ST ANDREW'S JUNIOR COLLEGE
JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME					
CLASS	2	0	S		

CHEMISTRY

Paper 3 Free Response

9729/03

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.

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

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.

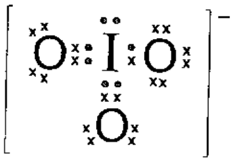
This document consists of **39** printed pages.

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]**

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 107° 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]

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

Step 2

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

$5H_2O_2 + I_2 \rightarrow 4H_2O + 2IO_3^- + 2H^+$ [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,

$$\frac{Rate_3}{Rate_1} = \frac{k[0.100]^1[0.140]^y[0.025]^z}{k[0.0500]^1[0.070]^y[0.025]^z}$$

$y = 1$

First order wrt $[IO_3^-]$

Comparing expt 1 and 2,

$$\frac{Rate_2}{Rate_1} = \frac{k[0.100]^1[0.070]^1[0.050]^z}{k[0.050]^1[0.070]^1[0.025]^z}$$

$z = 0$

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^{3}s^{-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

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

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

(ii) Explain how the value and sign of ΔG_r° would compare to the value and sign of ΔH° 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, $\Delta S^\circ > 0$.

Given that $\Delta H^\circ < 0$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, ΔG° will have a negative sign and be of a bigger value than ΔH°.

(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

$$\frac{4.00}{x+2(126.9+16.0\text{x}3)} = \frac{0.947}{x+16}$$

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

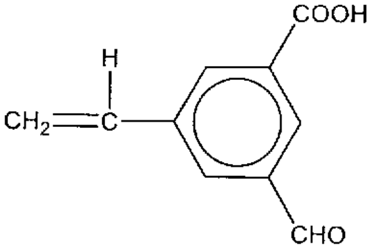
Ba^{2+} has larger ionic radius and hence has a lower charge density and lower polarising power.

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.

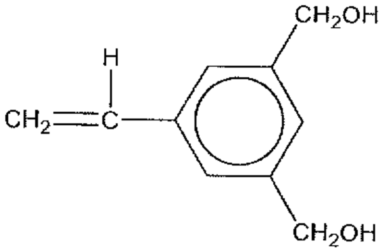
(a) Lithium aluminium hydride is often in reactions to reduce organic compounds. However, it is not the only reducing agent available, and different reducing agents work on different functional groups.



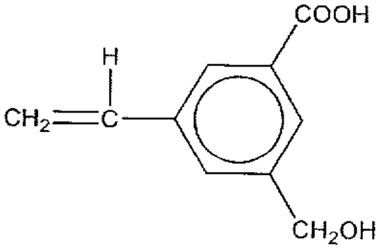
Compound **A**

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

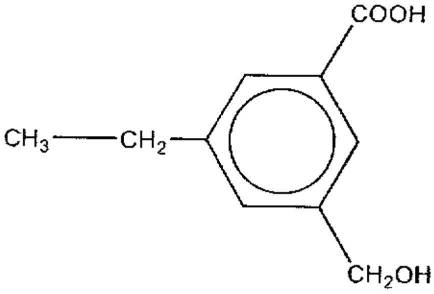
(i) LiA/H₄ **[1]**



(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.

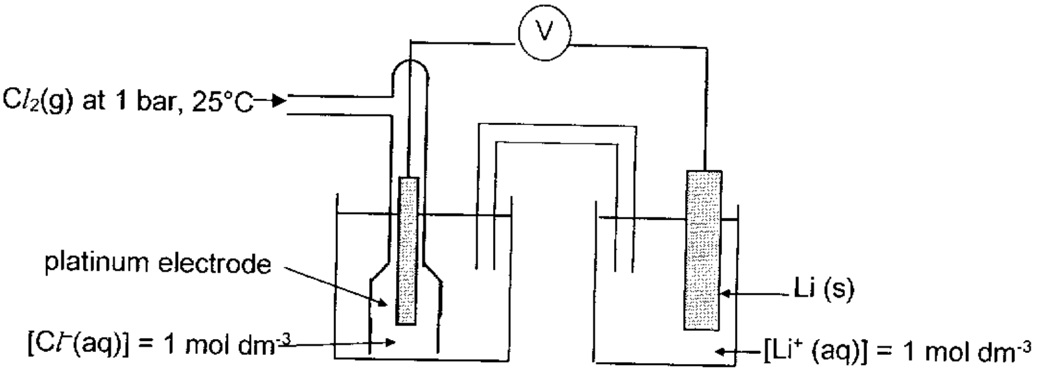


Fig 2.1

(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,

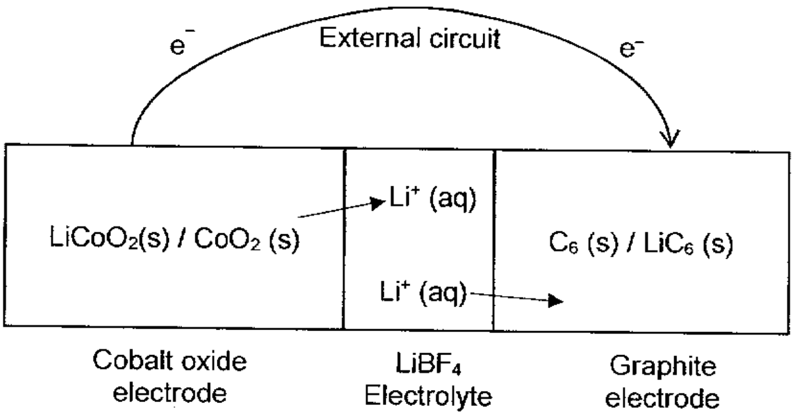
For the equilibrium $Cl_2 + 2e \rightleftharpoons 2Cl^-$,

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°_{cell} of the lithium cobalt oxide battery.

$CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2$ $E^\circ = +1.00V$

$Li^+ + C_6 + e^- \rightleftharpoons LiC_6$ $E^\circ = -3.00V$ **[1]**

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

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

$\Delta G^\circ = -nFE^\circ = -1 \times 96500 \times (+4.00)$

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

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

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

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

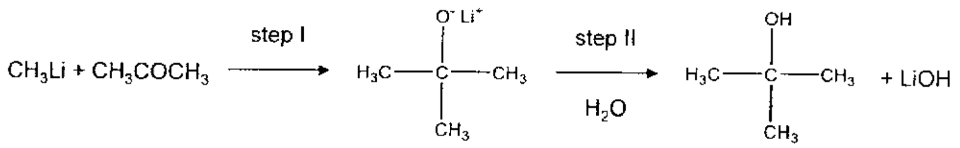
(ii) Based on your answers in **(a)(i)**, suggest why CH_3Li is formed by mixing Li and bromomethane in the ratio of 2:1. **[1]**

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.



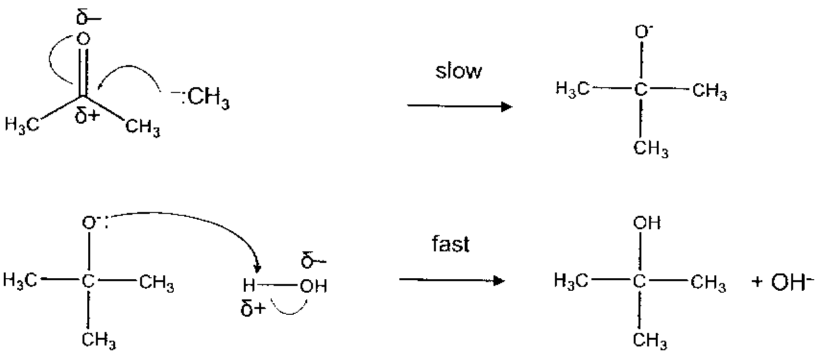
$$CH_3Li + CH_3COCH_3 \xrightarrow{\text{step I}} H_3C\text{—}\overset{O^-Li^+}{\underset{CH_3}{C}}\text{—}CH_3 \xrightarrow[H_2O]{\text{step II}} H_3C\text{—}\overset{OH}{\underset{CH_3}{C}}\text{—}CH_3 + LiOH$$

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

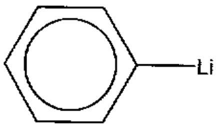
In your answer you should show all charges, dipoles and lone pairs and show the movement of electrons using curly arrows. **[3]**

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

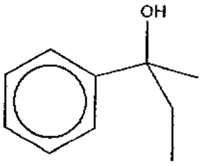
- lone pair on CH_3^- and O^-
- arrows on slow step
- arrows on fast step



(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)**.



