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SUPERVISOR'S USE ONLY

NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

QUALIFY FOR THE FUTURE WORLD
KIA NOHO TAKATŪ KI TŌ ĀMUA AO!

Tick this box if you have NOT written in this booklet

Scholarship 2022
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 may be cut off when the booklet is marked.

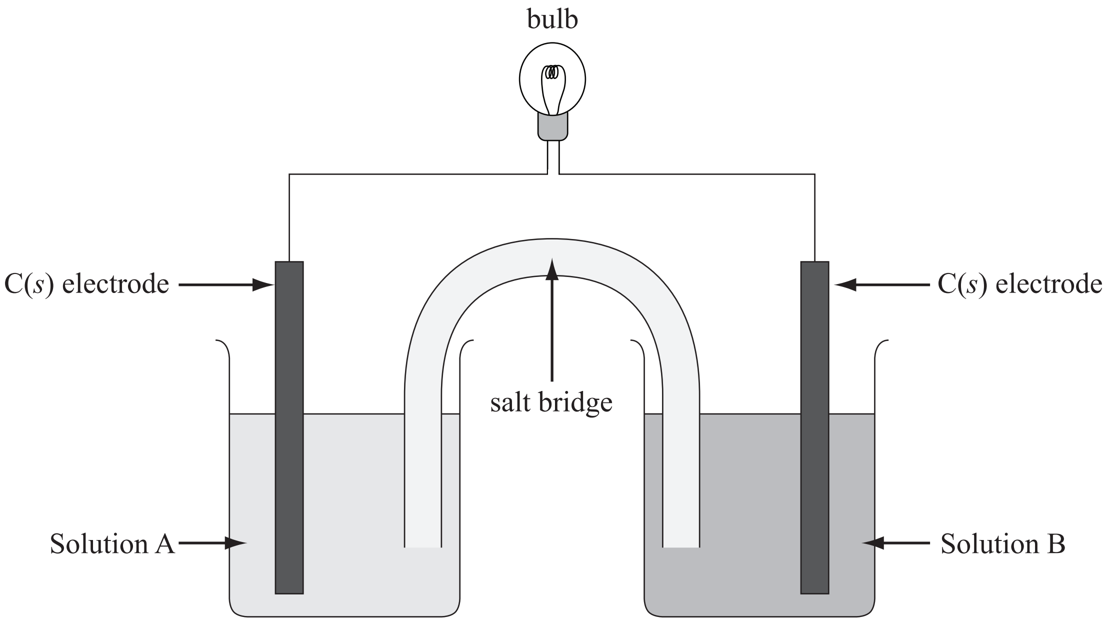
YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.

Question	Score
ONE	
TWO	
THREE	
FOUR	
TOTAL	

ASSESSOR'S USE ONLY

QUESTION ONE

(a) An electrochemical cell was constructed using two beakers, each containing acidified solutions of different reagents under standard conditions. Inert graphite electrodes, a salt bridge, and a small light bulb connected by wires to the electrodes, were used to construct the remainder of the cell.



Solution A contained a mixture of aqueous bromine, $Br_2(aq)$, and potassium bromide, $KBr(aq)$. Solution B contained a mixture of potassium permanganate, $KMnO_4(aq)$, and manganese(II) sulfate, $MnSO_4(aq)$. Both solutions were acidified using dilute sulfuric acid, $H_2SO_4(aq)$.

Once the apparatus was constructed, the bulb was observed to light up, and changes were observed in both beakers. The colour of the solution in one beaker became lighter, while the colour in the other beaker became darker.

(i) Justify the observations made for each solution while the bulb was illuminated. You should refer to the reactant and the product species involved, and write a description of the direction of electron flow in the apparatus.

