RAFFLES INSTITUTION
2023 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME

CLASS

INDEX NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

20 September 2023
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and index 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.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything in it.
You are reminded of the need for good English and clear presentation in your answers.

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			**Section B**			**Total**
1	**/ 20**		(Circle the question you have answered)			**/ 80**
2	**/ 20**		**4**	**/ 20**		
3	**/ 20**		**5**	**/ 20**		

This document consists of **27** printed pages and **1** blank page.

Section A

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

1 **(a)** Elemental silicon does not occur naturally and is obtained from SiO_2 in rocks.

(i) Silicon has a similar structure to diamond. However, the melting point of silicon at 1414 °C is lower than that of diamond at 3550 °C.

Explain this difference with reference to the structure and bonding of silicon and diamond. [2]

(ii) Describe the difference in the acid-base behaviour of Al_2O_3 and SiO_2. Write relevant equations to illustrate your answer. [3]

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(b) The standard enthalpy change of formation, $\Delta H_f^{\ominus}$, of SiO_2 and CO are listed in Table 1.1.

Table 1.1

compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
SiO_2	–910.9
CO	–110.5

Reactions 1 and 2 show two possible ways of extracting Si from SiO_2.

reaction 1 $SiO_2(s) \rightarrow Si(s) + O_2(g)$ $\Delta G^{\ominus}_{2500K} = +450.9$ kJ mol^{-1}

reaction 2 $SiO_2(s) + 2C(s) \rightarrow Si(s) + 2CO(g)$ $\Delta S^{\ominus} = +361$ J mol^{-1} K^{-1}

(i) In practice, the extraction of Si from SiO_2 is carried out at 2500 K.

Calculate $\Delta G^{\ominus}$ for reaction 2 at 2500 K and explain why reaction 2 is preferred for the extraction of Si from SiO_2.

Assume that $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are independent of temperature. [3]

(ii) Comment on the sign of $\Delta S^{\ominus}$ of reaction 2 with respect to the reaction. [1]

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(c) Using the data in Table 1.2 and the *Data Booklet*, calculate the lattice energy of Ca_2SiO_4 with the aid of an energy cycle.

You may assume that the lattice of Ca_2SiO_4 comprises Ca^{2+} and SiO_4^{4-} ions.

Table 1.2

	value / kJ mol^{-1}
standard enthalpy change of atomisation of Ca(s)	+121
standard enthalpy change of formation of Ca_2SiO_4(s)	−2306
enthalpy change of the following reaction $Si(s) + 2O_2(g) + 4e^- \rightarrow SiO_4^{4-}(g)$	+13872

[3]

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(d) Rusting occurs when iron is exposed to oxygen and water. The initial process involves the oxidation of Fe to Fe^{2+} ions and the reduction of O_2 to OH^- ions. The migration of ions eventually results in the formation of rust.

Use the table of standard redox potentials given in the *Data Booklet* to answer the questions below.

(i) Define the term *standard electrode potential,* $E^\ominus$, of a half-cell. [1]

(ii) Write the overall equation for the initial process of rusting and calculate its $E^\ominus_{cell}$. [2]

(iii) Use your answer in **(d)(ii)** to calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the initial process of rusting. [1]

(iv) Using information from the *Data Booklet* where relevant, explain why iron in the following objects rust slowly or not at all.

(I) A well-oiled iron bicycle chain.
(II) A piece of zinc is attached to the iron hull of a ship. [2]

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(e) The process of coating aluminium objects with aluminium oxide, Al_2O_3, via electrolysis is called anodising. Draw a labelled diagram of the electrolysis cell used for the anodising of aluminium. Include details of the cathode, anode and electrolyte. [2]

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2 **(a)** **(i)** State two conditions in which real gases behave ideally. [1]

(ii) Calculate the volume, in dm^3, of 5.2 mol of an ideal gas at 101300 Pa and 15 °C. [1]

(iii) A sample of 5.2 mol of ammonia gas measured under the same conditions as in **(a)(ii)** occupied a volume of 117 dm^3.

