2013 SRJC Prelim Paper H2 Chemistry P2 Suggested Solutions

1 Hard water, or water that contains high mineral content, such as calcium ions, pose serious problems in many industries. Other potential ions that could be present include zinc (through corrosion of pipings) and aluminium ions (whereby aluminium salts are added during the water purification process to start certain precipitation reactions).

You are provided with a water sample that may contain the cations Ca^{2+}, Al^{3+} and Zn^{2+}. The solution may also contain carbonate ions, CO_3^{2-}, and halide ions (either bromide or iodide).

You are given only the following to conduct your test.

Reagent	**Apparatus**
aqueous ammonia	tests tubes
aqueous sodium hydroxide	funnel
dilute sulfuric acid	filter paper

(a) Using the above only, write out a plan to separate each cation into three separate solutions.

In your plan you should:
- give a full description of the procedures you would use;
- indicate the expected observations in each step.

[5]

Steps	Test	Observations
1	Add **1 cm^3** of the sample solution into a **test tube**.	-
2	Add **excess** sodium hydroxide	**White ppt** of $Ca(OH)_2$ will be produced. There may be slight **dissolving** of white ppt when NaOH is added in excess due to presence of Al^{3+} and Zn^{2+} ions.
3	**Filter** any precipitate being formed.	**White ppt** of $Ca(OH)_2$ will be collected as residue. Al^{3+} and Zn^{2+} ions will be soluble and collected in the filtrate as $Al(OH)_4^-$ and $Zn(OH)_4^{2-}$ ions as a **colourless** solution.
4	Add **dilute sulfuric acid**	Effervescence may be seen if CO_3^{2-} is present.
5	Add aqueous ammonia in **excess**.	**White ppt** of $Al(OH)_3$ may be formed. **White ppt** of $Zn(OH)_2$ may be formed, which is **soluble in excess**.
6	**Filter** any precipitate being formed.	**White ppt** of $Al(OH)_3$ will be collected as residue. **Zn^{2+}** ions will be soluble and collected in the filtrate as $Zn(OH)_4^{2-}$ ions as a colourless solution.

	(b)	A student proposed to use concentrated sulfuric acid instead of dilute sulfuric acid in **(a)**.	
		(i)	Discuss how this change may affect the expected observations in **(a)**.
			In the presence of a halide ion, concentrated sulfuric acid will act as an **oxidising agent** and react with the halide ions. This will interfere with the results as the coloured halogens produced may **mask the white ppt** of the metal hydroxides formed.
		(ii)	Identify **one** potential safety hazard when the student make this change and state how you would minimise this risk.
		[4]	
		Concentrated sulfuric acid is a **corrosive acid**. The student may adopt any one of the following : 1. Conduct the experiment in a fume hood 2. Wear safety goggles and gloves to prevent any contact with the eyes and skin.	
	(c)	You are also required to identify the anions present in the solution.	
		(i)	Propose two reagents to identify and distinguish between CO_3^{2-} and halide ion.
			For CO_3^{2-}: dilute sulfuric acid. For halide ions: aqueous silver nitrate.
		(ii)	Outline how you would use your chosen reagents, including conditions, to determine the anions present in the solution. In your plan you should: $H_2O_2 = 0.03\ mol\ dm^{-3}$ • give a full description of the of the order of addi • quantity of reagent and apparatus used; • indicate the expected observations.
		[3]	
			To **1 cm^3** of the sample in a **test tube**, add **dilute sulfuric acid** first, followed by the **aqueous silver nitrate**. No marks for switching sequence as the ppt produced will mask the CO_2 effervescence being formed. Observations: Effervescence will be produced if carbonate ions are present. Ppt will be produced if halides are present: 1. For bromide: cream ppt of AgBr 2. For iodide: yellow ppt of AgI
			[Total : 12]

2 Iodometry is a technique used to analyse the concentration of an oxidising agent.

To a sample of hydrogen peroxide, excess but known amount of iodide is used which the oxidising agent oxidises the iodide to triiodide ion. The triiodide ion solution is then titrated against standard thiosulfate solution using starch indicator. The reactions are illustrated below.

Reaction 1 : $H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O$

Reaction 2 : $I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$

(a) Iodine exists as a black solid at standard conditions. An aqueous solution of iodine can only be prepared by dissolving iodine in excess potassium iodide, KI (aq) to form a dark reddish-brown solution.

