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Scholarship 2018
Chemistry

9.30 a.m. Thursday 8 November 2018
Time allowed: Three hours
Total marks: 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 2–24 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	Mark
ONE	
TWO	
THREE	
FOUR	
TOTAL	
	/32

ASSESSOR'S USE ONLY

QUESTION ONE

Ammonium perchlorate composite propellant (APCP) is a solid-fuel mixture of ammonium perchlorate, $NH_4ClO_4(s)$ and powdered aluminium metal, $Al(s)$. This fuel is used in rocket engines, particularly in aerospace propulsion. In the absence of oxygen, the mixture burns rapidly once ignited and the reaction cannot be stopped. There are several reactions occurring in quick succession, initially producing the gases hydrogen chloride, $HCl(g)$, nitrogen, $N_2(g)$, and water vapour, $H_2O(g)$, along with solid aluminium oxide, $Al_2O_3(s)$. All the $HCl(g)$ produced is consumed by reacting with some of the aluminium oxide to form aluminium chloride, $AlCl_3(s)$. Heat from the reaction causes the gaseous products to expand and lift the rocket boosters with a tremendous force.

(a)   Write a balanced equation for the reaction.

Describe the oxidation and reduction processes occurring in the fuel reaction by discussing changes in oxidation numbers, discussing electron transfer processes, and identifying the oxidant(s) and reductant(s) in the reaction mixture.

(b) Each solid rocket booster carries a total mass of around 590 000 kg of solid rocket fuel. This is made up of 74% by mass of ammonium perchlorate and 11% by mass of aluminium. One of these reagents will be present in excess to increase the efficiency of the reaction. The rest of the fuel is made up of additives such as catalysts and binders.

If the temperature of the reaction is reduced, nitric oxide, $NO(g)$ is produced instead of nitrogen gas.

$$3NH_4ClO_4(s) + 3Al(s) \rightarrow Al_2O_3(s) + 3NO(g) + AlCl_3(s) + 6H_2O(g)$$
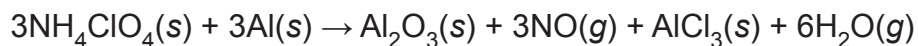
Calculate the energy released in this reaction when 590 000 kg of fuel of the composition described above are reacted.

Use the data given below.

$$M(Al) = 26.98 \text{ g mol}^{-1} \qquad M(NH_4ClO_4) = 117.46 \text{ g mol}^{-1}$$

	Standard Enthalpy of Combustion/kJ mol⁻¹
$Al(s)$	−838.0
$H_2(g)$	−285.8

	Standard Enthalpy of Formation/kJ mol⁻¹
$HCl(g)$	−92.3
$NH_4ClO_4(s)$	−295.3
$AlCl_3(s)$	−704.0
$NO(g)$	90.3

	Standard Enthalpy of Vaporisation/kJ mol⁻¹
$H_2O(\ell)$	44.0

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

(c) Thallium and oxygen form two ionic oxides with the following characteristics:

	Oxide I	Oxide II
Mass percentage Tl	89.49%	96.23%
Melting point	717°C	596°C

Determine the formula of each oxide, and, using your knowledge of structure and bonding, account for the difference in the melting points.

$M(Tl) = 204.38$ g mol^{-1} $M(O) = 16.00$ g mol^{-1}

QUESTION TWO

INFORMATION

In an **ozonolysis** reaction, the double bond (C=C) of an alkene is broken. Two products are formed, each having C=O at the carbon atom that was originally double-bonded. The actual products of the reaction depend on the reaction conditions.

When a reductant such as zinc metal in acid is used, the products are ketones or aldehydes.

When an oxidant such as H_2O_2 is used, the products are ketones or carboxylic acids.
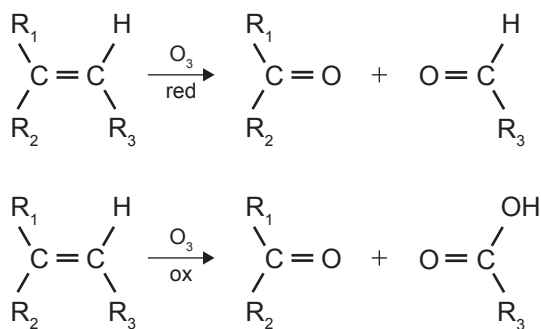
(a) Compound **A** has the molecular formula $C_5H_{10}O$ and is not optically active. In the ^{13}C NMR spectrum of Compound **A** there are four signals. None of these signals lies above 100 ppm.