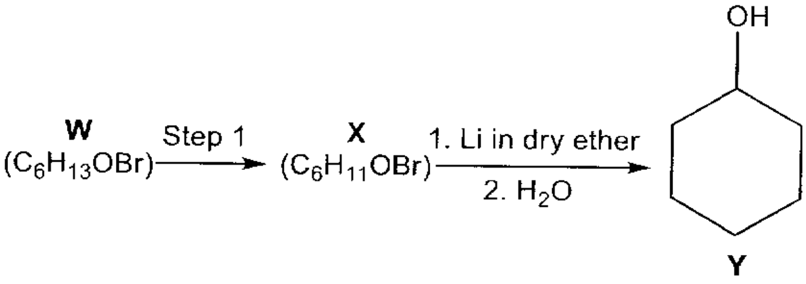
(ii) With reference to the mechanism identified in **(b)**, suggest whether the final product mixture in **(c)(i)** will rotate plane-polarised light. Explain why. **[2]**

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.

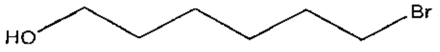
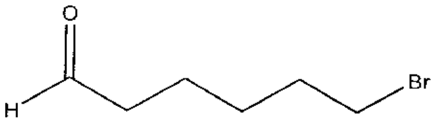
State the reagents and conditions for step 1, and draw the structures of **W** and **X**.



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.

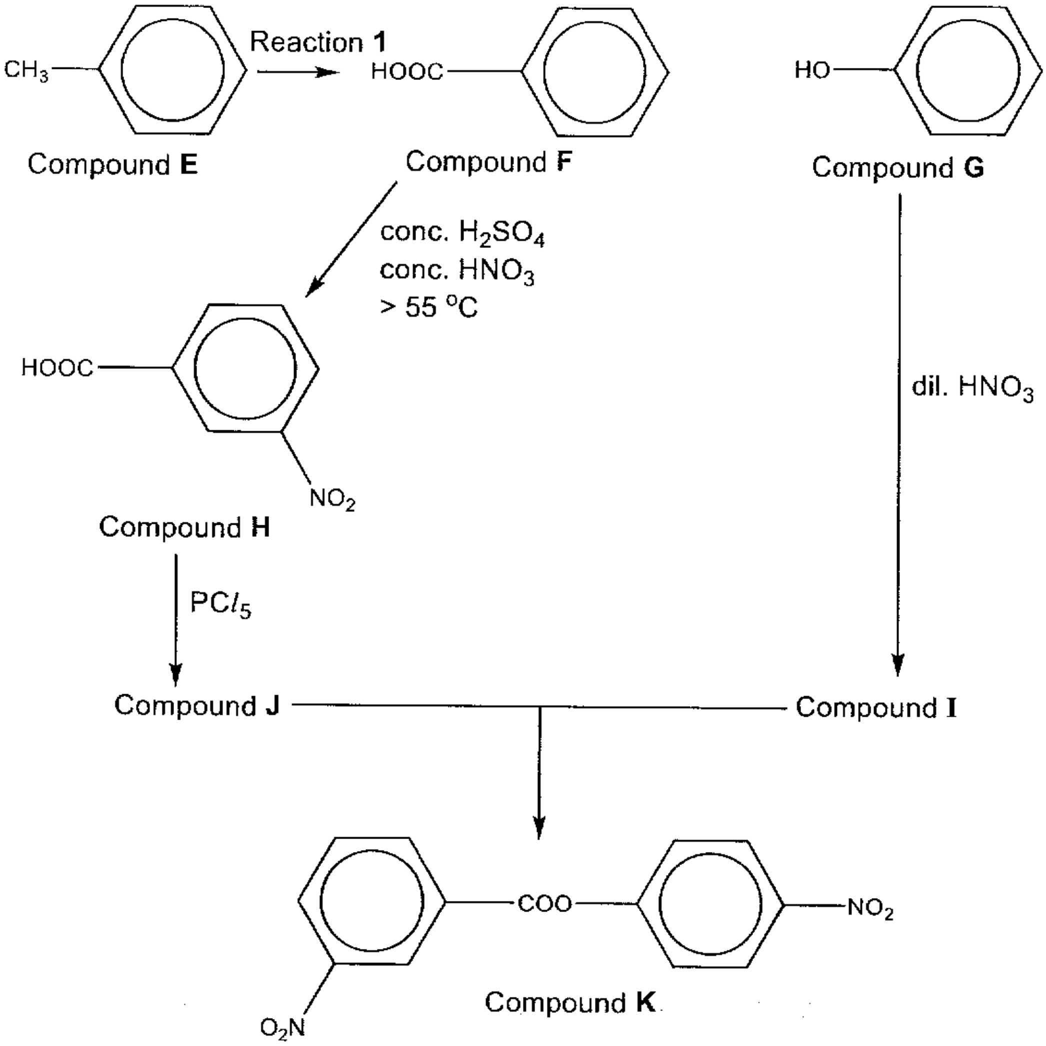
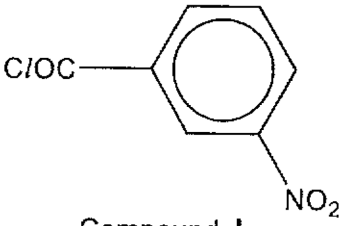
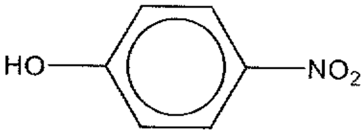


Fig 3.1

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



Compound **J**



Compound **I**

(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 $E^\ominus$ values.

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $\quad E^\ominus = +1.36V$

$Br_2 + 2e^- \rightleftharpoons 2Br^-$ $\quad E^\ominus = +1.07V$

$I_2 + 2e^- \rightleftharpoons 2I^-$ $\quad E^\ominus = +0.54V$

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 $x = 0.0180 x 10/78.1 = 2.30 x 10^{-4}\ mol\ dm^{-3}$

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

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

$= x(2x)^2$

$= 4x^3$

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

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

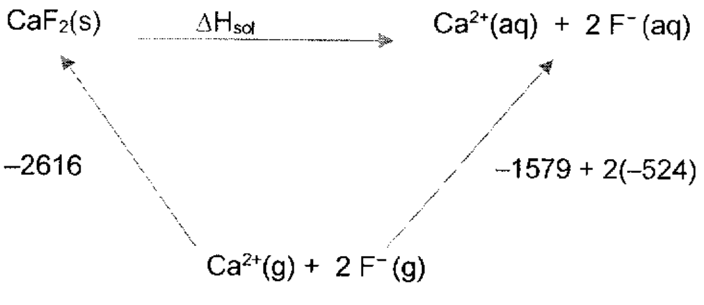
expression

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	**ΔH°/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

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

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

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

$Kr(g) + F_2(l) \rightarrow KrF_2(g)$ .... **Reaction (1)**

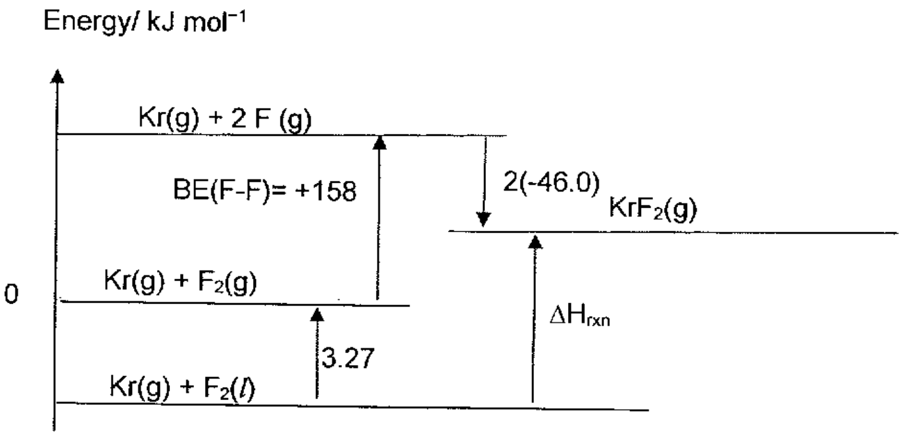
(i) Define the term *bond energy*. **[1]**

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

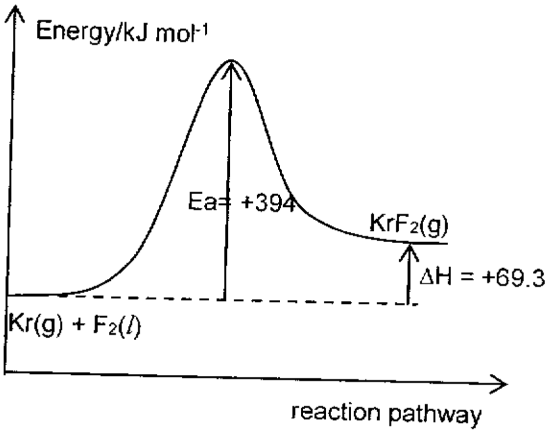


By Hess's Law $3.27+158+(-92) = \Delta H_{rxn}$

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

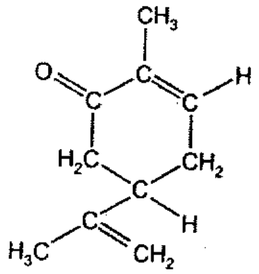
(iii) The activation energy, E_a, for Reaction (1) is +394 kJ mol^{-1}. **[1]**

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.



