EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2022
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CIVICS GROUP	**2**	**1**	**–**		

INDEX NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

21 September 2022
2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
Section A	
1	**/ 20**
2	**/ 20**
3	**/ 20**
Section B	
4	**/ 20**
5	**/ 20**
Total	**/ 80**

This document consists of **32** printed pages.

[Turn Over

Question 1 starts on the next page.

Section A

Answer **all** the questions in this section.

1 **(a)** Elements in Period 3 of the Periodic Table form chlorides and oxides with varying properties.

(i) Equal amounts of $MgCl_2$ and PCl_5 dissolve in equal volumes of water to form solutions with pH 6.5 and 1.0 respectively. Construct two equations to account for the different pH values. [2]

(ii) Explain why the first ionisation energies of aluminium and sulfur are lower than the element before it. [2]

(iii) Element **L** is an element in Period 3. **L** forms a chloride with a simple molecular structure but an oxide with a giant molecular structure. Identify element **L** and construct an equation for the reaction of its chloride with NaOH(aq). [2]

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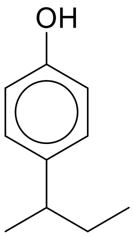
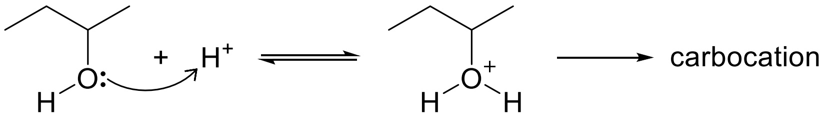
(b) 4-(butan-2-yl)phenol is an important intermediate in organic synthesis. It must be handled carefully as it is corrosive to the eyes and skin.



4-(butan-2-yl)phenol

4-(butan-2-yl)phenol can be synthesised by heating phenol and butan-2-ol in the presence of acid. The mechanism of this synthesis is thought to proceed via an acid-catalysed Friedel-Crafts alkylation, where butan-2-ol is first protonated by H^+, before forming a carbocation.



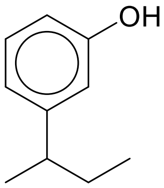
intermediate **X**

(i) Draw the structure of the carbocation formed from intermediate **X**. [1]

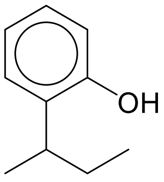
(ii) Hence, describe the mechanism for the formation of 4-(butan-2-yl)phenol from the carbocation in **(b)(i)** and phenol. [3]

(iii) Describe a simple chemical test that could distinguish between butan-2-ol and 4-(butan-2-yl)phenol. [2]

(iv) Compounds **M** and **N** are two minor products in the reaction.



compound **M**



compound **N**

Briefly explain why each of them is the minor product. [2]

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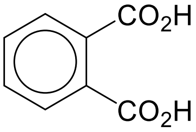
(c) Compound **R**, $C_{10}H_{14}O$, is a constitutional isomer of 4-(butan-2-yl)phenol. When **R** is heated strongly with acidified $K_2Cr_2O_7$(aq), **S** ($C_{10}H_{12}O$) is formed. **S** gives an orange precipitate with 2,4-DNPH. When **R** is heated strongly with concentrated sulfuric acid, **T** ($C_{10}H_{12}$) is formed, which decolourises Br_2(aq). When **T** is heated with acidified $KMnO_4$(aq), **U** is formed.



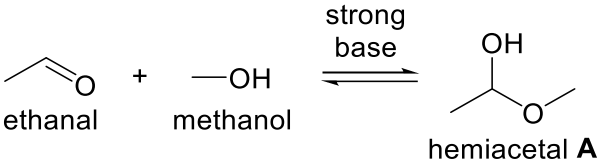
U

Deduce the structures of **R**, **S**, and **T** and explain the reactions involved. [6]

[Total: 20]

Question 2 starts on the next page.

