YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
CG		INDEX NO	

CHEMISTRY 9729/03

Paper 3 Free Response **16 September 2020**

Candidates answer on the Question Paper. **2 hours**
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
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** the questions.

Section B
Answer **one** question.

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

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	/16
3	/24
Section B	
4	/20
5	/20
Penalty	
	/80

This document consists of **26** printed pages and **6** blank pages.

Section A

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

1 Chlorine is an element in Group 17 of the Periodic Table. It exists as a diatomic gas at room temperature. Chlorine can also be found in many inorganic and organic compounds.

(a) Predict the colour of the final solutions when

- Cl_2(aq) is added to KBr(aq)
- I_2(aq) is added to KC*l*(aq)

Write equations for any reactions that occur. State clearly if no reaction occurs. [2]

(b) Describe and explain the trend in the thermal stabilities of the hydrogen halides HC*l*, HBr and HI. [2]

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(c) Chlorine dioxide, ClO_2 was discovered in 1811 and has been widely used for bleaching purposes in the paper industry and for treatment of drinking water.

(i) ClO_2 can be synthesised from the reaction between $NaClO_3$ and H_2O_2 in an acidic medium.
Construct a balanced equation for the reaction between ClO_3^- and H_2O_2. [2]

(ii) In the process of handling ClO_2, the concentration of the ClO_2 in aqueous solution must not exceed 45 parts per million by mass, as it will cause irritation to the eyes and nose.

1 part per million can be expressed as 1 mg of the substance in 1 kg of water.

An aqueous solution of ClO_2 was prepared by adding 150 cm^3 of 1.0×10^{-3} mol dm^{-3} $NaClO_3$ to 100 cm^3 of 2.0×10^{-3} mol dm^{-3} H_2O_2.

Using your equation in **(c)(i)**, calculate the concentration of the $ClO_2(aq)$ in **parts per million**, State whether it has exceeded the safety limit.

[Assume the density of the final solution is 1 g cm^{-3}.] [3]

The electrode potential for the reduction of chlorine dioxide is shown.

$$ClO_2(aq) + 4H^+(aq) + 5e^- \rightleftharpoons Cl^-(aq) + 2H_2O(l) \qquad E^\ominus = +1.50V$$

(iii) State what is meant by the term *standard electrode potential*. [1]

(iv) Draw a fully labelled diagram of the electrochemical cell you would set up in order to measure the standard reduction potential of ClO_2/Cl^- in the laboratory. Indicate clearly the positive and negative electrodes. [3]

Another cell composing of a standard ClO_2/Cl^- half-cell and a standard Fe^{3+}/Fe^{2+} half-cell was set up.

(v) Calculate $\Delta G^\ominus$, in kJ mol^{-1}, for the reaction that occurs [2]

(vi) State and explain what happens to the standard cell potential, $E^\ominus_{cell}$, when chlorine gas is bubbled into the Fe^{3+}/Fe^{2+} half-cell. [2]

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(d) Describe and explain the relative ease of hydrolysis of chloroethane, chlorobenzene and ethanoyl chloride. [3]

[Total: 20]

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2 **(a)** Propanone reacts with iodine in acidic conditions as shown below.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

The rate of the reaction may be followed by measuring the concentration of the iodine at regular time intervals.

Four separate sets of experiments were carried out in which the initial concentrations of the reactants were varied as shown in Table 2.1.

Table 2.1

experiment	initial concentration × 10^{-2} / mol dm^{-3}		
	propanone	hydrochloric acid	iodine
1	5	5	5
2	5	5	10
3	2	5	5
4	5	10	5

The results of experiment 1 and 2 are shown in Figure 2.1.

