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.

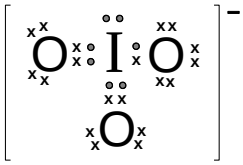
For Examiner's Use		
Q1		**24**
Q2		**17**
Q3		**19**
Q4/5		**20**
Total		**80**

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]**

Electron pairs repel each other and arrange themselves as far apart as possible to maximise stability and minimize (electrostatic) repulsion

Lone pair-lone pair repulsion are stronger than lone pair-bond pair repulsion which are stronger than bond pair-bond-pair repulsion.

IO_3^- has trigonal pyramidal[√] shape and 107º since there are 3 bond pairs and 1 lone pair of electrons around the central atom I.

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

Br is more electronegative than I, hence it draws the bond pair of electrons closer to itself, resulting in greater bond pair-bond pair repulsion, and a larger bond angle.

(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.

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

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

Step 1

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $\qquad E^\ominus = +0.68$

$5H_2O_2 + 2H^+ + 2IO_3^- \rightarrow I_2 + 5O_2 + 6H_2O$ [1/2 for either half-eqn or full eqn]

$E^\ominus_{cell} = +1.19 - (+0.68) = +0.51$ V

Step 2

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $\quad E^\ominus = +1.77$

$5H_2O_2 + I_2 \rightarrow 4H_2O + 2IO_3^- + 2H^+$ [1/2 for either half-eqn or full eqn]

$E^\ominus_{cell} = +1.77 - (+1.19) = +0.58$ V

(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 rate of the catalysed decomposition of H_2O_2 using acidified $KMnO_4$. **[3]**

Add (1 cm^3 or any small amount < 10 cm^3) of IO_3^- catalyst to a solution of H_2O_2 and start the stopwatch.

At regular time interval (of 5 min), pipette 25.0 (or 10) cm^3 aliquot of the reaction mixture and quench using a large volume of cold water.

Titrate the quenched mixture with the standard acidified $KMnO_4$

Since volume of $KMnO_4$ used $\propto$ amount of H_2O_2 remaining, plot the graph of volume of $KMnO_4$ used against time.

(Instantaneous) rate is found by drawing a tangent to the curve and finding its gradient g_1, where rate = $-g_1$.

(d) (i) A student collects some data for the reaction of H_2O_2 with acidified IO_3^-, as shown in Table **1.2**. **[3]**

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.

Let Rate = $k[H_2O_2]^x[IO_3^-]^y[H^+]^z$

Comparing expt 3 and 4, when $[H_2O_2]$ is 1.5 times, initial rate is 1.5 times.

First order wrt $[H_2O_2]$

Comparing expt 1 and 3,

$$\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{k[0.100]^1[0.140]^y[0.025]^z}{k[0.0500]^1[0.070]^y[0.025]^z}$$

$y = 1$

First order wrt $[IO_3^-]$

Comparing expt 1 and 2,

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[0.100]^1[0.070]^1[0.050]^z}{k[0.050]^1[0.070]^1[0.025]^z}$$

$z = 0$

Zero order wrt $[H^+]$

(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]**

Rate = $k[H_2O_2][IO_3^-]$

$k = 1.47 \times 10^{-5}/(0.05)(0.07) = 0.0042$ $mol^{-1}dm^3s^{-1}$

(e) (i) NH_4IO_3 is an unstable compound that readily decomposes when warmed as shown: **[1]**

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

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

Substance	Standard enthalpy change of formation / kJ mol^{-1}
NH_4IO_3	– 417.4
H_2O	– 286

Table 1.1

$\Delta H^{\ominus} = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$

$= 2(-286) - (-417.4) = -154.6 \text{ kJ mol}^{-1}$

(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]**

Since there is an increase in the number of gaseous molecules (from 0 to 1 mol) hence increase in disorderliness of system, $\Delta S^{\ominus} > 0$.

Given that $\Delta H^{\ominus} < 0$ and $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$, $\Delta G^{\ominus}$ will have a negative sign and be of a bigger value than $\Delta H^{\ominus}$.

(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. **[1]**

Determine the identity of the Group 2 metal.

Let x be the A_r of the Group 2 metal

$$\frac{4.00}{x+2(126.9+16.0x3)} = \frac{0.947}{x+16}$$

$x = 87.5$

which is close to A_r of Strontium

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

$Sr(IO_3)_2(s) \longrightarrow SrO(s) + I_2(g) + \frac{5}{2}O_2(g)$

(iii) To deduce which compound, calcium iodate or barium iodate, has a higher decomposition temperature. The following explanation was provided by a student: **[3]**

'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.

Lattice energy should not be used to determine relative thermal stability of Group 2 iodates and barium iodate should have a higher decomposition temperature.