2 Aldehyde reacts with alcohol in the presence of a base catalyst to give hemiacetal. The reaction between ethanal and methanol is shown below.



This reaction occurs via a three-step mechanism.

Step 1 The base removes an H^+ ion to form a methoxide anion, CH_3O^-.

Step 2 The methoxide anion undergoes nucleophilic addition with the carbonyl group generating an anionic intermediate.

Step 3 The anionic intermediate abstracts a proton from a H_2O molecule.

(a) **(i)** Draw the mechanism for steps 2 and 3. In your answer, you should show all relevant charges, dipoles, and lone pairs; and show the movement of electrons by curly arrows. [2]

(ii) A student suggests using NaOH to generate the methoxide ion. Suggest why this is not feasible. Hence, state a Period 3 element that is able to generate the methoxide needed for this reaction. [2]

(iii) Suggest a simple chemical test to differentiate between ethanal and methanol. State the observations and write a balanced equation for the positive reaction. [2]

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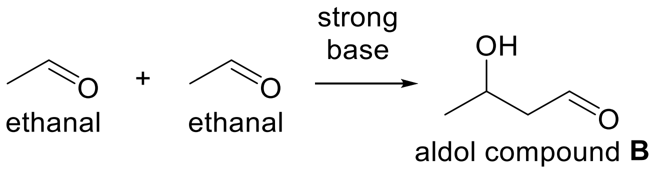
Aldehydes that have acidic α-hydrogens react with themselves when mixed with a dilute aqueous acid or base. The resulting compounds, β-hydroxy aldehydes, are referred to as aldol compounds.



(b) **(i)** State the functional groups that are present in aldol compound **B**. Hence, state the nucleophile that is generated from ethanal for the given aldol reaction. [2]

(ii) Hence, draw the skeletal structure of the aldol compound formed when the α-hydrogens of propanal undergoes the above reaction. [1]

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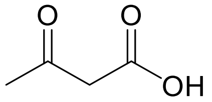
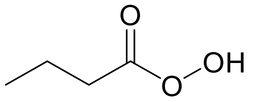
When compound **B** reacts with acidified $K_2Cr_2O_7$, 3-oxobutanoic acid, $CH_3COCH_2CO_2H$ is formed. The pK_a values of 3-oxobutanoic acid and peroxybutanoic acid ($CH_3CH_2CH_2CO_3H$) are 3.6 and 8.2, respectively.



3-oxobutanoic acid



peroxybutanoic acid

A mixture containing 3-oxobutanoic acid and peroxybutanoic acid was titrated using the double-indicator method. 25.0 cm^3 of the solution required 13.50 cm^3 of 0.250 mol dm^{-3} sodium hydroxide to decolourise the first indicator. A few drops of the second indicator was added and the titration continued until the indicator changed colour. The total volume of sodium hydroxide needed for the titration was 35.00 cm^3.

(c) **(i)** The smaller the pK_a value, the stronger is the acid. Explain why 3-oxobutanoic acid is a stronger acid than peroxybutanoic acid. [1]

(ii) Hence, calculate the concentrations of 3-oxobutanoic acid and peroxybutanoic acid. [2]

(iii) During the course of titration, the pH remains relatively constant around pH 3.6 at the mid-point of the first titration. Explain why this is so. [1]

(iv) Calculate the concentration of the peroxybutanoate ions ($CH_3CH_2CH_2CO_3^-$) at the mid-point of the first titration. [2]

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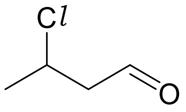
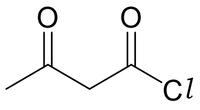
Chlorine-containing compounds **C** and **D** can be obtained from compound **B** and 3-oxobutanoic acid, respectively.



compound **C**



compound **D**

Unlike chlorobenzene which does not reacts with sodium hydroxide, compound **D** reacts with NaOH much more readily than compound **C**.