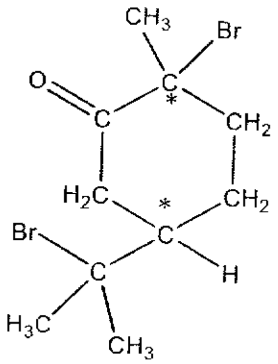
Correct axis and units with reactants and products and indication of E_a and ΔHr

(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]**

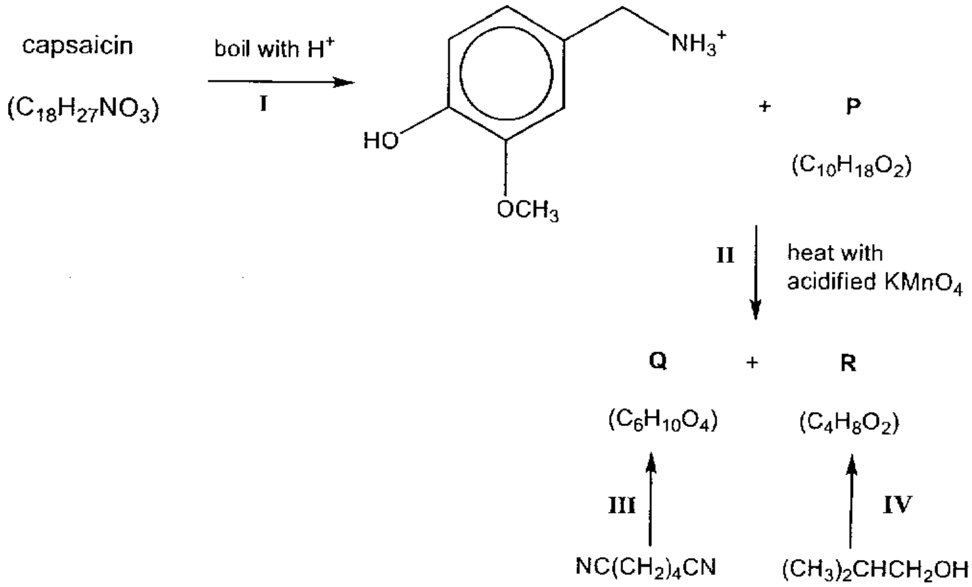


Structure

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

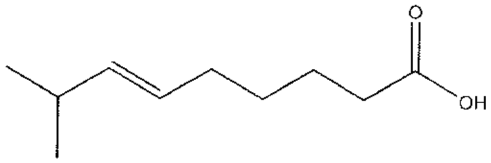
(ii) Suggest the reagent and conditions for reaction **IV**. **[1]**

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

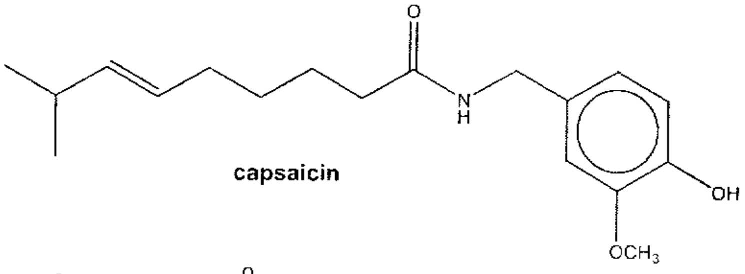
(iii) Name the *type of reaction* in reaction **III**. **[1]**

(Acidic) hydrolysis

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

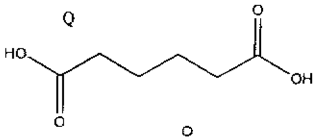


P

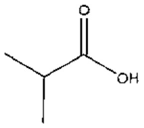


capsaicin

Q



R



[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.

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

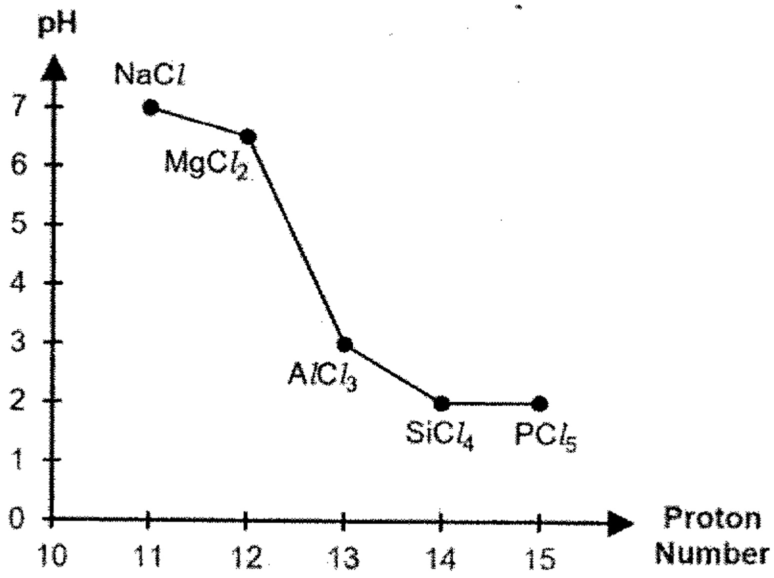
$Al_2O_3 + 2NaOH + 3\,H_2O \rightarrow 2NaAl(OH)_4$

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]**



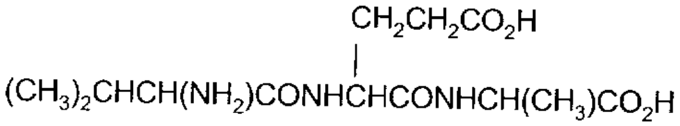
Diagram

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

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

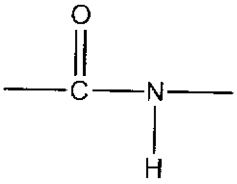
$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$

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



$$(CH_3)_2CHCH(NH_2)CONH\overset{\overset{\displaystyle CH_2CH_2CO_2H}{|}}{C}HCONHCH(CH_3)CO_2H$$

(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) **<u>Heating</u>** 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

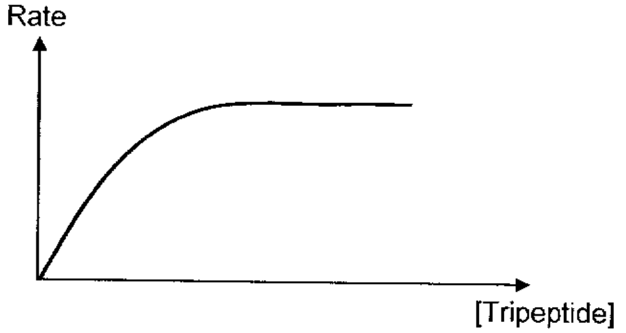
$H_3N^+\text{-}CH(CH_3)\text{-}CO_2^-$ / $H_3N^+CH(CH_2CH_2CO_2H)CO_2^-$/ $(CH_3)_2CHCH(NH_3^+)CO_2^-$

How it acts as a buffer:

$H_3N^+\text{-}CH(CH_3)\text{-}CO_2^- + \underline{H^+} \rightarrow H_3N^+\text{-}CH(CH_3)\text{-}CO_2H$

$H_3N^+\text{-}CH(CH_3)\text{-}CO_2^- + \underline{\mathbf{OH^-}} \rightarrow H_2N\text{-}CH(CH_3)\text{-}CO_2^- + H_2O$

(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**:

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

step I $\downarrow$

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

step II $\downarrow$

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

step III $\downarrow$ $H_2NCH_2CO_2H$

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

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 HCl 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 HC*l* required $= \frac{1.789 \times 10^{-2}}{0.500}$

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

$= 35.8$ cm^3

[Total 20 marks]

Name:		Class:	

ST ANDREW'S JUNIOR COLLEGE

JC 2 PRELIMINARY EXAMINATION

CHEMISTRY
Paper 4 Practical

9729/04
16 Aug 2021
2 hours 30 minutes

Additional Materials: Qualitative Analysis Notes

READ THESE INSTRUCTIONS FIRST.

Shift
Laboratory

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory in the boxes provided above.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.

The number of marks is given in the brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	13
2	18
3	10
4	14
Total	55

This document consists of **21** printed pages including this page.

1. Determination of the value of *x* in the oxyanion of iodine, IO_x^-

Iodine is able to form more than one oxyanion, IO_x^-, polyatomic ions that contain oxygen, each containing a different number of oxygen atoms.