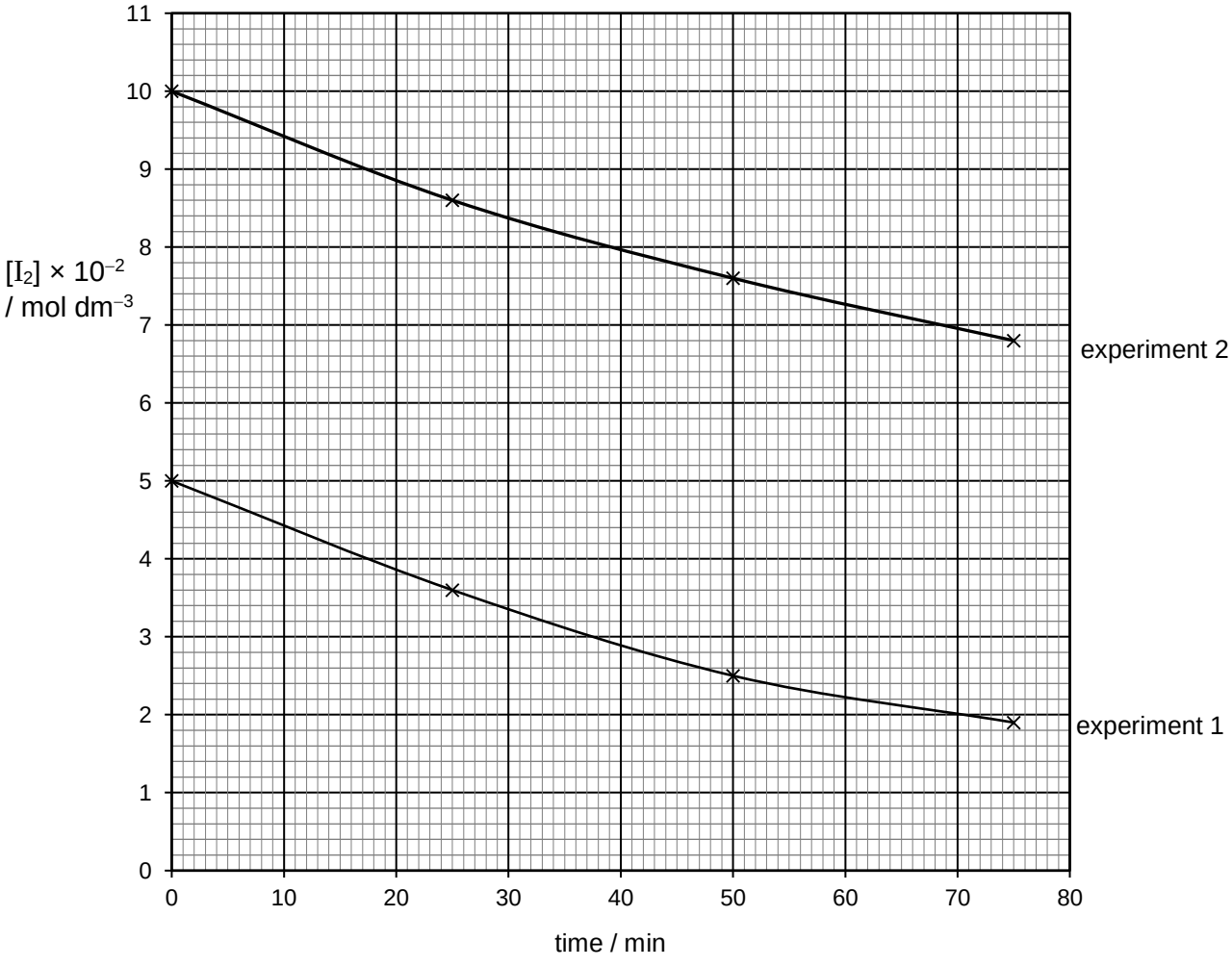


Fig. 2.1

The results shown in Table 2.2 were obtained for experiment 3 and 4.

Table 2.2

experiment	initial rate / mol dm^{-3} min^{-1}
3	2.70×10^{-4}
4	1.25×10^{-3}

(i) Using Fig. 2.1, determine the order of reaction with respect to $[I_2]$. Draw clearly any construction lines on Fig. 2.1 and show all your working. [1]

(ii) Determine the orders with respect to $[H^+]$ and $[CH_3COCH_3]$ [2]

(iii) Hence write the rate equation for the reaction, and calculate a value of the rate constant. Include units in your answer. [3]

(iv) The reaction of propanone with iodine proceeds via a three-step mechanism.

The first step is the protonation of propanone, which is a fast step. The second step is the deprotonation of the intermediate formed in the first step to produce another intermediate, $CH_2=C(OH)CH_3$.

Suggest a mechanism, which is consistent to your rate equation in **(a)(iii)** and indicate the rate determining step.