(i) Suggest a reason for the insolubility of iodine in water.

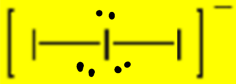
Iodine do have favourable interaction with water molecules as the extensive **<u>intermolecular VDW is incompatible with the hydrogen bonding between water</u>**, thus iodine does not dissolve in water.

(ii) Suggest with an equation, how the addition of excess potassium iodide aids in making iodine more soluble.

In the presence of excess KI, iodine dissolve due to complex formation:

$\mathbf{I^- + I_2 \rightleftharpoons I_3^-}$

(iii) Draw the structure of I_3^- formed and suggest its shape.



linear

[4]

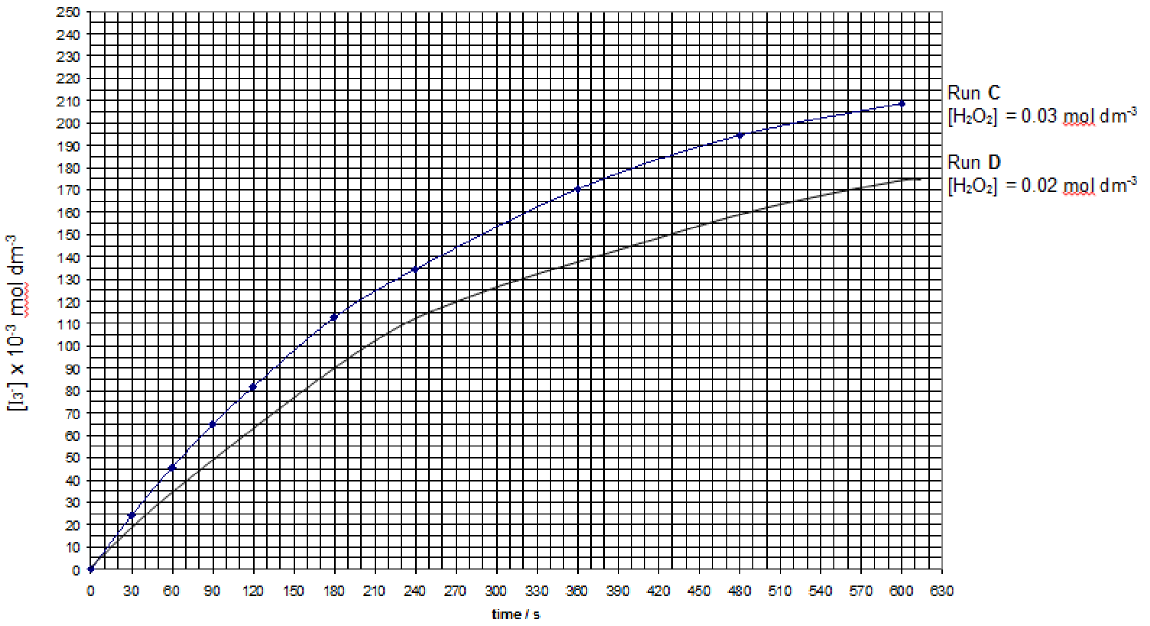
(b) 250 cm^3 of hydrogen peroxide was reacted with acidified iodide ions of various concentrations in a series of experiment named Run **C**.

The concentration of the triiodide liberated at respective times can be determined via the iodometric titration.