In this experiment, you will determine the value of ***x*** in the oxyanion of iodine, IO_x^-. You will first react IO_x^- ions with an excess of iodide ions, I^-, to form iodine, I_2 as shown in equation 1.

equation 1 $$IO_x^- + \mathbf{y}\,I^- + \mathbf{z}\,H^+ \rightarrow \frac{1+y}{2} I_2 + \frac{z}{2} H_2O$$

where **x**, **y** and **z** are all integers

The amount of iodine produced will then be determined by titration with thiosulfate ions, $S_2O_3^{2-}$.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

FA 1 is a solution containing 0.0150 mol dm^{-3} IO_x^- ions.
FA 2 is dilute sulfuric acid, H_2SO_4.
FA 3 is 1.00 mol dm^{-3} potassium iodide, KI.
FA 4 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
starch indicator

(a) Procedure

1. Fill the burette with **FA 4**.
2. Pipette 25.0 cm^3 of **FA 1** into a conical flask.
3. Use a measuring cylinder to add 25 cm^3 of **FA 2** to the conical flask.
4. Use another measuring cylinder to add 10 cm^3 of **FA 3** to the conical flask. The solution will turn brown as iodine is produced.
5. Add **FA 4** from the burette until the solution in the conical flask turns yellow.
6. Add 5 drops of starch indicator to the conical flask. The solution will turn blue-black.
7. Continue to add more **FA 4** from the burette until the blue-black colour just disappears. This is the end-point of the titration.
8. Record your titration results, to an appropriate level of precision, in the space provided on page 3.
9. Repeat points 2 to 7 until consistent results are obtained.

1 (a) **Results**

☐ M1

☐ M2

☐ M3

[3]

(b) From your titrations, obtain a suitable volume of **FA 4**, to be used in your calculations. Show clearly how you obtained this value. **[2]**

☐ M4

☐ M5

volume of **FA 4** = ...

(c) (i) Calculate the number of moles of iodine formed when **FA 1** reacts with **FA 3**. **[1]**

☐ M6

number of moles of I_2 = ...

[Turn Over

1 (c) (ii) Calculate the number of moles of IO_x^- ions in 25.0 cm^3 of **FA 1**. [1]

M7

number of moles of IO_x^- ions = ...

(iii) Using equation 1 and your answers in **1(c)(i)** and **1(c)(ii)**, calculate the value of **y**. Show your working. [1]

(Note that **y** is an odd integer such as 1, 3, 5, 7 etc.)

M8

y = ...

[Turn Over

1 (c) (iv) Use your value of **y** in **1(c)(iii)** and considering the number of electrons transferred, determine the oxidation number of I in IO_x^- ion. Hence, determine the value of **x** in IO_x^- ion. **[2]**

M9

M10

oxidation number of I in IO_x^- ion = ...

x = ...

(v) A student suggested that a more accurate value of **x** could be obtained if a 10.0 cm^3 pipette was used to measure **FA 3** rather than the measuring cylinder. **[1]**

State whether you agree with the student. Explain your answer.

....

....

....

M11

[Turn Over

1 (c) (vi) Explain how the titre volume of $Na_2S_2O_3$ will change when the value of **x** in IO_x^- is greater. [1]

....

....

....

☐ M12

(d) Chlorine is also able to form more than one oxyanion, ClO_x^-. [1]

Similar to IO_x^-, oxyanions of chlorine are also oxidising agents. The table below shows the standard electrode potential of different chlorine oxyanions.

Electrode Reaction	**E° / V**
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	+0.89
$ClO_2^- + 2H_2O + 4e^- \rightleftharpoons Cl^- + 4OH^-$	+0.78
$ClO_3^- + 3H_2O + 6e^- \rightleftharpoons Cl^- + 6OH^-$	+0.63
$ClO_4^- + 4H_2O + 8e^- \rightleftharpoons Cl^- + 8OH^-$	+0.56
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

However, unlike IO_x^-, the value of **x** in the oxyanion of chlorine, ClO_x^- cannot be determined by reacting ClO_x^- with its corresponding halide, Cl^-.

Use the data given in the above table, explain why it is not possible to determine the value of **x** in the oxyanion of chlorine, ClO_x^-, with the reaction with Cl^-, under standard conditions.

....

....

....

M13

[Total: 13]

[Turn Over

2. **Investigation of the effect of [$S_2O_8^{2-}$] on the rate of reaction between I^- and $S_2O_8^{2-}$**

Sulfur forms the peroxodisulfate anion, $S_2O_8^{2-}$. This ion can oxidise iodide ions, I^-, to iodine, I_2, as shown in the equation.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

You will carry out a series of experiments to investigate how the rate of this reaction is affected by changing the concentration of the solutions.

The rate can be measured by adding thiosulfate ions, $S_2O_3^{2-}$, and starch indicator. As the reaction between $S_2O_8^{2-}$ and I^- occurs, iodine is produced. The I_2 produced reacts immediately with the thiosulfate.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

When all the thiosulfate has reacted, the iodine will remain in the mixture and cause the starch indicator to turn blue-black. The rate of reaction may be determined by measuring the time taken for the reaction mixture to turn blue-black.

FA 5 is 0.0200 mol dm^{-3} potassium peroxodisulfate, $K_2S_2O_8$.
FA 6 is 1.00 mol dm^{-3} potassium iodide, KI.
FA 7 is 0.00500 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
starch indicator

(a) (i) Procedure

Experiment 1

1. Use the marker to label one of the 100 cm^3 beakers '**A**' and the other 100 cm^3 beaker '**B**'.
2. Use the marker to label one of the measuring cylinders '**A**' and the other measuring cylinder '**B**'.
3. Use the measuring cylinder **A** to transfer 20.0 cm^3 of **FA 5** into beaker **A**.
4. Use the measuring cylinder **B** to add 20.0 cm^3 of **FA 6** into beaker **B**.
5. Use the measuring cylinder **B** to add 10.0 cm^3 of **FA 7** to beaker **B**.
6. Add 10 drops of starch indicator to beaker **B**.
7. Add the contents of beaker **A** to beaker **B**. Start the stopwatch during this addition.

[Turn Over

8. Stir the mixture **once** and place the beaker on a white tile.
9. Stop the stopwatch when the solution **first** turns blue-black.
10. Record this reaction time to the nearest second.
11. Wash out both beakers and shake to remove excess water.

Experiment 2

1. Use the measuring cylinder **A** to transfer 10.0 cm^3 of **FA 5** into beaker **A**.
2. Use the measuring cylinder labelled **A** to transfer 10.0 cm^3 of distilled water into beaker **A**.
3. Use the measuring cylinder **B** to add 20.0 cm^3 of **FA 6** into beaker **B**.
4. Use the measuring cylinder **B** to add 10.0 cm^3 of **FA 7** to beaker **B**.
5. Add 10 drops of starch indicator to beaker **B**.
6. Add the contents of beaker **A** to beaker **B**. Start the stopwatch during this addition.
7. Stir the mixture once and place the beaker on a white tile.
8. Stop the stopwatch when the solution **first** turns blue-black.
9. Record this reaction time to the nearest second.
10. Wash out both beakers and shake to remove excess water.

Experiments 3 to 5

Choose suitable volumes that will enable you to investigate further the effect of changing the concentration of potassium peroxodisulfate, **FA 5**, on the rate of the reaction.

Note that the total volume of **FA 5** and distilled water must always be constant. Do not use a volume of **FA 5** that is less than 6.0 cm^3.

The relative rate of the reaction can be calculated as shown.

$$\text{Relative rate} = \frac{900}{\text{reaction time}}$$

In the space provided, record in a single table for each of your five experiments:

- volume of **FA 5**
- volume of distilled water
- the reaction time
- the relative rate of the reaction

[Turn Over

For Examiner's Use

2 (a) (i) **Results**

☐ M14

☐ M15

☐ M16

☐ M17

☐ M18

[5]

(ii) Using data from **Experiments 1** and **2**, show by calculation that the volume of potassium peroxodisulfate, **FA 5**, used was directly proportional to the concentration of peroxodisulfate. You can ignore the volume of starch used. **[2]**

☐ M19

☐ M20

[Turn Over

For Examiner's Use

2 **(b)** **(i)** Use the grid below to plot a graph of rate against volume of **FA** 5. **[3]**

Include the origin in your plot.

M21

M22

M23

2 **(b)** **(ii)** Explain, by referring to your graph or your table of results, how the rate of reaction is affected by an increase in the concentration of potassium peroxodisulfate, **FA 5**. **[1]**

....

....

....

☐ M24

(iii) Use your graph to calculate the reaction time you would expect to measure if you carried out an experiment using 5.00 cm^3 of **FA 5**. Show on the graph how you obtained your answer. **[2]**

☐ M25

☐ M26

reaction time = ...