Explain why the volume measured was lower than that of an ideal gas, in terms of the properties of ammonia molecules. [1]

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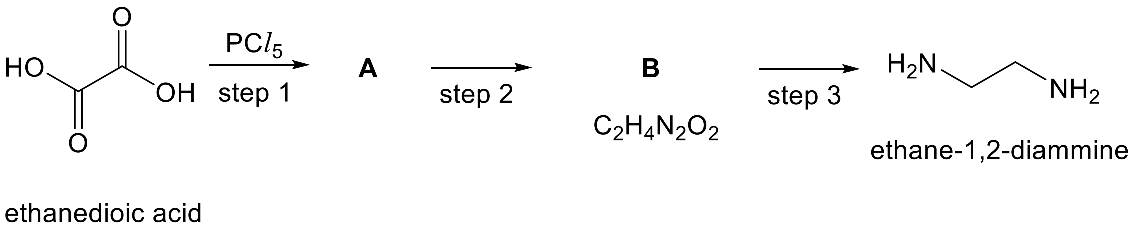
(b) Ethane-1,2-diamine can be synthesised from ethanedioic acid as shown below.



State the reagents and conditions needed for steps 2 and 3. Suggest structures for **A** and **B**. [2]

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(c) **(i)** Draw labelled diagrams of the d_{xy} and $d_{x^2-y^2}$ orbitals on separate axes. [1]

(ii) Explain why the five degenerate orbitals in the 3d subshell are split into two energy levels in the presence of ligands in an octahedral environment. You should specify the d orbitals in each level. [2]

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(d) Fig. 2.1 shows a sequence of reactions involving chromium.

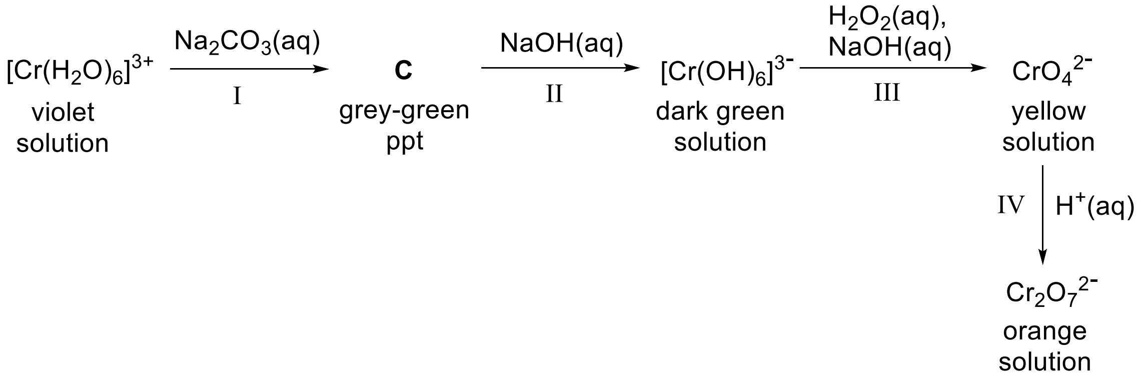

Fig. 2.1

(i) Identify the chromium-containing precipitate present in **C**. [1]

(ii) State the type of reaction in step III with respect to the chromium-containing species. [1]

(iii) Write an ionic equation for the reaction occurring in step IV. Hence, explain why it is a condensation reaction. [2]

(iv) Suggest why the aqueous solutions of $[Cr(H_2O)_6]^{3+}$ and $[Cr(OH)_6]^{3-}$ ions display different colours. [2]

(v) The ability of chromium-containing compounds to display different colours and form complexes are characteristic properties of transition elements.

State one other property of transition elements that is illustrated by the reaction scheme in Fig. 2.1. Explain why transition elements exhibit this property. [2]

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(e) $Cr(NH_3)_4X_3$ contains one cation and one anion.

When excess aqueous $AgNO_3$ is added to an aqueous solution containing 1 mol of $Cr(NH_3)_4X_3$, 1 mol of white precipitate is observed. The white precipitate dissolves in aqueous NH_3.