The use of curly arrows is **not** required. [3]

(b) The boiling points of propanone, propan-1-ol and ethanoic acid increase, as shown in Table 2.3.

Table 2.3

compound	formula	M_r	boiling point / ^oC
propanone	CH_3COCH_3	58	56
propan-1-ol	$CH_3CH_2CH_2OH$	60	97
ethanoic acid	CH_3CO_2H	60	118

Suggest explanations for these differences. [2]

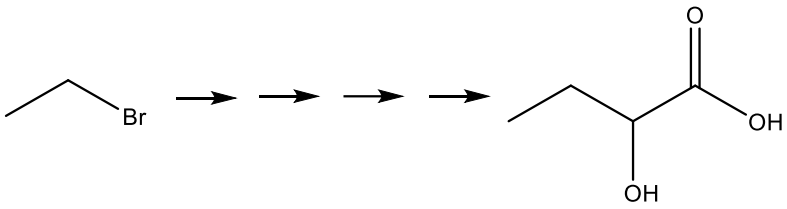
(c) Lithium aluminium hydride, $LiAlH_4$, sodium boron hydride, $NaBH_4$, and di-isobutyl aluminium hydride, DIBAL, are commonly used reducing agents in organic synthesis.

Carboxylic acids can be reduced to primary alcohols by $LiAlH_4$, but not by $NaBH_4$ because it is a stronger reducing agent.

Nitriles, –CN, are reduced to primary amines by $LiAlH_4$, but are reduced to aldehyde by DIBAL.

(i) Suggest why $LiAlH_4$ is a stronger reducing agent than $NaBH_4$. [1]

(ii) 2-hydroxybutanoic acid can be synthesised in 4 steps from bromoethane.



bromoethane 2-hydroxybutanoic acid

Suggest a synthesis of 2-hydroxybutanoic acid starting from bromoethane using DIBAL in one of the steps. Include reagents and conditions for all reactions, and the structures of all intermediate compounds in your answer. [4]

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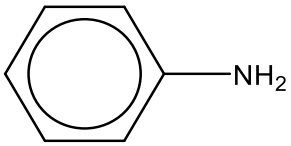
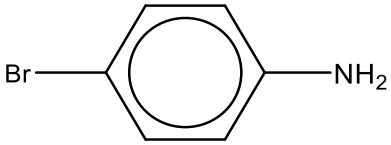
3 **(a)** The K_b values of 3 bases, at 25°C, are shown in Table 3.1.

Table 3.1

base	formula	K_b / mol dm^{-3}
ethylamine	$CH_3CH_2NH_2$	4.5×10^{-4}
phenylamine		7.4×10^{-10}
4-bromophenylamine		5.3×10^{-11}

(i) Ethylamine can behave as a *Brønsted-Lowry* base in aqueous medium.

Explain what is meant by this statement. [1]

(ii) Write the K_b expression for ethylamine. [1]

(iii) Calculate the pH of 0.50 mol dm^{-3} solution of ethylamine. [2]

(iv) Explain the relative magnitudes of the K_b values in Table 3.1. [3]

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(b) Compound **A**, $C_8H_{11}NO$ is weakly basic. It dissolves in dilute hydrochloric acid to give a solution from which a crystalline solid **B** is isolated.

A decolourises aqueous bromine and a white precipitate **C**, $C_8H_9NOBr_2$, is formed.

When **A** is heated with alkaline aqueous iodine and then followed by careful acidification, some yellow crystals are produced together with **D**, $C_7H_7NO_2$. However, no orange crystals are observed when 2,4–dinitrophenylhydrazine is added to **A**.