(iv) Assume that the error in the time measured for each reaction was ±0.5 s in total. Calculate the percentage error in the reaction time you measured in **Experiment 1**. Show your working. **[2]**

☐ M27

☐ M28

percentage error = ...

[Turn Over

2 (b) (v) A student suggested that this error could be reduced if 0.00200 mol dm^{-3} sodium thiosulfate was used in place of **FA 7**. Do you agree with this student? Explain your answer. **[1]**

....

....

....

M29

(vi) A student carries out the same investigation as in **2(a)(i)** but the solutions are mixed in a different order. The student places **FA 5** and an appropriate volume of distilled water in beaker **A**. He then added **FA 7** and starch into beaker **A**. He added **FA 6** last and started the stopwatch immediately. **[2]**

Tick the box for the statement you consider correct. Explain your answer.

The student's method is better than that in **(a)**.	☐
The two methods are equally good.	☐
The student's method is not as good as that in **(a)**.	☐

You may use the data in the table below to explain your answer.

Electrode Reaction	**E° / V**
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.09
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

Reason: ....

....

....

M30

M31

[Total: 18]

3. Planning

A student suggested that the temperature at which the experiment was carried out would also affect the rate of the reaction.

(a) Plan an investigation, based on the experiment described in **2(a)(i)**, to determine the effect of temperature on the rate of reaction. **[4]**

You may assume that you are provided with the same reagents as experiment **2(a)(i)** as well as the equipment normally found in a school laboratory

Give a step-by step description of how you would carry out the experiment by considering

- what you would keep constant in all the experiments,
- a suitable number of experiments you would do, and a reasonable temperature range,
- the apparatus that you would use in addition to that specified in **2(a)(i)**
- the procedure that you would follow and the measurements that you would take
- how you would determine the rate for each experiment.

....

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[Turn Over

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(b) The activation energy, E_A, for the reaction can be obtained using the "Arrhenius Equation".

$$k = Ae^{\frac{-Ea}{RT}}$$

where k is the rate constant at reaction temperature T in Kelvin, A is the frequency factor and R is the ideal gas constant (8.314 J $K^{-1}mol^{-1}$). A can be regarded as a constant for this experiment.

Taking the natural logarithm of the "Arrhenius equation", gives the following equation.

$$\ln k = \ln A - \frac{E_a}{R}(\frac{1}{T_K})$$

(i) Given that rate = k [reactants], state the relationship between k and the time taken for the reaction mixture to turn blue-black. **[1]**

……………………………………………………………………………… M36

………………………………………………………………………………

[Turn Over

For Examiner's Use

3 **(b)** **(ii)** Sketch a graph that you would use to determine the activation energy, E_A, for the reaction on the axes in **Figure 3.1**. Describe how you would use your graph to determine the value of E_A. **[3]**

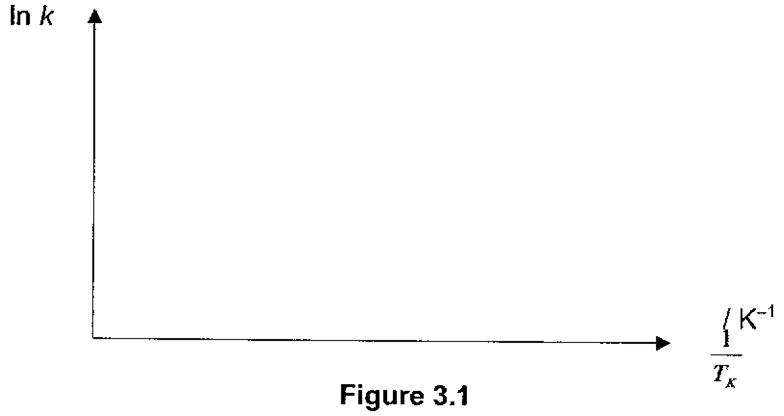


Figure 3.1

....

....

....

....

☐ M37

☐ M38

☐ M39

(iii) Briefly describe how you would use results obtained from **3(a)** to determine all necessary values in order to plot the graph in **3(b)(ii)**. You do **not** need to calculate any of the calculations. **[2]**

....

....

....

....

☐ M40

☐ M41

[Total: 10]

[Turn Over

4. **Investigation of some inorganic and organic reactions**

(a) **FA 8** is a mixture that contains two cations and two anions.

Distilled water was added to **FA 8**, where the mixture was stirred and then filtered. You are provided with the dried residue, **FA 9**, and the filtrate, **FA 10**, from this filtration process.

Carry out the tests described in **Table 4.1** and carefully record your observations in the table.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identity any gas evolved.

Table 4.1

	tests	observations
1.	(a) Add one spatula of **FA 9** into a dry boiling tube and add dilute hydrochloric acid until no further reaction occurs.	
	(b) To 1 cm depth of the solution from **test 1(a)** in another test tube, add aqueous sodium hydroxide dropwise until no further change is seen. **Keep the remaining solution from test 1(a) for 4(b)(iii).**	

M42

M43

M44

2.	To 1 cm depth of **FA 10** in a test tube, add aqueous ammonia dropwise until no further change is seen. Note: There is no need to perform this test.	Blue ppt formed, soluble in excess aqueous ammonia to form a dark blue solution.
3.	To another 1 cm depth of **FA 10** in a boiling tube, add a piece of aluminium foil and 2 cm depth of aqueous sodium hydroxide. Heat the mixture. Cool the mixture and filter.	
4.	Use a glass rod to transfer the residue in **test 3** into a test tube and add 2 cm^3 of **FA 2**.	

M45

M46

M47

[6]

(b) **(i)** Identify the cation that is **definitely** present in **FA 8** and **two possible** identities for the other cation present in **FA 8**. **[1]**

Cation that is **definitely** present: ....

Two possible identities for the other cation present: ....

M48

4 **(b)** **(ii)** Describe a test, which will allow you to determine which of the two possible cations that you listed in **4(b)(i)** is present in **FA 8**. **[1]**

....

....

....

M49

(iii) Perform the test you describe in **4(b)(ii)** using the remaining solution from **test 1(a)** of **Table 4.1**. Record your observations and hence deduce the other identity of the cation present in **FA 8**. **[1]**

....

....

M50

Cation is ....

(iv) Given that **FA 8** does not contain nitrite ions, NO_2^-, or sulfite ions, SO_3^{2-}, identify the two anions that are present in **FA 8**. Use evidence from your observations in **4(a)** to support your deduction. **[2]**

Anion: ....

Evidence: ....

....

M51

Anion: ....

Evidence: ....

....

M52

[Turn Over

4 (c) (i) Write an equation to show the change in observation in **test 4**. **[1]**

....

M53

(ii) The solution prepared in **test 4** can be used to prepare a reagent to test for the carbonyl functional group.
Use this information and the observation given in **Table 4.2** to plan an experiment using the reagent prepared in **test 4** to confirm the presence of aldehyde in 1 cm^3 of C_8H_8O.

In your plan you should include brief details of:

- the quantity and the identity of the reagent to be used
- the condition and apparatus you would use

Table 4.2

Test	Observation
	Brick red ppt is formed.

[1]

M54

(iii) A student carried out the plan in **4(c)(ii)** and obtained the expected observation to confirm the functional group in C_8H_8O. Draw the structure of C_8H_8O. **[1]**

M55

[Total: 14]

[Turn Over

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	*reaction with*	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt.. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

[Turn Over

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated on warming with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

Name:		**Class:**	

ST ANDREW'S JUNIOR COLLEGE

JC 2 PRELIMINARY EXAMINATION

CHEMISTRY 9729/04

Paper 4 Practical **16 Aug 2021**

2 hours 30 minutes

Additional Materials: Qualitative Analysis Notes

READ THESE INSTRUCTIONS FIRST.

Shift
Laboratory

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory in the boxes provided above.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.

The number of marks is given in the brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/ 13
2	/ 18
3	/ 10
4	/ 14
Total	/ 55

This document consists of **21** printed pages including this page.

1. **Determination of the value of *x* in the oxyanion of iodine, IO_x^-**

Iodine is able to form more than one oxyanion, IO_x^-, polyatomic ions that contain oxygen, each containing a different number of oxygen atoms.

In this experiment, you will determine the value of **x** in the oxyanion of iodine, IO_x^-. You will first react IO_x^- ions with an excess of iodide ions, I^-, to form iodine, I_2 as shown in equation 1.

equation 1 $IO_x^- + \mathbf{y}\, I^- + \mathbf{z}\, H^+ \rightarrow \frac{1+y}{2} I_2 + \frac{z}{2} H_2O$

where **x**, **y** and **z** are all integers

The amount of iodine produced will then be determined by titration with thiosulfate ions, $S_2O_3^{2-}$.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

FA 1 is a solution containing 0.0150 mol dm^{-3} IO_x^- ions.

