RAFFLES INSTITUTION
2014 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CHEMISTRY 9647/03

Paper 3 Free Response **23 September 2014**

Candidates answer on separate paper. **2 hours**

Additional Materials: Writing Paper
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 in the spaces provided on the cover page.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
Begin each question on a fresh sheet of paper.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

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

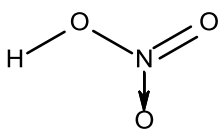
Answer any **four** questions.
Begin each question on **a fresh sheet of paper**.

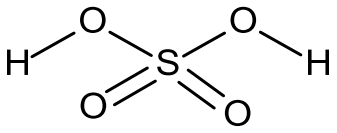
1 **(a)** Nitrobenzene is formed when benzene is treated with concentrated nitric acid and concentrated sulfuric acid. The reaction proceeds via the formation of an electrophile, a nitronium ion, NO_2^+.

(i) Draw a dot-and-cross diagram of NO_2^+.

Nitric acid accepts a proton from sulfuric acid to form $H_2NO_3^+$ and HSO_4^-. This is followed by the loss of water from $H_2NO_3^+$ to produce the nitronium ion. The mechanism is initiated by the donation of a lone pair of electrons from the oxygen atom of the O─H bond in nitric acid to a hydrogen atom in sulfuric acid.

(ii) Use the information given above to draw out the full "curly arrows" mechanism for the formation of the nitronium ion. You are advised to use structural formulae to show clearly the charges on all the species and which bonds are broken and formed.





(iii) With the aid of an equation, show how H_2SO_4 behaves as a catalyst in the nitration reaction.

(iv) Explain why the nitration of phenol

- occurs more readily than the nitration of benzene,
- gives two products, 2-nitrophenol and 4-nitrophenol.

[6]

(b) Chlorobenzene can be converted to phenylamine at low temperature using the amide ion (NH_2^-) as a nucleophile. This reaction involves the formation of a very reactive intermediate called benzyne, C_6H_4. Benzyne contains a carbon-carbon triple bond.

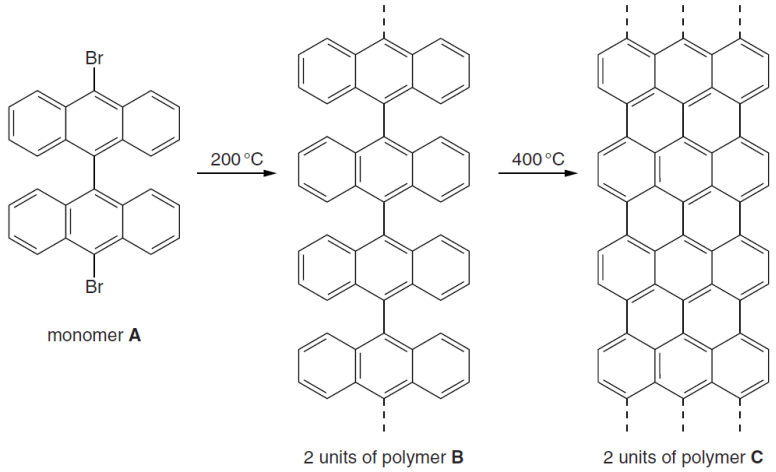
(i) Draw the structural formula of benzyne and explain why this intermediate is highly reactive.

4-Chloromethylbenzene reacts with sodium amide in liquid ammonia to produce two isomers **J** and **K**, with the molecular formula C_7H_9N. Both compounds decolourise Br_2(aq) with the formation of white precipitates. Compound **J** reacts with Br_2(aq) to give a compound **L**, $C_7H_7NBr_2$, whereas compound **K** reacts with Br_2(aq) to give a compound **M**, $C_7H_6NBr_3$.

(ii) Suggest structures for compounds **J**, **K**, **L** and **M**. Write a balanced equation for the reaction of compound **J** with Br_2(aq).