Barium iodate has a higher decomposition temperature because

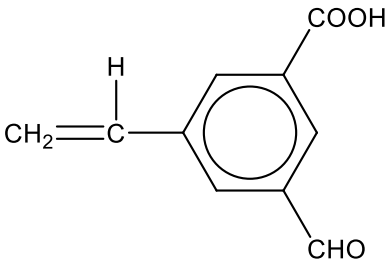
Ba^{2+} has larger ionic radius and hence has a lower charge density and lower polarising power.

Hence, Ba^{2+} polarises the electron cloud of the iodate ion to a lesser extent, weakening the I–O bonds to a lesser extent in barium iodate.

[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.

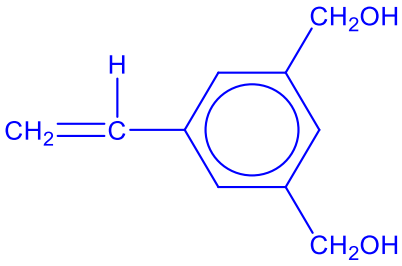
(a) Lithium aluminium hydride is often in reactions to reduce organic compounds. However, it is not the only reducing agent available, and different reducing agents work on different functional groups.



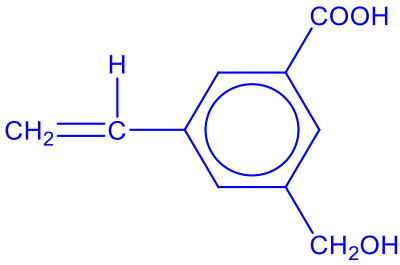
Compound **A**

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

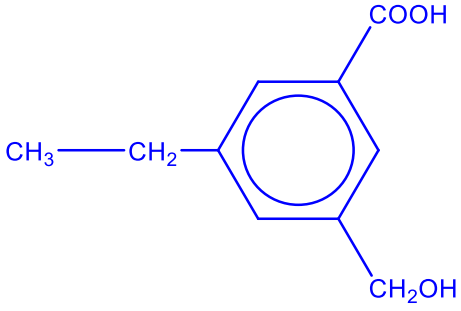
(i) $LiAlH_4$ **[1]**



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



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



(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.

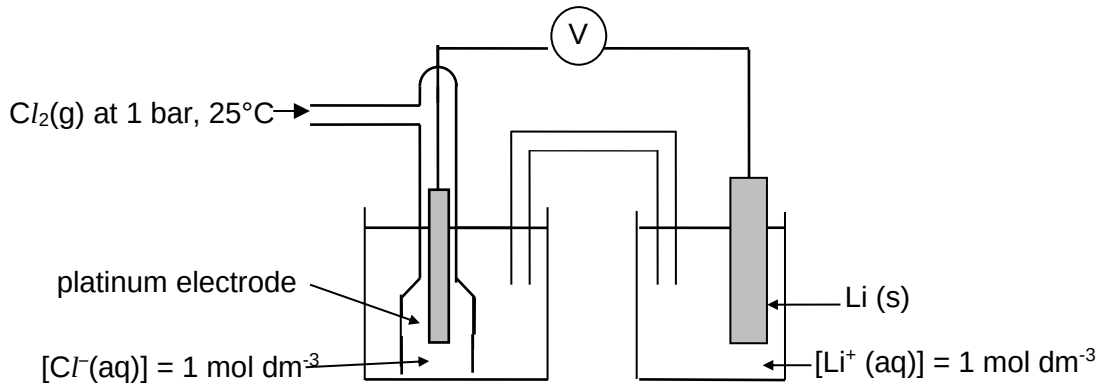


Fig 2.1

(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]**

$Li^+ + e \rightleftharpoons Li$ E = -3.04 V (more negative, likely to be oxidised)

$Cl_2 + 2e \rightleftharpoons 2Cl^-$ E = +1.36 V (more positive, likely to be reduced)

Hence Li is oxidised and Cl_2 is reduced.

Flow of electrons in the external circuit is from Li electrode to Pt electrode

(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]**

When the pressure is increased at the Cl_2/Cl^- half-cell,

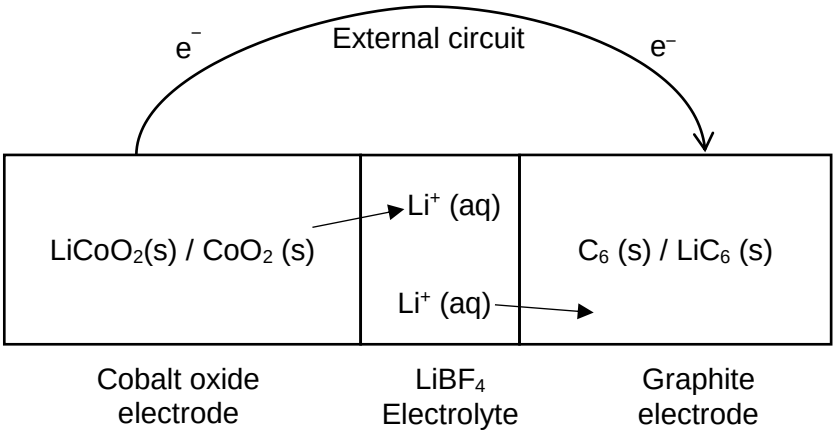
For the equilibrium $Cl_2 + 2e \rightleftharpoons 2Cl^-$,

The POE shifts right/(forward reaction favoured), $E_{cathode}$ becomes more positive.

