ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME					
CLASS	**2**	**0**	**S**		

CHEMISTRY **9729/03**

Paper 3 Free Response **15 September 2021**

2 hours

Candidate answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use a 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		
Q1		**24**
Q2		**17**
Q3		**19**
Q4/5		**20**
Total		**80**

This document consists of **39** printed pages.

Section A

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

1 **(a)** Iodates are compounds that contain the IO_3^- anion.

(i) Draw the dot-and-cross diagram of IO_3^-. **[1]**

(ii) Use your knowledge of VSEPR theory to name the shape of and state the bond angle for IO_3^-. Explain your reasoning. **[3]**

(iii) Explain why BrO_3^- has a larger bond angle than IO_3^-. **[1]**

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(b) The decomposition of hydrogen peroxide, H_2O_2, can be catalysed by acidified IO_3^-.

$$2H_2O_2 \rightarrow 2\ H_2O + O_2$$

With the aid of relevant data from the *Data Booklet* and the information below, show that IO_3^- is a suitable catalyst for the decomposition of H_2O_2 under standard conditions.

$$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O \qquad E^\ominus = +1.19\ V$$

In your answer, give relevant equations for the reactions that occur. **[3]**

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(c) The kinetics of the catalytic decomposition of H_2O_2 by IO_3^- can be investigated.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The concentration of H_2O_2 remaining can be determined by titrating with standard acidified $KMnO_4$.

Briefly outline how you would determine the rate of the catalysed decomposition of H_2O_2 using acidified $KMnO_4$. **[3]**

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(d) (i) A student collects some data for the reaction of H_2O_2 with acidified IO_3^-, as shown in Table **1.2**.

Experiment	$[H_2O_2]$/ mol dm^{-3}	$[IO_3^-]$/ mol dm^{-3}	$[H^+]$/ mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
1	0.050	0.070	0.025	1.47×10^{-5}
2	0.100	0.070	0.050	2.94×10^{-5}
3	0.100	0.140	0.025	5.88×10^{-5}
4	0.150	0.140	0.025	8.82×10^{-5}

Table 1.2

Determine the order of reaction with respect to $[H_2O_2]$, $[IO_3^-]$ and $[H^+]$. Show your reasoning. **[3]**

(ii) Hence, write the rate equation for the reaction, and calculate a value for the rate constant using experiment **1**. Include units in your answer. **[2]**

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(e) (i) NH_4IO_3 is an unstable compound that readily decomposes when warmed as shown:

$$NH_4IO_3(s) \rightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}I_2(s) + 2H_2O(l) \quad \Delta H_r^{\ominus}$$

Using the information given below in Table **1.1**, calculate the standard enthalpy change $\Delta H_r^{\ominus}$ for the above reaction. **[1]**

Substance	**Standard enthalpy change of formation / kJ mol^{-1}**
NH_4IO_3 (s)	– 417.4
H_2O (*l*)	– 286

Table 1.1

(ii) Explain how the value and sign of $\Delta G_r^{\ominus}$ would compare to the value and sign of $\Delta H^{\ominus}$ for the decomposition of NH_4IO_3. **[2]**

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(f) **(i)** When 4.00 g a Group 2 metal iodate was heated strongly, 0.947 g of a metal oxide, a purple gas and a colourless gas which rekindles a glowing splint were produced.

Determine the identity of the Group 2 metal. **[1]**

(ii) Using your answer in **(f)(i)**, write a balanced equation, with state symbols, for the decomposition of the Group 2 iodate. **[1]**

(iii) To deduce which compound, calcium iodate or barium iodate, has a higher decomposition temperature, the following explanation was provided by a student:

'Calcium iodate has a higher decomposition temperature than barium iodate. The Ca^{2+} ion is a smaller ion than Ba^{2+}, hence the lattice energy of calcium iodate is more exothermic than that of barium iodate.'