Draw the **five** constitutional isomers of $C_5H_{10}O$ that satisfy the information given.
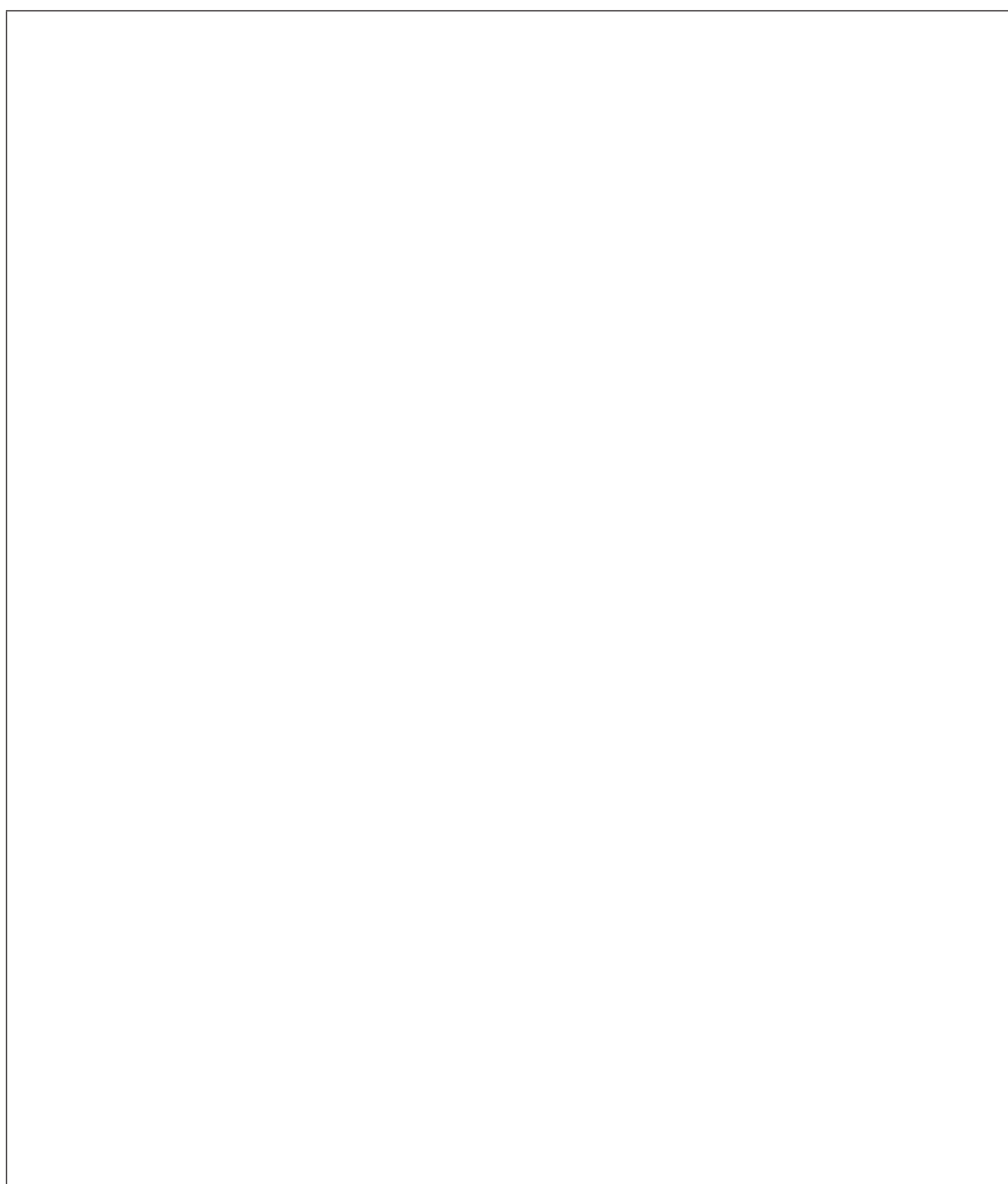
(b) When Compound **A** is reacted with thionyl chloride, $SOCl_2$, followed by alcoholic potassium hydroxide, KOH(alc), the resulting Compound **B** is found to be optically active. The ^{13}C NMR of Compound **B** has five signals.

Reductive ozonolysis of Compound **B** produces Compound **C** which, on reaction with sodium borohydride, $NaBH_4$, produces Compound **D**, which has the molecular formula $C_5H_{12}O_2$. Compound **D** is optically active.

When Compound **D** is treated with thionyl chloride, $SOCl_2$, followed by gaseous ammonia, $NH_3(g)$, under pressure, Compound **E** is produced.

Oxidative ozonolysis of Compound **B** produces Compound **F** which, in turn, forms Compound **G** on reaction with thionyl chloride.

Draw the structures of Compounds **A** to **G**, including both optical enantiomers of Compound **B** (no other optical isomers are required).

(c) Compound **E** and Compound **G** from part (b) on the previous page can be reacted under different conditions to produce different products.

Method One: One litre of an inert, non-polar solvent is placed in a large round-bottom flask. Two dropping funnels, one containing an 0.04 mol L^{-1} solution of Compound **G** and the other containing an 0.08 mol L^{-1} solution of Compound **E**, are loaded into the flask (see diagram). The two solutions are added dropwise to the flask, with continuous stirring, to produce two organic products, Compounds **H** and **I**. These two compounds are constitutional isomers with the molecular formula $C_{10}H_{18}N_2O_2$. The reaction requires an excess of Compound **E** to ensure the products are neutral.
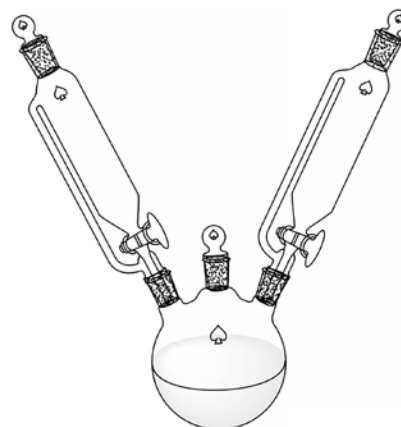
Method Two: Compound **E** and excess sodium hydroxide, NaOH(*s*), are added to a beaker and dissolved in sufficient water to give a concentration of 1 mol L^{-1} for Compound **E**. Compound **G** is dissolved in hexane in a separate beaker to give a 1 mol L^{-1} solution. The solution of Compound **G** is then gently poured into the aqueous solution of Compound **E** and the formation of two layers is observed. Compound **J** is formed between the two layers and is drawn out of the beaker and wound around a glass rod.

Identify and draw structural formulae for the compounds **H, I** and **J**.

Explain why the two sets of conditions given above produce different products.

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QUESTION THREE

(a) The soil in New Zealand is low in iodine, and hence food grown in New Zealand will have low levels of iodine. A diet deficient in iodine can lead to health issues such as goitre, and impaired physical and mental development. To increase iodine in the diet, it can be added to salt using potassium iodate, KIO_3.

The Australia New Zealand Food Standards Code requires iodised salt to contain "*equivalent to no less than 25 mg/kg of iodine; and no more than 65 mg/kg of iodine*".

The amount of iodine present in a sample of iodised salt can be determined by titration against a standard solution of sodium thiosulfate, $Na_2S_2O_3$. The iodate is converted to iodine and the resulting solution is used in the titration. Iodine is sparingly soluble in water but, in the presence of iodide ions forms the soluble tri-iodide ion.

$$I_2(s) + I^-(aq) \rightleftharpoons I_3^-(aq)$$
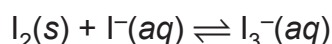
Method for analysis of iodate ions in salt
A 50.00 g sample of iodised salt is added to a 250.0 mL volumetric flask and is made up to the mark with distilled water. The mixture is shaken until the salt has completely dissolved.

A 50.00 mL sample of the iodised salt solution is placed in a conical flask, and mixed with 5 mL of 1 mol L^{-1} HCl solution, and 5 mL of 0.6 mol L^{-1} KI solution. The solution changes to a brown colour indicating the formation of I_2.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$
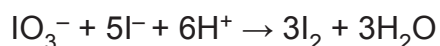
A fresh solution of sodium thiosulfate, $Na_2S_2O_3(aq)$, is prepared by placing 2.456 g of solid $Na_2S_2O_3 \cdot 5H_2O$ into a 100.0 mL volumetric flask and making it up to the mark with distilled water. This solution is then diluted by taking a 5.000 mL sample and diluting it to 250.0 mL in a volumetric flask.

