



VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE
NAME

CT GROUP

CHEMISTRY

9729//03

Paper 3 Free Response

20 September 2021

Candidates answer on the Question Paper.

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your index number, name and CT group in the spaces at the top of this page.

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** questions.

Section B

Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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

For Examiner's Use	
1	/21
2	/17
3	/22
4 or 5	/20
Total	/80

This document consists of **34** printed pages and **2** blank pages.

Section A

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

- 1 (a) Elements in the same group tend to form products with similar physical properties.

However, the oxides of carbon and silicon have very different physical structures. While CO_2 exists as a gas at room temperature, SiO_2 is a solid.

- (i) Explain, in terms of structure and bonding, the difference in the physical states of CO_2 and SiO_2 .

[2]

- (ii) Describe the bonding in **a single** CO_2 molecule. Include a fully labelled diagram showing how the different types of bonds are formed in terms of orbital overlap.

[2]

- (iii) By considering the extent of overlap of the orbitals, suggest a reason why SiO_2 does not form bonds similar to that of CO_2 .

[1]

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- (b) The extraction of iron from its ores typically involves the use of a Blast Furnace. One of the most common impurities in iron ore is silicon dioxide. To remove silicon dioxide, limestone is added. The calcium carbonate in limestone decomposes due to the high temperatures in the Blast Furnace to form calcium oxide. The calcium oxide then reacts with silicon dioxide to form calcium silicate, Ca_2SiO_4 , which runs to the bottom of the Blast Furnace to be removed easily.

(i) State the type of reaction between silicon dioxide and calcium oxide.

[1]

(ii) Define the term *lattice energy*.

[1]

(iii) Using the information given in **Table 1.1** and relevant data from the *Data Booklet*, draw an energy level diagram and calculate a value for the lattice energy of calcium silicate, $\text{Ca}_2\text{SiO}_4(\text{s})$.

Table 1.1

enthalpy change	value / kJ mol^{-1}
standard enthalpy change of atomisation of $\text{Ca}(\text{s})$	+178
standard enthalpy change of atomisation of $\text{Si}(\text{s})$	+456
$\text{O}(\text{g}) + 2\text{e}^- \rightarrow \text{O}^{2-}(\text{g})$	+650
$\text{Si}^{4+}(\text{g}) + 4\text{O}^{2-}(\text{g}) \rightarrow \text{SiO}_4^{4-}(\text{g})$	-9304
standard enthalpy change of formation of $\text{Ca}_2\text{SiO}_4(\text{s})$	-994

[4]

(iv) The reaction between calcium oxide and silicon dioxide also forms another form of calcium silicate, CaSiO_3 .

Deduce whether the magnitude of the lattice energy of CaSiO_3 is expected to be larger or smaller than that of Ca_2SiO_4 . Explain your answer.

[2]

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[illegible]

- (c) Compound **A**, $\text{C}_9\text{H}_9\text{NO}_2$, is insoluble in both aqueous acids and alkalis and does not react with sodium metal. When heated with aqueous hydrochloric acid, followed by careful addition of aqueous sodium hydroxide, compound **B**, $\text{C}_8\text{H}_{11}\text{NO}$ is formed. Gentle warming of **A** with acidified KMnO_4 gives the salt of compound **C**, $\text{C}_8\text{H}_9\text{NO}$. Further strong heating of the mixture forms the salt of compound **D**, $\text{C}_7\text{H}_7\text{NO}_2$.

Each mole of compounds **B**, **C** and **D** decolourises two moles of aqueous bromine. Compound **C** gives a pale yellow precipitate on warming with alkaline aqueous iodine.

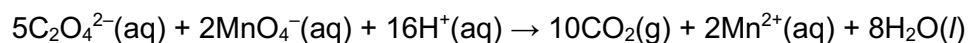
Suggest structures for **A**, **B**, **C** and **D** and explain the reactions described.

[8]

[illegible]

[Turn over

- 2 (a) (i) The reaction between an aqueous solution of permanganate(VII) ions, MnO_4^- , and ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, can be represented by the following equation:



The presence of Mn^{2+} , which are produced in the reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$, is thought to catalyse this reaction.

An experiment was performed to measure the volume of CO_2 gas produced at regular time intervals until the reaction goes to completion.

The graph of volume of CO_2 gas produced against time has three distinct regions.

Sketch on **Figure 2.1**, the graph of volume of CO_2 gas produced against time you would expect to obtain.