Since $E_{cell} = E_{cathode} - E_{anode}$, E_{cell} becomes **more positive**.

(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]**

Graphite electrode

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

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

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

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

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

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

$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = +1 - (-3) = +4.00\ V$

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

$\Delta G^{\ominus} = -nFE^{\ominus} = -1 \times 96500 \times (+4.00)$

$\Delta G^{\ominus} = -386000\ J\ mol^{-1}$ **[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]**

The answer in part (iii) assumes standard conditions.

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

The electrolyte solution allows for the movement of ions (from one electrode to the other)

OR

to maintain charge / electric neutrality.

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

Lithium has high energy density as it has the lowest mass per charge / highest electrical voltage per mass.

or

Lithium is lighter and hence more portable than lead-acid batteries.

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

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

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

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

(I) the charging process,

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

During charging, at the graphite cathode, C_6 can undergo reduction with either Li^+ or K^+. Since the $E^\ominus$ (K^+ / KC_6) is less negative / more positive than $E^\ominus$ (Li^+ / LiC_6), K^+ is preferentially reduced to KC_6. There is no effect at the cobalt oxide anode.

During discharge, at the cobalt oxide cathode, CoO_2 can undergo reduction with either Li^+ or K^+. Since the $E^\ominus$ (CoO_2 / $LiCoO_2$) is more positive than $E^\ominus$ (CoO_2 / $KCoO_2$), Li^+ will still be preferred to be reduced to $LiCoO_2$. There is no effect at the graphite anode.

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

It cannot be recharged any more since K^+ instead of Li^+ would be preferentially reduced.

OR

Although the potassium ions did not affect the discharge voltage, the amount of charge the battery can hold is still decreased due to the presence of potassium ions. Hence, the batteries are defective.

[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]**

C in CH_3Br: . . . . . C in CH_3Li: . . . . . .

C in CH_3Br: –2 C in CH_3Li:–4

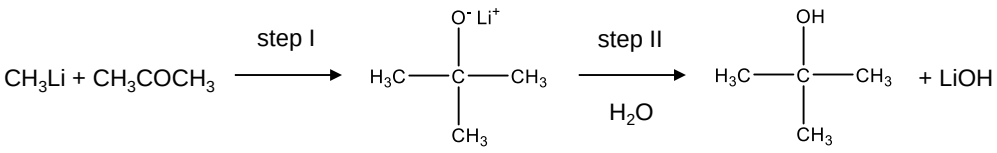
(ii) Based on your answers in **(a)(i)**, suggest why CH_3Li is formed by mixing Li and bromomethane in the ratio of 2:1. **[1]**

1 mol of C needs to take in 2 mol of electrons but 1 mol of Li only gives out 1 mol of electrons.

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

Lithium will reduce / react with water instead of the bromomethane.

(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.

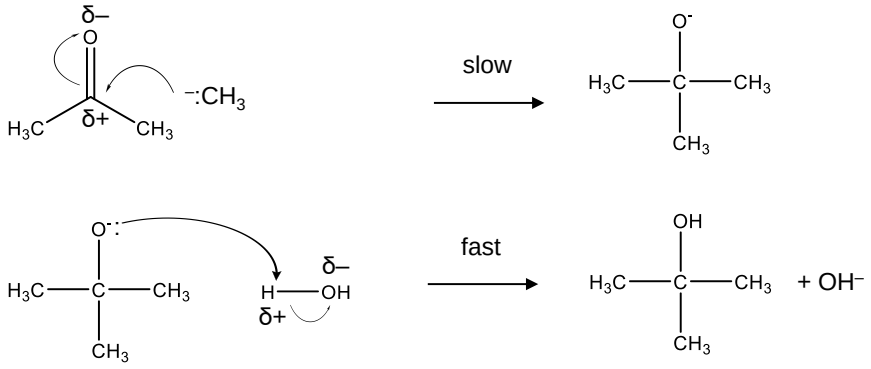


Assuming that CH_3Li produces the methyl carbanion, $:CH_3^-$, as the reacting species, name and describe the two-step mechanism for the reaction.