The solution in the conical flask is titrated against the sodium thiosulfate solution using starch solution as an indicator. The reaction for the titration is:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$
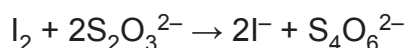
(i) Calculate the lower limit for the titre values (burette readings) for the given sodium thiosulfate solution when the procedure described above is used to determine whether a sample of iodised salt meets the standards quoted.

$M(Na_2S_2O_3 \cdot 5H_2O) = 248.2$ g mol^{-1} $M(KIO_3) = 214.0$ g mol^{-1} $M(I) = 126.9$ g mol^{-1}

(ii) To ensure the accuracy of the results, the titration used in part (i) must be carried out without vigorous mixing of the solutions, and the titration should be performed without delay.

Explain the consequences of vigorous mixing or delayed titrating on the accuracy of the results in question (a) (i).

Justify your answer using the electrode potentials given.

$E°(O_2/H_2O) = +1.23$ V $\quad\quad$ $E°(I_2/I^-) = +0.53$ V $\quad\quad$ $E°(S_4O_6^{2-}/S_2O_3^{2-}) = +0.08$ V

$E°(S_2O_3^{2-}/S) = +0.60$ V $\quad\quad$ $E°(IO_3^-/I_2) = +1.20$ V

(b) The strength of oxygen-containing acids depends on the structure and bonding in the acid molecules. This is illustrated in the following table.

Acid	Structure	pK_a
HOCl	H — O — Cl	7.5
HOBr	H — O — Br	8.7
HOI	H — O — I	10.6
HOClO ($HClO_2$)	H — O — Cl = O	2.0
HOClO$_2$ ($HClO_3$)	H — O — Cl = O $\parallel$ O	−3.0

(i) Explain how the structure and bonding in these molecules influence their acidity.

(ii) Rank the following acids from highest to lowest acid strength, giving reasons for your answer.

H_2SO_3 $((HO)_2SO)$ $\qquad$ FSO_3H $((HO)(F)SO_2)$ $\qquad$ H_2SO_4 $((HO)_2SO_2)$

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The examination continues on the following page.

QUESTION FOUR

(a) 3-carboxy-3-hydroxypentanedioic acid, more commonly known as citric acid, is a triprotic, organic acid found in citrus fruits. Lemons and limes contain a particularly high concentration of citric acid, sometimes up to 8% of the dry weight of the fruit. In the purified form, it exists as transparent colourless crystals.

http://premaasianstore.com/
supreme-citric-acid-100g.html

$M(H_3Cit) = 192.1$ g mol^{-1}

$$H_3Cit + H_2O \rightleftharpoons H_2Cit^- + H_3O^+ \qquad pK_a = 3.13$$
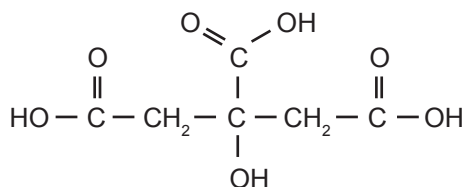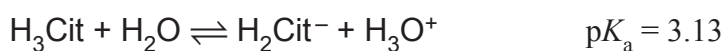
A lemon was crushed and dried, resulting in 32.00 g of powder. 9.00 g of the powder was weighed and placed into a beaker with hot distilled water and left to soak for 30 minutes to completely extract the citric acid. The mixture was then filtered and washed, and the filtrate was made up to 150.0 mL with distilled water.

The pH of the final solution was 2.47.

(i) Calculate the mass percentage of citric acid in the dry weight of the lemon.

You can assume there are no other compounds affecting the pH of the solution and that there is no ionisation of H_2Cit^-.

(ii)   Solid sodium hydroxide was added to the citric acid from the 150.0 mL volumetric flask (pH of 2.47) until the pH of the mixture reached 3.45.

Calculate the mass of sodium hydroxide added. Assume there is no change in the volume of the mixture.

$M(NaOH) = 40.00$ g mol^{-1}

(b) A number of different organic acids are found in different types of fruit. For example, the three predominant acids in grapes are citric acid (3-carboxy-3-hydroxypentanedioic acid), tartaric acid (2,3-dihydroxybutanedioic acid), and malic acid (2-hydroxybutanedioic acid). There is also likely to be a smaller amount of iso-citric acid (3-carboxy-2-hydroxypentanedioic acid).

Acid	Structure	Molar mass /g mol^{-1}	Melting point / °C
Citric acid		192	153
Tartaric acid		150	173
Malic acid		134	132
Iso-citric acid		192	105

Compare and contrast the factors that affect the melting points of these four acids.

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