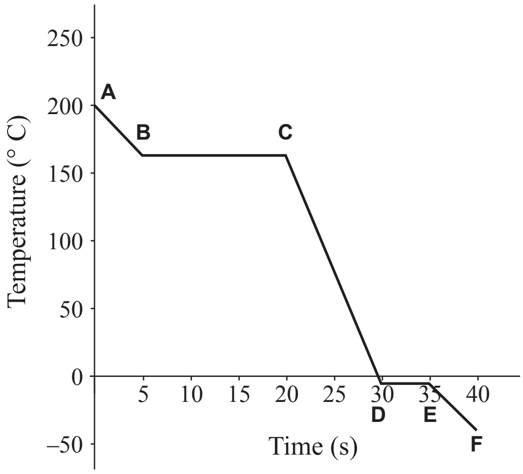
You should use cell potential calculations and balanced chemical equations to support your answer.

$E°(Br_2/Br^-) = +1.10$ V	$E°(SO_4^{2-}/SO_2) = +0.16$ V	$E°(O_2/H_2O) = +1.23$ V
$E°(H_2O/H_2) = -0.83$ V	$E°(MnO_4^-/Mn^{2+}) = +1.51$ V	$E°(K^+/K) = -2.94$ V
$E°(Cl_2/Cl^-) = +1.36$ V	$E°(NO_3^-/NO_2) = +0.80$ V	$E°(H^+/H_2) = 0.00$ V

(ii) Using the electrochemical data provided, justify the identity of an acid that would **not** be appropriate to use when acidifying the solutions in this electrochemical cell.

(b) A sample of initially gaseous butanoic acid at standard pressure was rapidly cooled over a 40-second period. During this time, energy was consistently removed from the sample; however, a simple linear decrease in the temperature of the sample was not observed.

The graph below shows the data that was gathered.



(i) Justify the gradient of the line between sections **B–C** and **D–E** of the graph, including the differences in the length of each section.

Include clear links to kinetic energy of particles and attractive forces.

(ii) Explain how the information in the graph can be used to determine the specific heat capacity of liquid butanoic acid, and describe what further information would be necessary to determine this.

No calculations are required.

(c) Sterling silver is a common silver alloy used in fine cutlery and jewellery. It is an alloy of various metals, with silver as the base, and most commonly copper within the alloy mixture. Sterling silver must be a minimum of 92.50% (by mass) silver.

To confirm the composition of a particular silver alloy used in jewellery, a ring with mass of 4.824 g was reacted completely with a small excess of hot concentrated nitric acid, HNO_3(*conc*).

The resulting solution was then transferred to a 250.0 mL volumetric flask, and diluted to the mark using distilled water.

20.00 mL volumes of the diluted solution were titrated with a 0.1450 mol L^{-1} potassium thiocyanate solution, KSCN(*aq*), using an iron(III) solution indicator. An average volume of 22.13 mL KSCN solution was required to reach the end point on repeat titrations.

$$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(s)$$

From the remaining diluted solution, 10.00 mL volumes were pipetted into conical flasks. 5.00 mL of dilute sodium chloride solution, NaCl(*aq*), was then added to each flask to precipitate out the Ag^+ ions from the solution. Following this, 5.00 mL of approximately 2 mol L^{-1} sulfuric acid solution, H_2SO_4(*aq*), was then added to each flask, followed by 10.00 mL of 1% potassium iodide solution, KI(*aq*). Each flask was then titrated with 0.02370 mol L^{-1} sodium thiosulfate solution, $Na_2S_2O_3$(*aq*). An average volume of 12.58 mL $Na_2S_2O_3$ solution was required to reach the end point on repeat titrations.

$$4I^-(aq) + 2Cu^{2+}(aq) \rightarrow 2CuI(s) + I_2(aq)$$

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

Determine the percentage of silver and copper metals in the alloy, and state whether this alloy meets the standard required to be called sterling silver.

You may assume that any other metals present do not affect either analysis.

QUESTION TWO

(a) The molecules in fats (solids at room temperature, often of animal origin) and oils (liquids at room temperature, often of plant origin) are triglycerides. A single triglyceride molecule is a tri-ester of glycerol (propan-1,2,3-triol) and three fatty acids (long chain carboxylic acids). The molecules can be saturated or unsaturated, and the three fatty acids in a single triglyceride molecule can be the same or different.

(i) Triglycerides **X**, **Y**, and **Z** are three different molecules found in common food products. Within each molecule, the three fatty acids are identical.

Use the two fatty acids given below to draw a possible structure for triglycerides **X**, **Y**, and **Z**, considering the descriptions given. With reference to these structures, justify the observed variation in the states of the three different food products. You do not need to use expanded structural formulae, and any stereochemistry in the structures may be labelled, rather than drawn.

$CH_3(CH_2)_{16}COOH$ $\quad\quad$ $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

Triglyceride X is saturated and a major component of butter, which is a solid at room temperature:

Triglyceride Y is unsaturated and a major component of olive oil, which is a liquid at room temperature:

Triglyceride Z is unsaturated and a major component of margarine, which is a solid at room temperature:

(ii) It is difficult to clean fats and oils from dining plates, cutlery, or our skin, using hot water alone. Detergents and soaps contain substances known as anionic surfactants, which are often used to assist with the cleaning process. The anionic surfactants found in soaps are produced from the hydrolysis of naturally occurring fats and oils.

A common water-soluble surfactant in soap is sodium dodecanoate, $CH_3(CH_2)_{10}COONa$, which is produced from the hydrolysis of triglycerides found in coconut oil.

Explain why water alone is not able to clean away fats and oils, and propose reasons for the use of surfactants, such as sodium dodecanoate, in the cleaning process.

(b) During a classroom demonstration, a teacher prepared a small beaker of dilute copper(II) sulfate solution, $CuSO_4(aq)$, which was pale blue in colour.

Addition of a small volume of ammonia solution, $NH_3(aq)$, to the beaker caused a pale blue precipitate to form. Addition of further ammonia solution caused the precipitate to disappear, and the solution to darken into a deep royal-blue colour.

Addition of dilute hydrochloric acid solution, $HCl(aq)$, to the beaker caused the solution to lighten in colour, and a pale blue precipitate to form. Addition of further dilute hydrochloric acid solution led to the precipitate disappearing, leaving a pale blue solution.

Justify the observations made during each stage of this classroom demonstration. You should identify the species responsible for the observations, and use equilibrium principles and balanced chemical equations to support your justification.

QUESTION THREE

(a) A saturated solution of calcium hydroxide, $Ca(OH)_2(aq)$, was prepared by mixing an excess of solid calcium hydroxide with a small volume of water at 25 °C. The solution was filtered to remove remaining undissolved solid, and the filtrate was then used to fill a 50.0 mL burette.

20.0 mL of 0.0308 mol L^{-1} ethanoic acid solution, $CH_3COOH(aq)$, was pipetted into a conical flask, and titrated with the calcium hydroxide solution using an appropriate pH indicator.

(i) Calculate the volume of calcium hydroxide solution that was required to reach the equivalence point in the titration.

$K_s(Ca(OH)_2) = 6.40 \times 10^{-6}$

(ii) Determine the pH of the solution in the conical flask: at the start of the titration; at the equivalence point; and after 35.0 mL of calcium hydroxide solution had been added.

Include a brief outline of any assumptions made when calculating either the initial pH or equivalence pH.

If you were unable to solve the volume in (i), use 25.00 mL for the equivalence point in these calculations.

$pK_a(CH_3COOH) = 4.76$

There is more space for your answer to this question on the following page.

(iii) Bromothymol blue is a pH indicator which can be used in acid base titrations. In solutions of low pH, the indicator is yellow in appearance. In solutions of high pH, the indicator is blue in colour. During a weak acid–strong base titration, the solution is observed to transition through a green colour as the pH rises.

Discuss these observations, with reference to how the composition and colours of pH indicators change during acid-base titrations, and comment on whether this indicator would be appropriate for the titration between CH_3COOH and $Ca(OH)_2$.

No calculations are required.

pK_a(bromothymol blue) = 7.2

(b) The industrial production of acetylene gas, also known as ethyne, $C_2H_2(g)$, is carried out in three distinct stages:

- In the first stage, calcium carbonate, $CaCO_3(s)$, is heated to high temperatures, causing it to decompose and produce calcium oxide, $CaO(s)$, and carbon dioxide gas, $CO_2(g)$.
- In the second stage, the calcium oxide is reacted with a refined form of carbon, $C(s)$, known as coke, inside a blast furnace. This stage requires large amounts of heat, and results in the formation of calcium carbide, $CaC_2(s)$, alongside carbon monoxide gas, $CO(g)$, as the by-product of the reaction.
- In the final stage, the calcium carbide is reacted with water, $H_2O(\ell)$, to produce acetylene gas, as well as calcium hydroxide, $Ca(OH)_2(s)$.

(i) Using the thermochemical data provided, determine the energy that would be absorbed or released during the final stage of the process in the production of 50.0 kg of acetylene gas.

$\Delta_f H°(CaO(s)) = –635 \text{ kJ mol}^{-1}$ $\quad$ $\Delta_f H°(CO(g)) = –111 \text{ kJ mol}^{-1}$

$\Delta_f H°(CaC_2(s)) = –60.0 \text{ kJ mol}^{-1}$ $\quad$ $\Delta_c H°(C_2H_2(g)) = –1301 \text{ kJ mol}^{-1}$

$\Delta_c H°(C(s)) = –394 \text{ kJ mol}^{-1}$

$$CaO(s) + H_2O(\ell) \rightarrow Ca(OH)_2(s) \quad \Delta_r H° = –65.0 \text{ kJ mol}^{-1}$$

(ii) Suggest reasons for the differences in $\Delta_f H°$ values for calcium oxide and carbon monoxide.

QUESTION FOUR

(a) The spectra for Compound **A** can be found in the resource booklet.

(i) Use the spectra provided to identify and name Compound **A**, and give a brief justification, linking aspects of the spectra to the structure of Compound **A**.

(ii) Compound **A** can be used as one of the starting reagents in a multi-step reaction process that yields a more complex organic product.

Compound **A** can be reacted with $NaBH_4$ to form Compound **B**, which then reacts with Reagent **X** to form Compound **C**. Compound **C** can be further reacted with Reagent **Y** to form Compound **D**, which turns damp red litmus paper blue.

Compound **E** is another starting reagent in the reaction process. It is a branched chain secondary alcohol, that has the molecular formula $C_5H_{11}OCl$. It can rotate plane polarised light, and it produces four distinct peaks in a ^{13}C NMR spectra. Reaction of Compound **E** with concentrated H_2SO_4 yields three products, Compounds **F**, **G**, and **H**. Compounds **G** and **H** are geometric isomers.

Compound **F** reacts with aqueous potassium permanganate to give Compound **I** and a brown precipitate. Compound **I** is reacted with aqueous potassium hydroxide to form Compound **J**, which can then be reacted further into Compound **K** using excess acidified potassium dichromate. Spectroscopic analysis of Compound **K** using MS and ^{13}C NMR yields a M+ peak at 132 m/z, and four unique carbon bonding environments, with two of the spectrum peaks situated above 150 ppm.

Compounds **K** and **D** react by proton transfer to form Compound **L**.

Use the information provided to identify the Reagents **X** and **Y**, and the structures of Compounds **B** to **L**. You do not need to name any of the compounds.

Reagents X and Y and Compounds B to L:

Question Four continues on the next page.

(b) Sodium chloride, $NaCl(s)$, has a high solubility in water, $H_2O(\ell)$, with the dissolution being a mildly endothermic process, with minimal temperature changes observed at room temperature. Despite this solubility, when an open beaker containing sodium chloride solution, $NaCl(aq)$, is left in a warm room, the solution is observed to decrease in volume, with the spontaneous formation of salt crystals throughout the solution.

Discuss all the favourable and unfavourable entropy changes occurring as sodium chloride dissolves into a solution at room temperature, and spontaneously crystallises out of the solution when left out in a warm room. Use these entropy changes to justify why, in each case, the observed process is spontaneous overall.

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