NAME:___________________________ PDG:_________ Register No: ____

ANDERSON JUNIOR COLLEGE

Preliminary Examinations 2012

CHEMISTRY **9647/02**

Higher 2 **13 September 2012**

Paper 2 Structured Questions **2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **ALL** questions.
A Data Booklet is provided.

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

For Examiner's Use	
1	
2	
3	
4	
5	
Total	

This document consists of **20** printed pages.

1 Planning (P)

Suppose you are given a solution containing Zn^{2+}, Al^{3+}, Cl^- and I^- ions.

You are also provided with the following:

reagents	apparatus
· NaOH(aq),	· test tubes,
· NH_3(aq),	· filter funnel and
· HNO_3(aq),	· filter paper
· HC*l*(aq),	
· $AgNO_3$(aq) and	
· distilled water	

(a) **(i)** Name the reagent, from the list provided, that can be used to convert both the Cl^- and I^- ions to precipitates.

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(ii) Name another reagent, from the list provided, that can be used to dissolve one of the precipitates formed in **(a)(i)**.

…………………………………………………………………………………………………..

[2]

(b) Using the reagents you have identified in **(a)**, you are to devise a sequence of steps, by which the halides in the mixture could be separated such that each halide is present in a separate precipitate.

In your plan, you need to include details on the reagents you will use, expected observations and state the location of each anion (i.e. in a solution or precipitate) after each step. You may present your answer in the form of a table or flow chart.

[2]

(c) A small amount of dilute nitric acid is usually added before the addition of the reagent you have chosen in **(a)(i)**.

Suggest a reason why this is done.

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…….

[1]

(d) One of the cations present in the above mixture, Zn^{2+} or Al^{3+}, can be removed as a precipitate, on reaction with excess of *either* NaOH(aq) *or* NH_3(aq).

Identify the reagent to be added in excess and which cation, Zn^{2+} or Al^{3+}, can be removed as a precipitate. Explain your answer using relevant equations.

Reagent to be added in excess …………………………………………………………………….

Cation precipitated ……………………………………………………………………………..

Explanation…………………………………………………………………………………………….

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[2]

You are provided with 3 unlabeled bottles each containing one of the following organic halogen derivatives.

- bromobenzene, C_6H_5Br
- (bromomethyl)benzene, $C_6H_5CH_2Br$
- ethanoyl bromide, CH_3COBr

You are also provided with the following:

reagents	apparatus
· NaOH(aq),	· test tubes,
· NH_3(aq),	· filter funnel,
· HNO_3(aq),	· filter paper and
· HCl(aq),	· Bunsen burner
· $AgNO_3$(aq) and	
· distilled water	

(e) Outline a logical sequence of chemical tests that would enable you to identify each of the compounds.

You need to describe in a clear, stepwise manner, the tests used to identify each compound.

For each test, you need to include

- details on the reagents and conditions you will use,
- their quantities and
- the expected observations for each compound tested