(d) **(i)** State the reagents and conditions for the conversion 3-oxobutanoic acid to compound **D**. [1]

(ii) Explain why the rate of reaction with sodium hydroxide differs between chlorobenzene, compound **C**, and compound **D**. [3]

(iii) Describe a simple chemical test to distinguish between compound **C** and compound **D**. [1]

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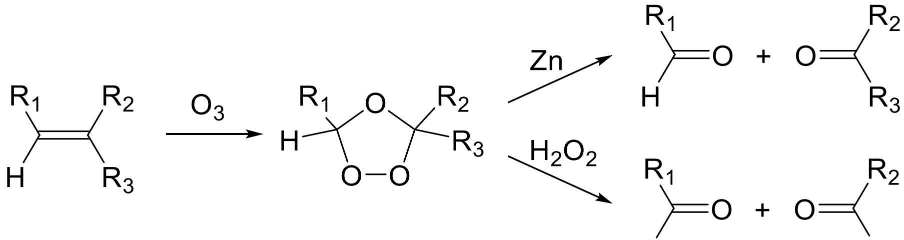
3 Ozonolysis is a reaction where the unsaturated bonds of alkenes are cleaved with ozone, followed by adding excess Zn, to form carbonyl compounds.

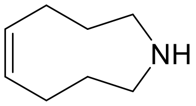


R_1, R_2 and R_3 are alkyl groups

If Zn is replaced by excess acidified H_2O_2, a carboxylic acid (R_1CO_2H) is obtained instead of the aldehyde (R_1CHO).

(a) **(i)** State the role of Zn in the ozonolysis process. [1]

(ii) Draw the skeletal formula of the product that is formed when compound **X** undergoes ozonolysis in the presence of excess Zn.



compound **X**

[1]

(iii) Suggest a simple chemical test to check that the ozonolysis process of compound **X** is completed. State the observations. [2]

(iv) State the oxidation states of the carbon in C=O in both the aldehyde (R_1CHO) and the carboxylic acid (R_1CO_2H). [1]

(v) Construct the oxidation half-equation for the conversion of R_1CHO to R_1CO_2H in an acidic medium. Hence, with reference to the *Data Booklet*, write the overall redox equation between R_1CHO and acidified H_2O_2. [2]

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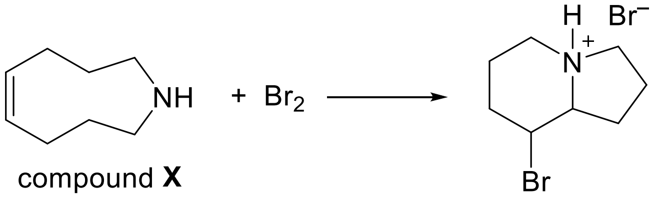
(b) When compound **X** reacts with Br_2 in CCl_4, it forms a bicyclic compound **Y** as shown below.



compound **X**

compound **Y**

(i) Compound **X** exhibits stereoisomerism. State the type of stereoisomerism and draw the pair of stereoisomers. [2]

(ii) Describe the mechanism for the formation of the bicyclic compound **Y** formed in the above reaction. [2]

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Ozone undergoes decomposition as shown below.

step 1 $O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$

step 2 $O_3 + O \xrightarrow{k_2} 2O_2$

Step 1 reaches dynamic equilibrium producing a constant concentration of O radicals.

Chlorofluorocarbon (CFC) is known to destroy stratospheric ozone through the production of the C*l* radical. The C*l* radical can react with the O atom through the following mechanism.

$$Cl + O \rightarrow ClO$$
$$ClO + O \rightarrow Cl + O_2$$

(c) **(i)** Explain the term *dynamic equilibrium*. [1]

(ii) Write down the equilibrium constant for step 1 with units. Hence, express the equilibrium constant in terms of the rate constants, k_1 and k_{-1}. [2]

(iii) Explain the role of the C*l* radical in the decomposition of stratospheric ozone. [1]

(iv) Hence, explain how the C*l* radical affects the reaction in step 1. [2]

(v) Suggest whether step 1 is exothermic or endothermic. Hence, suggest how an increase in temperature would affect the position of equilibrium for step 1. [2]

(vi) Explain why step 1 is spontaneous at high temperatures. [1]

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Section B

Answer **one** question from this section.