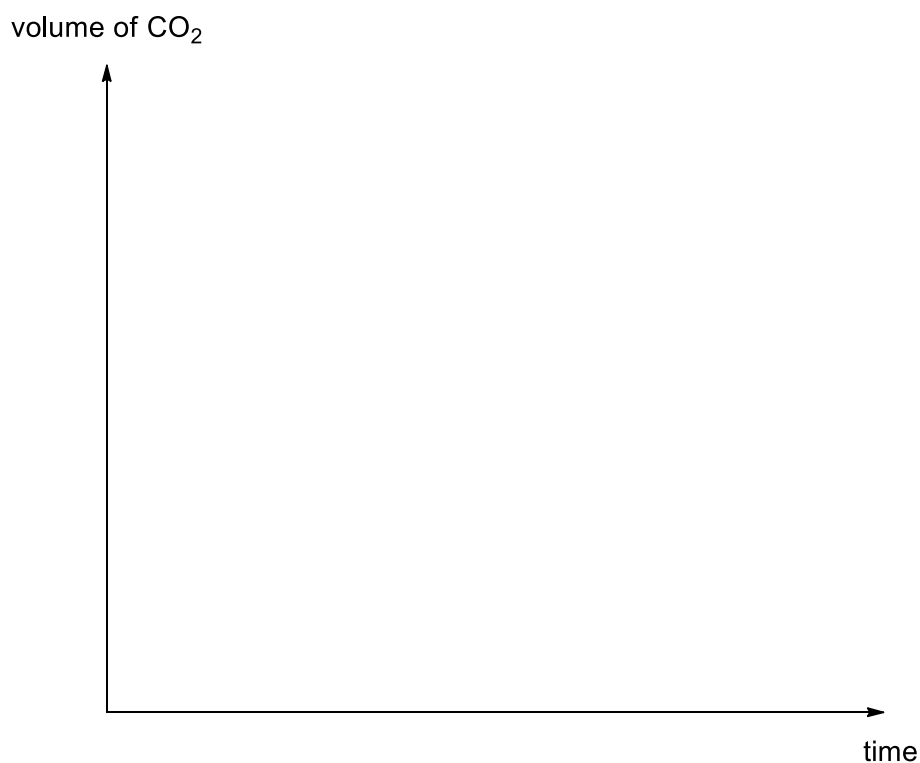


Figure 2.1

[1]

- (ii) Explain why there are three distinct regions of the graph you have drawn in (a)(i). [3]

- (iii) Using your answer in (a)(ii), sketch on **Figure 2.2**, the graph of rate against time you would expect to obtain for the same reaction in (a)(i).

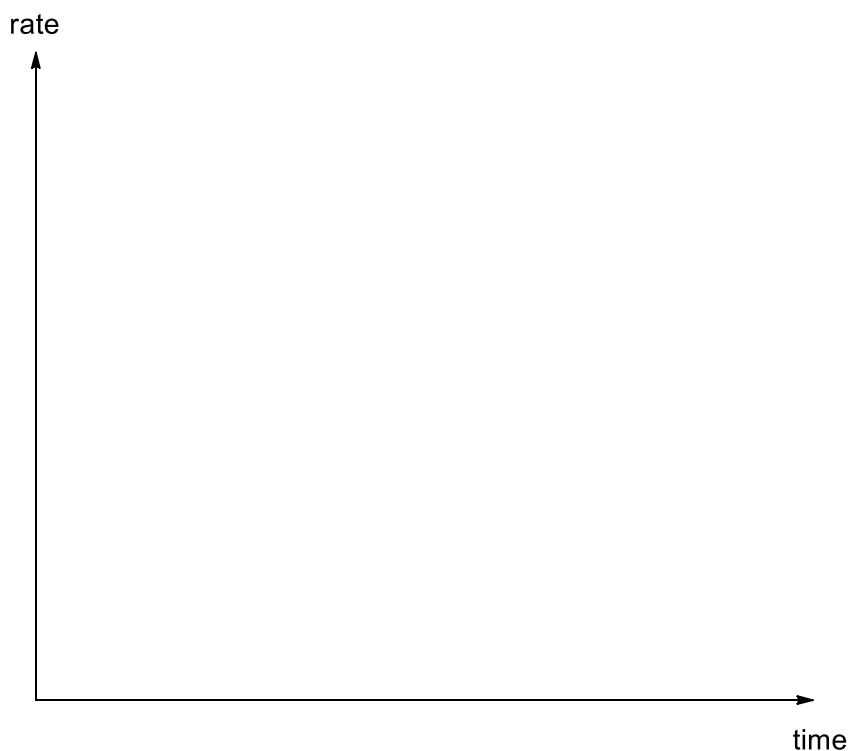


Figure 2.2

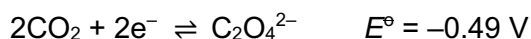
[1]

- (iv) The reaction mechanism for the **second** region of the graph you have drawn in (a)(i) can be described as follows.

step 1: MnO_4^- reacts with Mn^{2+} , producing Mn^{3+} as one of the products.

step 2: $\text{C}_2\text{O}_4^{2-}$ is then oxidised to form CO_2 gas as one of the products.

Using the information given above, write down the balanced equations for both steps of the mechanism. You may find the half-equation given below useful.



[2]

- (v) *Use of the Data Booklet is relevant to this question.*

Calculate E^\ominus_{cell} for **each** step you have written in (a)(iv). Explain how your calculated values support or contradict the proposed mechanism in (a)(iv).

[2]

- (vi) State the step in (a)(iv) you would expect to be the rate determining step. Explain your answer.

[1]

- (vii) The same experiment was repeated but with Mn^{2+} added at the **beginning** of the reaction.

The initial concentrations of the different chemical species in the second experiment are given in **Table 2.1**.

Table 2.1

species	initial concentration in reaction mixture / mol dm ⁻³
MnO ₄ ⁻	0.00594
C ₂ O ₄ ²⁻	0.0200
H ⁺	0.990
Mn ²⁺	9.90 x 10 ⁻⁴

Using your answers to **(a)(iv)** and **(a)(vi)**, determine the initial rate for the second experiment.

Note:

The rate equation can be written as $\text{rate} = k [\text{MnO}_4^-]^m [\text{C}_2\text{O}_4^{2-}]^n [\text{H}^+]^p [\text{Mn}^{2+}]^q$ where $k = 4.11 \times 10^{11} \text{ mol}^{-12} \text{ dm}^3 \text{ min}^{-1}$.

[1]

[illegible]



[2]

[illegible]

- (c) (i) Ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4$, also known as oxalic acid, can be found in leafy greens, vegetables, fruits, cocoa, nuts and seeds.

Figure 2.4 shows a reaction scheme involving $\text{H}_2\text{C}_2\text{O}_4$ and $\text{C}/\text{CH}_2\text{CH}_2\text{Cl}$ as starting materials.

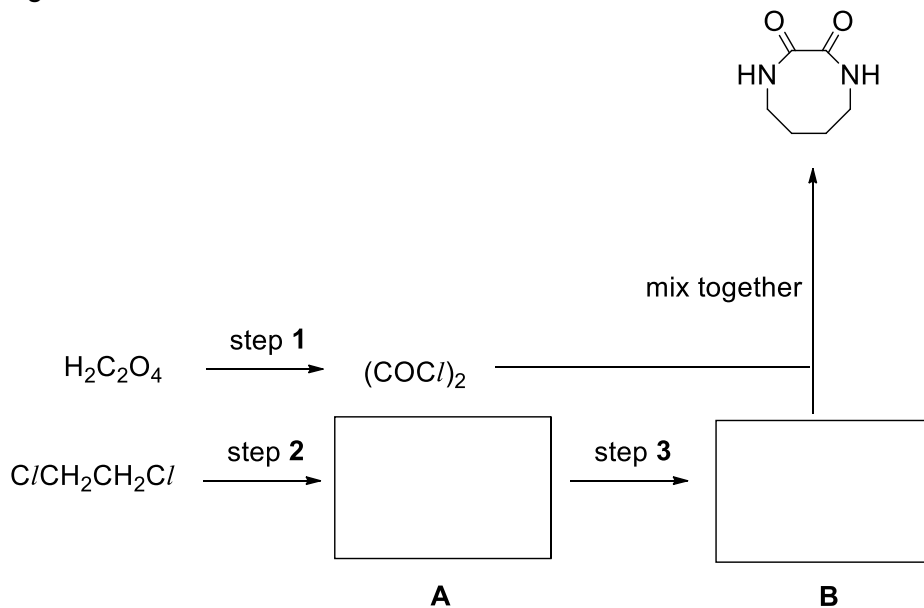


Figure 2.4

Suggest the reagents and conditions for steps **1** to **3** and draw the structures of the **A** and **B**.

[2]

- (ii) Explain the difference in the rate of hydrolysis of $(\text{COCl})_2$ and $\text{C}/\text{CH}_2\text{CH}_2\text{Cl}$.

[2]

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- 3 (a) **Table 3.1** shows the first five ionisation energies (I.E.) of some Period 4 elements:

Table 3.1

element	K	Ca	Fe	Ga	As	Se
1 st I.E.	418	590	762	577	944	941
2 nd I.E.	3070	1150	1560	1980	1790	2050
3 rd I.E.	4600	4940	2960	2960	2740	3060
4 th I.E.	5860	6480	5400	6190	4840	4140
5 th I.E.	7980	8140	7240	8300	6060	6590

- (i) With reference to the electronic configurations of As and Se, explain why the 1st I.E. of Se is lower than that of As. [2]
- (ii) With reference to the electronic configurations of Ca²⁺ and Ga²⁺, explain why the 3rd I.E. of Ca is higher than that of Ga. [2]
- (iii) **Table 3.2** shows the increment for the first five I.E. of Fe.

Table 3.2

element	1 st I.E.	2 nd I.E.	3 rd I.E.	4 th I.E.	5 th I.E.
Fe	762	1560	2960	5400	7240
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With reference to the electronic configuration of Fe³⁺, suggest a reason for the anomaly in increment from 3rd to 4th I.E. of Fe.

[1]

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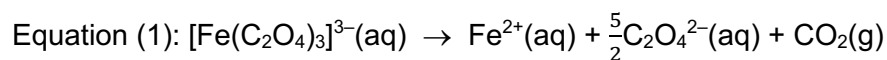
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- (b) Potassium trisoxalatoferrate(III), $K_3[Fe(C_2O_4)_3]$, is a green crystalline salt made up of potassium cations, K^+ , and ferrioxalate anions, $[Fe(C_2O_4)_3]^{3-}$.

The ferrioxalate anion is photo-sensitive. In the presence of light, $[Fe(C_2O_4)_3]^{3-}$ undergoes a redox reaction as shown in equation (1):



- (i) State and explain whether equation (1) is a disproportionation reaction. [1]
- (ii) Using the information given in **Table 3.3**, construct an energy cycle and calculate the standard Gibbs' free energy change of the reaction in equation (1).

Table 3.3

half-equation	$\Delta G^\circ / \text{kJ mol}^{-1}$
$[Fe(C_2O_4)_3]^{3-}(aq) + e^- \rightleftharpoons [Fe(C_2O_4)_3]^{4-}(aq)$	-4.8
$[Fe(C_2O_4)_3]^{4-}(aq) + 2e^- \rightleftharpoons Fe(s) + 3C_2O_4^{2-}(aq)$	+113.9
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	+85.0
$2CO_2(g) + 2e^- \rightleftharpoons C_2O_4^{2-}(aq)$	+123.5

- (iii) Hence, calculate the E°_{cell} value of equation (1). [1]
- (iv) With reference to your answers in (b)(ii) and (b)(iii), suggest a reason why light is needed for the reaction in equation (1) to occur. [1]

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- (c) To produce the medals for the Olympics Games, the Tokyo 2020 organising committee launched a campaign to collect unwanted electronic devices to harvest the necessary metals. The two-year campaign led to the collection of over 145,000 items, contributing 32 kg of gold, 3500 kg of silver and 2200 kg of bronze to the production of 5000 medals.

The medals for the Tokyo Olympic Games are made fully from the recovered metals. However, many replicas are produced by electroplating a layer of the necessary metal onto a relatively inexpensive base object.

- (i) **Figure 3.1** shows an inaccurate diagram for electroplating silver onto a base object made of iron.

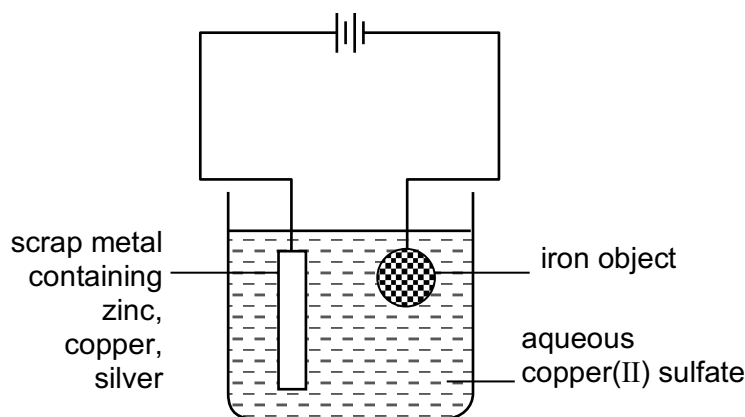


Figure 3.1

Identify and explain the error in **Figure 3.1**.

[2]

- (ii) The error in **Figure 3.1** was corrected and a current of $4.0 \times 10^{-3} \text{ A cm}^{-2}$ was passed through the set-up.

Given that the iron object has a surface area of 135 cm^2 , calculate the time, to the nearest minute, needed for 0.5 g of silver to be plated.

[2]

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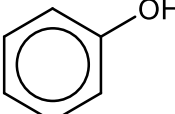
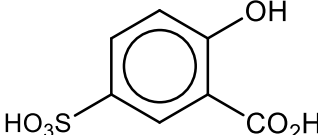
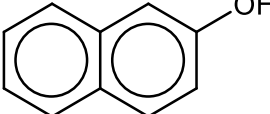
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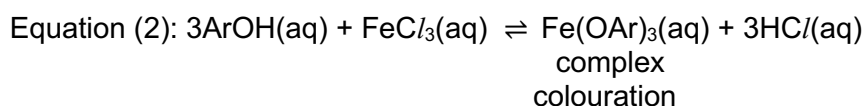
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- (d) The ferric chloride test is used to test for the presence of phenols in a given sample, with a number of phenolic compounds showing a characteristic complex colouration in the presence of neutral FeCl_3 .

Some examples are given below:

compound	structure	complex colouration
phenol		violet
sulfosalicylic acid		red
2-naphthol		green

The ferric chloride test can be represented using equation (2):



where Ar represents an aromatic substituent

- (i) With the aid of an equation, explain why a solution of FeCl_3 is acidic. [2]
- (ii) The ferric chloride test solution is prepared by adding a controlled amount of $\text{NH}_3\text{(aq)}$ to a solution of FeCl_3 .
Explain why the complex colouration may not be observed if a solution of FeCl_3 is not neutralised. [1]
- (iii) State the expected observation if an excess of $\text{NH}_3\text{(aq)}$ is added to a solution of FeCl_3 . Write an equation, including state symbols, to support the observation. [2]
- (iv) Using your answer in (d)(iii), outline the experimental steps you would take to confirm the identity of the anion in FeCl_3 . [2]

No details regarding use of specific glassware are required.

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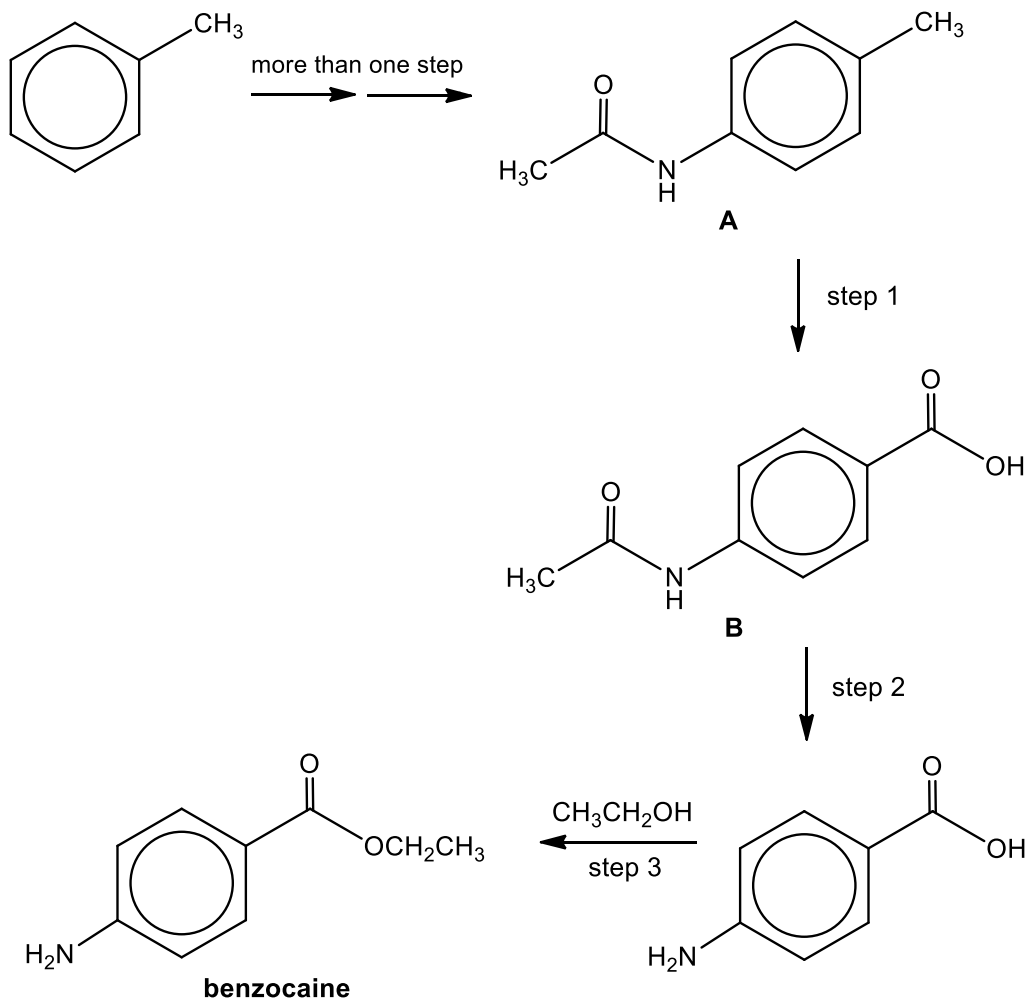
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Section B