(i) Write an equation for the dissolution of the white precipitate in aqueous NH_3. [1]

(ii) Suggest the formulae of the cation and anion in $Cr(NH_3)_4X_3$. [1]

(iii) The cation in $Cr(NH_3)_4X_3$ exists as two isomeric forms.

Draw the 3-dimensional structures of the two isomers. [2]

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3 **(a)** But-2-yne, $H_3C–C{\equiv}C–CH_3$, can be reduced to *cis*-but-2-ene, as shown below.

$$H_3C–C{\equiv}C–CH_3(g) + H_2(g) \xrightarrow{\text{Lindlar's catalyst}} \textit{cis}\text{-but-2-ene(g)}$$

Lindlar's catalyst is a solid mixture of palladium and other compounds.

(i) By reference to the hybridisation of the carbon atoms and orbital overlap, describe the covalent bonding in C≡C. You may use a labelled diagram to illustrate your answer. [3]

(ii) Draw the structure of *cis*-but-2-ene. [1]

(iii) Outline the mode of action of the catalyst in increasing the rate of the reaction. [2]

(iv) By considering your answer to **(a)(iii)**, suggest a reason to explain why this reduction forms **only** *cis*-but-2-ene, but not *trans*-but-2-ene. [1]

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(b) The Hofmann elimination is a two-step process which converts an amine to a quaternary ammonium salt before undergoing elimination to produce an alkene. The alkene with fewer substituents is obtained as the major product.

Fig. 3.1 shows an example involving 2-aminobutane.

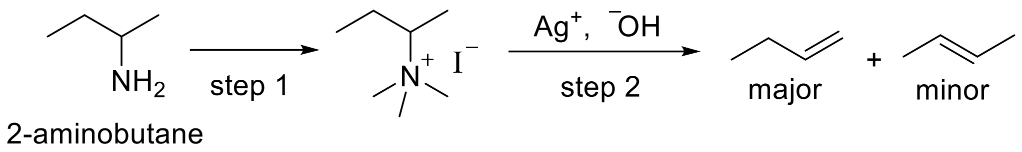


Fig. 3.1

(i) 2-Aminobutane exhibits stereoisomerism. Draw the 3-dimensional structures for the two stereoisomers. [1]

(ii) Suggest reagents and conditions for step 1. [1]

(iii) Fig 3.2 shows the mechanism of step 2 of the reaction.

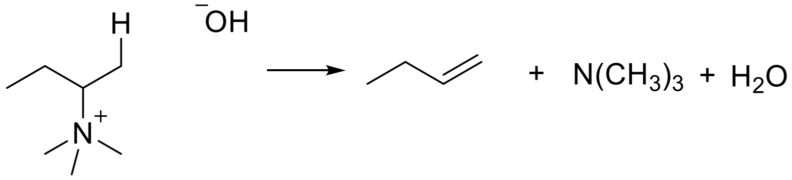
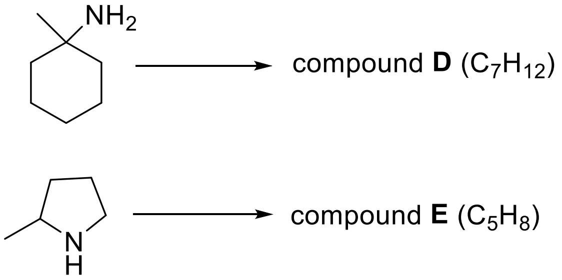


Fig. 3.2

Complete the mechanism by drawing curly arrows and relevant lone pairs on Fig. 3.2. [1]

(iv) Draw the structures of the **major** alkene products, **D** and **E**, obtained when the following compounds underwent Hofmann elimination.



[2]

(c) Compound **R**, $C_{10}H_{18}O$, forms white fumes with PCl_5. 1 mol of **R** also reacts with 1 mol of Br_2. Heating **R** with concentrated H_2SO_4 gives compound **S**, $C_{10}H_{16}$, as the only organic product.

When heated with acidified $KMnO_4$, **S** gives two products, **T**, $C_5H_8O_4$, and **U**, $C_5H_8O_3$.