4 Fluorine is the most reactive of all elements. It forms compounds, under appropriate conditions, with every other element except He, Ar and Ne, frequently combining directly and with such vigour that the reaction becomes explosive.

One reason for the great reactivity of F_2 compared to the rest of the halogens can be related to the weak F–F bond.

In fact, F_2 is the only halogen which reacts directly with the noble gases, notably xenon, to give binary fluorides, such as XeF_2, XeF_4 and XeF_6.

(a) **(i)** Unlike the other halogens, fluorine almost exclusively assumes an oxidation state of −1 in its compounds. Explain why this is so. [2]

(ii) Suggest a reason for the weak F–F bond. [1]

(iii) By quoting suitable data from the *Data Booklet* and considering the weak F–F bond, suggest another factor which explains why only F_2 reacts with xenon vigorously, but not the other halogens. [2]

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Fluorine derives its name from the early use of fluorspar (CaF_2) as a flux (Latin *fluor*, flowing). However, all attempts to isolate the element were foiled by the extreme reactivity of free fluorine.

Success was finally achieved on 26 June 1886 by H. Moissan who electrolysed a cooled solution of potassium bifluoride, KHF_2, in anhydrous liquid HF, using platinum-iridium electrodes sealed into a platinum U-tube sealed with fluorspar caps.

(b) KHF_2 is an ionic compound containing the HF_2^- ion.

(i) Draw the dot-and-cross diagram of the HF_2^- ion. [1]

(ii) Using your answer to **(b)(i)**, suggest why only fluorine forms a stable HX_2^- ion, while that of the rest of the halogens are unstable. [1]

(iii) Define the term *lattice energy*. [1]

(iv) Use the data in Table 4.1, together with data from the *Data Booklet*, to calculate a value for the lattice energy of potassium bifluoride, $KHF_2(s)$. Show your working.

Table 4.1

	value / kJ mol^{-1}
electron affinity of fluorine, $F(g) + e^- \rightarrow F^-(g)$	–328
enthalpy change for the reaction, $HF(g) + F^-(g) \rightarrow HF_2^-(g)$	–240
standard enthalpy change of atomisation of K(s)	+89
standard enthalpy change of formation of $KHF_2(s)$	–928

[4]

(v) Compare the magnitude of the lattice energy of KHF_2 to that of KF. Explain the difference. [1]

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Like ethanoic acid, its structural analogue trifluoroethanoic acid, CF_3CO_2H, is also a colourless liquid with a vinegar smell.

Trifluoroethanoic acid is prepared industrially by the electrofluorination of ethanoyl chloride, to give first trifluoroethanoyl fluoride, CF_3COF.

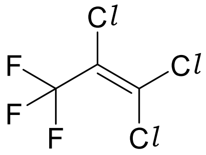
$$CH_3COCl + 4HF \rightarrow CF_3COF + 3H_2 + HCl$$

(c) **(i)** State and explain the relative acidity of CF_3CO_2H and CH_3CO_2H. [2]

(ii) Suggest the reagent and condition for the conversion of CF_3COF into CF_3CO_2H, and state the type of reaction involved. [2]

(iii) Explain why the two carboxylic acids, CF_3CO_2H and CH_3CO_2H, cannot be distinguished by a simple chemical test. [1]

(iv) An older route to trifluoroethanoic acid commences from 1,1,2-trichloro-3,3,3-trifluoroprop-1-ene.