Answer **one** question from this section.

- 4 (a) Benzocaine is a local anesthetic used in many over-the-counter products. It acts by preventing transmission of impulses along nerve fibers and at nerve endings. It may be synthesised from methylbenzene by the reaction route shown below.



- (i) Suggest a 3-step synthetic route to form compound **A** from methylbenzene. You should state the reagents and conditions for each step and draw the structures of the intermediates formed. [5]
- (ii) Suggest the reagents and conditions for steps 1 and 2. [2]
- (iii) In step 3, concentrated H₂SO₄ is used. By considering the products of step 3, suggest how concentrated H₂SO₄ helps to improve the yield of benzocaine. [1]

(iv) Compound **B** reacts separately with the two reagents shown in the table below.

Copy out and complete the table by drawing the **skeletal formula** of the organic products formed and stating the types of reaction involved in each case.

reaction	reagent	organic product formed	type of reaction
I	LiAlH ₄ in dry ether	(C ₉ H ₁₃ NO)	
II	Br ₂ (aq)	(C ₉ H ₈ NO ₃ Br)	

[3]

(v) Write a balanced equation for Reaction I.

[1]

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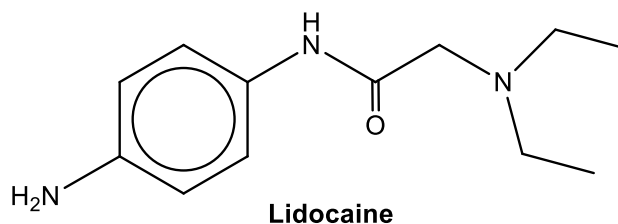
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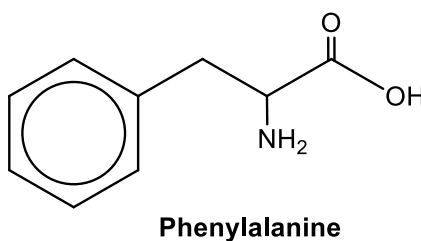
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(b) Lidocaine is also a local anesthetic.



- (i) Suggest the reagents and conditions for a reaction that could be used to distinguish between benzocaine and lidocaine. [2]
- (ii) To inhibit the sensation of pain, lidocaine act on peripheral nerves by binding to the inner pore of voltage-gated Na channels on the neurons. The drug is believed to interact with phenylalanine on the surface of the binding site.



Suggest two intermolecular interactions that can occur between lidocaine and phenylalanine.

[2]

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- (i) Calculate the K_{sp} of Ag_2CO_3 and state its units.

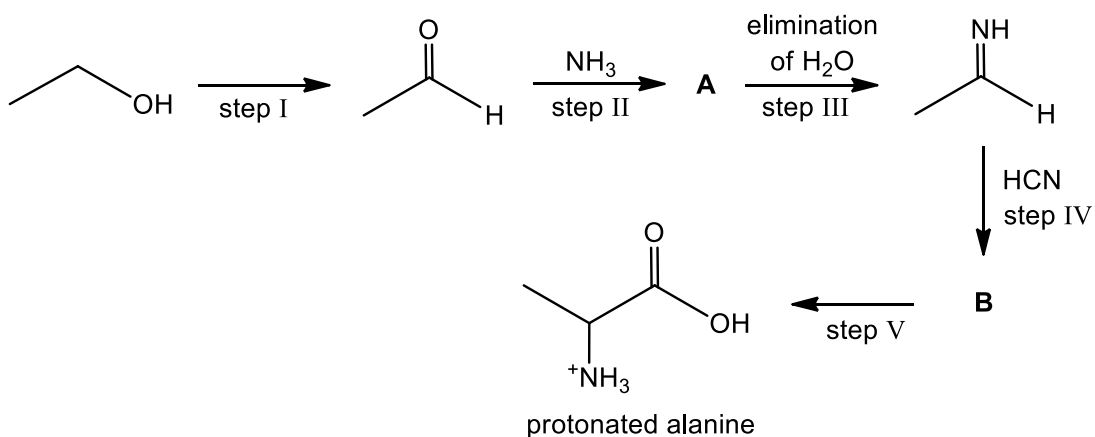
(ii) Hence, calculate the solubility of Ag_2CO_3 when 2.00 g of Na_2CO_3 solid was added to 100 cm^3 of the solution above.

[2]

[illegible]

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- 5 (a) The Strecker synthesis is a route to prepare amino acids. The protonated form of alanine, 2-aminopropanoic acid, can be prepared in the laboratory from ethanol in five steps as shown in the reaction scheme below.



- (i) In step I, the student is provided with a set of instructions to prepare the ethanal.

1. Add concentrated sulfuric acid to x g of ethanol in a round-bottomed flask, a few drops at a time.
2. Dissolve y g of potassium dichromate(VI) in a few cm^3 of distilled water.
3. Add this aqueous potassium dichromate(VI) slowly to the mixture in the round-bottomed flask.
4. Heat the mixture with immediate distillation.
5. Collect the ethanal from the reaction mixture.

Complete **Figure 5.1** to show the distillation set-up used to separate ethanal from the reaction mixture. Label your diagram fully including the location of ethanol and ethanal after distillation has taken place. It is not necessary to include clamps.

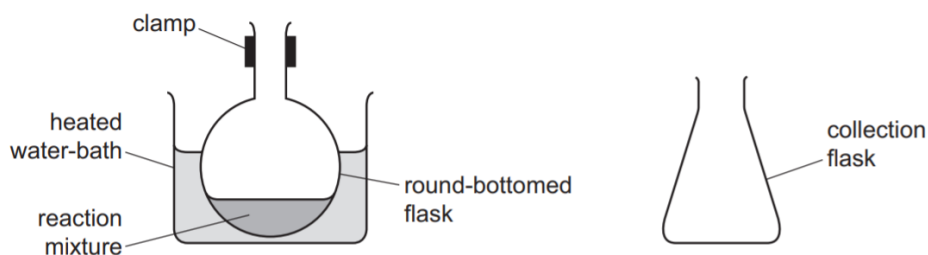


Figure 5.1

[3]

- (ii) Suggest the structure of compounds **A**.

[1]

- (iii)** The product of step III is an imine, which has a C=N bond.

Given that imines are the nitrogen analogues of carbonyl compounds, name the type of reaction in step IV.

Hence suggest the structure of compound **B**.

[2]

- (iv) Ethanal reacts with 2,4-dinitrophenylhydrazine to form an orange solid **C** which also has a C=N bond.

Draw the structure of solid **C**. Use the VSEPR Theory to predict the shape around the =N in solid **C**. Suggest a value for its bond angle.

[2]

- (v) Suggest reagents and conditions for step V.

[1]

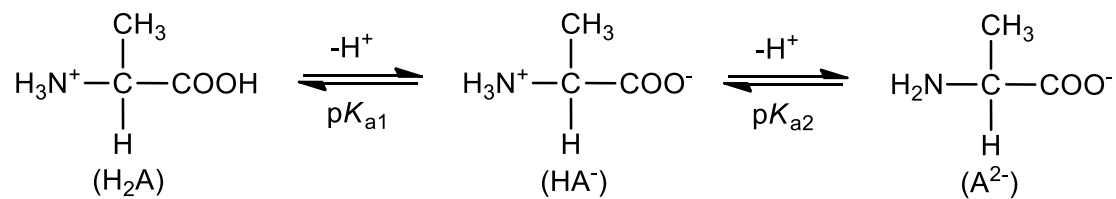
- (vi) The student proposed an alternative synthetic route by reacting ethanal directly with HCN and traces of aqueous NaOH. The route will also produce compound **B** as the precursor to protonated alanine.

Suggest how this synthetic route can proceed. You should state the reagents and conditions for each step and draw the structures of the intermediates formed. Omit the last step that converts compound **B** to protonated alanine.

[4]

[illegible]

- (b) Protonated alanine, H_2A , dissociates in two stages as shown below.



The percentage composition of H_2A , HA^- and A^{2-} changes with pH as shown in Figure 5.2.

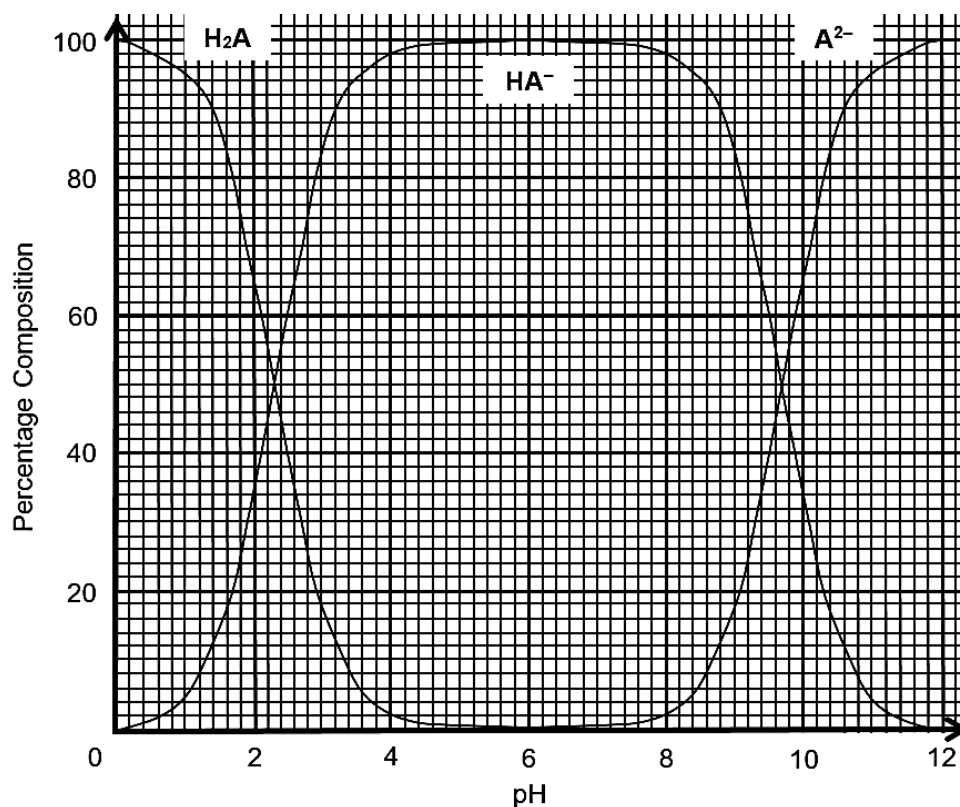


Figure 5.2

- (i) State the values of pK_{a1} and pK_{a2} of alanine. [1]
- (ii) A buffer of pH 10.0 is prepared by adding solid NaOH to $0.100 \text{ mol dm}^{-3}$ of protonated alanine, H_2A .

Using the graph above, determine the amount of HA^- and A^{2-} present in the buffer and hence, calculate the mass of solid NaOH added. [2]

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- (c) The solubility of alanine under different pH was investigated and the results are shown in **Figure 5.3**.

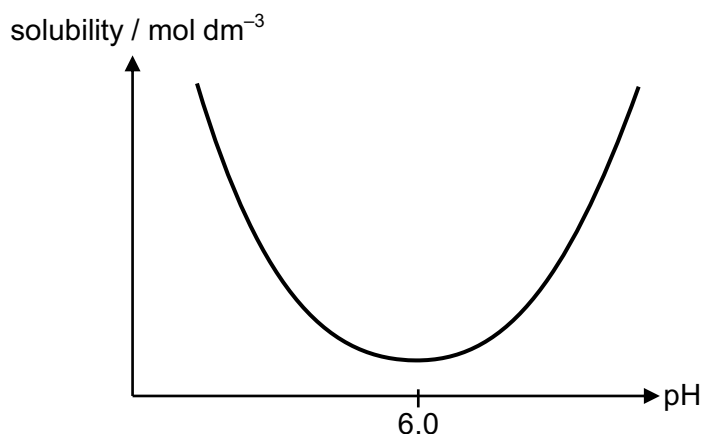


Figure 5.3

The isoelectric point of alanine is 6.0. The isoelectric point is the pH at which an amino acid has no net electrical charge.

With reference to the electrostatic forces involved, explain

- (i) the low solubility of alanine at its isoelectric point of 6.0.

[2]

- (ii)** the high solubility of alanine at low and high pH.

You may refer to alanine as H_2A , HA^- or A^{2-} where appropriate.

[2]

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This image shows a full page of a handwriting practice worksheet. It consists of multiple rows of horizontal dotted lines spaced evenly apart, providing a guide for letter height and placement. The background is plain white, and there are no other markings or text on the page.

