the correct element in each box in the table below. The first one has been done as an example for you.

Description	**Element symbol**
The lightest element with one electron in the 1s orbital.	**H**
Found in Period 2, this element has no paired p electrons and does not follow the general trend in ionisation energy across a period.	
This element has the highest ionisation energy of any element.	
Ions of this Period 3 element have the smallest ionic radius of all ions in this period.	
This element exists as a gaseous diatomic molecule, with the highest bond enthalpy of any of the diatomic molecules.	

(ii) For THREE of the elements you have identified, discuss your choices, with clear references to the details provided in the descriptions.

(1) Element: _____

Discussion: _____

(2) Element: _____

Discussion: _____

(3) Element: _____

Discussion: _____

QUESTION THREE

(a) In the standardisation of a solution of hydrochloric acid, HCl(*aq*), students were advised to measure 2.691 g of anhydrous sodium carbonate, $Na_2CO_3(s)$, and carefully transfer it into a 250.0 mL volumetric flask. This flask was then to be filled to the line using distilled water and labelled.

10.00 mL aliquots of the sodium carbonate solution were then to be titrated against a provided hydrochloric acid solution, HCl(*aq*).

Two students independently gathered results by following the method, and their measurements are shown in the tables below:

Student A results (mL)		
Initial	**Final**	**Titre**
0.00	16.55	
16.55	32.35	
32.35	48.05	
0.05	15.75	
15.75	31.40	

Student B results (mL)		
Initial	**Final**	**Titre**
0.00	22.25	
22.25	42.45	
0.15	20.70	
20.70	40.60	
0.25	19.75	

The teacher then determined the hydrochloric acid concentration to be 0.1040 mol L^{-1} using the same method.

Use the data collected by each student to calculate their final HCl(*aq*) concentrations.

For each student, comment on the **validity** of their method and the **accuracy** of their results, and suggest any possible sources of error in each of the their procedures.

$M(Na_2CO_3) = 106.0$ g mol^{-1}

(b) The enthalpy change for a reaction can be calculated using a number of different methods. Relevant chemical data book values at 25 °C, which can be utilised in thermochemical calculations are:

Bond enthalpies / kJ mol^{-1}			
C–O	358	O–H	463
C=O	745	O=O	498

Enthalpies of formation / kJ mol^{-1}	
$CO_2(g)$	–393
$H_2O(\ell)$	–286
$C_6H_{13}OH(\ell)$	–320

Enthalpies of reaction / kJ mol^{-1}	
$C(g) + 4H(g) \rightarrow CH_4(g)$	$\Delta_r H°$ –1652
$2C(g) + 6H(g) \rightarrow C_2H_6(g)$	$\Delta_r H°$ –2826

The specific heat capacity of water is 4.18 J g^{-1} °C^{-1}. $M(C_6H_{13}OH(\ell))$ = 102.2 g mol^{-1}

(i) Calculate the enthalpy of combustion, $\Delta_c H°$, for hexan-1-ol, $C_6H_{13}OH(\ell)$, using the three methods below.

$$C_6H_{13}OH(\ell) + 9O_2(g) \rightarrow 6CO_2(g) + 7H_2O(\ell)$$

Method 1: Using experimental data

1.35 g of hexan-1-ol was completely combusted by a student, and the heat produced raised the temperature of 300 mL of water from 22.3 °C to 51.5 °C.

Method 2: Using enthalpies of formation

Method 3: Using bond enthalpies and enthalpies of reaction

(ii) Compare the answers obtained for each of the three methods, suggesting reasons for any differences observed.

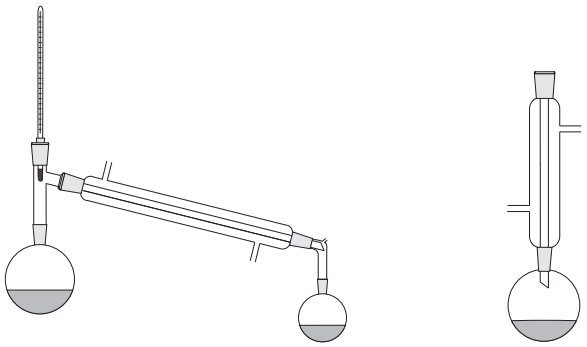
(c) (i) Identify, by name and structural formula, the ester formed between butanoic acid and ethanol.

(ii) Outline two different reactions that could be used to prepare this ester in a chemistry laboratory.

In your answer:

- give structural equations and include clear references to any other reagents or steps which might be required
- compare and contrast the experimental conditions and safety considerations for these reactions.

(iii) Acid hydrolysis of the ester, to give butanoic acid and ethanol, will require use of both apparatuses shown below.



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Discuss how each apparatus would be used in the preparation and separation of ethanol and butanoic acid from the ester.