Comment on why the student's answer was wrong and hence suggest a more appropriate answer. **[3]**

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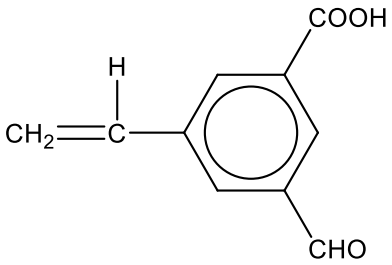
[Total:24 marks]

2 Lithium is one of the most abundant elements on the Earth, and has gained widespread use in a variety of applications, from chemical synthesis to battery technology.

(a) Lithium aluminium hydride is often used in reactions to reduce organic compounds. However, it is not the only reducing agent available, and different reducing agents work on different functional groups.



Compound **A**

Draw the structures of the organic products formed when Compound **A** reacts with the following reducing agents:

(i) $LiAlH_4$ **[1]**

(ii) $NaBH_4$ **[1]**

(iii) H_2 with Ni catalyst, heat **[1]**

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(b) Fig **2.1** shows how the standard cell potential between the Li^+/Li half-cell and the Cl_2/Cl^- half-cell is measured.

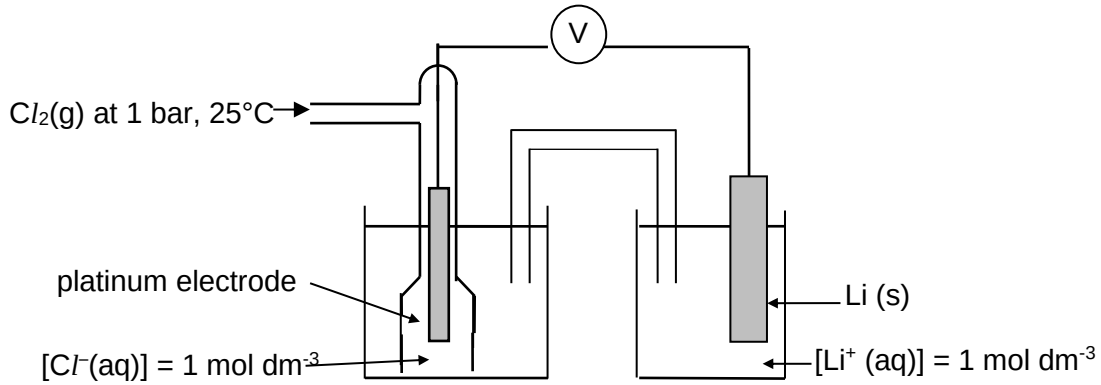

Fig 2.1

(i) Use of the *Data Booklet* is relevant to this question.
Describe the flow of electrons in the external circuit in the above electrochemical cell. Explain your reasoning. **[2]**

(ii) Predict the effect, if any, on the voltmeter reading when the pressure is increased at the Cl_2/Cl^- half-cell. Explain your answer. **[2]**

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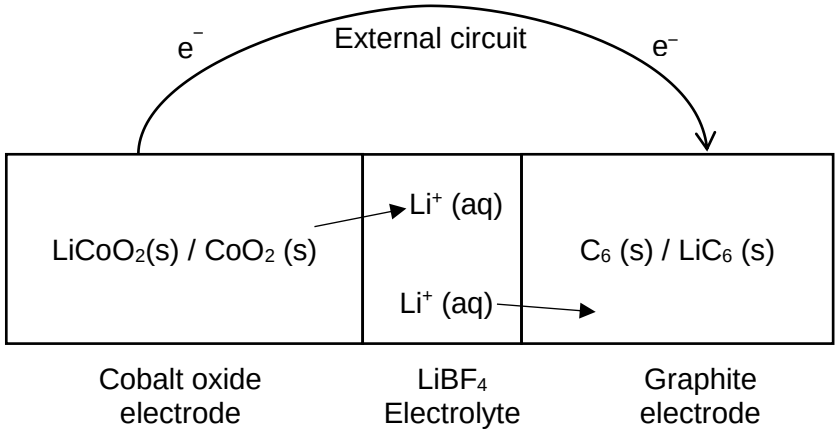
(c) Lithium-ion batteries are lightweight and can hold a large amount of charge. The lithium-cobalt oxide battery was the first lithium-ion battery to be developed and sold by Sony in 1991. It consisted of a cobalt oxide electrode, and a graphite electrode with lithium intercalated within the graphite structure.