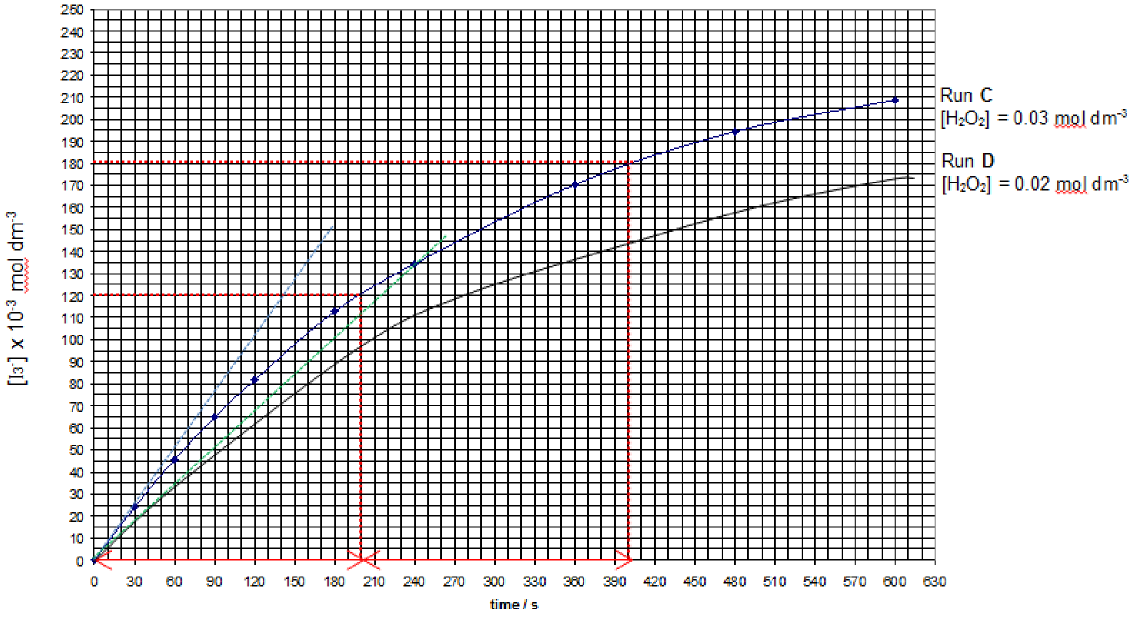
Run **C** was conducted with concentration of hydrogen peroxide held constant at 0.0300 mol dm^{-3} while varying the concentration of iodide. It is known that the rate of reaction is independent to hydrogen ions.

The rate of reaction can be measured by the increase in the concentration of triiodide formed over time and it was found out that the maximum concentration of triiodide produced was 240 x 10^{-3} mol dm^{-3} in Run **C**.

The concentration of hydrogen peroxide used in run **D** was 0.0200 mol dm^{-3}.



(i) Using the graph above and relevant information, determine the order of reaction with respect to hydrogen peroxide, iodide and hydrogen ion.



Consistent $t_{½}$ = 180 s observed when $[H_2O_2]$ is kept constant while varying $[I^-]$

Rate of reaction is independent to change in $[H^+]$
➔ **zero order w.r.t. H^+**

Taking Run C only, since $[H_2O_2]$ is constant at 0.30 and order of reaction is zero wrt H^+, the varied $[I^-]$ causes the product of $[I_3^-]$ to change.

Mentioned in the question the maximum concentration of $[I_3^-]$ obtained is 240 x 10^{-3} mol dm^{-3}, using half-life method from the graph **(show clear working on graph)**

Consistent half-life of 180 s was observed ➔ **1st order reaction wrt to I^-**

			Taking the initial rate for Run C and Run D where [I$^-$] are constant while [H_2O_2] is varied. Let rate = k [H_2O_2]^y[I$^-$] From Run C, initial rate = $\frac{50\times10^{-3}}{60}=8.33\times10^{-4}$ mol dm^{-3} s^{-1} From Run D, initial rate = $\frac{70\times10^{-3}}{120}=5.83\times10^{-4}$ mol dm^{-3} s^{-1} Comparing Run C and Run D: $\frac{rate_{runC}}{rate_{runD}}=\frac{k[I^-]\ [0.03]^y}{k[I^-]\ [0.02]^y}$ $\frac{8.33\times10^{-4}}{5.83\times10^{-4}}=\frac{k[I^-]\ [0.03]^y}{k[I^-]\ [0.02]^y}$ $\Rightarrow y=0.8$ $\Rightarrow y\approx1$ Therefore, order of reaction w.r.t. hydrogen peroxide = **1** Rate = k[H_2O_2][I$^-$] (not required by question)
		(ii)	In run **C**, the excess hydrogen peroxide was titrated with 10.00 cm^3 of 0.10 mol dm^{-3} of acidified potassium manganate(VII). Determine the total amount of triiodide formed.
			Amt of H_2O_2 initial = (250/1000) x 0.03 = 7.5 x 10^{-3} mol From the reaction b/w H_2O_2 and $KMnO_4$: $5H_2O_2 \equiv 2MnO_4^-$ Amt of MnO_4^- = (10/1000) x 0.10 = 1 x 10^{-3} mol Amt of H_2O_2 remaining = 5/2 x 1 x 10^{-3} = 2.5 x 10^{-3} mol Amt of H_2O_2 reacted = 7.5 x 10^{-3} – 2.5 x 10^{-3} = 5.0 x 10^{-3} mol $H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O$ Amt of I_3^- produced = **5.0 x 10^{-3} mol**
			[8]
			[Total : 12]

3 In the 1970s, a new compound, fukinolic acid, was isolated from the leaves, leaf stems, and flower stalks of the plant, *Petasites japonicus*. Hydrolysis of fukinolic acid produced other compounds, one of which is fukiic acid, $C_{11}H_{12}O_8$.