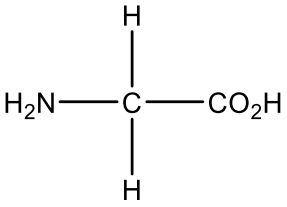
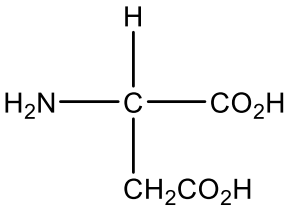
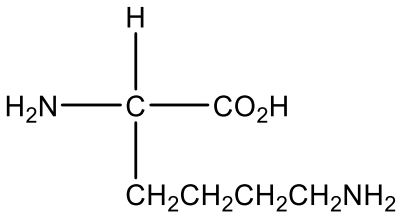
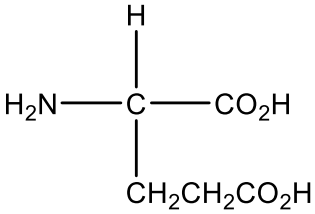
D can be produced from 4–nitromethylbenzene in a two–step reaction via an intermediate **E**. 4–nitromethylbenzene is first heated with tin in the presence of concentrated hydrochloric acid, followed by aqueous sodium hydroxide to form **E**, and then followed by adding hot acidified potassium manganate(VII) to produce **D**.

Deduce the structures of the compounds **A, B, C, D** and **E**, explaining the reactions described. [11]

(c) (i) Isoelectric point, pI, is the pH at which a molecule is electrically neutral. At a pH below their pI, amino acids carry a net positive charge; above their pI, they carry a net negative charge.

The structures of four amino acids and their respective isoelectric points are given in Table 3.2.

Table 3.2

amino acid	formula	isoelectric point, pI
glycine		6.07
aspartic acid		2.98
lysine		9.74
glutamic acid		3.08

Electrophoresis is used to separate protein molecules or amino acids. An electric field is applied and the particles will be separated based on their charge and size. In the preparation for electrophoresis, the four amino acids were dissolved together in the same buffer solution kept at pH 6.07.

During electrophoresis, a potential difference is applied across the solution containing the four amino acids and the results are obtained as shown in Figure 3.1.

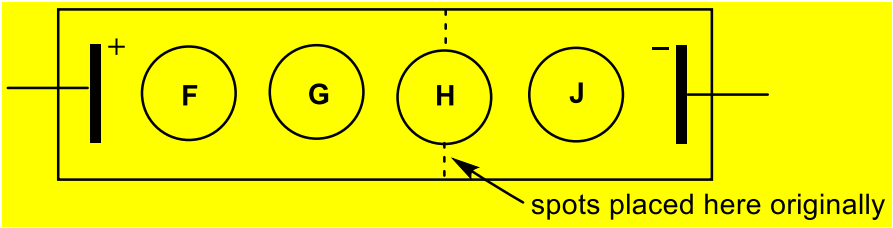


Figure 3.1

With reference to the isoelectronic point pI data provided in Table 3.2, draw the corresponding structure of the four amino acids present in the buffer solution of pH 6.07 and hence, deduce the identities of the amino acids **F**, **G**, **H** and **J**.

[4]

(ii) Amino acids can act as buffer in solutions. By means of equations, show how glycine can act as a buffer when

- dilute hydrochloric acid and
- dilute sodium hydroxide

is added separately into its solution. [2]

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[Total: 24]

Section B

Answer **one** questions in this section.

4 The modern Periodic Table in use today was developed by Henry Moseley in 1913 in which the elements are arranged in order of increasing atomic number.

The position of an element in the Periodic Table is defined by its period number and group number. Elements with similar chemical properties are grouped into specific columns and also blocks such as *s*-, *p*- and *d*-blocks, with each block denoting the type of valence subshell.

(a) Describe and explain the trend of first ionisation energy down a group. [2]

(b) The elements in Period 3 of the Periodic Table reacts with oxygen to form oxides that have different acid-base behaviour.

The acid-base behaviour of aluminium oxide, Al_2O_3 is similar to that of sodium oxide, Na_2O, on the one hand, and phosphorus(V) oxide, P_4O_{10}, on the other.

Describe what these similarities are.
Write equations for all the reactions you choose to illustrate your answer. [4]