A simplified diagram of the lithium-cobalt oxide battery during the charging process is shown below. LiC_6 represents the lithium intercalated within the graphite structure.



During charging, the following process occurs at the cobalt oxide electrode:

$LiCoO_2 \longrightarrow CoO_2 + Li^+ + e^-$

At the same time, at the graphite electrode, the following process occurs:

$Li^+ + C_6 + e^- \longrightarrow LiC_6$

(i) Identify the electrode that is the anode during the ***discharging*** process. **[1]**

(ii) Write half equations for the processes at the anode and cathode during ***discharge***. **[1]**

(iii) Given the following information, determine the $E^{\ominus}_{cell}$ of the lithium cobalt oxide battery.

$CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2$ $\quad E^{\ominus} = +1.00$ V

$Li^+ + C_6 + e^- \rightleftharpoons LiC_6$ $\quad E^{\ominus} = -3.00$ V **[1]**

(iv) Calculate the standard Gibbs free energy change that occurs in the battery during discharge using your answer in **(c)(iii)**. **[1]**

(v) The actual voltage of the lithium cobalt oxide battery is 3.60 V. Suggest why this value differs from your answer in **(c)(iii)**. **[1]**

(vi) Explain the purpose of the electrolyte solution. **[1]**

(vii) Suggest why modern lithium-ion batteries are superior to lead-acid batteries. **[1]**

(viii) A batch of lithium-cobalt oxide batteries were defective due to the presence of potassium ions in the graphite electrode. Given that

$CoO_2 + K^+ + e^- \rightleftharpoons KCoO_2$ $\quad E^{\ominus} = +0.79$V

$K^+ + C_6 + e^- \rightleftharpoons KC_6$ $\quad E^{\ominus} = -2.88$V

State and explain the effect, if any, of the presence of potassium ions on

(I) the charging process,

(II) the discharging process **[2]**

(ix) Explain why the batteries in **(c)(viii)** are considered defective. **[1]**

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[Total:17 marks]

3 **(a)** Organolithium reagents, RLi, are compounds which contains carbon-lithium bonds. They act as sources of negatively charged carbon, i.e. carbanions, and are useful reagents in organic synthesis involving carbon-carbon bond formation.

Organolithium reagents can be formed by reacting powdered lithium with halogenoalkanes in dry ether, as shown in the example below with bromomethane.

$$CH_3Br + 2Li \xrightarrow{\text{dry ether}} CH_3Li + LiBr$$

(i) State the oxidation state of carbon in CH_3Br and CH_3Li. **[1]**

(ii) Based on your answers in **(a)(i)**, suggest why CH_3Li is formed by mixing Li and bromomethane in the ratio of 2:1. **[1]**

(iii) Suggest why the ether solvent used needs to be dry in this reaction. **[1]**

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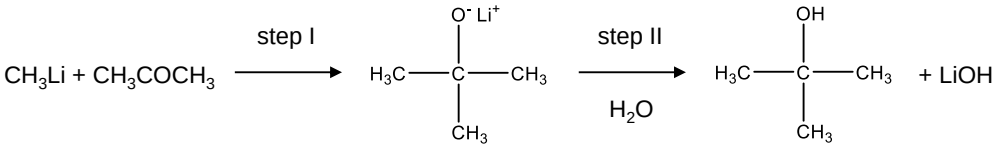
(b) A typical example of the use of an organolithium reagent is the two-step mechanism of CH_3Li with propanone, CH_3COCH_3, to form 2-methylpropan-2-ol.



Assuming that CH_3Li produces the methyl carbanion, $:CH_3^-$, as the reacting species, name and describe the two-step mechanism for the reaction.

In your answer you should show all charges, dipoles and lone pairs and show the movement of electrons using curly arrows. **[3]**

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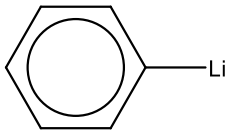
(c) **(i)** Suggest the **skeletal formula** of the final organic product formed when



is reacted with butanone, $CH_3CH_2COCH_3$, in a similar two-step mechanism as in **(b)**. **[1]**

(ii) With reference to the mechanism identified in **(b)**, suggest whether the final product mixture in **(c)(i)** will rotate plane-polarised light. Explain why. **[2]**

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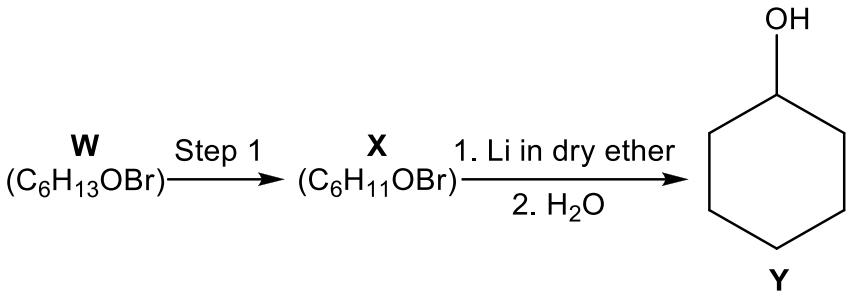
(d) Compound **Y** can be synthesised by the following route involving an intramolecular organolithium reaction.

X gives a silver mirror when boiled with Tollens' reagent. **X** also gives a cream precipitate when heated with ethanolic silver nitrate.

State the reagents and conditions for step 1, and draw the structures of **W** and **X**.



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(e) Fig. **3.1** shows a reaction synthesis.