The data given in the table below are based on **1 mole** of **fukiic acid**.

Reaction	**Reagent**	**Amount required in mol**	**Observation(s)**
1	Potassium metal	6	Colourless gas collected. White solid formed which is soluble in water.
2	Dilute NaOH	4	Colourless solution formed.
3	$Cr_2O_7^{2-}$ / H^+ heat under reflux	1	Unknown compound X (M_r = 270) gives orange precipitate with Brady's reagent.
4	Thionyl chloride	4	Pungent choking gas Thick white fumes obtained which bleaches damp blue litmus.
5	Concentrated HNO_3	3	Yellow liquid formed.
6	$LiAlH_4$ in dry ether	2	Colourless solution formed.
7	Ethanolic $NaBH_4$	1	No reaction

In this question, when identifying the functional groups, your answers should be unambiguous.

(a) Comment if ***fukiic acid*** is aromatic.

[1]

From the given molecular formula, fukiic acid has **comparable no. of C and H atoms** and **at least 6 C atoms**, hence it has a **benzene ring (aromatic)**.

(b) **(i)** State the number of moles of gas formed in reaction **1**.

3 moles of H_2.

(ii) List the likely functional groups present in reaction **1**.

alcohol, phenolic, and carboxylic acid groups

(iii) Which of the functional group(s) you have named in **(b)(ii)** is confirmed by reaction **4**?

[4]

Fukiic acid undergoes nucleophilic substitution with 4 moles of $SOCl_2$.
Fukiic acid has **2 phenolic groups** or (since only alcohol and carboxylic acid groups react with $SOCl_2$)

(c) **(i)** What is the type of reaction taking place in reaction **2** ?

Neutralisation

(ii) What is the role of the reagents used in reactions **6** and **7**?

Reducing agent

(iii) Suggest possible reason(s) to the difference in the observations made in reactions **6** and **7**.

$NaBH_4$ is not selective enough to reduce the carboxylic acid groups present. / $NaBH_4$ selectively reduces carbonyl compounds and there are no carbonyl compounds present in fukiic acid.

(iv) State which reaction, other than reaction **2**, confirms your deduction of the functional group present in ***fukiic acid***.

Explain your rationale clearly.

[5]

In **reaction 2**, fukiic acid has **2 carboxylic acid groups** (since only phenolic and carboxylic acid groups react with NaOH).

In **reaction 6**, only $LiAlH_4$ is selective enough a reducing agent to reduce carboxylic acids.

(d) **(i)** Deduce the molecular formula of unknown **X** formed in reaction **3**.

$C_{11}H_{10}O_8$

(ii) What type of reaction takes place when Brady's reagent is added to unknown **X** ?

Condensation

(iii) Suggest the functional group(s) present in **(d)(ii)** and make clear, logical deductions from reaction **3** only.

[5]

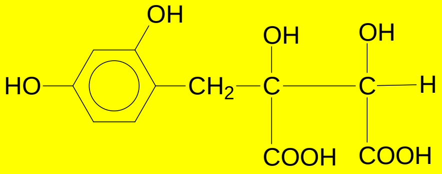
Carbonyl/ketone

Fukiic acid has 1 secondary alcohol and 1 tertiary alcohol group

[since from the formula no O was added (hence no primary alcohol resent as it wouuld be oxidized to carboxylic acid) and only 2H were removed (hence only 1 secondary alcohol and the remaining alcohol group must be tertiary].

(f) You now have enough information to determine the structural formula of ***fukiic acid***.

(i) Propose the structure of ***fukiic acid***.