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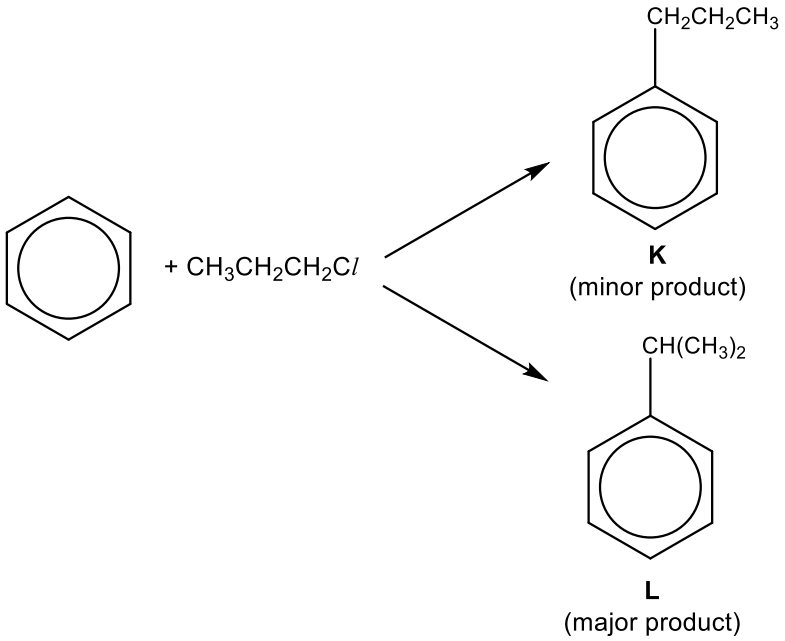
(c) Aluminium chloride, $AlCl_3$, is often used as a catalyst in the Friedel-Craft alkylation. When benzene is added to 1-chloropropane in the presence of $AlCl_3$, a mixture of two isomers, **K** and **L**, with different quantities are formed.



(i) The aluminium chloride used to react with 1-chloropropane must be anhydrous.

With the aid of equations, explain why anhydrous condition must be used in the reaction. [1]

(ii) The reaction between aluminium chloride and 1-chloropropane can be described as an *acid-base* reaction.

Explain why this is so. Write an equation for the reaction. [2]

(iii) Suggest a mechanism for the formation of isomer **K** from benzene, showing all charges and using curly arrows to show the movements of electron pairs. [2]

(iv) Another organic intermediate is also formed in the reaction between aluminium chloride and 1-chloropropane. This organic intermediate leads to the formation of isomer **L**.

Draw the structure of the organic intermediate in the formation of isomer **L** and hence explain why isomer **L** is formed in greater proportion. [2]

(v) In a similar reaction, 1 mole of benzene reacts with 1 mole of $BrCH_2CH_2CH_2CH_2Br$ to form two moles of HBr. Predict the structure of the product formed. [1]

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(d) Copper is a *d*-block element and can be found in period 4 of the Periodic Table.

(i) State the electronic configuration of Cu. [1]

(ii) When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with silver and tin as minor impurities. It contained no other metal. In order to purify it, this alloy was made the anode of an electrolysis cell, with a pure copper cathode and aqueous $CuSO_4$ as electrolyte.

Explain, with reference to relevant $E^{\ominus}$ values, what happened to the silver and tin impurities during this purification procedure. [3]

(iii) A current of 1.5 A was passed through the cell described in **(d)(ii)** for 48.0 minutes, and the cathode electrode removed, washed, dried and weighed.

Calculate the expected increase in mass of the cathode. [2]

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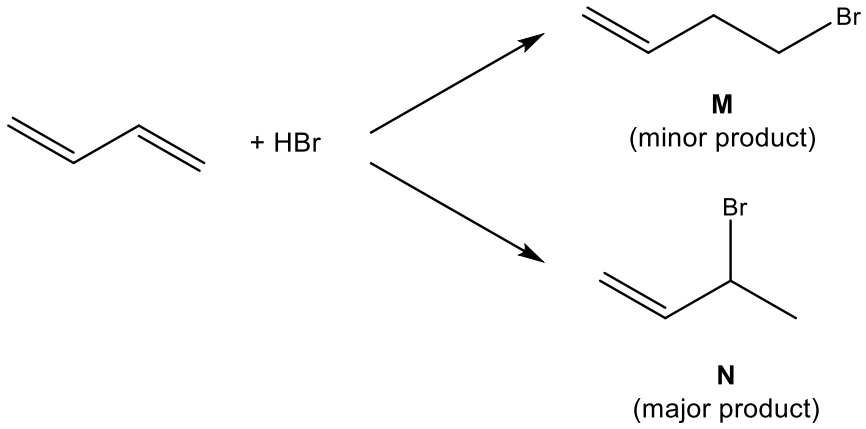
5 **(a)** Buta-1,3-diene reacts with HBr to form different isomers under different conditions as shown in Fig 5.1.

At low temperatures,



At high temperatures,

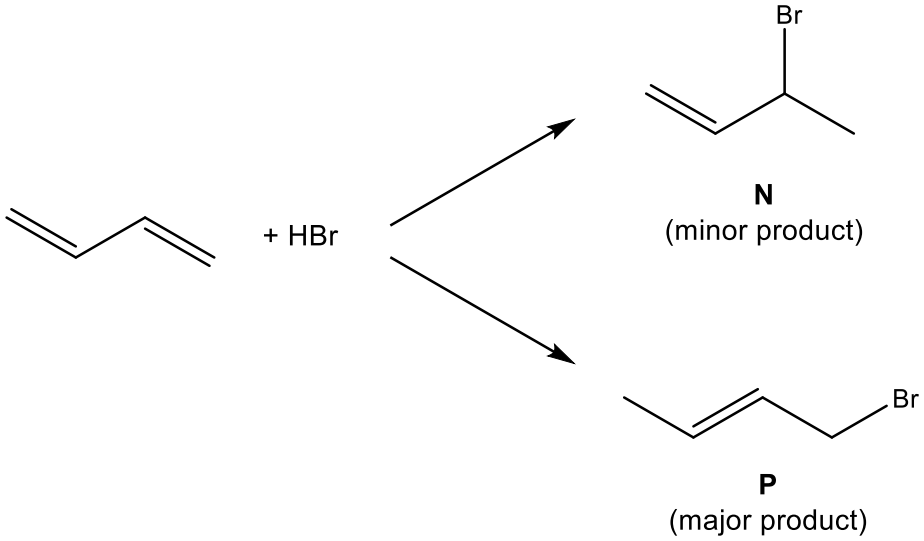


Fig 5.1

(i) Describe the hybridisation of the orbitals in, and the bonds between, the carbon atoms involved in the C=C bond of buta-1,3-diene. [3]

(ii) At low temperatures, isomer **N** is formed in a greater proportion than isomer **M**.

Suggest a mechanism for this reaction and use it to explain the preferential production of isomer **N**. [3]

(iii) At higher temperatures, isomer **P** is more likely to be formed as the organic intermediate formed is more stable than that formed in isomer **N**.

Draw the structure of the organic intermediate in the formation of isomer **P** and suggest a reason why it is more stable than the intermediate formed in isomer **N**. [2]

(iv) Buta-1,3-diene can also undergo hydrogenation to form butane.

$$CH_2=CH-CH=CH_2(g) + 2H_2(g) \rightarrow CH_3CH_2CH_2CH_3(g)$$

Construct a suitable energy cycle using this equation and use the data from Table 5.1 and your cycle to calculate the standard enthalpy change of hydrogenation of buta-1,3,diene. [3]

Table 5.1

Standard enthalpy change of formation of $CH_3CH_2CH_2CH_3(g)$	−126 kJ mol^{-1}
Standard enthalpy change of formation of $CO_2(g)$	−393 kJ mol^{-1}
Standard enthalpy change of formation of $H_2O(l)$	−286 kJ mol^{-1}
Standard enthalpy change of combustion of $CH_2=CH-CH=CH_2(g)$	−2540 kJ mol^{-1}

(v) A beaker containing 150 cm^3 of water was heated up by burning 1.2 g of buta-1,3-diene in excess oxygen. The process was known to be 70% efficient.

Calculate the expected increase in the temperature of water. [3]

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(b) A mixture contains equal quantities of two isomers, **Q** and **R**. These isomers have the molecular formula C_4H_7BrO.

Both isomers form orange precipitate and pale yellow precipitate with 2,4–dinitrophenylhydrazine and alkaline aqueous iodine respectively, but does not form any precipitate with Tollens' reagent. When heated with ethanolic silver nitrate, a pale cream precipitate is formed.

(i) Suggest what these observations indicate about the functional groups in both the isomers. [1]

(ii) When plane-polarised light is passed through this mixture there is no effect, but pure **Q** rotates plane-polarised light.

Explain these observations. [3]

(iii) Draw the three-dimensional structures of **Q** and **R**. [1]

(iv) Write an equation for the reaction between **Q** and 2,4-dinitrophenylhydrazine. [1]

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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.