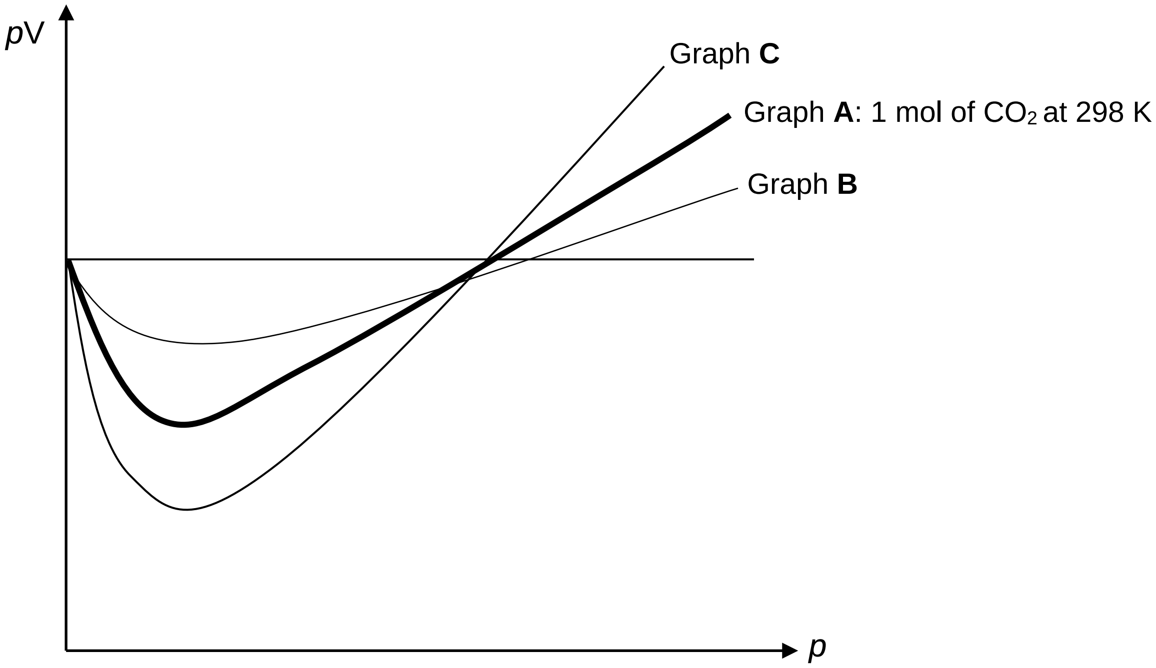
in that particular step.

You may present your answer in the form of a table or flow chart.

[5]
[Total: 12]

2 **(a)** **(i)** The value of *p*V is plotted against *p* for the following three gases, where *p* is the pressure and V is the volume of the gas.

1 mol CO_2 at 298 K
1 mol CO_2 at 473 K
1 mol SO_2 at 298 K



Given that graph **A** represents the graph for 1 mol of CO_2 at 298 K, identify and explain what graphs **B** and **C** represent.

Graph **B**: …………………………….. Graph **C**: ……………………………..

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The van der Waals' equation as shown below is often used to account for the discrepancies between experimental and theoretical behaviour of real gases.

$$(p + \frac{n^2a}{V^2})(V - nb) = nRT$$

p is the pressure, V the volume, T the temperature, n the amount of substance (in mol), and R the gas constant. The van der Waals' constants a and b are characteristic of the substance and are independent of temperature.

(ii) Given that the van der Waals' constants a and b for SO_2 is 0.687 Pa m^6 mol^{-2} and 5.68×10^{-5} m^3 mol^{-1} respectively, calculate the actual pressure exerted by 1 mol of SO_2 in a 0.5 dm^3 container at 25 °C.

(iii) Calculate the pressure exerted by SO_2 as described in **(a)(ii)** if it obeys the ideal gas law.

(iv) Suggest a reason for the discrepancy in the pressures obtained in **(a)(ii)** and **(a)(iii)**.

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[6]

(b) A wide range of sulfur oxoanions exist and many of them are widely used in laboratory synthesis. Four of such oxoanions have two sulfur (S) atoms. The average oxidation number of S and number of oxygen in the anions are shown in the table below.

oxoanion	**average oxidation number of S**	**number of oxygen atoms**
D	+2	3
E	+3	4
F	*x*	6
G	+6	*y*

All four sulfur oxoanions have a negative charge of 2–.

Only **D** has one central atom.

In **D**, **E** and **F** only,
- the sulfur atoms are bonded directly to each other and
- no oxygen atom is attached to another oxygen atom.

(i) Suggest a value for *x* and *y* in the table.

Value of *x*: ……………....... Value of *y*: ………………....

(ii) Suggest the structural formulae of **D** and **E**.

Structural formula of **D**	Structural formula of **E**

(iii) Using VSEPR theory, suggest the shape of oxoanion **E** with respect to each S atom.

…………………………………………………………………………………………..

(iv) Oxoanion **G** is a powerful oxidising agent.

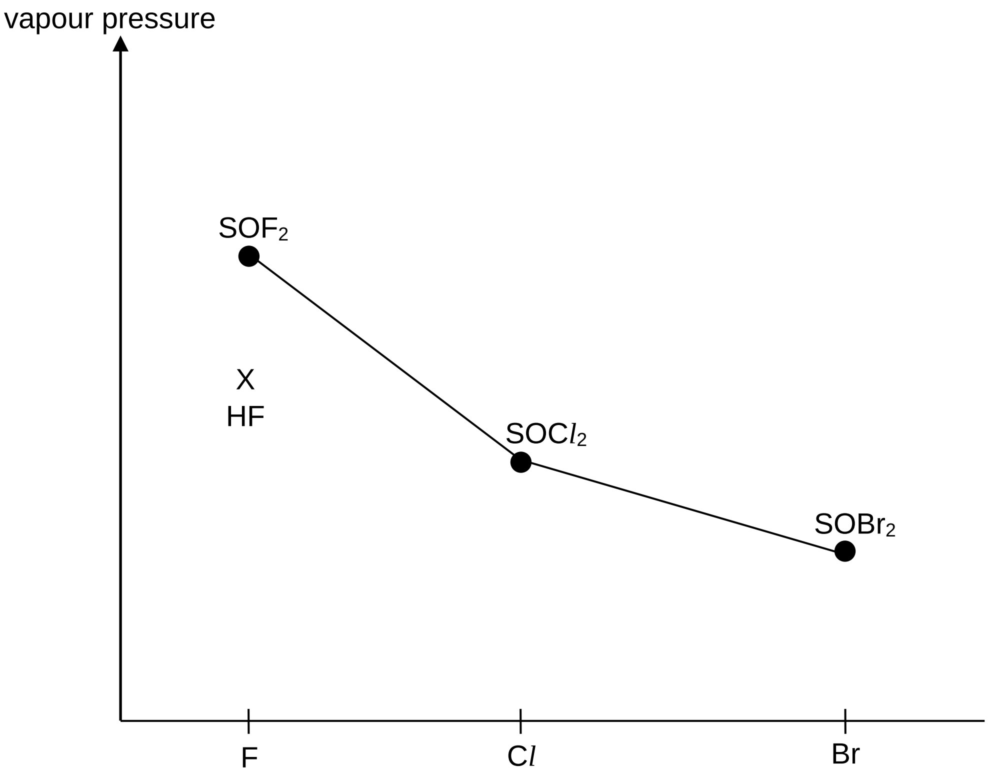
$$\mathbf{G} + 2e \rightleftharpoons 2SO_4^{2-} \qquad E^\ominus = +2.01\ \text{V}$$

Using the above data and information given in the question, draw the dot–and–cross diagram of oxoanion **G**.

[5]

(c) Thionyl halides such as $SOCl_2$ are commonly used in the halogenation of organic compounds. The reaction also results in the production of hydrogen halide vapour.

The following sketch shows the trend of vapour pressure exerted by the different thionyl halides at a given temperature.



(i) Explain the above trend in terms of structure of, and bonding in, each of these thionyl halides.

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....

(ii) The mark 'X' indicates the vapour pressure exerted by hydrogen fluoride at a given temperature.

On the same axes, indicate the expected vapour pressure exerted by each of the other two hydrogen halides at the same temperature.

(iii) Explain why the vapour pressure exerted by hydrogen fluoride is lower than that exerted by thionyl fluoride at the given temperature.

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[5]
[Total: 16]

3 In a typical laboratory, gas phase reactions are difficult to control and hence not common. Industrial production utilising gas phase reactions are similarly difficult to control and typically only used for manufacture of organic chemicals, sulfuric acid (Contact process) or ammonia (Haber process).

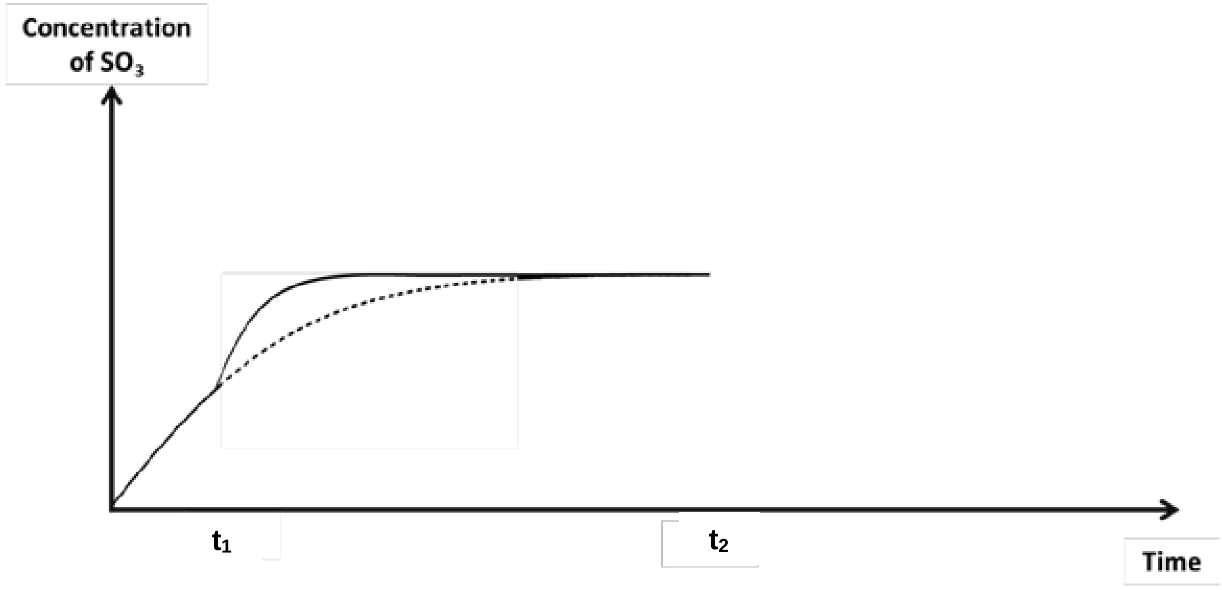
The Contact process used to produce sulfuric acid involves a three–stage process. Using V_2O_5 as a catalyst, reaction **II** achieves 99.5% conversion of sulfur dioxide to sulfur trioxide. The essential reactions are as follows:

I: $S(g) + O_2(g) \longrightarrow SO_2(g)$ $\Delta H = -308 \text{ kJ mol}^{-1}$
II: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -192 \text{ kJ mol}^{-1}$
III: $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$ $\Delta H = -130 \text{ kJ mol}^{-1}$

(a) **(i)** Write an expression **each** for K_c and K_p of reaction **II**.

Hence show that $K_p = K_c\left(\frac{1}{RT}\right)$.

The following graph shows how the concentration of SO_3 varies with time in reaction **II**.



(ii) A change in condition was introduced to the reaction mixture at $\mathbf{t_1}$ such that the concentration of SO_3 increases at a different rate after $\mathbf{t_1}$.
The dotted line in the graph above illustrates how the concentration of SO_3 would vary with time if no change in condition was introduced at $\mathbf{t_1}$.

Suggest what this change could be and explain your answer.

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(iii) The equilibrium mixture at $\mathbf{t_2}$ was suddenly heated to a higher temperature.

Sketch on the graph above to show how the concentration of SO_3 would change from $\mathbf{t_2}$ till equilibrium is reached.

(iv) Suggest and explain whether reaction **II** should be conducted at high or low pressure.

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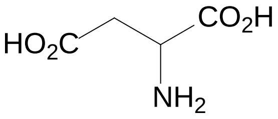
[6]

(b) Using the *Data Booklet*, calculate the average bond energy of the S=O bond in reaction **II**.

[2]
[Total: 8]

4 **(a)** Aspartic acid is a non–essential amino acid that can be synthesised by the human body. It plays a vital role in the construction of other amino acids and biochemicals in the citric acid cycle. It is also needed for stamina and assists the liver by removing excess ammonia and other toxins from the bloodstream.



aspartic acid

The three pK_a values associated with aspartic acid are given in the following table.

	pK_a
a–carboxyl	1.88
R group	3.65
a–amino	9.60

(i) Using the protonated form of aspartic acid, suggest a reason why the pK_a value of the *R* group of aspartic acid is higher than that of the a–carboxyl group.

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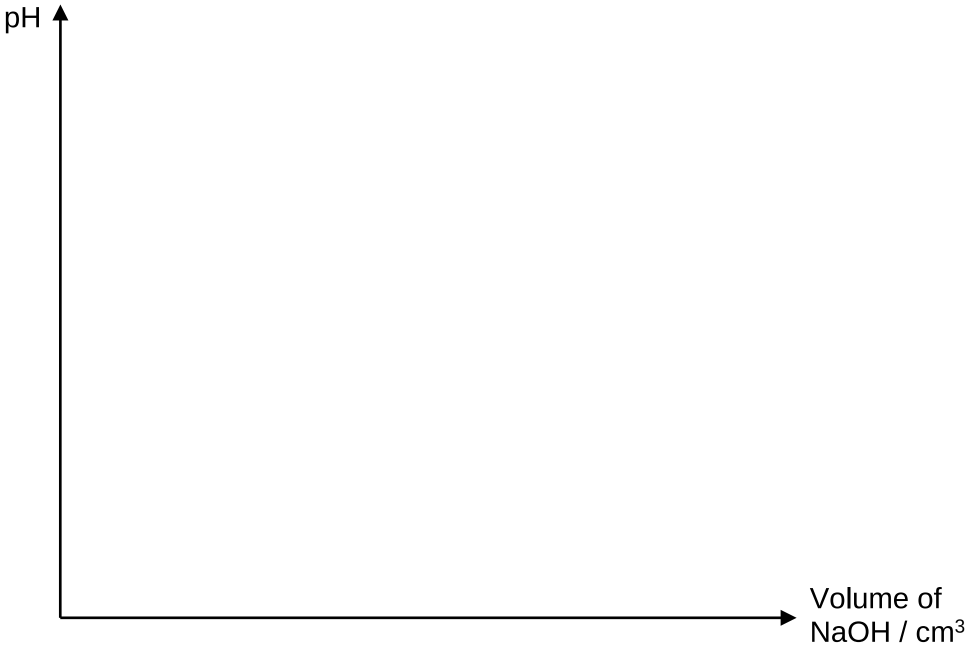
(ii) Sketch the pH–volume added curve you would expect to obtain when 30 cm^3 of NaOH is added to 10 cm^3 of the protonated form of aspartic acid of the same concentration. Show clearly on your curve where the three pK_a values occur.



(iii) Explain what is meant by the term *isoelectric point* of an amino acid. Hence suggest the structure of aspartic acid at its isoelectric point.

Indicate clearly the isoelectric point of aspartic acid on your curve obtained in **(a)(ii)** with an “X”.

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……………………………………………………………………………………………….....

Structure of aspartic acid
at isoelectric point

(iv) With the aid of an equation, explain how aspartic acid can maintain the pH of a solution at pH 3.65 on the addition of a small amount of H^+(aq). Show clearly the structure of aspartic acid in your equation.

Equation:

……………………………………………………………………………………………….....

……………………………………………………………………………………………….....

(v) Using your answers to **(ii)** and **(iv)**, calculate the change in pH when 50.0 cm^3 of 0.0200 mol dm^{-3} $HCl(aq)$ is added to 100.0 cm^3 solution of 0.100 mol dm^{-3} aspartic acid at pH 3.65.

You may represent the acid as HA and the conjugate base as A^- in your working.

[12]

(b) **(i)** Describe the reagents and conditions needed to hydrolyse a protein in the laboratory to form a mixture of its constituent amino acids.

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(ii) A polypeptide **H** was analysed and found to contain the following amino acids.

amino acid	*abbreviation*	*number of residues*
aspartic acid	Asp	1
glycine	Gly	1
serine	Ser	2
tyrosine	Tyr	1
valine	Val	1

Analysis gave the following results:

- The N–terminal was shown to be ser.
- On reaction with the enzyme chymotrypsin, which hydrolyses at the carboxylic acid end of tyr, **H** gave two tripeptides.
- On reaction with a special reagent which digests at the carboxylic acid end of val, **H** gave two peptides. One of these two was a dipeptide of sequence gly–ser.

Use the above information to determine the amino acid sequence of polypeptide **H**. Justify your answer.
[You should use the same 3–letter abbreviations as shown above to write out the amino acid sequence.]

[4]
[Total: 16]

5 **(a)** Compound **J**, is a non–narcotic analgesic commonly sold in pharmacy. Refluxing **J** in the presence of dilute sulfuric acid produces **K** and ethanoic acid.

Table 1 and Table 2 below show results of the analysis of compound **K**.

Table 1

Elemental Analysis (%)			**Melting point / °C**
C	H	O	
60.8	4.4	34.8	159

Table 2

Reaction	**Reagent**	**Result**
1	Excess aqueous Br_2	White solid, **L** formed which has M_r = 295.8.
2	Aqueous Na_2CO_3	Effervescence of gas.
3	Excess Na metal	About 174 cm^3 of a colourless gas is evolved when 1 g of **K** is used at room temperature.

(i) When vaporised in a suitable apparatus, 0.12 g of **K** occupies a volume of 37.5 cm^3 at 250 °C and a pressure of 101 kPa. Calculate the molar mass of **K**.

Molar mass of **K**:…………………………..

(ii) Hence using your answer in **(a)(i)** and Table 1, deduce the molecular formula of **K**.

Molecular formula of **K**:…………………………..

(iii) Name the functional group that reaction **1** shows to be present in **K**.

……………………………………………………………………………………………

(iv) Name the functional group present in **K** that is confirmed by reaction **2**.

……………………………………………………………………………………………

(v) Use your answers to **(a)(ii) – (a)(iv)** to account for the result in reaction **3**.

(vi) State the molecular formula of **L** in reaction **1.**

Molecular formula of **L**:…………………………..

(vi) Hence suggest two possible structural formulae of **K**. Draw the displayed formulae of your compounds in the boxes below.

Compound 1

Compound 2

(vii) Given that one of the compounds in **(a)(vi)** has a melting point of 214 ^{o}C, state the identity of **K** and explain your choice.

K is compound ………

Explanation: ……………………………………………………………………………………….

…………………………………………………………………………………………………….

(viii) Hence deduce the structure of compound **J**.

Structure of **J**

[12]

(b) Glycolic acid, $HOCH_2CO_2H$, is a colourless, odourless and hygroscopic crystalline solid that is highly soluble in water. It is commonly used in various skin–care products. It can be prepared from ethanedial by the Cannizzaro reaction, discovered in 1853.

When ethanedial, CHOCHO is reacted with aqueous NaOH and the product treated with dilute sulfuric acid, the following reaction sequence in the Cannizzaro reaction takes place.

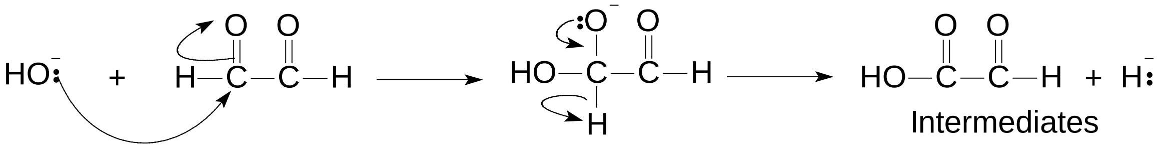
Stage I $CHOCHO + NaOH \longrightarrow HOCH_2CO_2Na$

Stage II $HOCH_2CO_2Na + H^+ \longrightarrow HOCH_2CO_2H + Na^+$

(i) What is unusual about the overall reaction?

……….…………………………………………………………………………………………

(ii) The following shows **part of** the mechanism in **stage I** where hydroxide ion attacks ethanedial in an aqueous medium.



Using the intermediates given above, propose a **further** 3–step mechanism to form $HOCH_2CO_2Na$.

In your answer, show relevant charges, lone pairs of electrons and movement of electrons.

(iii) What is the role of the H^- produced in **(b)(ii)**?

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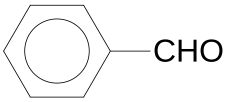
(iv) When a similar experiment is carried out using benzaldehyde as the starting material, two organic products are obtained.



benzaldehyde

Write the structural formulae of the two products and state the ratio in which they might be produced.

Structure of product		
Ratio of products		

[8]
[Total: 20]