Structure of fukiic acid

[Other possible structures are acceptable as long as they have 2 phenolic groups on positions 1 and 3, 2 carboxylic acid groups, 1 secondary alcohol and 1 tertiary alcohol]

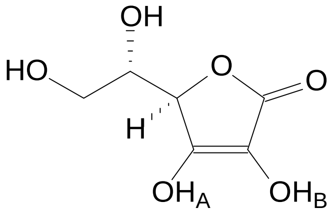
(ii) Explain clearly why you have placed the functional groups in their particular positions.

[2]

From reaction 5, multiple electrophilic substitutions can take place on the ring. Since 3 moles of conc HNO_3 are reacted, this suggests that the **phenolic groups** must be on **positions 1 and 3** and the **side chain** must be at **position 4**.

[Total : 17]

4 Ascorbic acid is an antioxidant commonly found in fruits, better known as vitamin C. Its structure is as shown below.



ascorbic acid
(M_r = 176.0)

When ascorbic acid dissociates in aqueous solution, the proton labelled H_A is released to form the ascorbate ion.

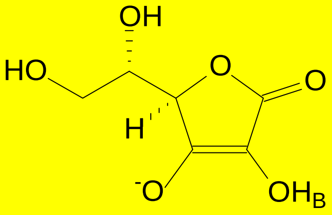
Values of the acid dissociation constant, K_a, for ascorbic acid and other organic acids are given below.

acid	**formula**	**K_a / mol dm^{-3}**
Ascorbic acid	given above	7.9×10^{-5}
Acetic acid	CH_3COOH	1.8×10^{-5}
Formic acid	HCOOH	1.8×10^{-4}

(a) **(i)** Write the acid dissociation constant expression for ascorbic acid.

$K_a = \frac{[RO^-]\,[H^+]}{[ROH]}$

where RO^- is



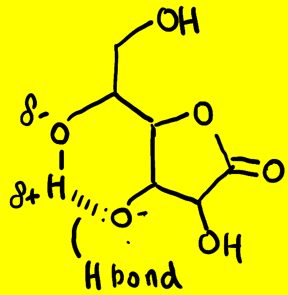
(ii) Hence or otherwise, calculate the pH of 0.5 mol dm^{-3} ascorbic acid.

$[H^+] = \sqrt{K_a \times c}$
$= \sqrt{7.9 \times 10^{-5} \times 0.5}$
$= 0.006285$ mol dm^{-3}
pH = –lg(0.006285) = <u>**2.20**</u>

(iii) With the aid of a labelled diagram, explain why H_A is the acidic proton.

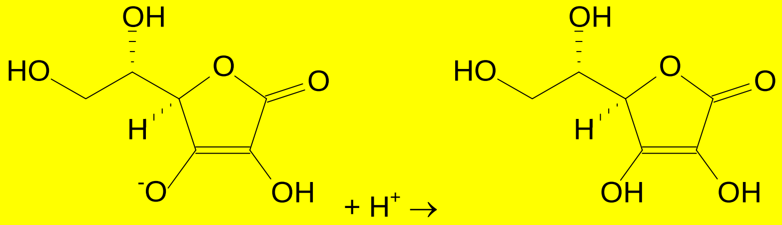
[5]

The conjugate base formed when H_A is released is stabilised via <u>intramolecular H bonding</u> as shown below.



(b) Kordel's Acid Free C is a health supplement that provides vitamin C in the form of the non-acidic calcium ascorbate. This is suitable for consumption by people with sensitive stomachs who are unable to tolerate vitamin C in its original acidic form.

(i) Write an equation to show how non-acidic vitamin C is effective in controlling acidity levels in the stomach.



(ii) Calculate the pH of a solution of ascorbic acid and calcium ascorbate at its optimal buffering capacity.

pH = pK_a = –lg(7.9×10^{-5}) = <u>**4.10**</u>

(iii) Given that the mass of ascorbic acid used to create the buffer solution in **(b)(ii)** is 5.00 g, find the change in pH when 0.01 g of calcium hydroxide is added to the buffer solution.

[4]

Initial amount of ascorbic acid = Initial amount of ascorbate ion
$= \frac{5.00}{176.0} = 0.02841$ mol

Amount of OH^- added = $\frac{0.01}{74.1} \times 2 = 2.700 \times 10^{-4}$ mol

$$\text{pH change} = \lg\frac{[ascorbate\ ion]}{[ascorbic\ acid]} = \lg\left(\frac{0.02841+2.700\times10^{-4}}{0.02841-2.700\times10^{-4}}\right) = \underline{\mathbf{0.00826}}$$

(c) Write balanced equations for any reaction that occurs when calcium ascorbate is added separately to acetic acid and formic acid. If nothing is formed, write 'no reaction' and explain your answer clearly.

[3]

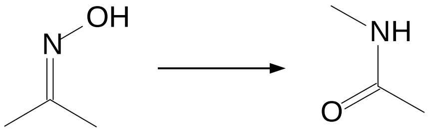
Let calcium ascorbate be $(RO)_2Ca$.

$CH_3COOH + (RO)_2Ca \rightarrow$ no reaction
$2HCOOH + (RO)_2Ca \rightarrow (HCOO)_2Ca + 2ROH$

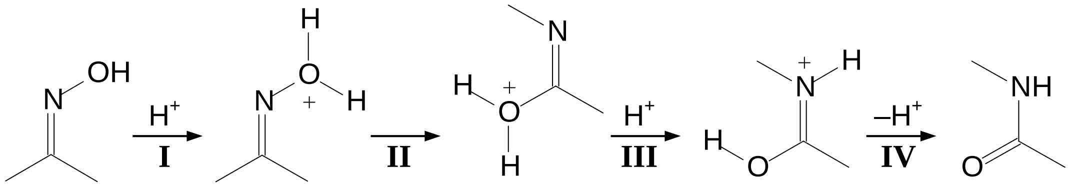
Formic acid is a stronger acid than ascorbic acid, since the K_a value of formic acid is larger than that of ascorbic acid. Hence, sodium ascorbate will undergo neutralisation with formic acid to form sodium formate and ascorbic acid.

[Total : 12]

5 **(a)** The Beckmann rearrangement reaction is one useful method of preparing amides by heating an oxime with concentrated sulfuric acid. An example for the synthesis of *N*-methylethanamide is shown below.



The reaction is thought to proceed via the following stages.



A

(i) Name the type of reaction occurring in step **I**.

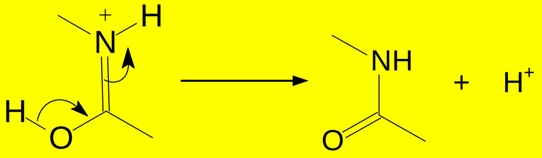
Neutralisation

(ii) State the oxidation number of nitrogen in compound **A**.

N: –1

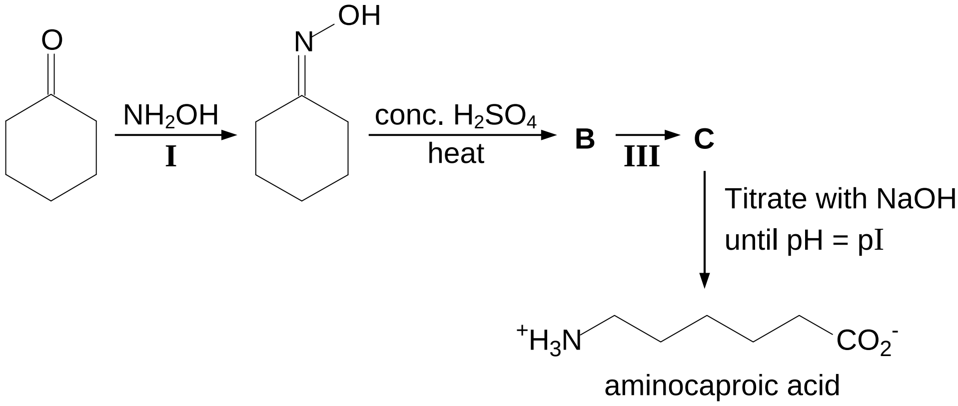
(iii) Outline the mechanism occurring in the step **IV**, showing clearly the movement of lone pairs of electrons with the use of curly arrows.

[3]



(b) Aminocaproic acid is commonly used to treat excessive postoperative bleeding.

The Beckmann rearrangement can be used as the second step in the synthesis of aminocaproic acid from cyclohexanone.



(i) Suggest the type of reaction occurring in step I.

Condensation

(ii) State the reagents and conditions used in step III.

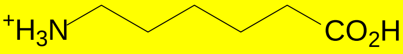
H_2SO_4(aq), heat

(iii) Draw the structures of compounds **B** and **C**.

[4]

B:

C:



[Total: 7]

6 **(a)** Group II alkali metal and its compounds are used extensively. In particular, strontium salts (such as oxides, nitrates and carbonates) are commonly used as an inexpensive colorant in pyrotechnics as they emit brilliant flames when combusted.

(i) State the colour emitted in the combustion of strontium salts.

Crimson Red / Brilliant Red/ Red.

(ii) Strontium carbonate acts as a weak Lewis base and can be used to produce strontium nitrate by simple use of the corresponding acid.

Write a chemical equation for the described chemical reaction.

$SrCO_3 + 2HNO_3 \rightarrow Sr(NO_3)_2 + CO_2 + H_2O$

(iii) 'Despite having similar thermal stabilities, carbonates are generally preferred over nitrates as they are not hygroscopic.'

Explain why nitrates are less preferred.

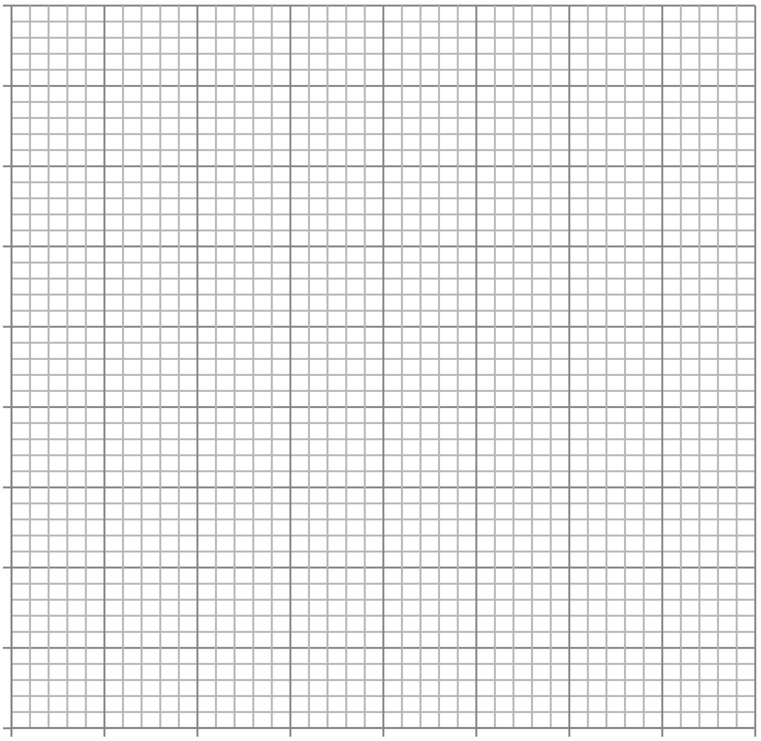
[3]

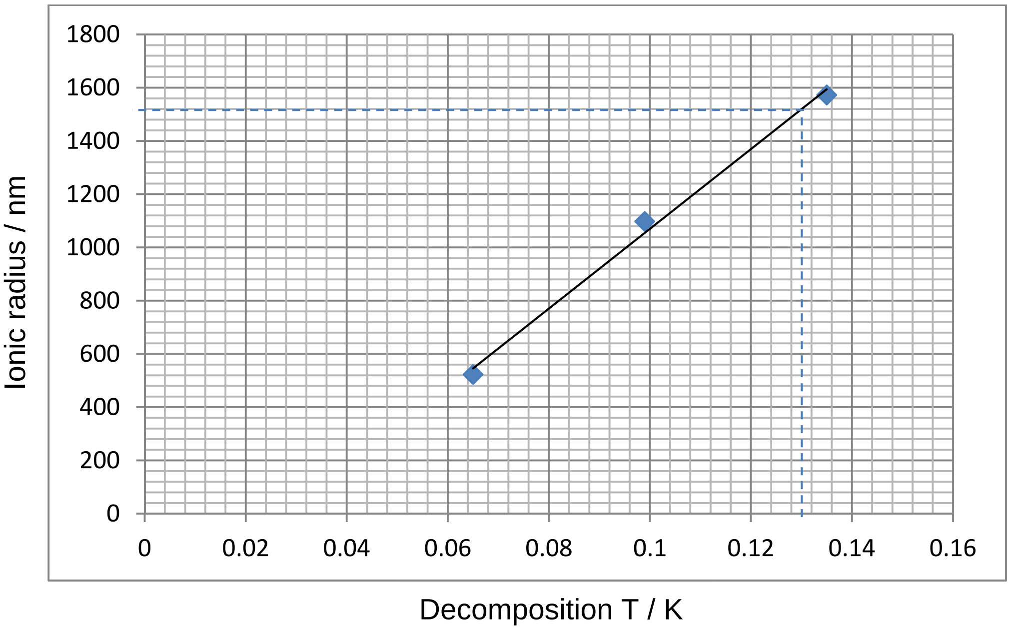
All **nitrates** are **soluble** hence more likely to absorb moisture in the air. The presence of water makes it more difficult to store as a desiccant, hence affects its performance.

(b) Group II carbonates decompose in a similar manner as the nitrates. The following table shows the temperature at which group II carbonates decompose.

Carbonate	**Ionic radius / nm**	**Decomposition temperature / K**
$MgCO_3$	0.065	523
$CaCO_3$	0.099	1098
$SrCO_3$	0.113	x
$BaCO_3$	0.135	1573

(i) Using the given data, plot a graph on the grid provided below for decomposition temperature against ionic radius.





(ii) From your graph, state the decomposition temperature of strontium carbonate.

Decomposition temperature of strontium carbonate = 1450 K

(iii) Using your plotted graph, comment on the trend of the thermal stability of group II carbonates.

As observed from the data, **decomposition temperature α thermal stability**.

Down group II,

- ionic size of cation increases
- charge density of cation decreases
- polarising power of cation decreases
- polarising effect on CO_3^{2-} anion decreases *or* the ability of the cation to distort the anion charge cloud of CO_3^{2-} decreases
- thermal stability of group II carbonates increases
- decomposition temperature increases

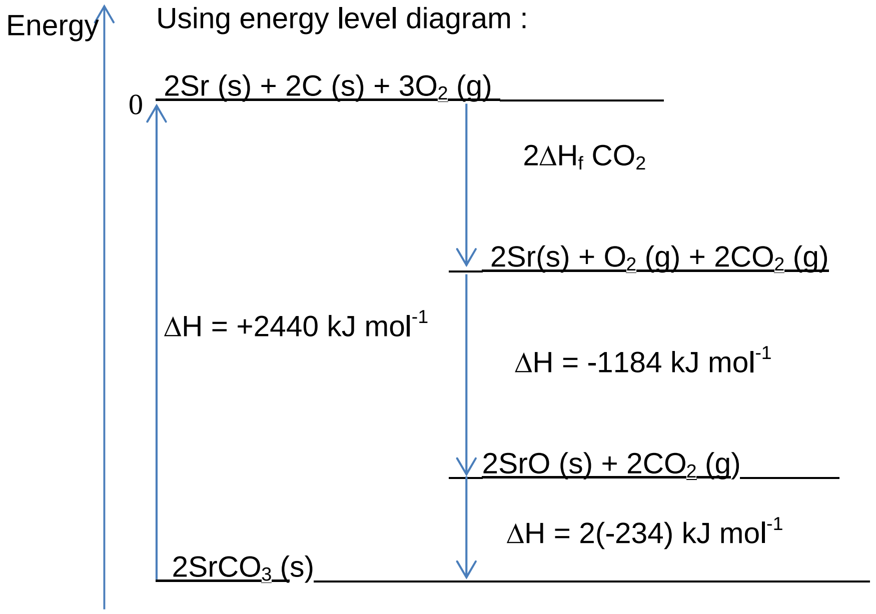
[6]

(c) Given the following information on strontium oxide and strontium carbonate, construct an energy level diagram to determine the enthalpy change of formation of carbon dioxide gas.

$SrO (s) + CO_2 (g) \rightarrow SrCO_3 (s)$	$\Delta H = -234 \text{ kJ mol}^{-1}$
$2SrO (s) \rightarrow 2Sr (s) + O_2 (g)$	$\Delta H = +1184 \text{ kJ mol}^{-1}$
$2SrCO_3 (s) \rightarrow 2Sr (s) + 2C (s) + 3O_2 (g)$	$\Delta H = +2440 \text{ kJ mol}^{-1}$

[3]

Using energy level diagram :



By Hess Law

$+ 2440 + 2\Delta H_f \, CO_2 - 1184 - 2(234) = 0$

$\Delta H_f \, CO_2 = -394 \text{ kJ mol}^{-1}$

[3]
[Total : 12]