[7]

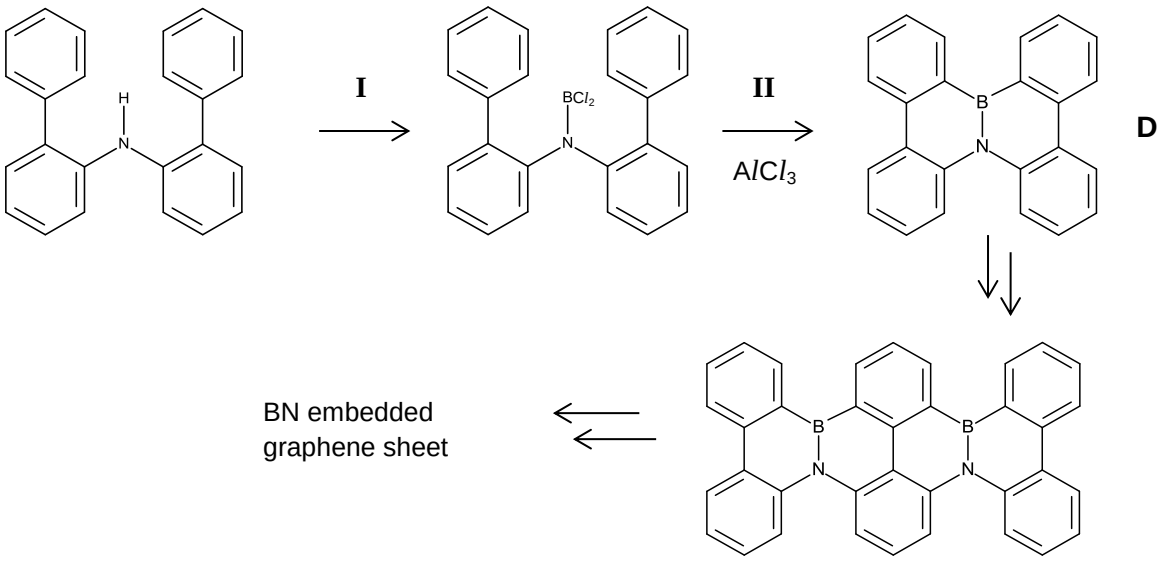
(c) A graphene sheet is a layer of graphite. A recent reaction scheme of the synthesis of graphene is shown below.



When monomer **A** is polymerised to make polymer **B**, an inorganic by-product **X** is formed. In the transformation of polymer **B** into polymer **C**, another inorganic by-product, **Y**, is produced.

(i) Give the molecular formulae of **X** and **Y**.

Another synthesis was developed in an effort to prepare graphene sheet in which one of the C=C bonds was replaced with a B-N unit.



(ii) Name the reaction mechanism for the formation of compound **D** in reaction **II** and suggest the role of $AlCl_3$.

(iii) Explain why compound **D** is non-planar.

(iv) Compare and explain the changes in the *electrical conductivity* and *softness* of graphene sheet with the newly synthesised BN embedded sheet in which one of the C=C bonds was replaced with a B-N unit.

[7]

[Total: 20]

2 Barium oxide is used to replace lead oxide for the development of lead-free glasses. Barium oxide can be prepared by the thermal decomposition of barium nitrate.

(a) Write a balanced equation for the thermal decomposition of barium nitrate. [1]

(b) Other oxides of magnesium, calcium and strontium may also be added to the formulations of lead-free glasses. Likewise, these oxides can be produced from the decomposition of their respective nitrates.

The variation in the decomposition temperatures can be explained in terms of enthalpy changes between the two ionic compounds involved in the reaction.

The calculated lattice energies of the nitrates and oxides of magnesium, calcium and strontium are shown in **Table 1** below.

Compound	Lattice energy/ kJ mol^{-1}	Compound	Lattice energy/ kJ mol^{-1}
$Mg(NO_3)_2$	–2481	MgO	–3889
$Ca(NO_3)_2$	–2268	CaO	–3513
$Sr(NO_3)_2$	–2176	SrO	–3310

Table 1

(i) What do you understand by the term *lattice energy*?