Compound **T** contains a chiral centre. At room temperature, **T** reacts with NaOH(aq) in a 1:2 ratio, while **U** reacts with NaOH(aq) in a 1:1 ratio.

Compound **U** also
- gives an orange precipitate with 2,4-dinitrophenylhydrazine.
- does not give a yellow precipitate with aqueous alkaline iodine.
- reacts with Cl_2 in the presence of UV light to give a mixture of 2 mono-chlorinated products.

Deduce the structures of compounds **R**, **S**, **T** and **U**, explaining the reactions described.
[8]

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Section B

Answer **one** question from this section.

4 Hydroxyapatite, $Ca_5(PO_4)_3(OH)$, is a mineral commonly found in tooth enamel.

It can be produced by the following reaction.

$$5Ca(OH)_2 + 3H_3PO_4 \longrightarrow Ca_5(PO_4)_3(OH) + 9H_2O$$

(a) Draw the dot-and-cross diagram of $Ca(OH)_2$. [1]

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(b) A decayed tooth lost 75% of its hydroxyapatite content. Assuming that the tooth originally contained 2.5 g of hydroxyapatite, calculate the mass of $Ca(OH)_2$ required to react with excess H_3PO_4 in order to restore its hydroxyapatite. [2]

[M_r of hydroxyapatite = 502.5]

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(c) Hydroxyapatite is a sparingly soluble salt.

$$Ca_5(PO_4)_3(OH)(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

When a tooth is treated with fluoride, the OH^- in hydroxyapatite is replaced by F^- to form fluorapatite, $Ca_5(PO_4)_3F$.

The solubility product values of hydroxyapatite and fluorapatite are listed in Table 4.1.

Table 4.1

compound	K_{sp} value
hydroxyapatite, $Ca_5(PO_4)_3(OH)$	6.8×10^{-37}
fluorapatite, $Ca_5(PO_4)_3F$	1.0×10^{-60}

(i) Write an expression for the solubility product, K_{sp}, of hydroxyapatite. [1]

(ii) Calculate the solubility of hydroxyapatite, in mol dm^{-3}, in pure water. [1]

(iii) State and explain how the solubility of hydroxyapatite would be affected by an acidic environment in the mouth. [2]

(iv) Tooth decay happens when the hydroxyapatite in tooth enamel is dissolved. Fluoride ions are added to drinking water to reduce tooth decay.

Using the data in Table 4.1, explain how fluoride reduces tooth decay. [1]

(d) Cumene can be synthesised from benzene using 2-chloropropane with $AlCl_3$ as a Lewis acid catalyst, as shown in Fig. 4.1.

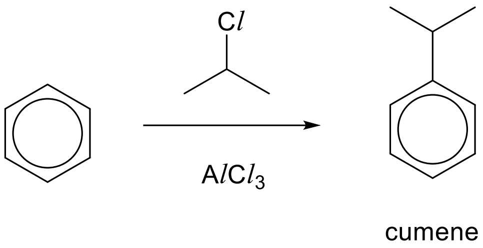
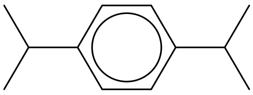


Fig. 4.1

(i) Describe the mechanism for the reaction in Fig. 4.1. Show all charges, relevant lone pairs and the movement of electron pairs by using curly arrows. [3]

(ii) Explain what is meant by the term *Lewis acid*. [1]

(iii) In the reaction in Fig. 4.1, di-substituted products, such as compound **X**, were also produced.



X

By considering electronic and steric effects, explain why:

- di-substituted products were formed.
- compound **X** was formed in a higher proportion compared to the 1,2 and 1,3 di-substituted products. [3]

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(e) Compound **H** can be synthesised from cumene in three steps as shown in Fig 4.2.