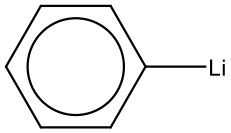
In your answer you should show all charges, dipoles and lone pairs and show the movement of electrons using curly arrows. **[3]**

- Nucleophilic addition
- Label slow step + correct anion intermediate
- δ+/δ– on carbonyl and H_2O

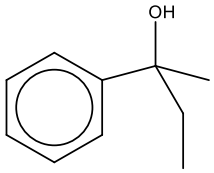
- lone pair on CH_3^- and O^-
- arrows on slow step
- arrows on fast step



(c) **(i)** Suggest the **skeletal formula** of the final organic product formed when **[1]**



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



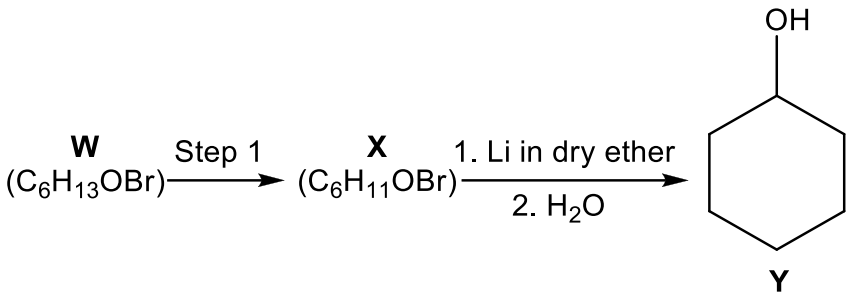
(ii) With reference to the mechanism identified in **(b)**, suggest whether the final product mixture in **(c)(i)** will rotate plane-polarised light. Explain why. **[2]**

No. Carbonyl carbon is sp^2 hybridised/ trigonal planar. The nucleophile has equal probability of attack above and below the plane, resulting in a racemic mixture / racemate / equal amount of each enantiomers.

(d) Compound **Y** can be synthesised by the following route involving an intramolecular organolithium reaction. **[3]**

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

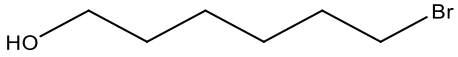
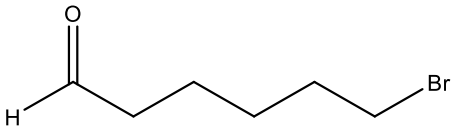
State the reagents and conditions for step 1, and draw the structures of **W** and **X**.



Reagents and conditions for step 1 . . . . . .

W	X

Step 1: $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat with immediate distillation [1]

W	X
	

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

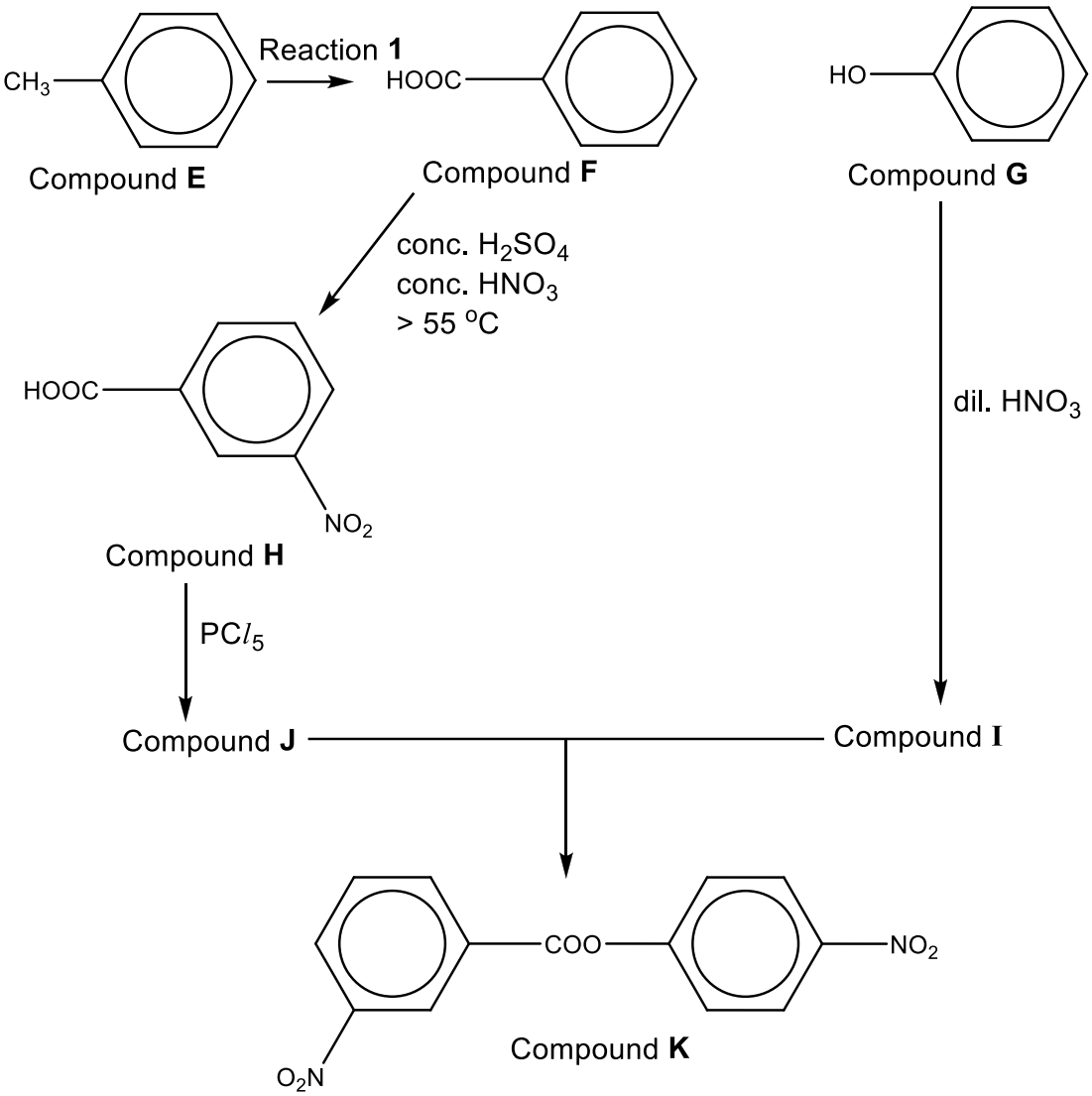
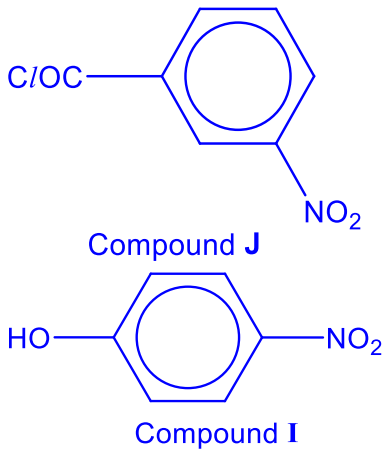