(ii) Explain the following trends observed in **Table 1**:

(I) The decrease in the magnitude of the lattice energies of both the nitrates and the oxides.

(II) The decrease in the magnitude of the lattice energy of oxides is greater than that of nitrates.

(iii) The enthalpy change of thermal decomposition of the Group II nitrates is found to be endothermic and can be represented by the following equation:

$$\Delta H_{\text{thermal decomposition}} = \text{LE of XO} - \text{LE of X(NO}_3)_2 + \text{constant}$$

where LE: lattice energy, and X: Group II metal

Deduce, in terms of enthalpy changes, the variation in the decomposition temperatures down the group.

[5]

(c) "Barium swallow" consists of a white fluid of barium sulfate, often given to patients to help diagnose problems that affect the large intestine.

Soluble barium salts, on the other hand, are highly poisonous.

The numerical value of the solubility product, K_{sp}, for $BaSO_4$ is 1.30×10^{-10} mol^2 dm^{-6}.

(i) Calculate $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$.

(ii) Suggest why barium carbonate is unsuitable to be administered as "barium swallow".

[3]

(d) Barium, which is a soft silvery metallic alkaline earth metal, is never found in nature in its pure form, due to its reactivity with air or water.

(i) Describe the reactions of barium with air and water, and give the relevant equations, with state symbols.

(ii) Describe and explain how the reactivity of Group II metals towards air and water varies down the group.

[6]

(e) When solid NH_4Cl is mixed with solid $Ba(OH)_2 \cdot 8H_2O$, the beaker freezes to the wooden table almost immediately.

Diagram I illustrates the observation and the equation for the reaction is given below.

$$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \longrightarrow 2NH_3(g) + 10H_2O(l) + BaCl_2(s)$$

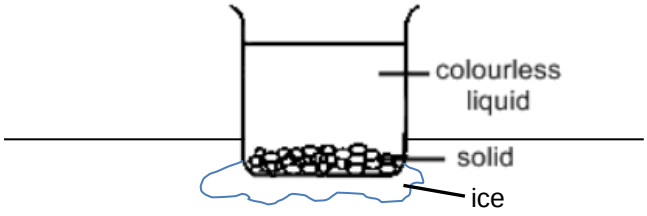


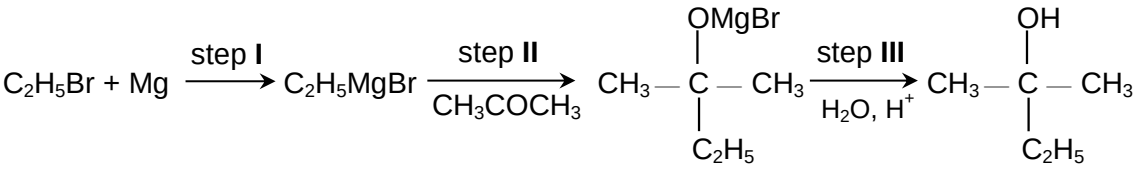
Diagram I

Comment on why the reaction is thermodynamically feasible.

[2]

(f) Grignard reagents are organometallic reagents derived from an alkyl halide and magnesium.

The use of a Grignard reagent in the conversion of bromoethane to 2-methylbutan-2-ol is given below. Step **II** is a nucleophilic addition reaction.



(i) Why is it necessary to convert bromoethane to ethylmagnesium bromide, C_2H_5MgBr, before reacting with propanone?

(ii) Explain why ethane is formed as a side product in both steps **I** and **II** if both reactions are **not** carried out under anhydrous conditions.

(iii) Suggest why the Grignard reagent can also react with a variety of carbonyl compounds but not alkenes.

[3]

[Total: 20]

3 This question is about the chemistry of halogens and halogen-containing compounds.

(a) Alcohols are converted into chloroalkanes by reacting alcohols with a mixture of solid sodium chloride and concentrated sulfuric acid. However, alcohols cannot be converted into iodoalkanes by reacting alcohols with a mixture of solid sodium iodide and concentrated sulfuric acid.

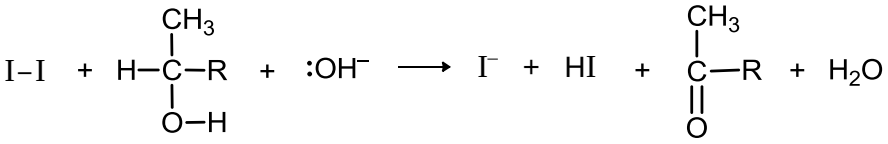
With the aid of suitable equations, explain the differences in the above reactions. [3]

(b) Alcohols with the structure $RCH(CH_3)OH$ can react with alkaline aqueous iodine to form yellow triiodomethane precipitate.

The mechanism of this reaction is as follows:

Step (1) Formation of IO^- ion

Step (2)



Step (3) $RCOCH_3 + 3IO^- \longrightarrow RCOCI_3 + 3OH^-$

Step (4) $RCOCI_3 + OH^- \longrightarrow RCOOH + CI_3^-$

Step (5) $RCOOH + CI_3^- \longrightarrow RCOO^- + CHI_3$

(i) Write an ionic equation to show the formation of IO^- and I^- ions from the reaction between I_2 and OH^- ion in step (1).

(ii) Copy the equation in step (2) onto your writing paper. Draw curly arrows to show the movement of electrons that led to the formation of the products.

(iii) Suggest the type of reaction in step (5).

[4]

(c) **(i)** Describe and explain how the ease of hydrolysis of CH_2=CHC*l* differs from that of CH_3CH_2C*l*.

(ii) Phenol, phenylmethanol and benzoic acid are three compounds containing benzene rings. None of these compounds is particularly soluble in water. Phenol and benzoic acid each dissolves in NaOH(aq), but only benzoic acid dissolves in Na_2CO_3(aq). State what these observations indicate about the relative acidities of the three compounds, and explain this trend in acidity.

[5]

(d) Compound **P**, $C_6H_{11}O_2Cl$, reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate and decolourises hot, acidified potassium manganate(VII).

When compound **P** is heated with excess aqueous sodium hydroxide, compound **Q**, $C_6H_{12}O_3$, is formed. Aqueous iodine is subsequently added to the hot mixture of this reaction and compound **R**, $C_4H_4O_5Na_2$, is formed.

P reacts with excess concentrated sulfuric acid at 170 °C to give **three** possible isomeric products **S**, **T** and **U**.

S, but not **T** and **U**, reacts with excess ammonia to form an amine.

Suggest the structures of **P**, **Q** and **R**, explaining your reasoning.

[8]

[Total: 20]

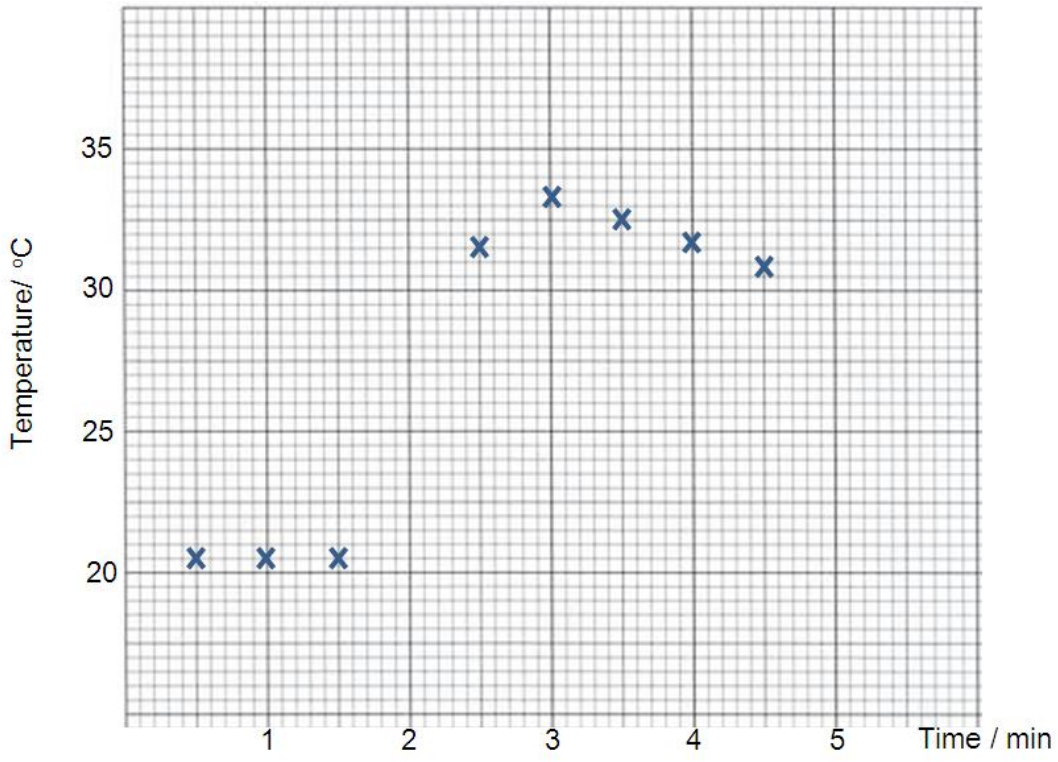
4 *Use of the Data Booklet is relevant to this question.*

(a) Aluminium forms many covalent compounds which are used in organic synthesis, for example, A*l*C*l*$_3$.

(i) Explain why aluminium has a high tendency to form covalent compounds.

(ii) A student attempted to determine the enthalpy change of solution of aluminium chloride, A*l*C*l*$_3$. He used a thermometer to measure the temperature of a 200 cm^3 sample of water in an insulated container, at 0.5 min intervals.

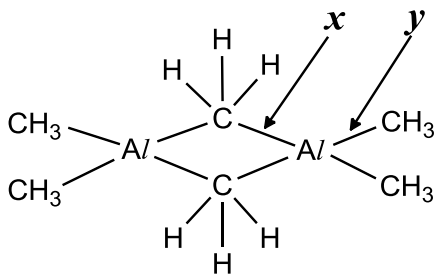
At 2.0 min, a 5.00 g sample of solid A*l*C*l*$_3$ was rapidly added to the 200 cm^3 sample of water. The temperature measurements are shown in the following graph.



Using the above graph, determine the maximum temperature change. Hence, calculate the enthalpy change of solution of A*l*C*l*$_3$.

[4]

(b) Trimethylaluminium, a co-catalyst for the industrial polymerisation of alkenes, exists as a dimer at room temperature with a molecular formula of $Al_2(CH_3)_6$. It has a shape similar to that of the aluminium chloride dimer, Al_2Cl_6.



Structure of $Al_2(CH_3)_6$

The two central methyl groups of $Al_2(CH_3)_6$ bind to both aluminium atoms, in which two electrons are shared across each Al–C–Al bridge. As such, the bridging methyl group does not violate the "octet rule".

(i) Sketch the shapes of the hybrid orbitals around the aluminium atom of $Al_2(CH_3)_6$.

(ii) State the oxidation number of the carbon atom in the bridging methyl group in $Al_2(CH_3)_6$.

(iii) Predict whether bond ***x*** would be longer than, equal to, or shorter than bond ***y*** labelled in the structure of $Al_2(CH_3)_6$. Explain your answer.

[4]

(c) Magnesium alanate, $Mg(AlH_4)_2$ is a potential material for hydrogen storage. It releases hydrogen gas according to the following reaction:

$$Mg(AlH_4)_2(s) \longrightarrow MgH_2(s) + 2Al(s) + 3H_2(g) \qquad \Delta H_r^{\ominus} = +1 \text{ kJ mol}^{-1}$$

Draw an appropriately labelled energy cycle, and use the following data, together with relevant data from the *Data Booklet*, to calculate the lattice energy of MgH_2, in kJ mol^{-1}, **to the nearest whole number**.

	$\Delta H^{\ominus}$ / kJ mol^{-1}
Standard enthalpy change of formation of $Mg(AlH_4)_2$	–66
1st electron affinity of hydrogen	–73
Standard enthalpy change of atomisation of Mg	+146

[5]

(d) The following table shows the relevant pK_a values of two compounds.

	pK_{a1}	pK_{a2}
$HOOC–CH_2–COOH$ malonic acid	2.83	5.69
$HOCH_2–CH_2–COOH$ 3-hydroxypropanoic acid	4.51	–

(i) Suggest a possible reason why the pK_{a1} of malonic acid is lower than

- the pK_{a2} of malonic acid,
- the pK_a of 3-hydroxypropanoic acid.

(ii) Sketch a titration curve that shows the pH change when a 10 cm^3 mixture of 0.100 mol dm^{-3} malonic acid **and** 0.100 mol dm^{-3} 3-hydroxypropanoic acid was titrated with 40 cm^3 of 0.100 mol dm^{-3} aqueous sodium hydroxide.

(iii) Calculate the pH of 0.100 mol dm^{-3} sodium malonate solution, $Na^+ {}^-OOC–CH_2–COO^- Na^+$.

[7]

[Total: 20]

5 **(a)** Gaseous hydrogen iodide is synthesised from hydrogen gas and iodine vapour.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

In one experiment, 0.010 atm of H_2, 0.005 atm of I_2 and 0.500 atm of HI are introduced into a sealed flask at a fixed temperature. When equilibrium is reached, the partial pressure of H_2 is 0.0455 atm.

(i) Calculate the equilibrium pressures of HI and I_2, and hence calculate the K_p value at this temperature.

(ii) By using the ideal gas equation, or otherwise, show that the value of K_c for this equilibrium is equal to the value of K_p.

[3]

(b) I_2 can be oxidised by a strong oxidising agent to produce iodic(V) acid, HIO_3 (M_r = 176).

When heated to 240 °C, iodic(V) acid dehydrates with **no change** in oxidation state to form white crystals **W**, an oxide of iodine whose M_r is 89.7 % larger than the M_r of iodic(V) acid.

Deduce the molecular formula of the white crystals **W** and construct a balanced equation for the dehydration reaction.

[3]

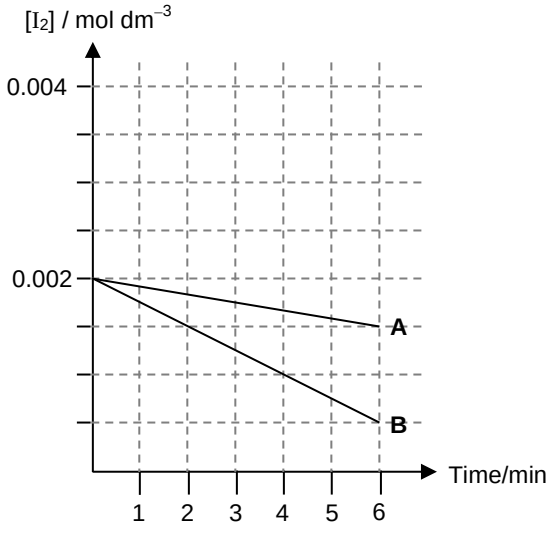
(c) Potassium iodate(V), KIO_3, in hydrochloric acid solution oxidises iodine to ICl_2^-.

(i) Construct a balanced ionic equation for this reaction, showing your working.

The rate of this reaction can be measured by following the decrease in colour intensity of brown iodine with the use of a colorimeter.

Two sets of experiments were performed in which the initial concentrations of KIO_3 and H^+ were varied. The results are shown below in graphical form.

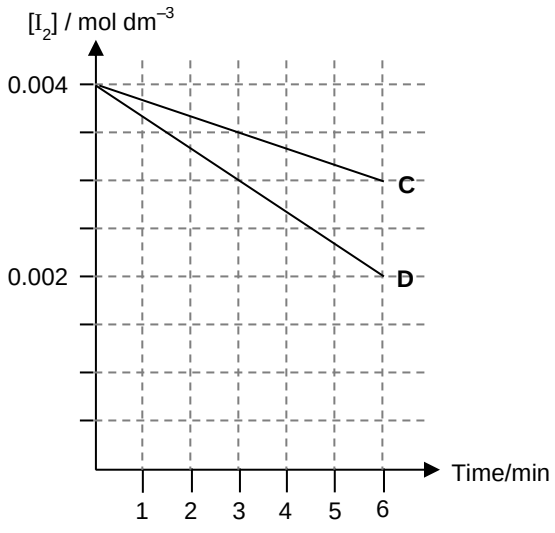
Set 1



A: $[KIO_3]$ = 0.4 mol dm^{-3}

B: $[KIO_3]$ = 1.2 mol dm^{-3}

Set 2



C: $[H^+]$ = 0.4 mol dm^{-3}

D: $[H^+]$ = 0.8 mol dm^{-3}

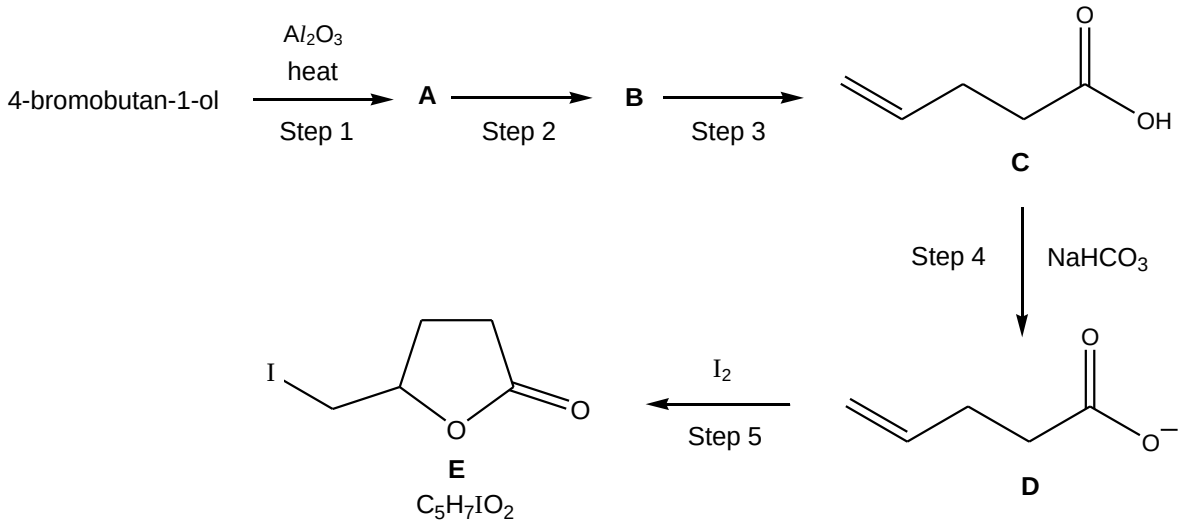
(ii) Use the graphs to determine the order of reaction with respect to the concentrations of KIO_3, iodine and H^+. Show your reasoning clearly.

(iii) Given that the reaction is zero order with respect to $C\mathit{l}^-$, write the rate equation for the reaction.

[6]

(d) Iodine is a commonly used reagent in lactonisation reactions where cyclic esters are formed. The products of iodolactonisation are particularly useful in the synthesis of many natural products.

Compound **E**, an iodolactone, can be synthesised from 4-bromobutan-1-ol using the reaction scheme proposed below.



(i) Suggest the

- structures of compounds **A** and **B**,
- reagents and conditions for Steps 2 and 3.

(ii) Explain the role of $NaHCO_3$ in Step 4.

(iii) Suggest another possible cyclic ester, with the same molecular formula as compound **E,** which can be formed in Step 5.

(iv) Comment on the optical activity of compound **E**.

(v) **F** is an isomer of **E**.
F gives only 2 monobrominated products when reacted with Br_2 under *uv* light.
F does **not** rotate plane-polarised light.
Suggest the structure of **F**.

[8]

[Total: 20]