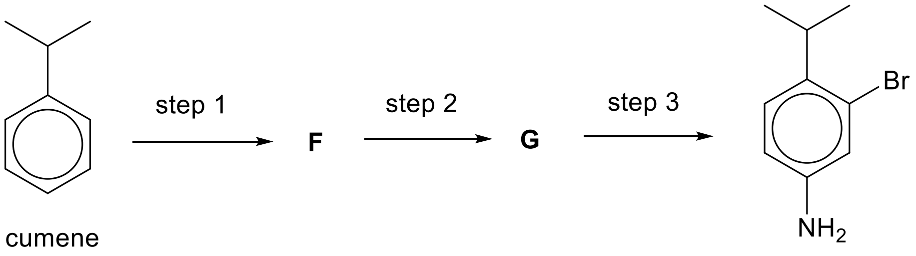

Fig. 4.2

(i) Suggest structures for the organic compounds **F** and **G**. [2]

(ii) Suggest reagents and conditions for each of the steps 1, 2 and 3. [3]

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5 **(a)** When BF_3 reacts with a trace amount of water to form $H_2O–BF_3$.

(i) Explain what is meant by the term *Lewis acid*. [1]

(ii) BF_3 acts as a *Lewis acid* in the reaction with water.

Draw a dot-and-cross diagram to show the bonding in $H_2O–BF_3$. [1]

(iii) State the shape and bond angle around the boron atom in $H_2O–BF_3$. [1]

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(b) High-value metals, such as nickel and cobalt, can be recovered from the cathode of recycled lithium-ion batteries.

In the process, the cathode is dissolved in acid to form a leach solution containing 4.93 g dm^{-3} of nickel ions and 5.84 g dm^{-3} of cobalt ions. The metals are then recovered by selective precipitation.

To recover cobalt, ethanedioate ions, $C_2O_4^{2-}$, were added to the leach solution. Cobalt was precipitated as CoC_2O_4.

The solubility product, K_{sp}, values for NiC_2O_4 and CoC_2O_4, at 298 K, are listed in Table 5.1.

Table 5.1

compound	K_{sp} value
NiC_2O_4	1.2×10^{-3}
CoC_2O_4	2.7×10^{-9}

(i) Write an expression for the K_{sp} of CoC_2O_4, giving its units. [1]

(ii) Calculate the concentration of ethanedioate ions in the leach solution, in mol dm^{-3}, when 94% of the cobalt has precipitated. [2]

(iii) Determine if NiC_2O_4 will precipitate when 94% of the cobalt has precipitated.

Use relevant calculations to support your answer. [2]

(iv) Ethanedioic acid, $H_2C_2O_4$, dissociates to form ethanedioate ions as follows.

$$H_2C_2O_4(aq) \rightleftharpoons H^+(aq) + HC_2O_4^-(aq)$$
$$HC_2O_4^-(aq) \rightleftharpoons H^+(aq) + C_2O_4^{2-}(aq)$$

Describe and explain how the solubility of CoC_2O_4 is affected by decreasing the pH of the solution. [2]

(v) At high concentrations of ethanedioate ions, the solubility of CoC_2O_4 was found to increase. Explain why. [2]

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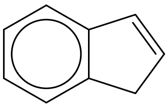
The structure of indene is shown below.



Indene

(c) Explain why indene does not exist as a pair of cis-trans isomers. [1]

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(d) When indene undergoes an addition reaction with hydrogen chloride, two possible products are formed.

(i) Suggest a mechanism for the reaction of indene with hydrogen chloride and use it to predict the major product. Show relevant lone pairs of electrons, dipoles and curly arrows. [2]

(ii) Explain your reasoning for the major product formed in **(d)(i)**. [1]

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(e) Indene undergoes the following reactions, as shown in Fig. 5.1.

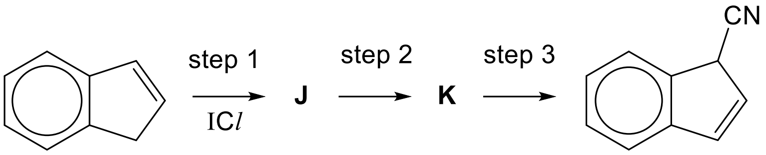

Fig. 5.1

(i) Compound **J** is the major product of the reaction between indene and iodine monochloride, IC*l*, in step 1. Draw the structure of compound **J**. [1]

(ii) State the reagents and conditions required for steps 2 and 3, and suggest the structure of compound **K**. [3]

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Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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