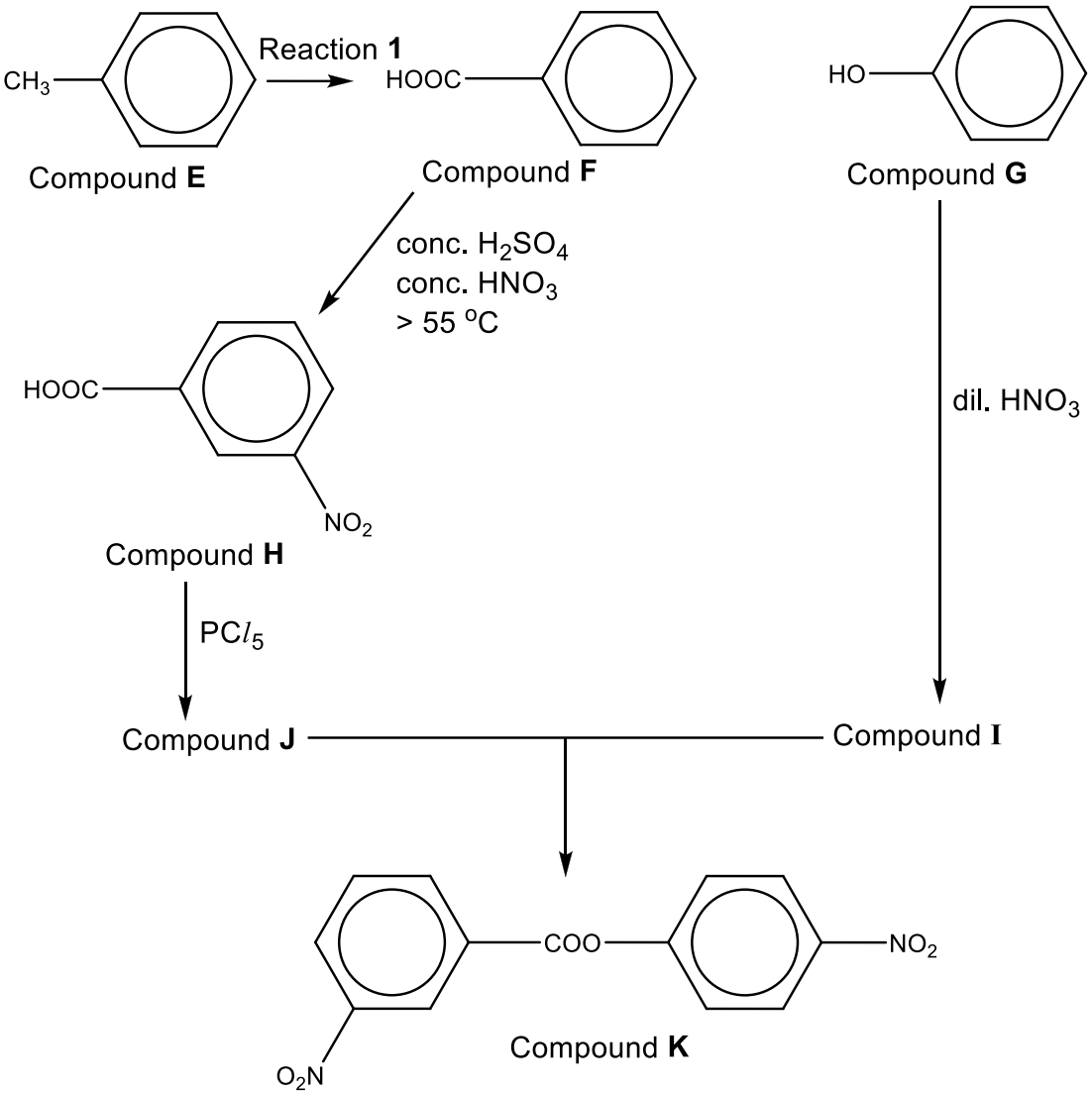

Fig 3.1

(i) Identify compound **J** and compound **I**. **[2]**

(ii) State the reagents and conditions required for Reaction **1**. **[1]**

(iii) Explain the differences in the conditions for the nitration of compound **F** and compound **G**. **[2]**

(iv) Suggest a simple chemical test to distinguish compound **F** and compound **G**. State any observations you would make with each compound. **[2]**

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[Total: 19 marks]

Section B

Answer **one** question from this section.

4 **(a)** **(i)** Use of the *Data Booklet* is relevant to this question. **[2]**

State how the reactivity of the halogens as oxidising agents varies down the group, and relate this variation to relevant E^{θ} values.

(ii) Describe reactions that illustrate the relative oxidising abilities of chlorine and iodine. Include all relevant observations. **[2]**

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(b) (i) Calcium fluoride is sparingly soluble in water. It has a solubility of 0.00180 g in 100 cm^3 of water at 0 °C.

Write an expression for the solubility product, $K_{sp,}$ for calcium fluoride.

Calculate the K_{sp} for calcium fluoride, stating its units **[2]**

(ii) Use the data in Table **4.1** to calculate a value for the enthalpy change of solution of calcium fluoride. **[2]**

Process	$\Delta H^{\ominus}$**/kJ mol^{-1}**
$Ca^{2+}(g) \longrightarrow Ca^{2+}(aq)$	–1579
$F^-(g) \longrightarrow F^-(aq)$	–524
$Ca^{2+}(g) + 2F^-(g) \longrightarrow CaF_2(s)$	–2616

Table 4.1

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(c) Krypton reacts with liquid fluorine in the presence of ultraviolet light to make gaseous krypton difluoride, KrF_2.

$$Kr(g) + F_2(l) \rightarrow KrF_2(g) \text{ ……} \textbf{Reaction (1)}$$

(i) Define the term *bond energy*. **[1]**

(ii) Use the data in Table **4.2**, together with relevant data from the *Data Booklet*, construct an energy level diagram to calculate the value for the enthalpy change of the above reaction. Show your working. **[3]**

	value/kJ mol^{-1}
Enthalpy change of vaporisation of fluorine	+ 3.27
Bond energy of Kr–F	+ 46.0

Table 4.2

(iii) The activation energy, E_a, for Reaction (1) is +394 kJ mol^{-1}.

Use all the information above to draw the reaction profile diagram for the formation of $KrF_2(g)$. Label E_a and ΔH_r on the diagram. Assume the reaction proceeds in one step. **[1]**

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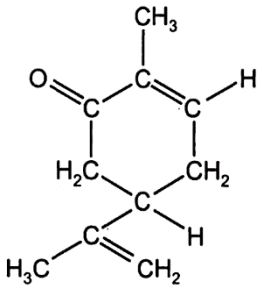
(d) Carvone is the main active ingredient of the flavouring agent oil of spearmint.



Carvone

Draw the structure of the major product when Carvone reacted with excess of HBr. State how many chiral centre(s) are present in the organic compound. **[2]**

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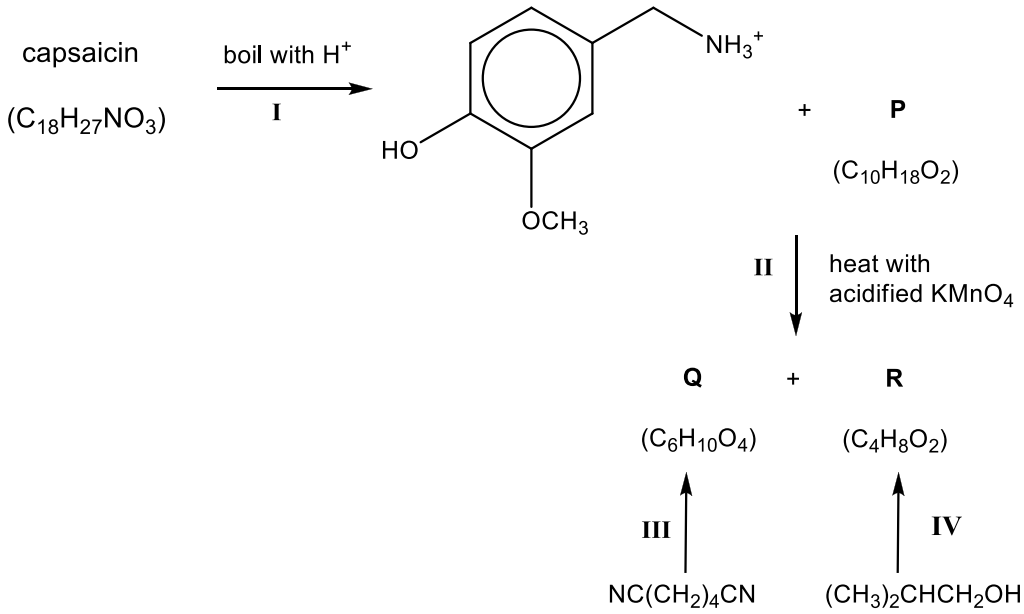
(e) The compound responsible for the hot taste of chilli peppers is capsaicin, which creates a burning effect on the tongue due to its weak acidic nature.

Its molecular structure can be deduced by the following reaction scheme:



(i) Suggest the functional group present in compound **P** that has reacted with hot acidified $KMnO_4$. **[1]**

(ii) Suggest the reagent and conditions for reaction **IV**. **[1]**

(iii) Name the *type of reaction* in reaction **III**. **[1]**

(iv) Suggest the structures of compound **P** and capsaicin. **[2]**

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5 **(a)** This part of the question is about the elements in Period 3.

The oxides MgO, Al_2O_3 and SiO_2 are all used as refractory materials due to their high melting points.

The last two are major constituents of gemstones, such as rubies, sapphires and amethysts.

(i) If a sample of one of the oxides was provided as a white powder, describe the reactions you could carry out on the powder to determine which of the three oxides it was. Write equation(s) to illustrate the reaction. **[3]**

(ii) Sketch a graph showing the variation of pH across the chlorides of Period 3 elements Na to P when they are added to water. Use relevant equations for NaCl, $AlCl_3$, and PCl_5, to show how these chlorides differ in their reactions with water. **[3]**

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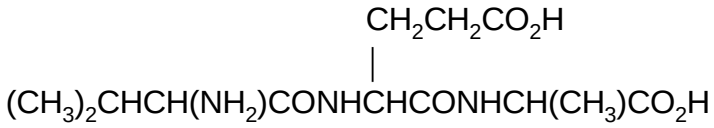
(b) The hormone insulin is responsible for regulating the blood glucose level in our body. Partial hydrolysis of insulin gives the following tripeptide:



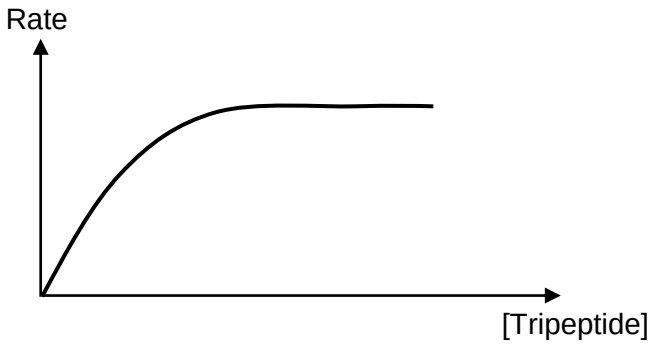
(i) Give the name and displayed formula of the linkage between amino acid residues in insulin. **[1]**

(ii) What reagents and conditions could you use to hydrolyse this tripeptide into its constituent amino acids? **[1]**

(iii) Draw the structural formula of the constituent amino acids that are obtained by further hydrolysis of the tripeptide. **[2]**

(iv) Amino acids exist as *zwitterions* in aqueous solution.
Draw the structural formula of the *zwitterion* formed from one of these amino acids, and write equations to show how it can act as a buffer. **[2]**

(v) The graph shows the results of an investigation of the initial rate of hydrolysis of the tripeptide by the enzyme amylase. In the experiments, the initial concentration of the tripeptide was varied but that of amylase was kept constant.



Explain the difference in the rate of hydrolysis at high and low concentrations of the tripeptide. **[2]**

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(c) The following scheme of reactions illustrates the reactions involving an amino acid to form compound **F**:

$C_6H_5CH_2Cl$ + $H_2N\text{-}CH(CH_3)\text{-}CO_2H$

step I ↓

$C_6H_5CH_2NH\text{-}CH(CH_3)\text{-}CO_2H$

step II ↓

$C_6H_5CH_2NH\text{-}CH(CH_3)\text{-}COCl$

step III ↓ $H_2NCH_2CO_2H$

$C_6H_5CH_2NH\text{-}CH(CH_3)\text{-}CO\text{-}NHCH_2CO_2H$

step IV ↓

$C_6H_5CH_2NH\text{-}CH(CH_3)\text{-}CH_2\text{-}NHCH_2CH_2OH$

F

(i) What *types of reaction* is step **I** and step **IV**? **[1]**

(ii) Suggest suitable reagents for step **II** and **IV**. **[2]**

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(d) *Lidocaine* and *Procaine* are two common local anaesthetics used in dental surgeries and minor operations. Table **5.1** shows their pK_b values. You may assume they are both monobasic.

Compound	**pK_b**
Lidocaine	6.1
Procaine	5.1

Table 5.1

(i) A sample of *Procaine* was found to have higher electrical conductivity than a sample of *Lidocaine* of equal concentration.
Explain this observation with reference to the pK_b values. **[1]**

(ii) Hydrochloric acid is added to 1 dm^3 of a 0.025 mol dm^{-3} *of Lidocaine* solution to produce a buffer solution. Determine the volume of 0.500 mol dm^{-3} HC*l* required to form a buffer solution of pH 7.5. **[2]**

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Additional Answer Space

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