Fig 3.1

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



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

H_2SO_4 (aq), $KMnO_4$ (aq), heat

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

Compound F contains a **deactivating group/EWG –COOH** which **decreases the electron density** of the benzene ring, hence it undergoes nitration less easily.

Compound G has an activating/electron-donating **–OH group**. The **lone pair of electrons on O delocalise into the benzene ring**, **increases the electron density** of the benzene ring, which allows phenol to undergo electrophilic substitution reaction more easily.

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

Br_2 (aq)

Compound G decolourises orange Br_2 (aq) solution and forms a white ppt.

Compound F does not decolourise orange Br_2 (aq) solution.

OR

Neutral $FeCl_3$

Compound G forms a violet coloration.

Compound F does not form a violet coloration.

Or Na_2CO_3(aq)

Compound F produces effervescence of CO_2 that produce white ppt in aqueous $Ca(OH)_2$.

Compound G has no effervescence of CO_2

[Total: 19 marks]

Section B

4 (a) (i) *Use of 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.

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $\quad E^{\theta} = +1.36V$

$Br_2 + 2e^- \rightleftharpoons 2Br^-$ $\quad E^{\theta} = +1.07V$

$I_2 + 2e^- \rightleftharpoons 2I^-$ $\quad E^{\theta} = +0.54V$

Reactivity of the halogen as oxidizing agents decreases down the group as is evident in the less positive $E^{\ominus}$ value down the group. The less positive the $E^{\ominus}$ value, the less tendency of halogen to accept electrons to become reduced hence it is a weaker oxidising agent.

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

Can choose any of these reactions:

(i) displacement reaction

Chlorine can displace iodine/oxidise iodide **from aq solution of iodide**, **Colourless solution turns brown**.

$Cl_2 + 2I^- \longrightarrow I_2 + 2\,Cl^-$

Iodine cannot displace chlorine from aq soluton of chlorde. The brown solution of iodine remains.

OR

(ii) reaction with Na

$Cl_2 + 2Na \rightarrow 2NaCl$ **vigorous** reaction; heating needed only to initiate

$I_2 + 2Na \rightarrow 2NaI$ **very slow** reaction even when heated

(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]**

Let the solubility be x = 0.0180x10/78.1 = 2.30x 10^{-4} mol dm^{-3}

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

$K_{sp} = [Ca^{2+}][F^-]^2$

$= x(2x)^2$

$= 4x^3$

$= 4(2.30 \times 10^{-4})^3 \text{ mol}^2\text{dm}^{-6}$

$= 4.87 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$

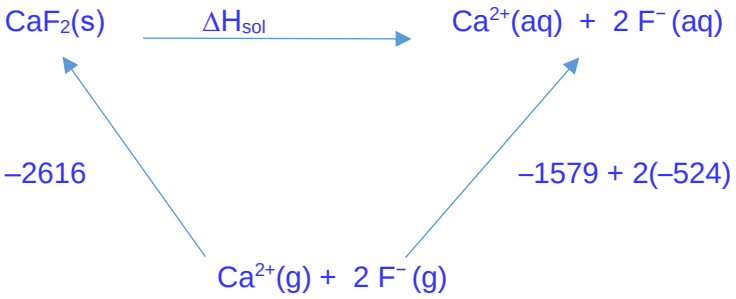
expression

K_{sp} value + units

(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



OR

$\Delta H_{sol} = -LE + \Sigma\Delta H_{hyd} = +2616 + [-1579 + 2(-524)]$

$= +2616 - 2627 = -11 \text{ kJmol}^{-1}$

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

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

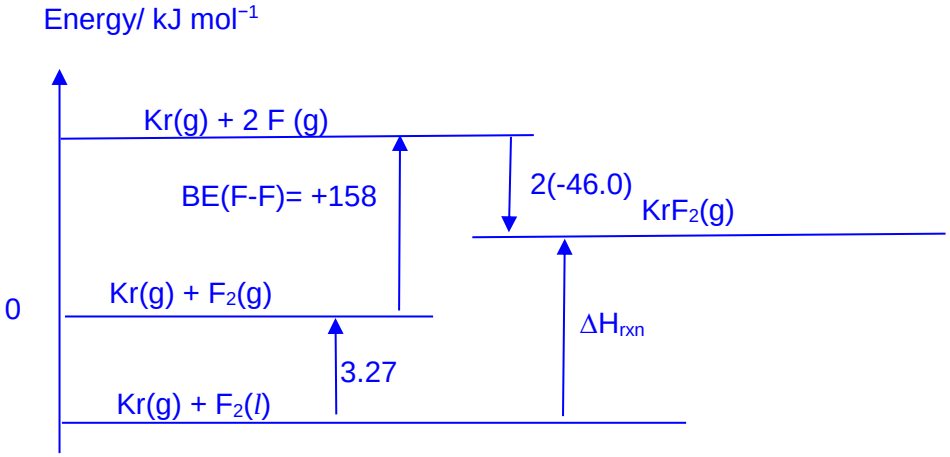
(i) Define the term *bond energy*. **[1]**

Bond energy is the enthalpy change/ energy required to break one mole of a covalent bond between two atoms in the gaseous state.

(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/kJmol^{-1}
Enthalpy change of vaporisation of fluorine	+ 3.27
Bond energy of Kr—F	+ 46.0

Table 4.2

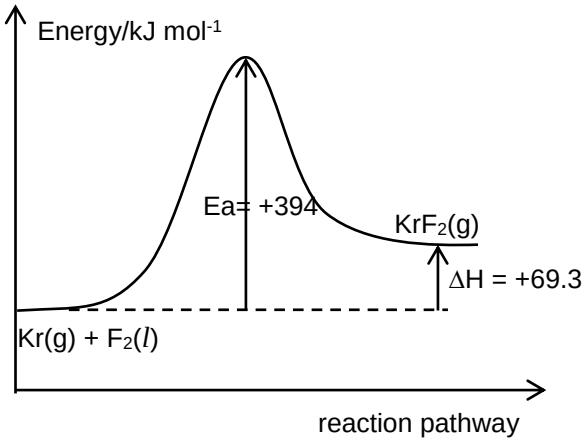


By Hess's Law $3.27+158+(-92) = \Delta H_{rxn}$

$\Delta H_{rxn} = +69.27 = +69.3$ kJmol^{-1}

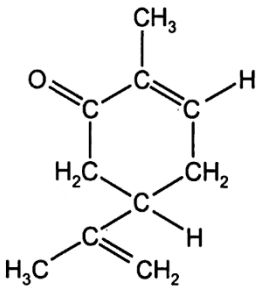
(iii) The activation energy, E_a, for Reaction (1) is +394 kJ mol^{-1}. **[1]**

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.



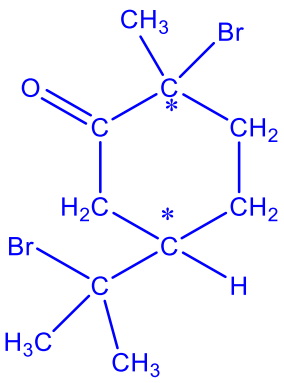
Correct axis and units with reactants and products and indication of E_a and ΔHr

(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 product. **[2]**

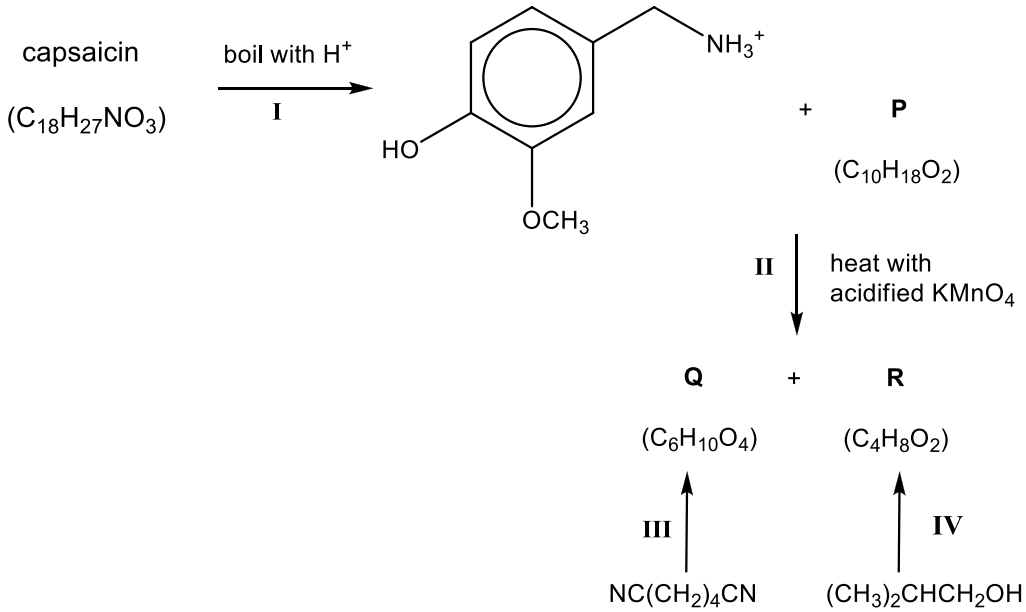


Structure

2 chiral centres are formed

(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]**

Alkene

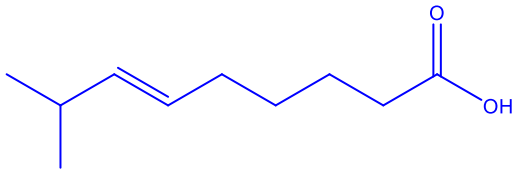
(ii) Suggest the reagent and conditions for reaction **IV**. **[1]**

$K_2Cr_2O_7$ or $KMnO_4/H_2SO_4$(aq), heat (under reflux)

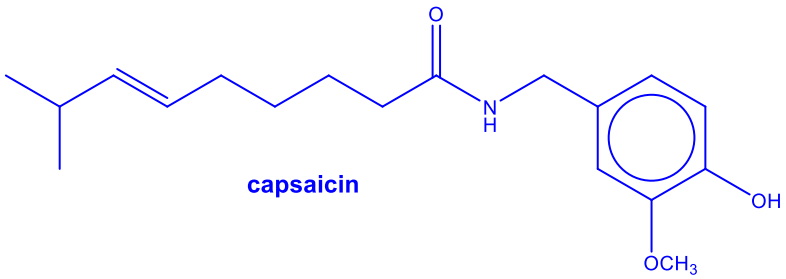
(iii) Name the *type of reaction* in reaction **III**. **[1]**

(Acidic) hydrolysis

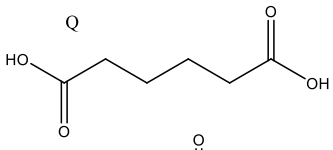
(iv) Suggest the structures of compound **P** and capsaicin. **[2]**

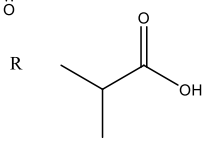


P



capsaicin





[Total: 20 marks]

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]**

Add dilute HCl and dilute NaOH separately to the sample of white powder

If the sample **dissolves in both**, then it is Al_2O_3.

$Al_2O_3 + 6\ HCl \rightarrow 2AlCl_3 + 3\ H_2O$

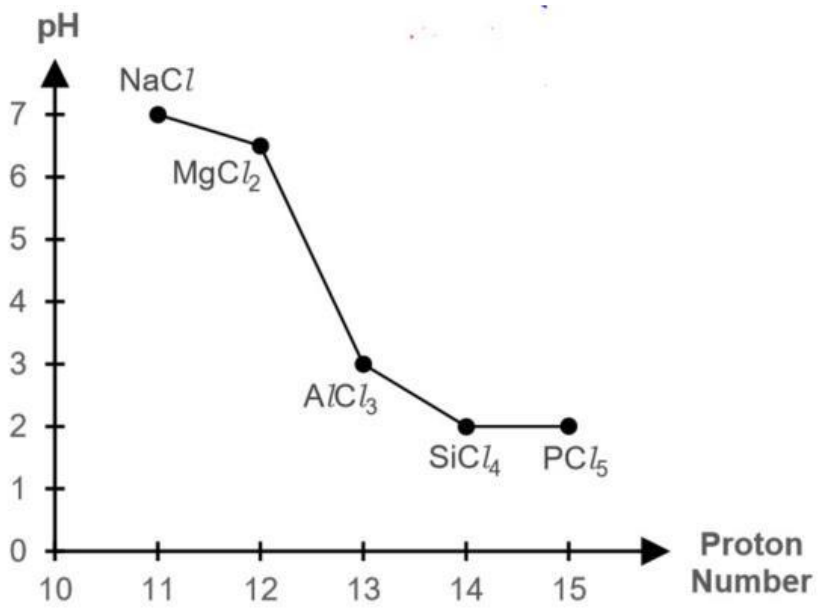
$Al_2O_3 + 2NaOH + 3\ H_2O \rightarrow 2NaAl(OH)_4$

If the sample **dissolves only in HCl(aq)**, it must be a basic oxide, which is MgO.

$MgO + 2\ HCl \rightarrow MgCl_2 + H_2O$

If the sample **does not dissolve in both**, then it is SiO_2

(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]**



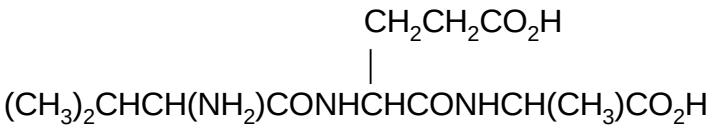
Diagram

$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$

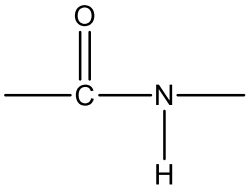
$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(OH)(H_2O)_5]^{2+} + H_3O^+$

$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5\,HCl(aq)$

(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]**



Peptide or amide linkage

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

(Prolonged) Heating with aqueous NaOH or aqueous H_2SO_4

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

$(CH_3)_2CHCH(NH_2)CO_2H$

$H_2NCH(CH_2CH_2CO_2H)CO_2H$

$H_2NCH(CH_3)CO_2H$

Neutral species or zwitterion acceptable, but if ionised form, must match reagents used in (ii). E.g. acidic hydrolysis shd have protonated species, basic hydrolysis shd have deprotonated species

(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]**

Any of the following

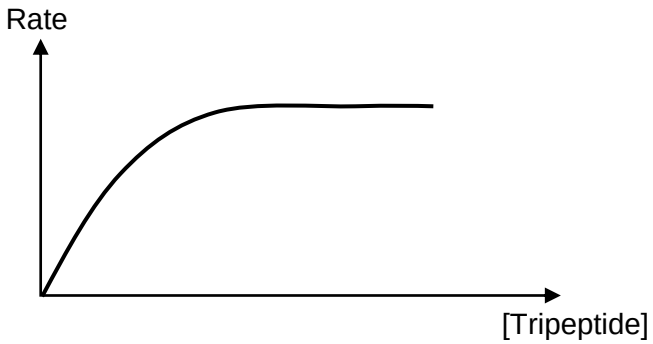
H_3N^+-CH(CH_3)-CO_2^- / $H_3N^+CH(CH_2CH_2CO_2H)CO_2^-$/ $(CH_3)_2CHCH(NH_3^+)CO_2^-$

How it acts as a buffer:

H_3N^+-CH(CH_3)-CO_2^- + **H^+** → H_3N^+-CH(CH_3)-CO_2H

H_3N^+-CH(CH_3)-CO_2^- + **OH^-** → H_2N-CH(CH_3)-CO_2^- + H_2O

(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]**

At low concentration of tripeptide,

- Rate of reaction increases linearly/reaction is first order wrt the concentration of tripeptide
- as active sites of the enzyme are not fully occupied

However, at high concentration of tripeptide,

- Rate of reaction is constant/rxn is zero order wrt the concentration of tripeptide
- as all active sites occupied

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

$C_6H_5CH_2Cl$ + H_2N-CH(CH_3)-CO_2H

step I ↓

$C_6H_5CH_2NH$-CH(CH_3)-CO_2H

step II ↓

$C_6H_5CH_2NH$-CH(CH_3)-$COCl$

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 *type of reaction* is step **I** and step **IV**? **[1]**

Step I Nucleophilic substitution
Step IV Reduction

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

Step II: PCl_5 or $SOCl_2$
Step IV: $LiAlH_4$ in dry ether

(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]**

K_b value of *Procaine* > K_b value of *Lidocaine*/pK_b value of *Procaine* < pK_b value of *Lidocaine*. For the 2 samples of equal concentration, number of free mobile ions for *Procaine* is greater than that of *Lidocaine.*

(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} HCl required to form a buffer solution of pH 7.5. **[2]**

Let B be Lidocaine

$HCl + B \rightarrow BH^+ + Cl^-$

Let *x* be the number of moles of HC*l* required, and v be the total volume.

$$pOH = pK_b + \lg \frac{[BH^+]}{[B]}$$

$$14 - 7.5 = 6.1 + \lg \frac{x/v}{(0.025 - x)/v}$$

$x = 1.789 \times 10^{-2}$ mol

Volume of HCl required $= \frac{1.789 \times 10^{-2}}{0.500}$

$= 3.578 \times 10^{-2}$ dm^3

$= 35.8$ cm^3

[Total 20 marks]