QUESTION FOUR

(a) A beaker was filled with 125 mL of a solution containing a mixture of 1.68×10^{-4} mol L^{-1} potassium chloride, KCl(*aq*), and 1.39×10^{-4} mol L^{-1} potassium chromate, $K_2CrO_4(aq)$. Small crystals of silver nitrate, $AgNO_3(s)$, were slowly added to the beaker, with stirring until the formation of two solids had been observed, each with different appearances. No change in volume was observed.

$K_s(AgCl) = 1.80 \times 10^{-10}$ $K_s(Ag_2CrO_4) = 2.60 \times 10^{-12}$

(i) Determine the identity of the first solid to precipitate from the solution.

(ii) Determine the concentration of the anion from the first solid that still remains in the solution when the second solid begins to precipitate. Use this to decide whether this procedure could be used to separate the Cl^- ions from CrO_4^- ions in this solution. For this to be the case, more than 99.9% of the first ion must have precipitated before the second solid begins to precipitate.

(iii) A second experiment was carried out. In this case, a dilute solution of $AgNO_3(aq)$ was instead slowly titrated into a beaker containing 125 mL of the solution described at the beginning of part (a).

The first precipitate was observed after a small volume of the $AgNO_3$ solution had been added, and the second precipitate was observed once a total of 16.8 mL $AgNO_3$ solution had been added.

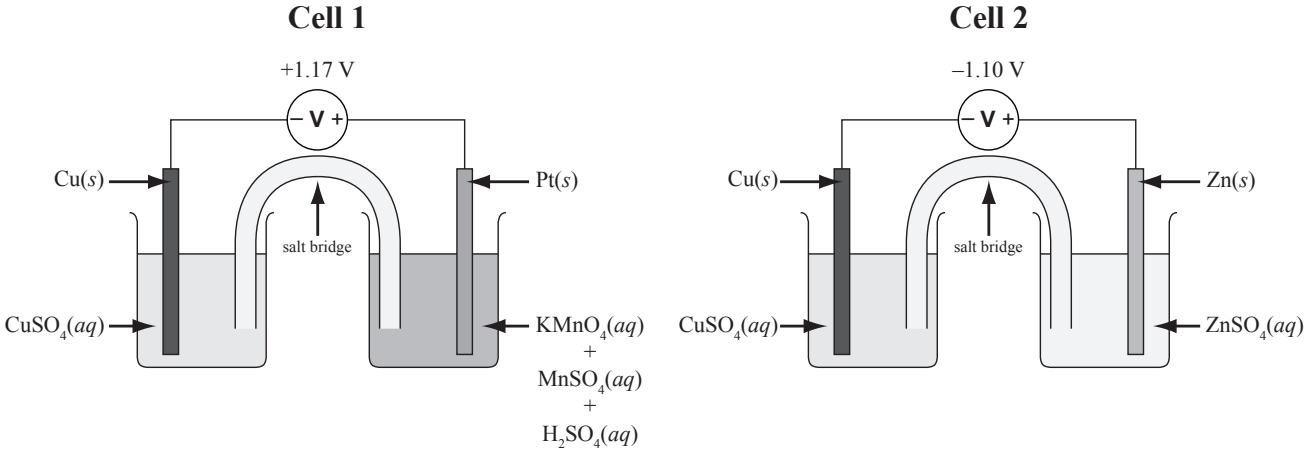
Calculate the concentration of the $AgNO_3(aq)$ solution used in the titration.

You should consider the amount of Ag^+ precipitated, as well as the amount remaining in solution.

(b) A student set up two electrochemical cells under standard conditions at 25 °C.

The internal circuit of both cells consisted of a salt bridge containing potassium sulfate solution, $K_2SO_4(aq)$, and the external circuit consisted of a voltmeter with wires connected to solid electrodes. The metals used for the electrodes, and solutions prepared, are indicated in the diagrams below.

The student recorded the voltages shown on each voltmeter.



The voltmeters were then removed and replaced with a conductive wire. After some time, the student recorded any observed changes that had occurred.

(i) Describe the changes that occurred in each of the electrochemical cells, and justify them in terms of oxidation-reduction processes, flow of charge, and movement of particles.

(ii) Determine the standard reduction potentials, $E^{o}(Cu^{2+} / Cu)$ and $E^{o}(MnO_4^{-} / Mn^{2+})$, and use appropriate calculations to justify what would be observed if a piece of zinc metal, Zn(*s*), was added to a beaker containing a solution of acidified potassium permanganate, $H^{+} / MnO_4^{-}(aq)$.

$E°(Zn^{2+} / Zn) = –0.76$ V

Question Four continues on the next page.

(c) The energy required to break apart an ionic crystal, to form gaseous ions, is different for magnesium chloride, $MgCl_2(s)$, and sodium chloride, $NaCl(s)$.

Justify which compound will require the greater amount of energy for this change to occur.

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