FA 2 is dilute sulfuric acid, H_2SO_4.

FA 3 is 1.00 mol dm^{-3} potassium iodide, KI.

FA 4 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.

starch indicator

(a) Procedure

1. Fill the burette with **FA 4**.
2. Pipette 25.0 cm^3 of **FA 1** into a conical flask.
3. Use a measuring cylinder to add 25 cm^3 of **FA 2** to the conical flask.
4. Use another measuring cylinder to add 10 cm^3 of **FA 3** to the conical flask. The solution will turn brown as iodine is produced.
5. Add **FA 4** from the burette until the solution in the conical flask turns yellow.
6. Add 5 drops of starch indicator to the conical flask. The solution will turn blue-black.
7. Continue to add more **FA 4** from the burette until the blue-black colour just disappears. This is the end-point of the titration.
8. Record your titration results, to an appropriate level of precision, in the space provided on page 3.
9. Repeat points 2 to 7 until consistent results are obtained.

[Turn Over

Results **[3]**

Initial burette reading /cm^3	0.00	0.00	
Final burette reading /cm^3	25.60	25.70	
Volume of **FA 4** /cm^3	25.60	25.70	

- Correct headers, units and final burette reading greater than initial burette reading
- Correct precision to 2 d.p
- 2 consistent values within ±0.10 cm^3

(b) From your titrations, obtain a suitable volume of **FA 4**, to be used in your calculations. Show clearly how you obtained this value. **[2]**

Volume of **FA 4** = $\frac{25.60 + 25.70}{2}$ = 25.65 cm^3

- Correct calculation of average titre volume to 2 d.p and correct calculation of volume of **FA 4** in the titration table
- Accuracy

volume of **FA 4** = ...

(c) **(i)** Calculate the number of moles of iodine formed when **FA 1** reacts with **FA 3**. **[1]**

Number of moles of I_2 = ½ x (25.65 / 1000 x 0.1)
= 1.28 x 10^{-3}

number of moles of I_2 = ...

(ii) Calculate the number of moles of IO_x^- ions in 25.0 cm^3 of **FA 1**. **[1]**

Number of moles of IO_x^- ions = 25 / 1000 x 0.015 = 3.75 x 10^{-4}

number of moles of IO_x^- ions = ...

[Turn Over

(iii) Using equation 1 and your answers in **1(c)(i)** and **1(c)(ii)**, calculate the value of **y**. Show your working. **[1]**
(Note that **y** is an odd integer such as 1, 3, 5, 7 etc.)

$$\frac{1.28 \times 10^{-3}}{3.75 \times 10^{-4}} = \frac{1+y}{2}$$

$y = 5.83 \approx 5$

y = ...

(iv) Use your value of **y** in **1(c)(iii)** and considering the number of electrons transferred, determine the oxidation number of I in IO_x^- ion. Hence, determine the value of **x** in IO_x^- ion. **[2]**

$IO_x^- + 5I^- + zH^+ \rightarrow 3I_2 + \frac{z}{2}H_2O$

$2I^- \rightarrow I_2 + 2e^-$

2 moles of I^- gives out 2 moles of electrons

$5I^- \rightarrow \frac{5}{2}I_2 + 5e^-$

<u>5 moles of I^-</u> gives out <u>5 moles of electrons</u>

<u>1 mole of IO_x^- gains 5 moles of electrons</u> to form I_2

Hence, <u>oxidation number of I in IO_x^- is +5</u>

$+5 + x(-2) = -1$

$x = 3$

oxidation number of I in IO_x^- ion = ...

x = ...

(v) A student suggested that a more accurate value of **x** could be obtained if a 10.0 cm^3 pipette was used to measure **FA 3** rather than the measuring cylinder. **[1]**
State whether you agree with the student. Explain your answer.
<u>I do not agree</u> as <u>KI is in excess</u> so precision of the apparatus does not matter.

[Turn Over

(vi) Explain how the titre volume of $Na_2S_2O_3$ will change when the value of **x** in IO_x^- is greater. **[1]**

When x is greater, higher amount of iodine will be produced, which require a higher titre volume of $S_2O_3^{2-}$.

(d) Chlorine is also able to form more than one oxyanion, ClO_x^-. **[1]**

Similar to IO_x^-, oxyanions of chlorine are also oxidising agents. The table below shows the standard electrode potential of different chlorine oxyanions.

Electrode Reaction	**E° / V**
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	+0.89
$ClO_2^- + 2H_2O + 4e^- \rightleftharpoons Cl^- + 4OH^-$	+0.78
$ClO_3^- + 3H_2O + 6e^- \rightleftharpoons Cl^- + 6OH^-$	+0.63
$ClO_4^- + 4H_2O + 8e^- \rightleftharpoons Cl^- + 8OH^-$	+0.56
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

However, unlike IO_x^-, the value of **x** in the oxyanion of chlorine, ClO_x^- cannot be determined by reacting ClO_x^- with its corresponding halide, Cl^-.

Use the data given in the above table, explain why it is not possible to determine the value of **x** in the oxyanion of chlorine, ClO_x^-, with the reaction with Cl^-, under standard conditions.

E^o_{cell} is negative for all reactions between ClO_x^- and Cl^-, hence reaction is not spontaneous / feasible.

[Total: 13]

[Turn Over

2. **Investigation of the effect of [$S_2O_8^{2-}$] on the rate of reaction between I^- and $S_2O_8^{2-}$**

Sulfur forms the peroxodisulfate anion, $S_2O_8^{2-}$. This ion can oxidise iodide ions, I^-, to iodine, I_2, as shown in the equation.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

You will carry out a series of experiments to investigate how the rate of this reaction is affected by changing the concentration of the solutions.

The rate can be measured by adding thiosulfate ions, $S_2O_3^{2-}$, and starch indicator. As the reaction between $S_2O_8^{2-}$ and I^- occurs, iodine is produced. The I_2 produced reacts immediately with the thiosulfate.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

When all the thiosulfate has reacted, the iodine will remain in the mixture and cause the starch indicator to turn blue-black. The rate of reaction may be determined by measuring the time taken for the reaction mixture to turn blue-black.

FA 5 is 0.0200 mol dm^{-3} potassium peroxodisulfate, $K_2S_2O_8$.
FA 6 is 1.00 mol dm^{-3} potassium iodide, KI.
FA 7 is 0.00500 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
starch indicator

(a) (i) Procedure

Experiment 1

1. Use the marker to label one of the 100 cm^3 beakers '**A**' and the other 100 cm^3 beaker '**B**'.
2. Use the marker to label one of the measuring cylinders '**A**' and the other measuring cylinder '**B**'.
3. Use the measuring cylinder **A** to transfer 20.0 cm^3 of **FA 5** into beaker **A**.
4. Use the measuring cylinder **B** to add 20.0 cm^3 of **FA 6** into beaker **B**.
5. Use the measuring cylinder **B** to add 10.0 cm^3 of **FA 7** to beaker **B**.
6. Add 10 drops of starch indicator to beaker **B**.
7. Add the contents of beaker **A** to beaker **B**. Start the stopwatch during this addition.

[Turn Over

8. Stir the mixture **once** and place the beaker on a white tile.
9. Stop the stopwatch when the solution **first** turns blue-black.
10. Record this reaction time to the nearest second.
11. Wash out both beakers and shake to remove excess water.

Experiment 2

1. Use the measuring cylinder **A** to transfer 10.0 cm^3 of **FA 5** into beaker **A**.
2. Use the measuring cylinder labelled **A** to transfer 10.0 cm^3 of distilled water into beaker **A**.
3. Use the measuring cylinder **B** to add 20.0 cm^3 of **FA 6** into beaker **B**.
4. Use the measuring cylinder **B** to add 10.0 cm^3 of **FA 7** to beaker **B**.
5. Add 10 drops of starch indicator to beaker **B**.
6. Add the contents of beaker **A** to beaker **B**. Start the stopwatch during this addition.
7. Stir the mixture once and place the beaker on a white tile.
8. Stop the stopwatch when the solution **first** turns blue-black.
9. Record this reaction time to the nearest second.
10. Wash out both beakers and shake to remove excess water.

Experiments 3 to 5

Choose suitable volumes that will enable you to investigate further the effect of changing the concentration of potassium peroxodisulfate, **FA 5**, on the rate of the reaction.

Note that the total volume of **FA 5** and distilled water must always be constant. Do not use a volume of **FA 5** that is less than 6.0 cm^3.