1,1,2-trichloro-3,3,3-trifluoroprop-1-ene

Suggest the reagent and condition for the one-step conversion of 1,1,2-trichloro-3,3,3-trifluoroprop-1-ene into CF_3CO_2H, and suggest the identities of the likely by-products. [2]

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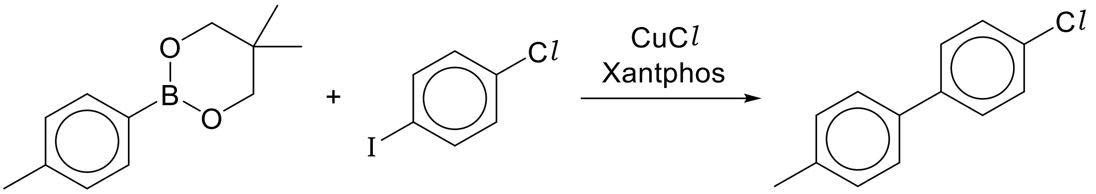
5 Copper is a transition element which use dates to prehistoric times. The metal, its compounds, and alloys have numerous applications in every sphere of life, making it one of the most important metals.

(a) Cross-coupling reactions are powerful tools for carbon-carbon bond formation and have been widely utilised in organic synthesis. These transformations are typically catalysed by palladium complexes. Recently, tremendous efforts have been invested in developing copper as an alternative, due to the high cost and low natural abundance of palladium.

Fig. 5.1 shows an example of the cross-coupling between 1-chloro-4-iodobenzene and boronic ester **1**, catalysed by copper(I) chloride in the presence of a neutral phosphorus-containing tridentate ligand, Xantphos.

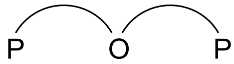


boronic ester **1** 1-chloro-4-iodobenzene

Fig. 5.1

(i) Define the term *tridentate ligand*. [1]

(ii) $CuCl$ and Xantphos form a tetrahedral complex in a 1:1 ratio. Draw the structure of the complex, showing its shape.

Use  to represent Xantphos. [1]

(iii) Copper(II) complexes are coloured, while copper(I) complexes, such as the complex between $CuCl$ and Xantphos, are generally colourless. Explain. [3]

(iv) The copper(I) halides, $CuCl$, $CuBr$ and CuI are white solids when pure. However, upon exposure to air, $CuBr$ turns light green, while CuI becomes light brown in colour. Suggest separate reasons for the two colour changes. [2]

The cross-coupling is interesting in that it involves the cleavage of a carbon-halogen bond in the halogenoarene.

(v) Explain why the carbon-halogen bond in halogenoarenes are difficult to break. [2]

(vi) There are two different carbon-halogen bonds in 1-chloro-4-iodobenzene. By quoting suitable data from the *Data Booklet*, suggest why the reaction took place as shown in Fig. 5.1. [2]

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(b) Soft, highly malleable, conductive, corrosion-resistant, and most importantly economical, copper is a perfect choice for many applications. While copper is great, the material is not suitable for applications where strength is desired. For such cases, copper electroplating can be an ideal solution. The outer layer will deliver the same properties that the application requires while the core provide the strength or any other mechanical properties that is needed.

For copper electroplating, an electrolytic cell is used where the metal core is made the cathode, while the anode is a copper rod.

(i) Suggest an electrolyte to use for the copper electroplating cell. [1]

(ii) Draw a labelled diagram of the cell for copper electroplating. [2]

(iii) The copper rod used does not need to be of high purity, it can contain impurities such as silver and iron. Explain. [2]

The same setup can be used to determine an accurate value for the Avogadro constant as well. However, in this case, the copper anode needs to be of very high purity (> 99.99% Cu). In one such experiment, when a current of 3.0 A is passed through the cell for 32 minutes, the mass of the cathode is found to increase by 1.896 g.

(iv) Calculate the amount of electrons, in moles, required to deposit the observed mass of copper at the cathode. [1]

(v) Using your answer to **(b)(iv)**, calculate a value for the Faraday's constant, F, the charge of one mole of electrons. [1]

(vi) Calculate, using your answer to **(b)(v)**, a value for the Avogadro constant, *L*. [1]

(vii) Explain why the copper anode must be of very high purity. [1]

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