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Tick this box if there is no writing in this booklet

Scholarship 2020
Chemistry

9.30 a.m. Tuesday 17 November 2020
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.

Pull out Resource Booklet S–CHEMR from the centre of this booklet.

You should answer ALL the questions in this booklet.

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 2–20 in the correct order and that none of these pages is blank.

You are advised to spend approximately 45 minutes on each question.

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

Question	Score
ONE	
TWO	
THREE	
FOUR	
TOTAL	

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QUESTION ONE

(a) Solution **X** is prepared by mixing 50.00 mL volumes of nitric acid solution, $HNO_3(aq)$, and ammonia solution, $NH_3(aq)$. The nitric acid had a pH of 1.50, while the ammonia solution had a pH of 11.00, at 25 °C.

Calculate the concentration of all species present in Solution **X**, and determine the pH of the solution.

$K_a(NH_4^+) = 5.75 \times 10^{-10}$ $\quad\quad$ $pK_a(NH_4^+) = 9.24$

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(b) Account for the following observations using thermodynamic principles:

1. Oxygen gas dissolves in water at room temperature.
2. The reaction between hydrogen gas, $H_2(g)$, and chlorine gas, $Cl_2(g)$, to form hydrogen chloride gas, $HCl(g)$, is spontaneous at room temperature.

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(c) Consider the following ionisation equations:

$Na(g) \rightarrow Na^+(g) + e^-$

$Na^+(g) \rightarrow Na^{2+}(g) + e^-$

$Mg(g) \rightarrow Mg^+(g) + e^-$

$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$

Predict the order of ionisation enthalpy values (from lowest to highest) for these four changes. Justify your predictions with reference to the atomic structures of Na and Mg.

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QUESTION TWO

(a) In electrolysis reactions, an electric current is used to force non-spontaneous reactions to occur. For electrolysis to take place, the voltage supplied must exceed the calculated cell potential under standard conditions. When electrolysis is carried out with aqueous solutions, the strongest oxidant in the solution reacts at one electrode, and the strongest reductant in the solution reacts at the other electrode.

A table of electrode potentials is provided in the resource booklet.

(i) A solution containing a mixture of tin(II) sulfate, $SnSO_4(aq)$, and zinc chloride, $ZnCl_2(aq)$, is electrolysed using inert electrodes.

Determine the changes observed at each electrode during the electrolysis process, the overall cell reaction, and the minimum voltage required for the reactions to occur.

Justify your decisions, with reference to the species in solution and use of balanced equations.

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(ii) Predict and justify how the reactions and expected observations will differ if the following changes are made to the cell described in (i):

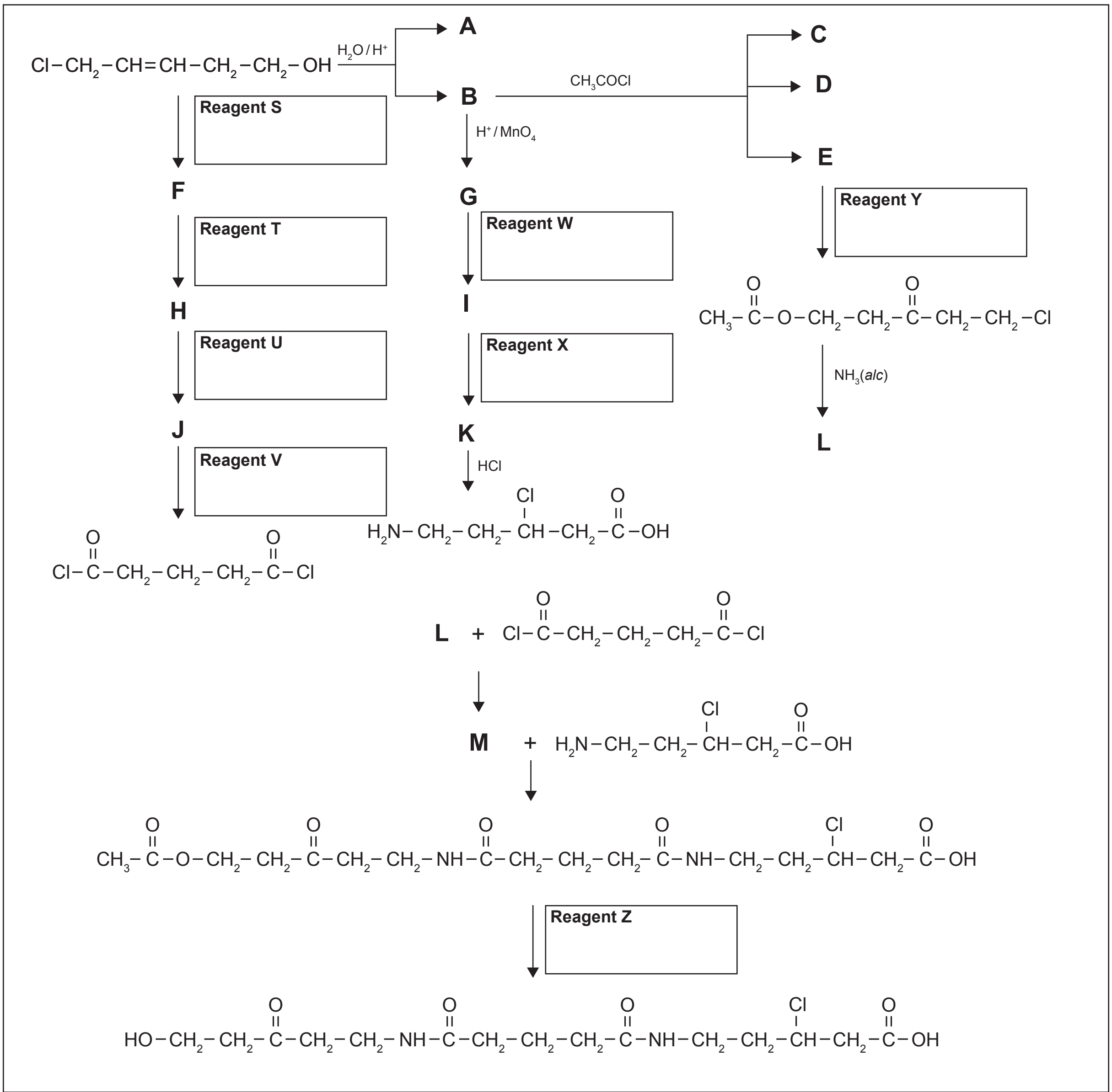
- the inert electrodes are replaced with zinc metal electrodes

- the tin(II) sulfate, $SnSO_4(aq)$, is replaced with iron(II) sulfate, $FeSO_4(aq)$.

(b) The versatility of the ester functional group makes it a useful tool for organic synthesis pathways. It can be added to or removed from organic molecules with relative ease. It is resistant to oxidation, but is less stable to hydrolysis than the amide functional group.

In theory, 5-chloropent-3-en-1-ol, $ClCH_2CH{=}CHCH_2CH_2OH$, could be used as a starting reagent to synthesise three different molecules, which can be combined to create the final product below.

Complete the scheme by identifying reagents **S–Z** below, and by determining and giving the structures for compounds **A–M** on the next page.



Additional Information

- Following separation of compounds **C**, **D**, and **E**, all three samples were analysed using IR spectroscopy. The spectra for compounds **C** and **E** both had distinctive peaks at 3550 cm^{-1} and 1740 cm^{-1}, while the spectra for compound **D** had only the one distinctive peak at 1740 cm^{-1}.
- Compound **M** needed to be isolated from a mixture of two organic products formed in the previous reaction step. Compound **M** was the lower mass product.

Compounds **A**–**M**

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QUESTION THREE

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(a) A 50.00 mL saturated solution of lead chloride, $PbCl_2(aq)$, in dilute nitric acid, $HNO_3(aq)$, at 25 °C, contains 0.225 g of dissolved lead chloride.

The solution is then diluted to 250.0 mL in a volumetric flask using distilled water, and a 50.00 mL sample is extracted from the flask and mixed with 25.00 mL of 2.35×10^{-3} mol L^{-1} hydrochloric acid, $HCl(aq)$.

(i) Determine whether any precipitate is present in the final mixture.

$M(PbCl_2) = 278$ g mol^{-1}

(ii) Justify the need for nitric acid in the original solution.

$K_s(Pb(OH)_2) = 8.00 \times 10^{-17}$

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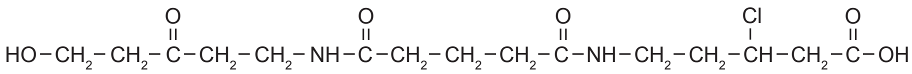
(b) Consider complete hydrolysis of the following compound from Question Two (b).



Predict the number of peaks, and their positions, in the ^{13}C NMR spectra for each of the organic products, and discuss the unique attributes of each spectra that could be used to distinguish the products from each other.

A spectroscopy data sheet is provided in the resource booklet.

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

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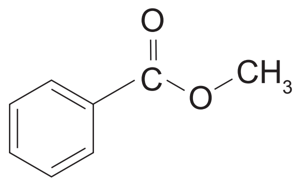
(c) Methyl benzoate is a liquid at room temperature. Addition of 6 mol L^{-1} sodium hydroxide solution, NaOH(*aq*), to a sample of methyl benzoate initially results in the formation of two immiscible liquid layers. When the mixture is heated under reflux, the two layers mix and on cooling, a single solution is observed. On addition of excess dilute sulfuric acid, H_2SO_4(*aq*), to the solution, a white crystalline solid is formed.



methyl benzoate

Explain these observations, with reference to the structure and bonding of the substances involved.

Note: The carbon double bonds in the ring structure do not react with NaOH(*aq*) or H_2SO_4(*aq*).

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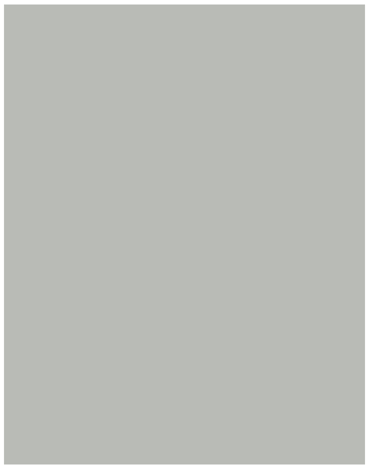
QUESTION FOUR

(a) Blackboard chalk sticks are primarily composed of refined natural chalk, $CaCO_3$. Other ingredients in the chalk sticks can include small amounts of other minerals, binding agents, and colouring pigments.

The average percentage mass of $CaCO_3$ in blackboard chalk sticks can be determined by mixing a sample of a chalk stick with an excess of a standardised solution of hydrochloric acid, HCl(*aq*), leaving sufficient time for all reactions to occur, and then titrating the remaining HCl with a solution containing a base of known concentration.



https://image.freepik.com/free-photo/aged-math-teacher-writing-chalkboard_23-2148201011.jpg

In analysis of blackboard chalk sticks, a standard solution of sodium carbonate, $Na_2CO_3(aq)$, was prepared by dissolving 1.473 g of sodium carbonate in distilled water in a 250.0 mL volumetric flask. A hydrochloric acid solution was standardised using the sodium carbonate solution, and determined to have a concentration of 1.060 mol L^{-1}.

A chalk stick was crushed, and a 4.017 g sample of the powder was added to a conical flask containing 100.0 mL of the hydrochloric acid solution, HCl(*aq*). The mixture was gently heated for 30 minutes and left to cool. The cooled mixture was then transferred to a 250.0 mL volumetric flask, and diluted to the mark using distilled water.

Finally, 25.00 mL samples of the sodium carbonate solution prepared above were pipetted into conical flasks and titrated against the HCl / chalk solution using methyl orange indicator. The data gathered in the titration is provided below.

Titre	Initial volume reading / mL	Endpoint volume reading / mL
1	1.46	28.42
2	2.62	28.22
3	1.24	27.12
4	2.34	28.66
5	3.48	29.24

$M(Na_2CO_3) = 106.0 \text{ g mol}^{-1}$ $\quad M(CaCO_3) = 100.1 \text{ g mol}^{-1}$

Determine the average percentage mass of $CaCO_3$ in the chalk sticks.

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(b) The limiting reagent in a chemical reaction is the reactant present in the smallest quantity, limiting, and therefore determining, the amount of product that can be formed. The reaction ends once this reactant is completely consumed, and all other reagents involved in the reaction are considered to be present in *excess*.

https://media.techeblog.com/images/potassium-chlorate-gummy-bear.jpg

12.0 g of potassium chlorate, $KClO_3(s)$, and a 4.50 g gummy bear, composed primarily of sucrose, $C_{12}H_{22}O_{11}(s)$, are placed in a boiling tube. The boiling tube is then heated, causing the potassium chlorate to start decomposing, rapidly releasing oxygen gas, which causes the gummy bear to ignite. The heat from the combustion decomposes the potassium chlorate further, accelerating the reactions, causing the tube to glow brightly and liberate clouds of white vapour.

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(g)$$

(i) Determine the limiting reagent, then calculate the theoretical energy released in this reaction.

Use the data values below, all given at 25 °C.

$$12C(s) + 11H_2(g) + 5\tfrac{1}{2}O_2(g) \rightarrow C_{12}H_{22}O_{11}(s) \qquad \Delta H_1 = -2226 \text{ kJ mol}^{-1}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \qquad \Delta H_2 = -483.6 \text{ kJ mol}^{-1}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_3 = -393.5 \text{ kJ mol}^{-1}$$

$$K(s) + \tfrac{1}{2}Cl_2(g) \rightarrow KCl(s) \qquad \Delta H_4 = -436.5 \text{ kJ mol}^{-1}$$

$$K(s) + \tfrac{1}{2}Cl_2(g) + 1\tfrac{1}{2}O_2(g) \rightarrow KClO_3(s) \qquad \Delta H_5 = -397.7 \text{ kJ mol}^{-1}$$

$M(KClO_3) = 122.5 \text{ g mol}^{-1}$ $\qquad$ $M(C_{12}H_{22}O_{11}) = 342.3 \text{ g mol}^{-1}$

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(ii) Give reasons for why the energy released in this experiment may be less than the theoretical value.

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

QUESTION NUMBER

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