The relative rate of the reaction can be calculated as shown.

$$\text{Relative rate} = \frac{900}{\text{reaction time}}$$

In the space provided, record in a single table for each of your five experiments:

- volume of **FA 5**
- volume of distilled water
- the reaction time
- the relative rate of the reaction

[Turn Over

Results

Expt	Volume of FA 5 / cm^3	Volume of distilled water / cm^3	Time / s	Relative Rate / s^{-1}
1	20.0	0.0	15	60.0
2	10.0	10.0	30	30.0
3	15.0	5.0	20	45.0
4	12.0	8.0	26	34.6
5	8.0	12.0	36	25.0

[5]

- Correct headers and units
- 3 additional volumes chosen
  Intervals not less than 2.0 cm^3 and
  All volumes of **FA 5** between 6.0 – 20.0 cm^3
- Correct volume of deionised water used and rate calculated
- Time taken increases with decreasing volume of **FA 5**
- Correct precision recorded:
  - Volume of **FA 5** to 1 d.p
  - Volume of deionised water to 1 d.p
  - Time to whole number
  - rate to 3 s.f.

(ii) Using data from **Experiments 1 and 2**, show by calculation that the volume of potassium peroxodisulfate, **FA 5**, used was directly proportional to the concentration of peroxodisulfate. You can ignore the volume of starch used. **[2]**

Expt 1:

Since $C_1V_1 = C_2V_2$

$C_1 = 0.02$ mol dm^{-3} and $V_1 = 20$ cm^3 and $V_2 = 50$ cm^3

$\Rightarrow [S_2O_8^{2-}] = 2/5 \times 0.02 = 8.00 \times 10^{-3}$ mol dm^{-3}

Expt 2:

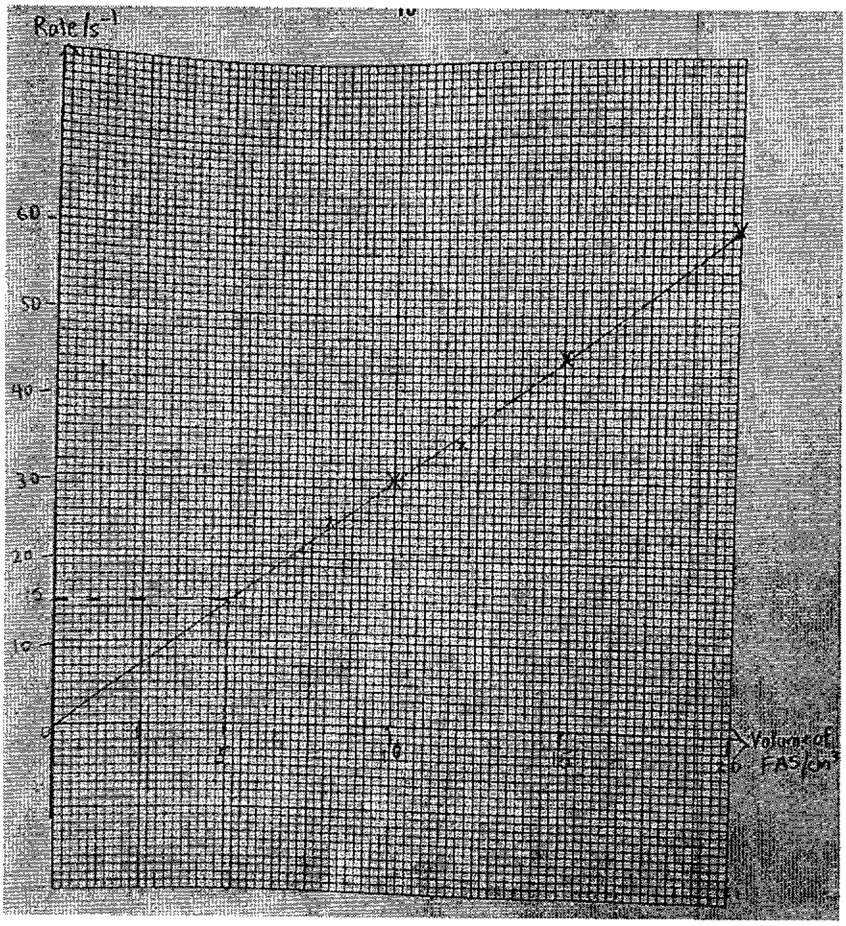
Since $C_1V_1 = C_2V_2$

$C_1 = 0.02$ mol dm^{-3} and $V_1 = 10$ cm^3 and $V_2 = 50$ cm^3

$\Rightarrow [S_2O_8^{2-}] = 1/5 \times 0.02 = 4.00 \times 10^{-3}$ mol dm^{-3}

When volume is doubled from 10 to 20 cm^3, [$S_2O_8^{2-}$] is doubled, hence volume of $S_2O_8^{2-}$ is directly proportional to [$S_2O_8^{2-}$].

(b) (i) Use the grid below to plot a graph of rate against volume of **FA 5**. **[3]**
Include the origin in your plot.



- Linear scales cover more than half the space in both directions including (0, 0).
- Axes correctly orientated and clearly labelled.
- Points plotted correctly.
- Points must be within half a small square of the correct position.
- Line of best fit drawn which ignores anomalous results identified by the candidate.
- The line may be straight or smooth curve AND use a minimum of 3 points.
- Reject if a point has been shown at the origin and the line of best fit does not pass within 5 small squares of (0,0).

[Turn Over

(b) **(ii)** Explain, by referring to your graph or your table of results, how the rate of reaction is affected by an increase in the concentration of potassium peroxodisulfate, **FA 5**. **[1]**

Straight line: Rate is proportional to concentration (of iodide ions) / proportional as line has a positive gradient.

Curve: As concentration / volume (of iodide ions) increases, rate increases more / not directly proportional as line is a curve / not a straight line.

OR

Table: Compares ratio of concentrations / volumes of FA 1 with ratio of rates. Directly proportional as rate doubled when volume doubled.

(iii) Use your graph to calculate the reaction time you would expect to measure if you carried out an experiment using 5.00 cm^3 of **FA 5**. Show on the graph how you obtained your answer. **[2]**

From graph, when volume = 5 cm^3, rate = 15.0 s^{-1}

Reaction time = $\frac{900}{rate}$

= $\frac{900}{15}$

= 60.0 s

reaction time = ...

(iv) Assume that the error in the time measured for each reaction was ±0.5 s in total. Calculate the percentage error in the reaction time you measured in **Experiment 1**. Show your working. **[2]**

% error = $\frac{\pm 0.5}{15} \times 100\ \% = \pm\ 3.33\ \%$

percentage error = ...

[Turn Over

(v) A student suggested that this error could be reduced if 0.00200 mol dm^{-3} sodium thiosulfate was used in place of **FA 7**. Do you agree with this student? Explain your answer. **[1]**

The student is wrong as the reaction time will be shorter and hence the percentage error would be greater.

(vi) A student carries out the same investigation as in **2(a)(i)** but the solutions are mixed in a different order. The student places **FA 5** and an appropriate volume of distilled water in beaker **A**. He then added **FA 7** and starch into beaker **A**. He added **FA 6** last and started the stopwatch immediately. **[2]**

Tick the box for the statement you consider correct. Explain your answer.

The student's method is better than that in **(a)**.	☐
The two methods are equally good.	☐
The student's method is not as good as that in **(a)**.	☐

You may use the data in the table below to explain your answer.

Electrode Reaction	**E° / V**
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.09
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

Reason: ....

....

....

Not as good.

$S_2O_8^{2-}$ will react with $S_2O_3^{2-}$ and less $S_2O_3^{2-}$ will be left in the reaction mixture to react with iodine. Hence, time will decrease for each run.

OR

$S_2O_8^{2-}$ will react with $S_2O_3^{2-}$ and a lower concentration of $S_2O_8^{2-}$ results in a slower rate of producing iodine. Hence, time will increase for each run.

[Total: 18]

[Turn Over

3. **Planning**

A student suggested that the temperature at which the experiment was carried out would also affect the rate of the reaction.

(a) Plan an investigation, based on the experiment described in **2(a)(i)**, to determine the effect of temperature on the rate of reaction. **[4]**

You may assume that you are provided with the same reagents as experiment **2(a)(i)** as well as the equipment normally found in a school laboratory

Give a step-by step description of how you would carry out the experiment by considering

- what you would keep constant in all the experiments,
- a suitable number of experiments you would do, and a reasonable temperature range,
- the apparatus that you would use in addition to that specified in **2(a)(i)**
- the procedure that you would follow and the measurements that you would take
- how you would determine the rate for each experiment.

1. After step 2 and step 4 in **2(a)(i)**, place beaker A and beaker B in a temperature controlled water bath (A) at 10°C.
2. Use a thermometer (A) to measure and ensure the temperature in beaker A and beaker B is the same as the water bath before mixing. (P)
3. When both solutions have reached 10.0°C, add the contents of beaker **A** to beaker **B** and start timing immediately. (P)
4. Repeat the experiment with the same volume of **FA 5, FA 6, FA 7** and starch indicator (Q) used but at temperature 20.0°C, 30.0°C, 40.0°C, 50.0°C. (P, R)
5. Calculate rate $\alpha \frac{1}{time}$ at each temperature. (P)

Procedure (P)	1. Measure and ensure the temperature in beaker A and beaker B is the same as the water bath before mixing

[Turn Over

	2. Add the contents of beaker **A** to beaker **B** and start timing immediately 3. Repeat the experiment at at temperature 20.0°C, 30.0°C, 40.0°C, 50.0°C 4. Calculate rate at each temperature
Apparatus (A)	• Temperature controlled water bath • Thermometer
Reliability (R)	• Temperatures should be less than 100 °C and cover at least a 10°C range of temperatures
Quantity (Q)	• Same volume of **FA 5, FA 6, FA 7** and starch indicator Credit if made reference to Q2 and repeated steps 1 – 6.

(b) The activation energy, E_A, for the reaction can be obtained using the "Arrhenius Equation".

$$k = Ae^{\frac{-Ea}{RT}}$$

where k is the rate constant at reaction temperature T in Kelvin, A is the frequency factor and R is the ideal gas constant (8.314 J $K^{-1}mol^{-1}$). A can be regarded as a constant for this experiment.

Taking the natural logarithm of the "Arrhenius equation", gives the following equation.

$$\ln k = \ln A - \frac{Ea}{R}(\frac{1}{T_K})$$

(i) Given that rate = k [reactants], state the relationship between k and the time taken for the reaction mixture to turn blue-black. **[1]**

Since [reactants] are constant, rate α k

Since rate α **1/t,**

k α 1/t

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(ii) Sketch a graph that you would use to determine the activation energy, E_A, for the reaction on the axes in **Figure 3.1**. Describe how you would use your graph to determine the value of E_A. **[3]**

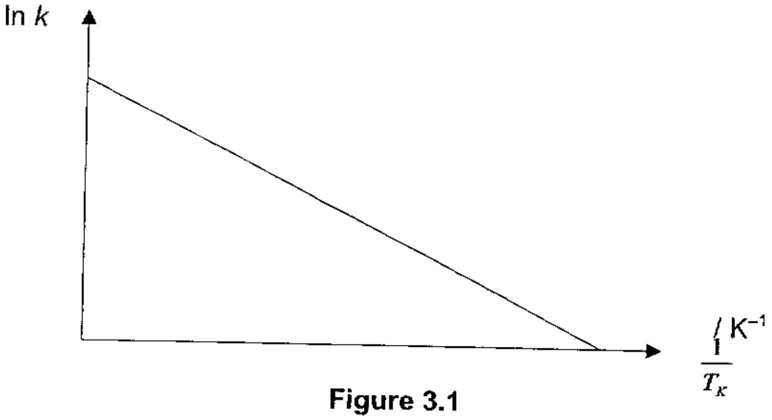

Figure 3.1

Calculate E_a by taking two sets of co-ordinates on the graph (x_1, y_1) and (x_2, y_2)

Find the gradient = $\frac{y_1 - y_2}{x_1 - x_2}$

Equate $\frac{y_1 - y_2}{x_1 - x_2} = -\frac{E_a}{R}$ and determine E_a by **multiplying –R with gradient**.

(iii) Briefly describe how you would use results obtained from **3(a)** to determine all necessary values in order to plot the graph in **3(b)(ii)**. You do **not** need to calculate any of the calculations. **[2]**

Since time $\alpha \frac{1}{rate}$ and rate α rate constant, k, calculate ln k by taking ln $(\frac{1}{t})$

Convert T/°C to T/K and calculate $\frac{1}{T_k}$

Expt	Time / s	ln k α ln $(\frac{1}{t})$	T/°C	T/K	$\frac{1}{T_k}$/ K^{-1}

[Total: 10]

[Turn Over

4. **Investigation of some inorganic and organic reactions**

(a) **FA 8** is a mixture that contains two cations and two anions.

Distilled water was added to **FA 8**, where the mixture was stirred and then filtered. You are provided with the dried residue, **FA 9**, and the filtrate, **FA 10**, from this filtration process.

Carry out the tests described in **Table 4.1** and carefully record your observations in the table.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identity any gas evolved.

Table 4.1

	tests	observations
1.	(a) Add one spatula of **FA 9** into a dry boiling tube and add dilute hydrochloric acid until no further reaction occurs.	Effervescence (✓) observed. White residue dissolved (✓) in HC*l* to form colourless solution. Gas evolved formed white ppt with $Ca(OH)_2(aq)$ / limewater (✓). Gas evolved is carbon dioxide (✓).
	(b) To 1 cm depth of the solution from **test 1(a)** in another test tube, add aqueous sodium hydroxide dropwise until no further change is seen. **Keep the remaining solution from test 1(a) for 4(b)(iii).**	White ppt (✓) formed, soluble in excess NaOH (aq) (✓) to form colourless solution.

[Turn Over

2.	To 1 cm depth of **FA 10** in a test tube, add aqueous ammonia dropwise until no further change is seen. Note: There is no need to perform this test.	Blue ppt formed, soluble in excess aqueous ammonia to form a dark blue solution.
3.	To another 1 cm depth of **FA 10** in a boiling tube, add a piece of aluminium foil and 2 cm depth of aqueous sodium hydroxide. Heat the mixture. Cool the mixture and filter.	Gas turned damp red litmus paper blue (✓). Gas evolved is ammonia (✓). Blue ppt turned into black / (dark) brown / grey ppt (✓). Black / (dark) brown / grey residue (✓) and blue / pale blue / colourless filtrate (✓).
4.	Use a glass rod to transfer the residue in **test 3** into a test tube and add 2 cm^3 of **FA 2**.	Black / (dark) brown / grey residue dissolved (✓) to form pale blue / colourless solution (✓).

[6]

(b) **(i)** Identify the cation that is **definitely** present in **FA 8** and **two possible** identities for the other cation present in **FA 8**. **[1]**

Cation that is **definitely** present: Cu^{2+}

Two possible identities for the other cation present:

Al^{3+} or Zn^{2+} or Pb^{2+}

(ii) Describe a test, which will allow you to determine which of the two possible cations that you listed in **4(b)(i)** is present in **FA 8**. **[1]**

Add 1 cm^3 aqueous ammonia. Al^{3+} forms white ppt that is insoluble in excess NH_3 (aq) while Zn^{2+} forms white ppt that is soluble in excess NH_3 (aq).

OR

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Add 1 cm^3 aqueous Na_2CO_3. Al^{3+} forms effervescence while Zn^{2+} does not form effervescence. Gas evolved formed white ppt with $Ca(OH)_2(aq)$ / limewater.

(iii) Perform the test you describe in **4(b)(ii)** using the remaining solution from **test 1(a)** of **Table 4.1**. Record your observations and hence deduce the other identity of the cation present in **FA 8**. **[1]**

White ppt formed is soluble in excess NH_3 (aq) to form a colourless solution.

Cation is Zn^{2+}.

(iv) Given that **FA 8** does not contain nitrite ions, NO_2^-, or sulfite ions, SO_3^{2-}, identify the two anions that are present in **FA 8**. Use evidence from your observations in **4(a)** to support your deduction. **[2]**

Anion: CO_3^{2-}

Evidence: CO_3^{2-} reacts with HCl to form CO_2, which gives white ppt with limewater.

Anion: NO_3^-

Evidence: NO_3^- reacts with NaOH and Al to give NH_3, which turns damp red litmus paper blue.

(c) **(i)** Write an equation to show the change in observation in **test 4**. **[1]**

$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$

Black residue Blue solution

OR

$CuO + 2H^+ \rightarrow Cu^{2+} + H_2O$

(ii) The solution prepared in **test 4** can be used to prepare a reagent to test for the carbonyl functional group.

Use this information and the observation given in **Table 4.2** to plan an experiment using the reagent prepared in **test 4** to confirm the presence of aldehyde in 1 cm^3 of C_8H_8O.

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In your plan you should include brief details of:

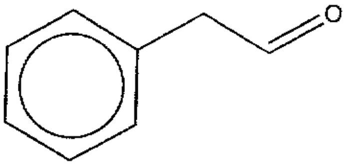
- the quantity and the identity of the reagent to be used
- the condition and apparatus you would use

Table 4.2

Test	Observation
To 1 cm^3 of C_8H_8O in a test-tube, add 1 – 2 cm^3 of Fehling's solution. Warm the mixture in a water bath for 3 – 5 min.	Brick red ppt is formed.

[1]

(iii) A student carried out the plan in **4(c)(ii)** and obtained the expected observation to confirm the functional group in C_8H_8O. Draw the structure of C_8H_8O. **[1]**



[Total: 14]

[Turn Over

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt.. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

[Turn Over

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple