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]

(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, $Ca_2SiO_4(s)$.

Table 1.1

enthalpy change	value / kJ mol^{-1}
standard enthalpy change of atomisation of Ca(s)	+178
standard enthalpy change of atomisation of Si(s)	+456
$O(g) + 2e^- \rightarrow O^{2-}(g)$	+650
$Si^{4+}(g) + 4O^{2-}(g) \rightarrow SiO_4^{4-}(g)$	−9304
standard enthalpy change of formation of $Ca_2SiO_4(s)$	−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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(c) Compound **A**, $C_9H_9NO_2$, 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**, $C_8H_{11}NO$ is formed. Gentle warming of **A** with acidified $KMnO_4$ gives the salt of compound **C**, C_8H_9NO. Further strong heating of the mixture forms the salt of compound **D**, $C_7H_7NO_2$.

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]

[Total: 21]

2 (a) (i) The reaction between an aqueous solution of permanganate(VII) ions, MnO_4^-, and ethanedioate ions, $C_2O_4^{2-}$, can be represented by the following equation:

$$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$

The presence of Mn^{2+}, which are produced in the reaction between MnO_4^- and $C_2O_4^{2-}$, 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.

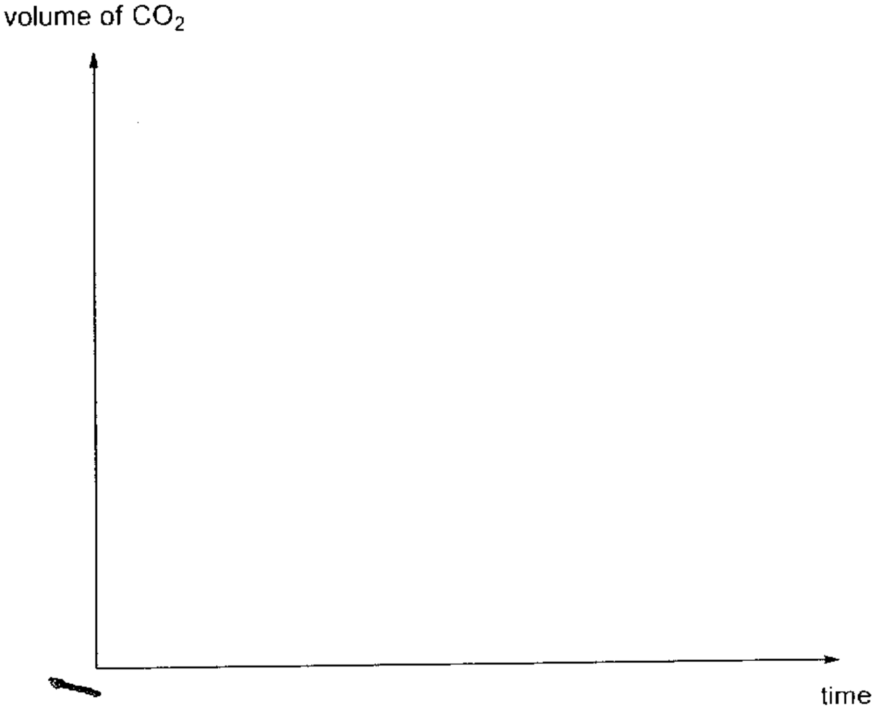

Figure 2.1

[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)**.

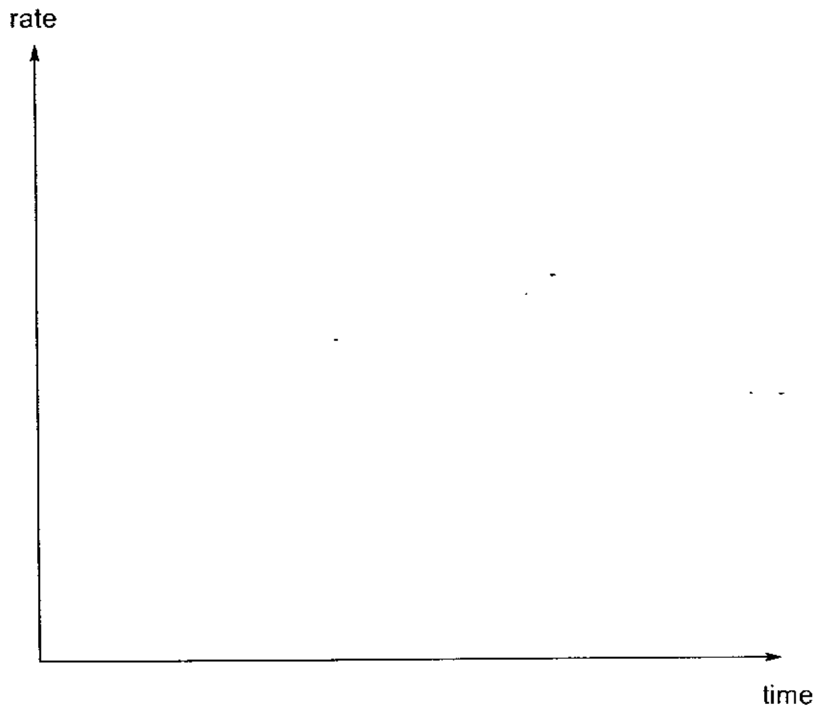

Figure 2.2

[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**: $C_2O_4^{2-}$ 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.

$$2CO_2 + 2e^- \rightleftharpoons C_2O_4^{2-} \qquad E^\ominus = -0.49\ V$$

[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
$C_2O_4^{2-}$	0.0200
H^+	0.990
Mn^{2+}	9.90×10^{-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 rate = $k\,[MnO_4^-]^m\,[C_2O_4^{2-}]^n\,[H^+]^p\,[Mn^{2+}]^q$
where $k = 4.11 \times 10^{11}$ $mol^{-12}\,dm^{36}\,min^{-1}$.

[1]

(b) $KMnO_4$ can also be used to determine the kinetics for the decomposition of H_2O_2 by withdrawing fixed aliquots at regular time intervals and perform titrimetric analysis. The graph of $[H_2O_2]$ against time for this decomposition reaction is shown in **Figure 2.3**.

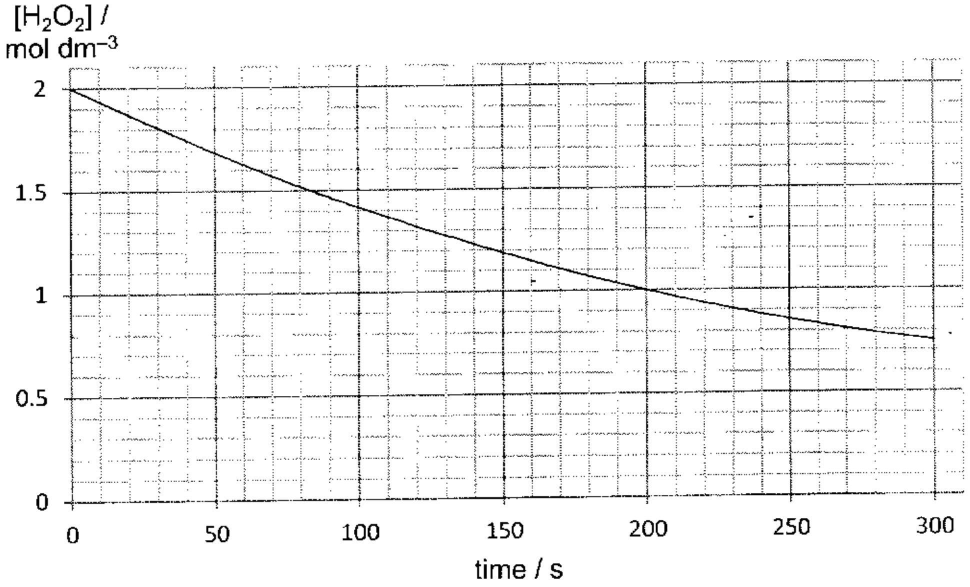

Figure 2.3

By drawing relevant construction lines on **Figure 2.3**, determine the order of reaction with respect to H_2O_2. Explain your answer.

[2]

(c) **(i)** Ethanedioic acid, $H_2C_2O_4$, 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 $H_2C_2O_4$ and $ClCH_2CH_2Cl$ as starting materials.

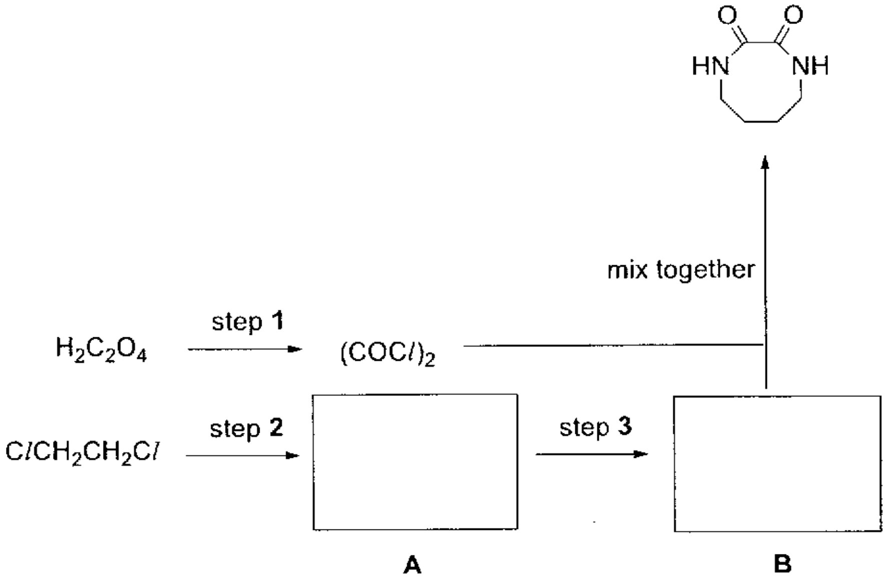

Figure 2.4

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 $(COCl)_2$ and $ClCH_2CH_2Cl$.

[2]

[Total: 17]

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
1st I.E.	418	590	762	577	944	941
2nd I.E.	3070	1150	1560	1980	1790	2050
3rd I.E.	4600	4940	2960	2960	2740	3060
4th I.E.	5860	6480	5400	6190	4840	4140
5th 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 Ca^{2+} and Ga^{2+}, 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	1st I.E.	2nd I.E.	3rd I.E.	4th I.E.	5th I.E.
Fe	762	1560	2960	5400	7240

798 1400 2440 1840

With reference to the electronic configuration of Fe^{3+}, suggest a reason for the anomaly in increment from 3rd to 4th I.E. of Fe.

[1]

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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):

$$\text{Equation (1): } [Fe(C_2O_4)_3]^{3-}(aq) \rightarrow Fe^{2+}(aq) + \tfrac{5}{2}C_2O_4^{2-}(aq) + CO_2(g)$$

(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	$\Delta G^\ominus$ / 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

[3]

(iii) Hence, calculate the $E^\ominus_{cell}$ 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.

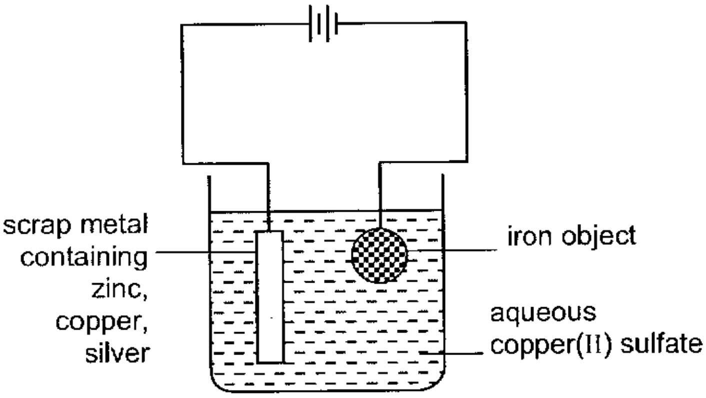

Figure 3.1

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 x 10^{-3} 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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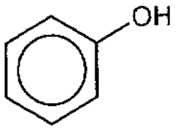
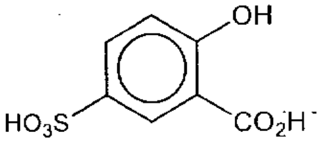
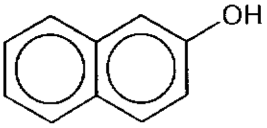
(d) The ferric chloride test is used to test for the presence of phenols in a given sample, with a number of phenolic compounds showing a characteristic complex colouration in the presence of neutral $FeCl_3$.

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):

$$\text{Equation (2): } 3ArOH(aq) + FeCl_3(aq) \rightleftharpoons \underset{\substack{\text{complex}\\ \text{colouration}}}{Fe(OAr)_3(aq)} + 3HCl(aq)$$

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 $NH_3(aq)$ 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 $NH_3(aq)$ 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 $FeCl_3$.

No details regarding use of specific glassware are required. [2]

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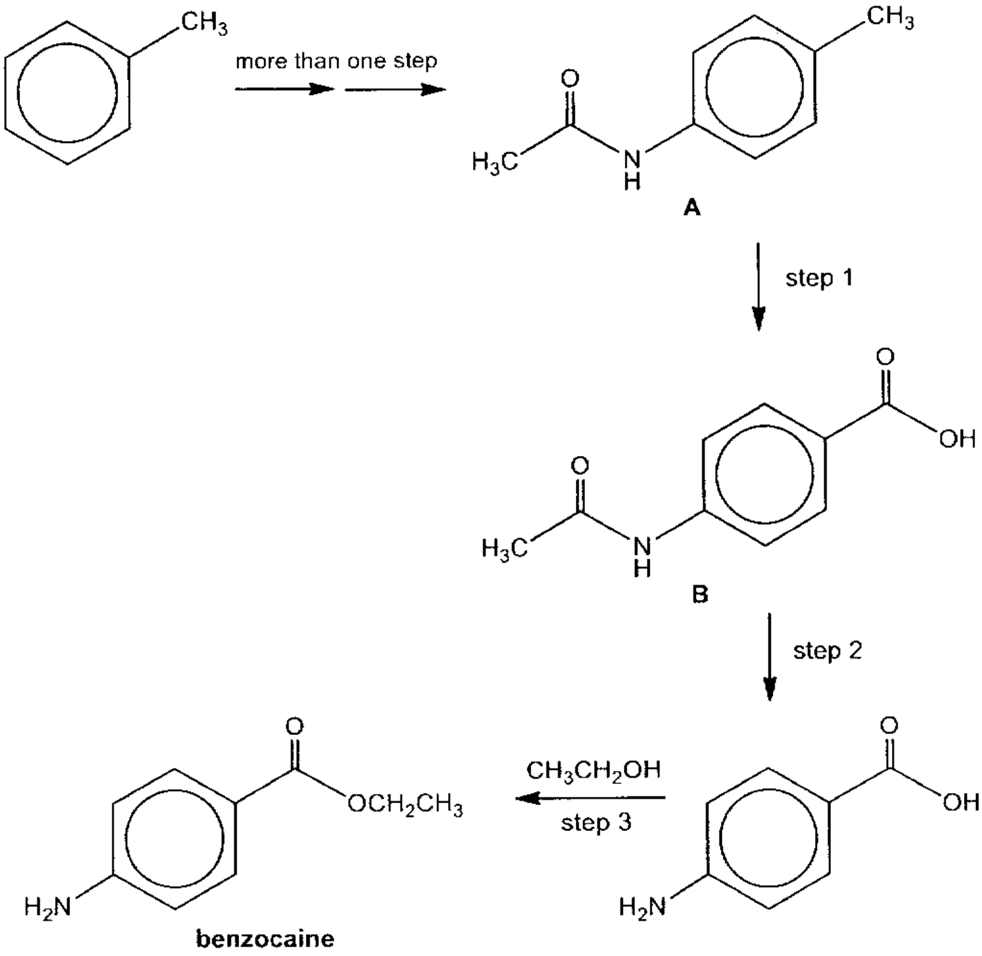
[Total: 22]

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 H_2SO_4 is used. By considering the products of step 3, suggest how concentrated H_2SO_4 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	LiA/H$_4$ in dry ether	($C_9H_{13}NO$)	
II	Br_2(aq)	($C_9H_8NO_3Br$)	

[3]

(v) Write a balanced equation for Reaction I. [1]

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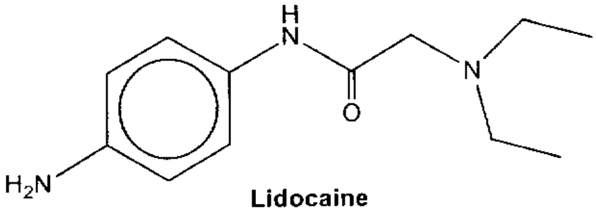
(b) Lidocaine is also a local anesthetic.

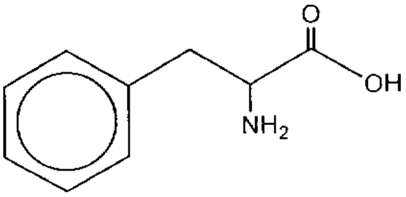


Lidocaine

(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.



Phenylalanine

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

[2]

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(c) Silver carbonate, Ag_2CO_3, is used as a catalyst in many organic synthesis. It is a sparingly soluble salt. A saturated solution of Ag_2CO_3 was found to contain 2.50×10^{-4} mol dm^{-3} of Ag^+ ions.

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

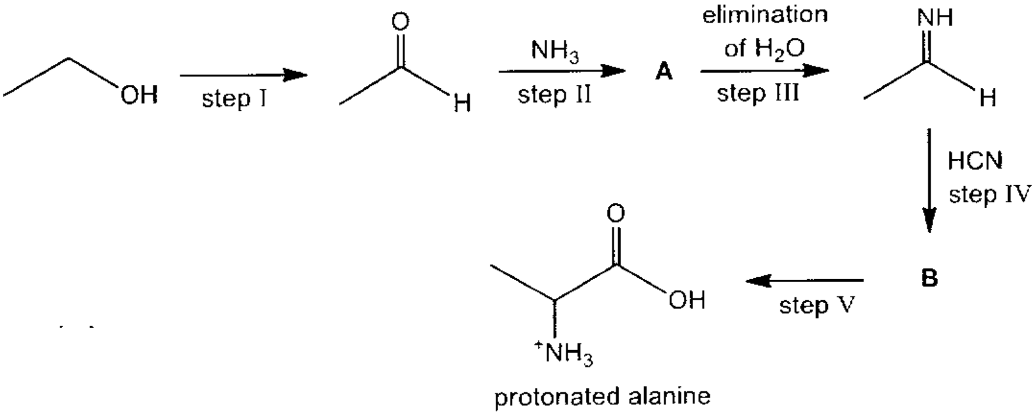
[2]

(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]

[Total: 20]

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.

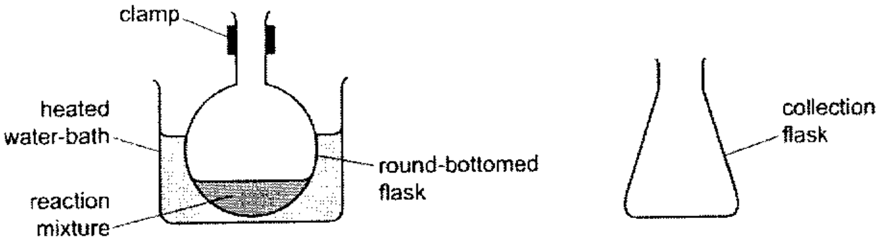


Figure 5.1

[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]

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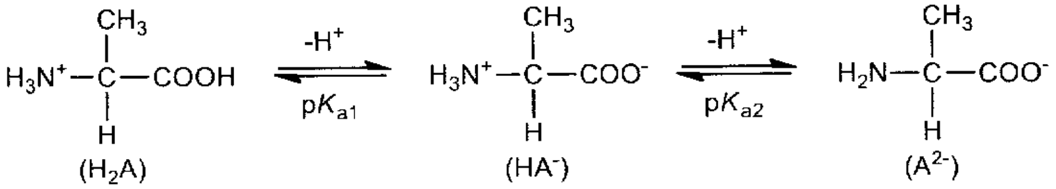
(b) Protonated alanine, H_2A, dissociates in two stages as shown below.



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

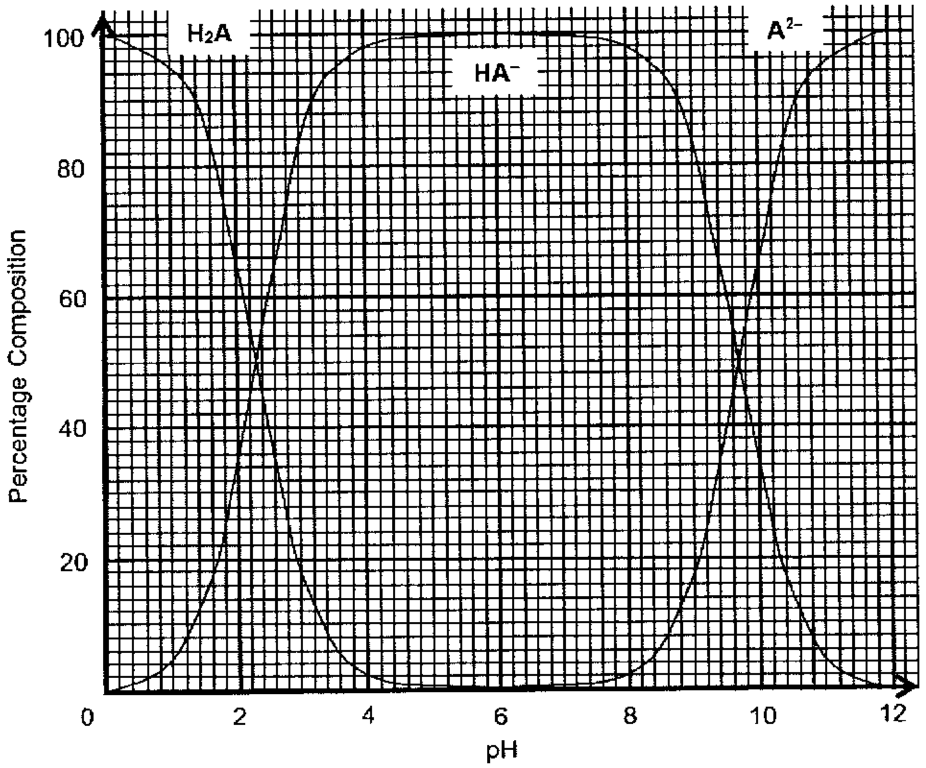


Figure 5.2

(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 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]

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

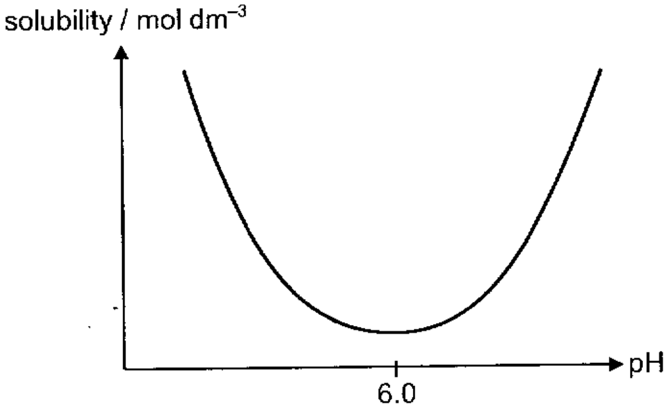


Figure 5.3

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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[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

Victoria Junior College
2021 H2 Chemistry Prelim Exam 9729/3
Suggested Answers

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.

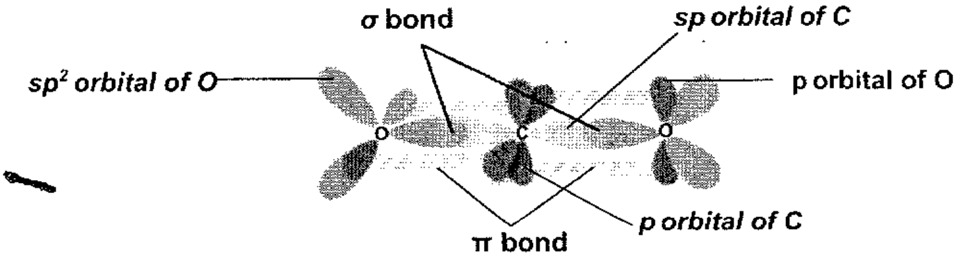
SiO_2 has a giant molecular structure where each Si atom is covalently bonded to 4 other O atoms. CO_2 has simple molecular structure with weak instantaneous dipole-induced dipole interactions (id-id) between the CO_2 molecules. Much more energy is required to break the strong covalent bonds in SiO_2 as compared to the weak id-id for CO_2. Hence, SiO_2 is a solid while CO_2 is a gas at room temperature.

[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.

C–O σ bond is formed via head-on overlap between sp hybridized orbital of C and sp^2 hybridised orbital of O (accept p orbital of O).

C–O π bond is formed via side-ways overlap between unhybridized p orbital of C and unhybridised p orbital of O.



[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.

Si atom has a larger atomic radius than C. This leads to less effective overlap of the p orbitals between Si and O. Thus, a π bond formed between S and O would be much weaker and less likely to be formed.

[1]

(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.

acid-base [OR neutralization]

[1]

(ii) Define the term *lattice energy*.

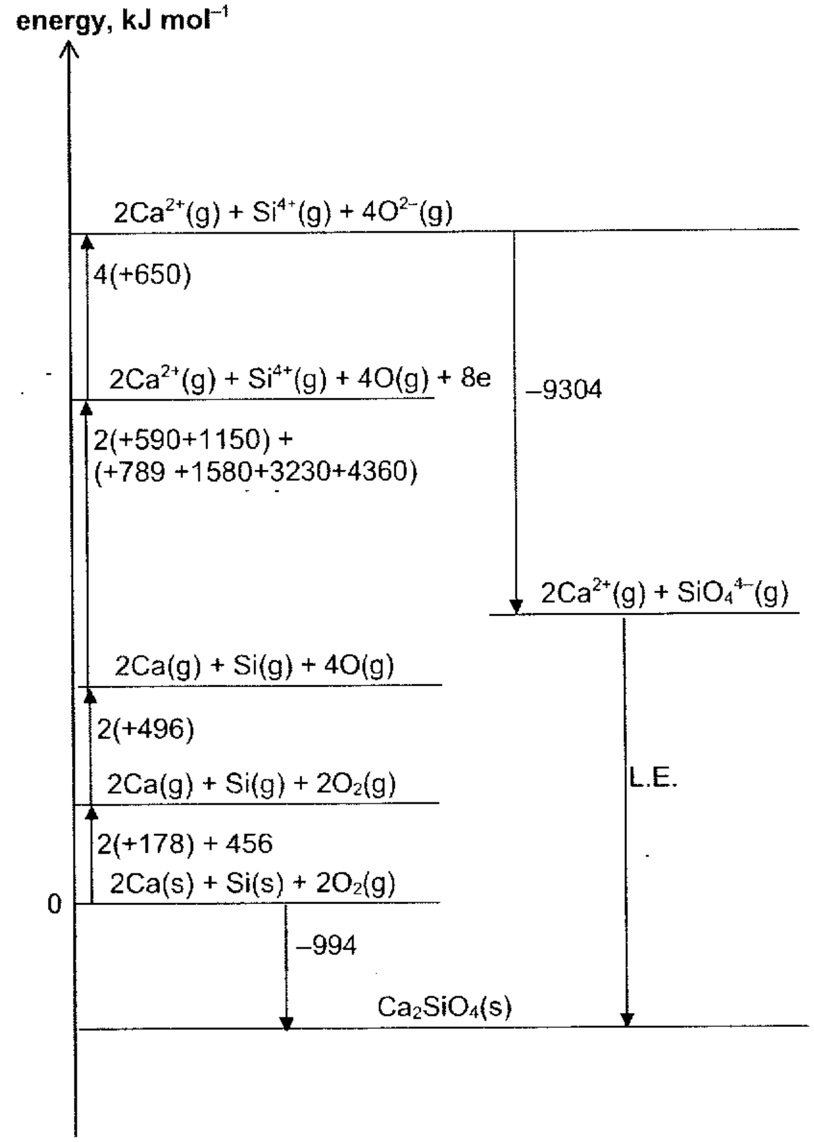
Lattice energy is energy released when one mole of solid ionic solid is formed from its isolated gaseous ions.

[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, $Ca_2SiO_4(s)$.

Table 1.1

enthalpy change	value/kJ mol^{-1}
standard enthalpy change of atomisation of Ca(s)	+178
standard enthalpy change of atomisation of Si(s)	+456
$O(g) + 2e^- \rightarrow O^{2-}(g)$	+650
$Si^{4+}(g) + 4O^{2-}(g) \rightarrow SiO_4^{4-}(g)$	–9304
standard enthalpy change of formation of $Ca_2SiO_4(s)$	–994



L.E. = 994 + 2(178) + 456 + 2(496) + 2(590 + 1150)
+ (789 + 1580 + 3230 + 4360) + 4(650) − 9304
= −9530 kJ mol^{-1}

[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.

L.E. $\propto \frac{q_+ \cdot q_-}{r_+ + r_-}$

The cationic charge and cationic radius are the same for both compounds. SiO_3^{2-} has a smaller anionic charge and smaller ionic radius than SiO_4^{4-}. Charge factor dominates and hence, $CaSiO_3$ will have a lattice energy with smaller magnitude.

[2]

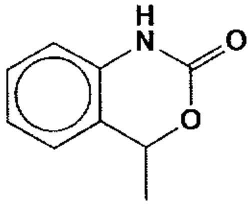
(c) Compound **A**, $C_9H_9NO_2$, is insoluble in both aqueous acids and alkalis and does not react with sodium metal. When heated with aqueous hydrochloric acid, followed by careful addition of aqueous sodium hydroxide, compound **B**, $C_8H_{11}NO$ is formed. Gentle warming of **A** with acidified $KMnO_4$ gives the salt of compound **C**, C_8H_9NO. Further strong heating of the mixture forms the salt of compound **D**, $C_7H_7NO_2$.

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.

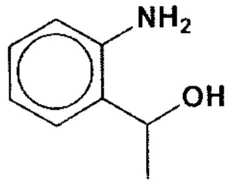
Suggest structures for **A**, **B**, **C** and **D** and explain the reactions described.

	Hints	**Deductions**
1	**Compound A has C:H = 1:1**	**A contains a benzene ring.**
2	**Compound A, $C_9H_9NO_2$, is insoluble in both aqueous acids and alkalis** **and does not react with sodium metal.**	**A is a neutral compound. A does not contain $-NH_2$ or $-COOH$. A contains amide / ester.** **A does not contain alcohol, phenol or carboxylic acid.**
3	**When heated with aqueous hydrochloric acid, followed by careful addition of NaOH, compound B, $C_8H_{11}NO$ is formed.**	**A undergoes acid hydrolysis of amide (and ester) followed by neutralisation. B contains an amine (and alcohol).** **Loss of carbon suggests the carboxyl carbon was removed upon hydrolysis.**
4	**Gentle warming of A with acidified $KMnO_4$ gives C, C_8H_9NO.**	**A undergoes hydrolysis to give B which undergoes oxidation of 2° alcohol to give ketone C**
5	**Further strong heating of the mixture forms D, $C_7H_7NO_2$.**	**Loss of carbon suggests C undergoes side–chain oxidation to give benzoic acid in D.**
6	**Each mole of compounds B, C and D decolourises two moles of aqueous bromine.**	**B, C and D undergoes electrophilic substitution.** **They contain phenylamine.** **The compounds are either 1,2 or 1,4 substituted.**
7	**Compound C gives a ~~pale~~ yellow precipitate on warming with alkaline aqueous iodine.**	**C undergoes oxidative cleavage to give CHI_3 yellow ppt.** **C contains $-COCH_3$ structural unit.**

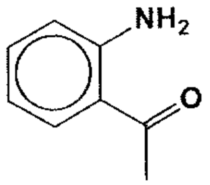
A:



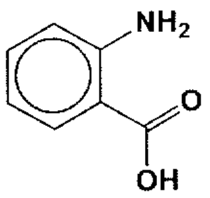
B:



C:



D:



[8]

[Total: 21]

2 **(a)** **(i)** The reaction between an aqueous solution of permanganate(VII) ions, MnO_4^-, and ethanedioate ions, $C_2O_4^{2-}$, can be represented by the following equation:

$$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$

The presence of Mn^{2+}, which are produced in the reaction between MnO_4^- and $C_2O_4^{2-}$, 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.

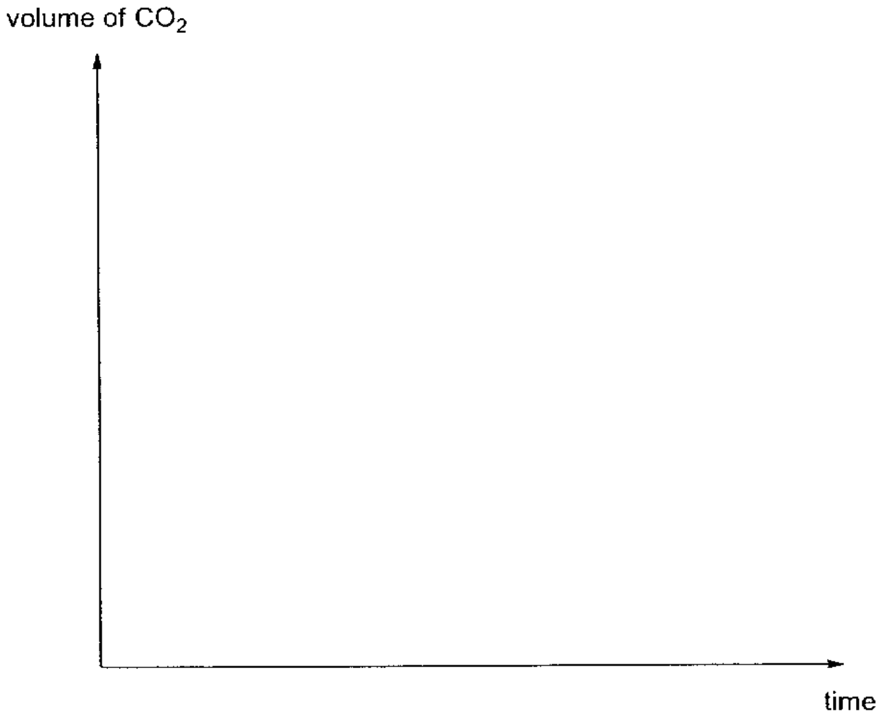


Figure 2.1

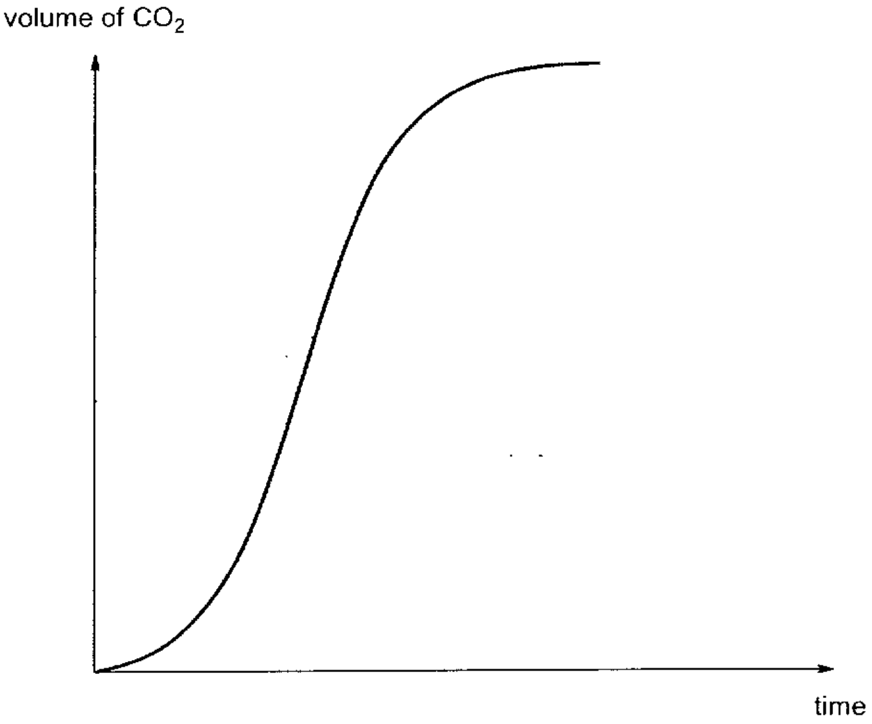


Figure 2.1

[1]

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

Initially, the rate of reaction will be slow due to the electrostatic repulsion between the negatively charged MnO_4^- and $C_2O_4^{2-}$, which results in high activation energy to overcome. Thus, the gradient will be gentle.

As the reaction progresses, the autocatalyst Mn^{2+} is formed. Mn^{2+} provides an alternative pathway of lowered activation energy for the reaction to take place. Thus, rate of reaction increases and gradient will be steeper.

Towards the end of the reaction, $[MnO_4^-]$ and $[C_2O_4^{2-}]$ would have decreased to a very low value. Less reactant particles will lead to less frequency of effective collisions. Thus, rate of reaction decreases and gradient will be gentle again.

[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)**.

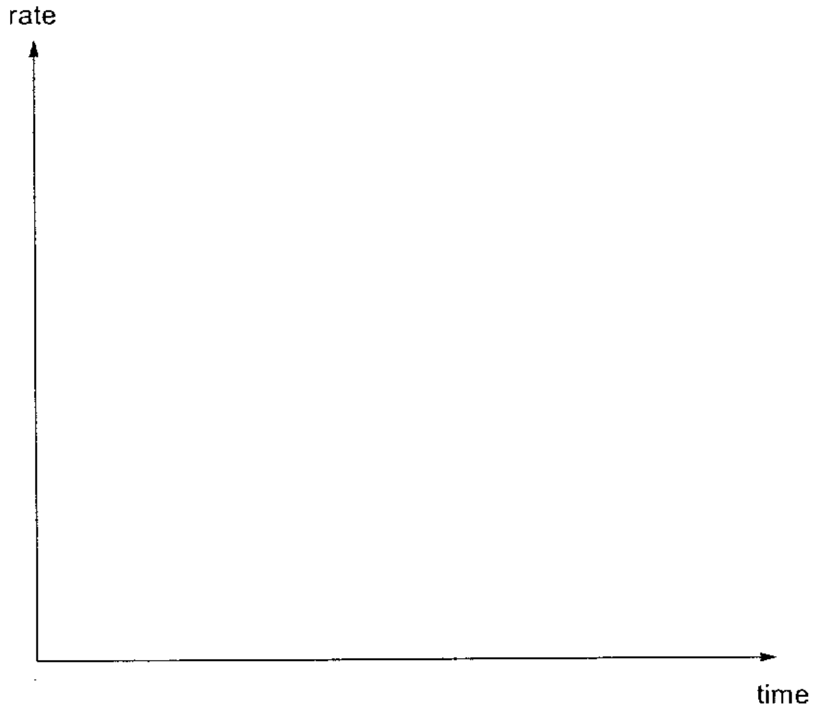


Figure 2.2

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**: $C_2O_4^{2-}$ 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.

$$2CO_2 + 2e^- \rightleftharpoons C_2O_4^{2-} \qquad E^\circ = -0.49\text{ V}$$

Step 1:
[R]: $MnO_4^- + 8H^+ + 4e^- \rightarrow Mn^{3+} + 4H_2O$
[O]: $Mn^{2+} \rightarrow Mn^{3+} + e^-$
Overall: $MnO_4^- + 8H^+ + 4Mn^{2+} \rightarrow 5Mn^{3+} + 4H_2O$

Step 2:
[R]: $Mn^{3+} + e^- \rightarrow Mn^{2+}$
[O]: $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$
Overall: $2Mn^{3+} + C_2O_4^{2-} \rightarrow 2Mn^{2+} + 2CO_2$

[2]

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

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

Step 1:
$E^\circ_{cell} = +1.52 - (+1.54) = -0.02$ V
Since $\underline{E^\circ_{cell} < 0}$, this step is <u>not expected to be spontaneous</u>, which contradicts the proposed mechanism. However, reaction is likely to still be possible if performed under non-standard conditions.

Step 2:
$E^\circ_{cell} = +1.54 - (-0.49) = +2.03$ V
Since $\underline{E^\circ_{cell} > 0}$, this step is <u>expected to be spontaneous</u>, which supports the proposed mechanism.

[2]

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

The rate determining step is likely to be <u>step 1</u> as the <u>(auto)catalyst Mn^{2+} is consumed</u> in step 1.

[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
$C_2O_4^{2-}$	0.0200
H^+	0.990
Mn^{2+}	9.90×10^{-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 rate = $k\,[MnO_4^-]^m\,[C_2O_4^{2-}]^n\,[H^+]^p\,[Mn^{2+}]^q$ where $k = 4.11 \times 10^{11}$ $mol^{-12}\,dm^{36}\,min^{-1}$.

Since step 1 is the rate determining step, the rate equation is rate = $k\,[MnO_4^-]\,[H^+]^8\,[Mn^{2+}]^4$

initial rate $= 4.11 \times 10^{11}\,[0.00594].[0.990]^8.[9.90 \times 10^{-4}]^4$
$= 2.17 \times 10^{-3}$ **mol dm^{-3} min^{-1}**

[1]

(b) $KMnO_4$ can also be used to determine the kinetics for the decomposition of H_2O_2 by withdrawing fixed aliquots at regular time intervals and perform titrimetric analysis. The graph of $[H_2O_2]$ against time for this decomposition reaction is shown in **Figure 2.3**.

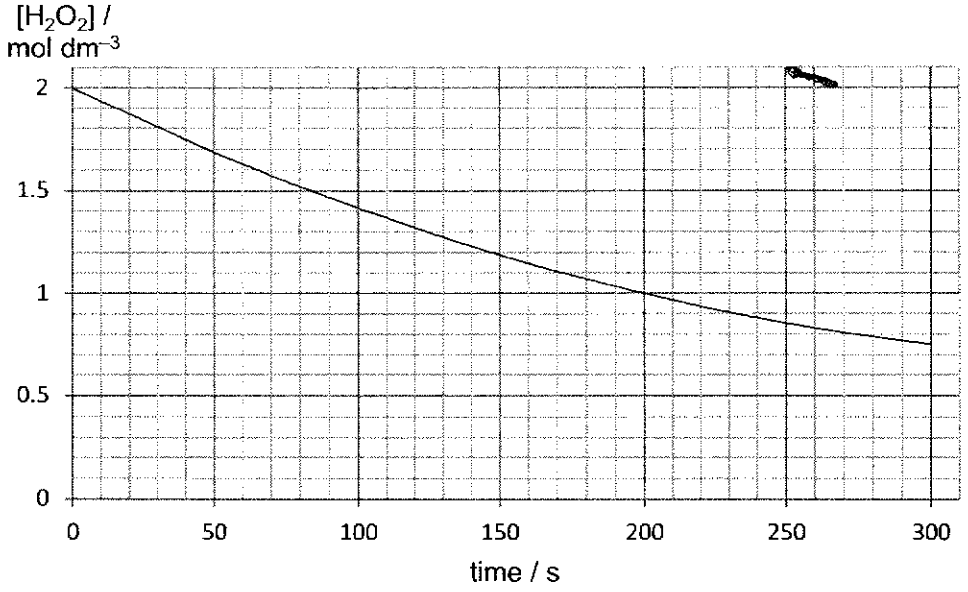


Figure 2.3

By drawing relevant construction lines on **Figure 2.3**, determine the order of reaction with respect to H_2O_2. Explain your answer.

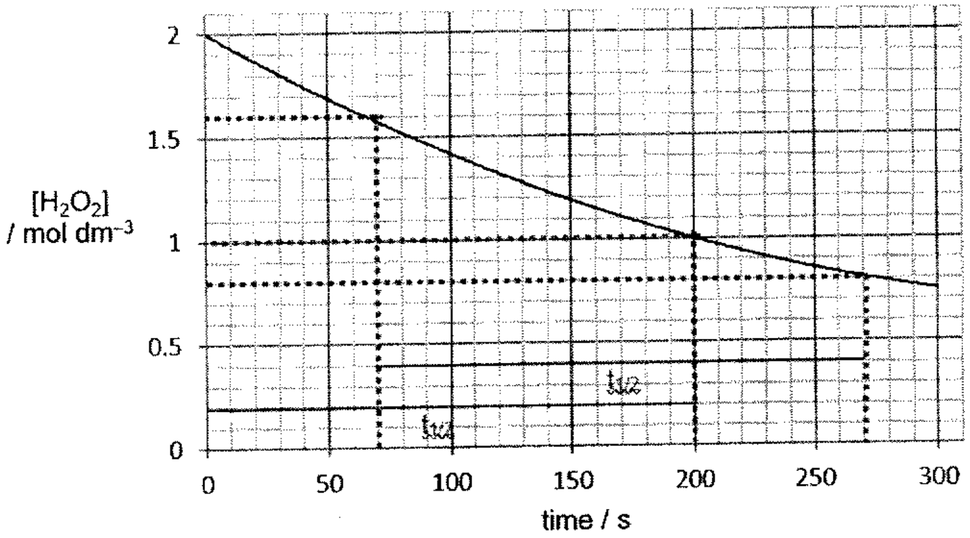


Figure 2.3

Time taken for $[H_2O_2]$ to fall from 2 mol dm^{-3} to 1 mol dm^{-3} ≈ 200 s.
Time taken for $[H_2O_2]$ to fall form 1.6 mol dm^{-3} to 0.8 mol dm^{-3} is ≈ 200 s.
(show two half lives on above graph)
Since half-life of the reaction is (approximately) constant at 200 s, the order of reaction with respect to H_2O_2 is one.

[2]

(c) **(i)** Ethanedioic acid, $H_2C_2O_4$, 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 $H_2C_2O_4$ and $ClCH_2CH_2Cl$ as starting materials.

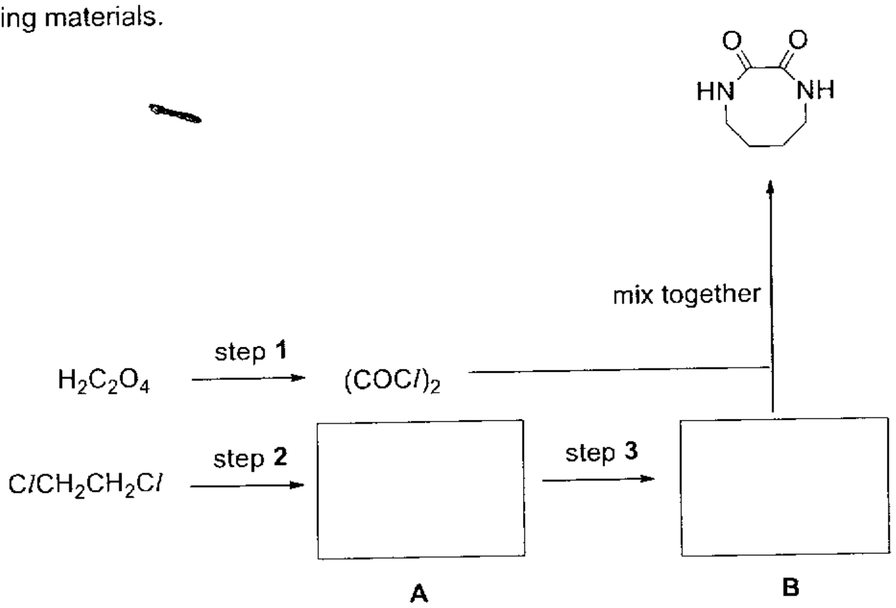


Figure 2.4

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

step 1: excess PCl_5, r.t.p. OR excess $SOCl_2$, heat OR excess PCl_3, heat
step 2: excess KCN(alcoholic), heat
step 3: excess $LiAlH_4$ in dry ether, r.t.p. OR H_2, Ni, heat OR H_2, Pt, r.t.p.

A: $NCCH_2CH_2CN$,
B: $H_2N(CH_2)_4NH_2$

[2]

(ii) Explain the difference in the rate of hydrolysis of $(COCl)_2$ and $ClCH_2CH_2Cl$.

$(COCl)_2$ undergoes hydrolysis more readily than $ClCH_2CH_2Cl$.
The presence of two highly electronegative O and Cl atoms makes the carboxyl C more electron deficient and thus more susceptible to nucleophilic attack.

In $ClCH_2CH_2Cl$, the alpha carbon bonded, which is only bonded to one highly electronegative Cl atom is less electron deficient and thus less susceptible to nucleophilic attack.

[2]

[Total: 17]

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
1st I.E.	418	590	762	577	944	941
2nd I.E.	3070	1150	1560	1980	1790	2050
3rd I.E.	4600	4940	2960	2960	2740	3060
4th I.E.	5860	6480	5400	6190	4840	4140
5th 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.

As: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$
Se: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^4$

The valence electron to be removed from Se is a paired 4p electron whereas the valence electron to be removed from As is an unpaired 4p electron. Less energy is required to remove the paired electron due to additional inter-electronic repulsion caused by the paired electrons.

[2]

(ii) With reference to the electronic configurations of Ca^{2+} and Ga^{2+}, explain why the 3rd I.E. of Ca is higher than that of Ga.

Ca^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Ga^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

Ca^{2+} has one less electron shell compared to Ga^{2+}. Thus, more energy is required to overcome the valence electron of Ca^{2+} which is closer and thus more strongly attracted to the nucleus.

[2]

(iii) **Table 3.2** shows the increment for the first five I.E. of Fe.

Table 3.2

element	1st I.E.	2nd I.E.	3rd I.E.	4th I.E.	5th I.E.
Fe	762	1560	2960	5400	7240

798 1400 2440 1840

With reference to the electronic configuration of Fe^{3+}, suggest a reason for the anomaly in increment from 3rd to 4th I.E. of Fe.

Fe^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

The fourth electron to be removed is from a stable $3d^5$ configuration/half-filled 3d orbitals. Thus, more energy is required to remove the fourth electron.

[1]

(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):

$$\text{Equation (1): } [Fe(C_2O_4)_3]^{3-}(aq) \rightarrow Fe^{2+}(aq) + \tfrac{5}{2}C_2O_4^{2-}(aq) + CO_2(g)$$

(i) State and explain whether equation (1) is a disproportionation reaction.

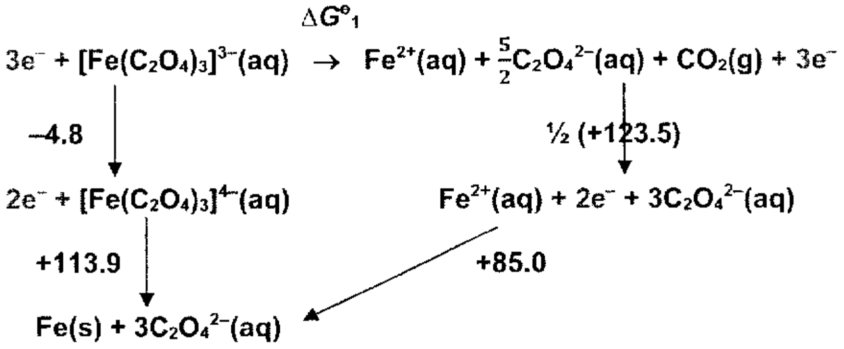
Fe is being reduced from +3 to +2 while C is being oxidized from +3 to +4. Since different elements are being reduced and oxidized, / there is no one element that is simultaneously oxidised and reduced, equation (1) is not a disproportionation reaction.

[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	$\Delta G^\ominus$, 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



By Hess' Law:
$\Delta G^\ominus_1 = (-4.8) + (+113.9) - (+85.0) - ½ (+123.5)$
$= -37.7$ kJ mol^{-1}

[3]

(iii) Hence, calculate the $E^\ominus_{cell}$ value of equation (1).

$\Delta G^\ominus_1 = -nFE^\ominus_{cell}$
$-37.7 \times 1000 = -(1).(96500).E_{cell}$
$E^\ominus_{cell} = +0.39$ V

[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.

The reaction could be associated with <u>high activation energy</u> due to the need to break strong covalent bonds within $C_2O_4^{2-}$.

[1]

(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.

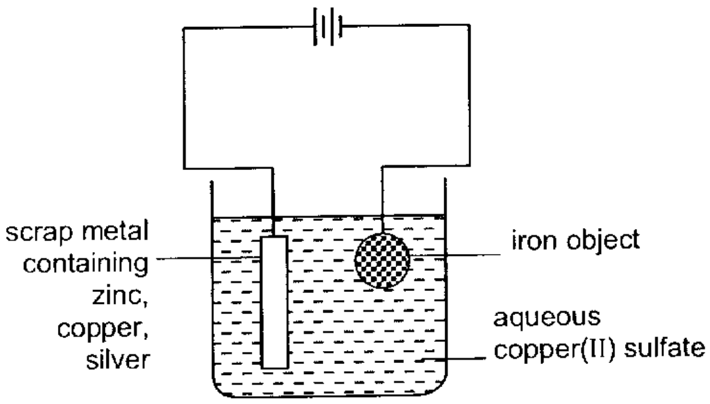


Figure 3.1

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

The electrolyte should not be a solution of $CuSO_4$(aq). At the start of the electrolysis process, Ag^+ is not present. Thus, Cu^{2+} will undergo reduction to form Cu on the iron object. In addition, due to the presence of SO_4^{2-}, Ag^+ formed will also be precipitated as Ag_2SO_4..

[2]

(ii) The error in **Figure 3.1** was corrected and a current of 4.0 x 10^{-3} 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.

$Ag^+ + e^- \rightarrow Ag$

n_{Ag} = 0.5 ÷ 107.9
= 4.63 x 10^{-3} mol

n_e = 4.63 x 10^{-3} mol

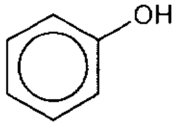
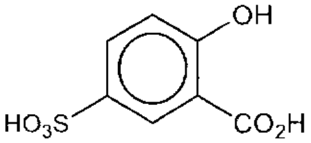
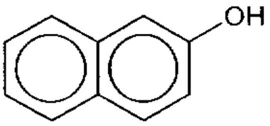
Q = n_eF
= (4.63 x 10^{-3}).(96500)
= 447 C

Q = It
447 = (4.0 x 10^{-3} x 135).t
t = 447 ÷ (4.0 x 10^{-3} x 135)
= 828 s
= 13.8 min
≈ 14 min

[2]

(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):

Equation (2): $3ArOH(aq) + FeCl_3(aq) \rightleftharpoons \underset{\text{complex colouration}}{Fe(OAr)_3(aq)} + 3HCl(aq)$

where Ar represents an aromatic substituent

(i) With the aid of an equation, explain why a solution of $FeCl_3$ is acidic.

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

Due to the high charge density of Fe^{3+}, it will hydrolyse H_2O to produce H^+, giving rise to an acidic solution.

[2]

(ii) The ferric chloride test solution is prepared by adding a controlled amount of $NH_3(aq)$ to a solution of $FeCl_3$.

Explain why the complex colouration may not be observed if a solution of $FeCl_3$ is not neutralised.

By Le Chatelier's Principle, if the solution is not neutralised, equilibrium position of equation (2) will shift left to counteract the higher $[H^+]$, resulting in less complex being formed. Thus the colour may not be observed.

[1]

(iii) State the expected observation if an excess of $NH_3(aq)$ is added to a solution of $FeCl_3$. Write an equation, including state symbols, to support the observation.

$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$

A red-brown ppt. of $Fe(OH)_3$ would be observed, which is insoluble in excess $NH_3(aq)$.

[2]

(iv) Using your answer in **(d)(iii)**, outline the experimental steps you would take to confirm the identity of the anion in $FeCl_3$.

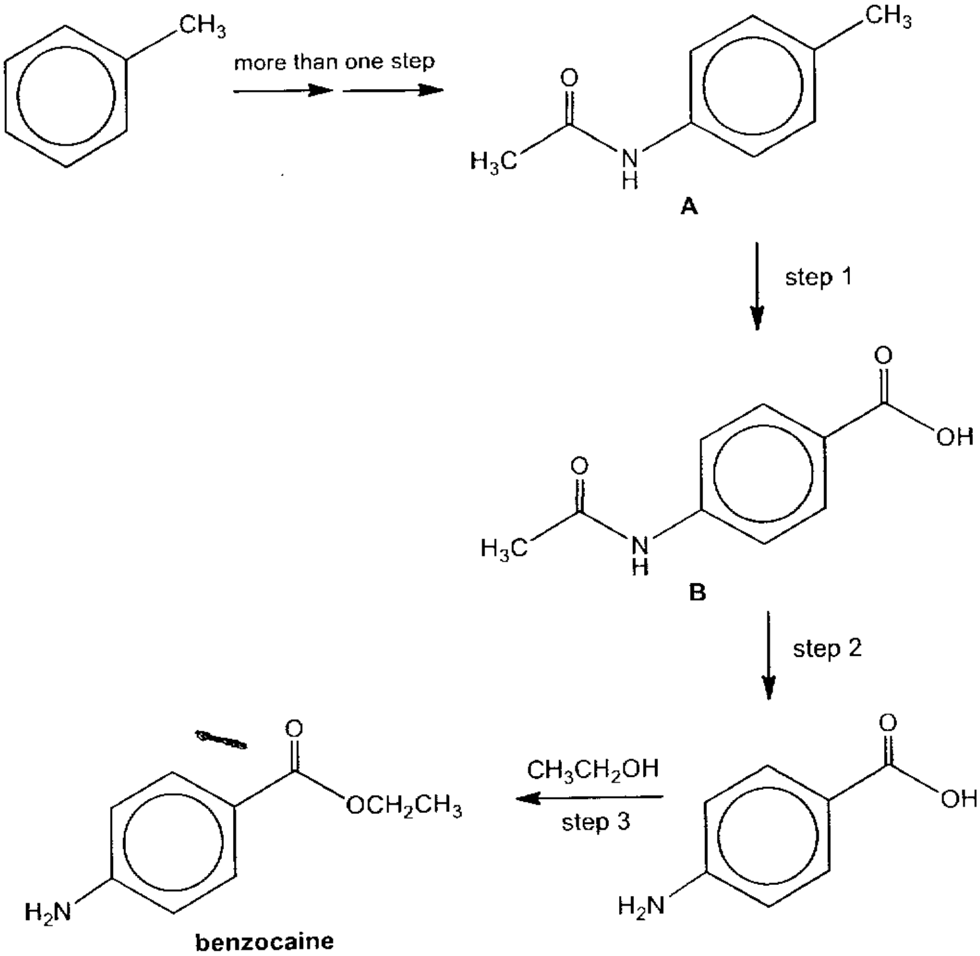
No details regarding use of specific glassware are required.

1. **To 1 cm depth of FeC*l*$_3$ solution, add an excess of NH$_3$(aq).**
2. **Filter and collect the filtrate.**
3. **Add excess HNO$_3$(aq) to the filtrate.**
4. **Add AgNO$_3$(aq) to the filtrate. A white ppt. of AgC*l* will be formed.**
5. **Add excess NH$_3$(aq). The white ppt. will completely dissolve.**

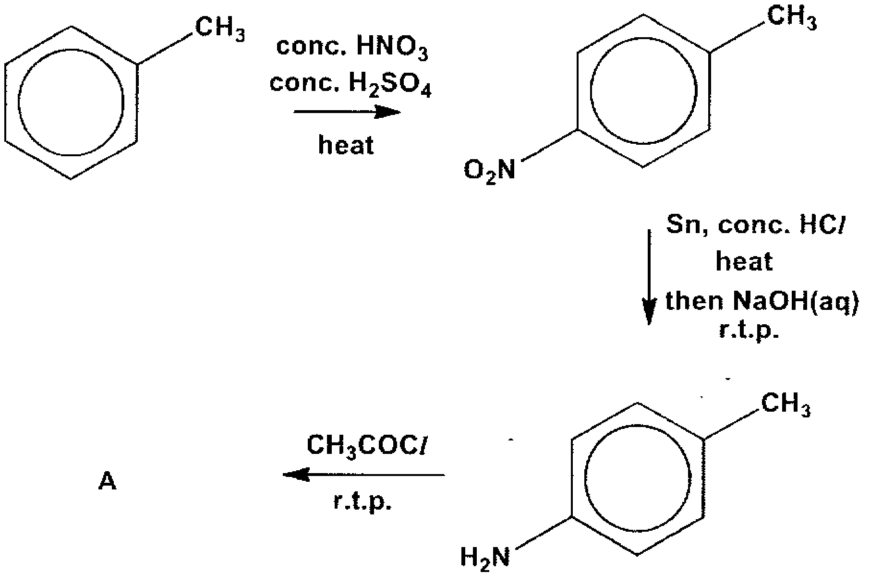
[2]

[Total: 22]

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.

Step 1: Conc. $KMnO_4$, heat
Step 2: H_2SO_4(aq), heat, then controlled addition of NaOH(aq) OR
NaOH(aq), heat, then controlled addition of H_2SO_4(aq)

[2]

(iii) In step 3, concentrated H_2SO_4 is used. By considering the products of step 3, suggest how concentrated H_2SO_4 helps to improve the yield of benzocaine.

$$RCO_2H + R'OH \overset{H^+}{\rightleftharpoons} RCO_2R' + H_2O$$

Step 3 is an <u>equilibrium reaction</u>. In addition to being a catalyst, concentrated H_2SO_4 is also a <u>dehydrating agent</u>, <u>removing H_2O</u> during the reaction. By Le Chatelier's Principle, <u>equilibrium position shifts right to counteract the loss of H_2O</u>, resulting in a higher yield of benzocaine formed.

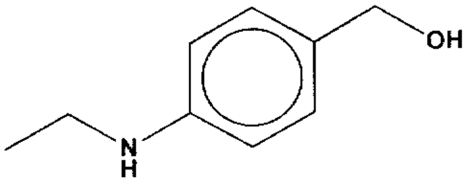
[1]

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

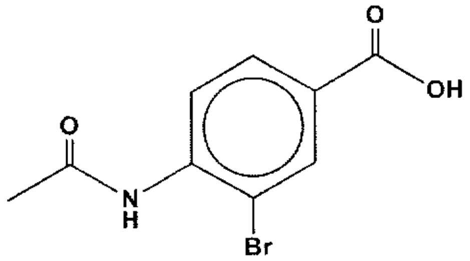
Copy out and complete the table by drawing the **skeletal formula** of the organic products formed and stating the types of reaction involved in each case.

reaction	reagent	organic product formed	type of reaction
I	$LiAlH_4$ in dry ether	($C_9H_{13}NO$)	
II	Br_2(aq)	($C_9H_8NO_3Br$)	

Reaction I: reduction

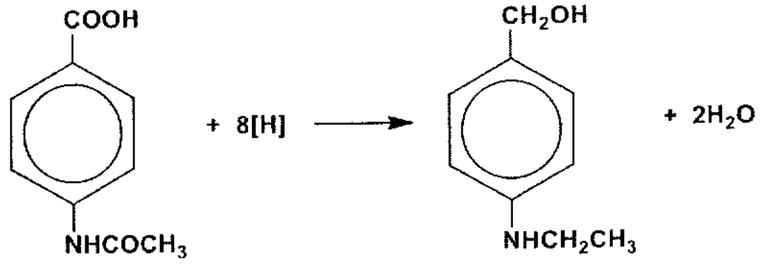


Reaction II: electrophilic substitution



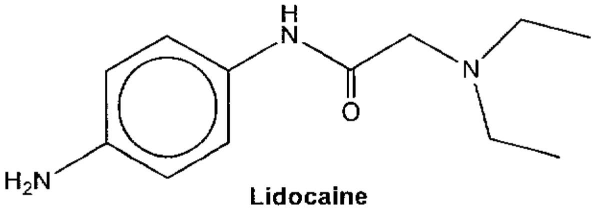
[3]

(v) Write a balanced equation for Reaction I.



[1]

(b) Lidocaine is also a local anesthetic.



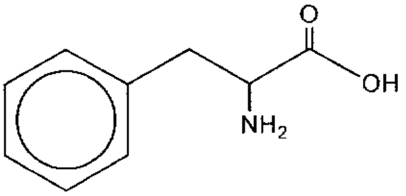
Lidocaine

(i) Suggest the reagents and conditions for a reaction that could be used to distinguish between benzocaine and lidocaine.

Test: I_2(aq), NaOH(aq), warm
Observations:
Benzocaine : pale yellow ppt. of CHI_3 formed
Lidocaine: no pale yellow ppt. formed

[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.



Phenylalanine

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

hydrogen bonds OR
permanent dipole-induced dipole interactions OR
instantaneous dipole-induced dipole interactions OR
ion-dipole interactions OR
electrostatic interactions between oppositely charged ions

Examiner's Comments:
Generally well done. For students answered wrongly, most misinterpreted intermolecular interactions as reactions.

[2]

(c) Silver carbonate, Ag_2CO_3, is used as a catalyst in many organic synthesis. It is a sparingly soluble salt. A saturated solution of Ag_2CO_3 was found to contain 2.50×10^{-4} mol dm^{-3} of Ag^+ ions.

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

$$K_{sp} = [Ag^+]^2[CO_3^{2-}]$$
$$= (2.50 \times 10^{-4})^2(2.50 \times 10^{-4} \div 2)$$
$$= 7.81 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$$

[2]

(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.

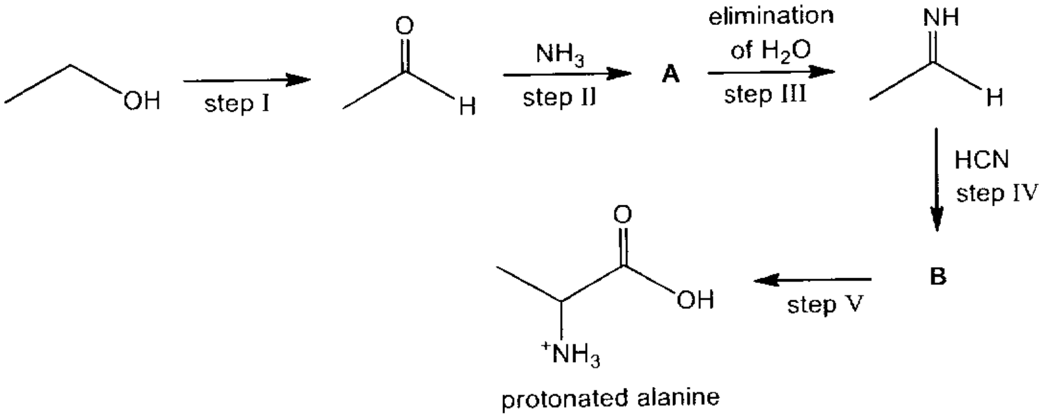
$K_{sp} = [Ag^+]^2[CO_3^{2-}]$
$7.81 \times 10^{-12} = [Ag^+]^2 \times [2.00 / 106.0 \div (100/1000)]$
$[Ag^+] = 6.43 \times 10^{-6}$ mol dm^{-3}

Solubility of Ag_2CO_3 = $\frac{1}{2} \times 6.43 \times 10^{-6} = 3.22 \times 10^{-6}$ mol dm^{-3}

[2]

[Total: 20]

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.



protonated alanine

(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.

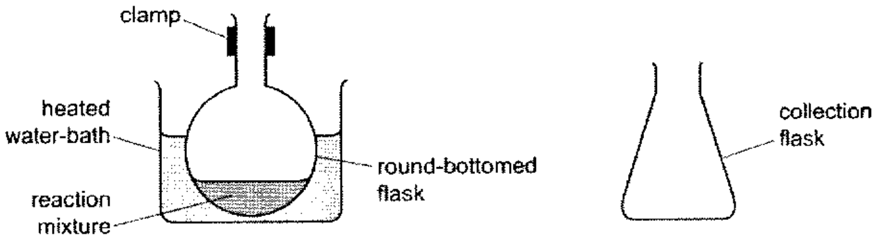


Figure 5.1

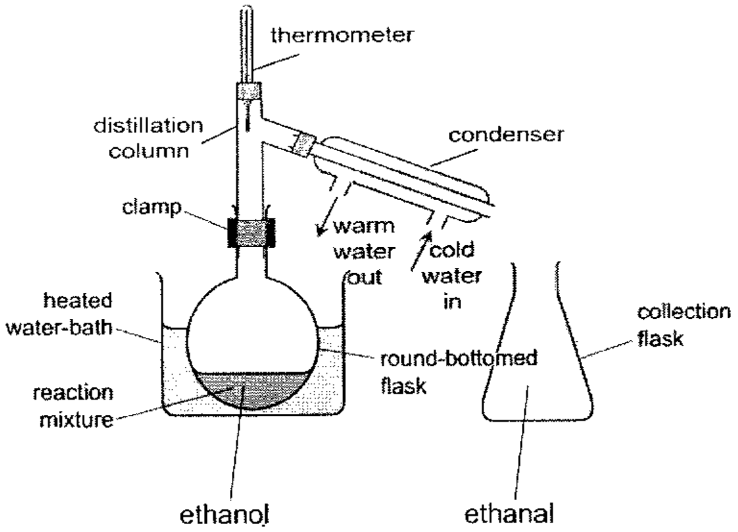


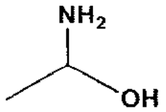
Figure 5.1

- **thermometer bulb level with side arm**
- **condenser with water in (at bottom) and out (at top)**
- **sealed around the round bottomed flask and thermometer, and not sealed around collection flask**

[3]

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

A:



[1]

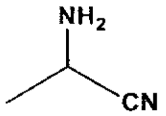
(iii) The product of step III is an imine, which has a C=N bond.

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**.

Nucleophilic addition

B:

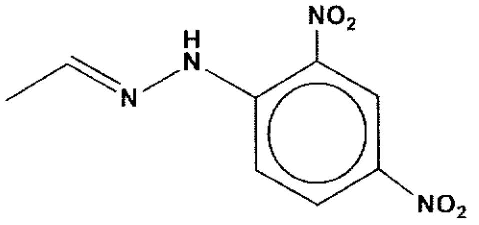


[2]

(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.

C:



Since there are 2 bond pairs and 1 lone pair,
shape: bent
bond angle: 117.5° or 118°

[2]

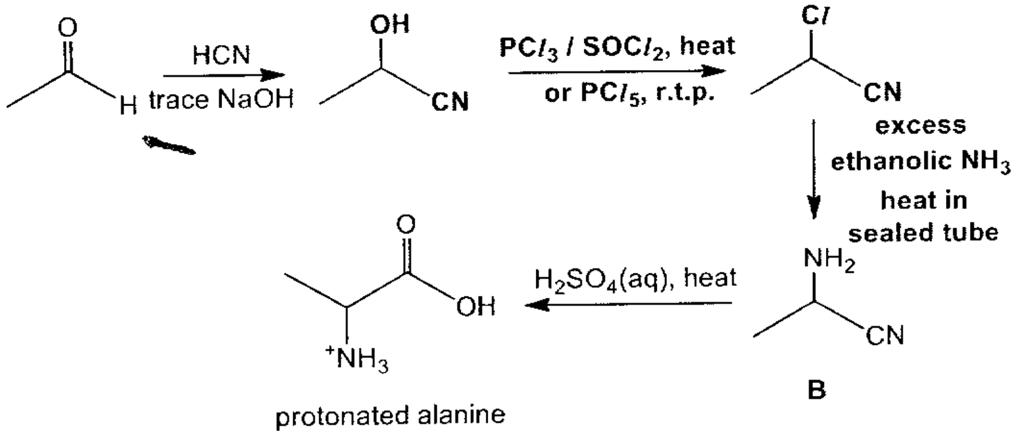
(v) Suggest reagents and conditions for step V.

step V: H_2SO_4(aq), heat OR HC*l*(aq), heat

[1]

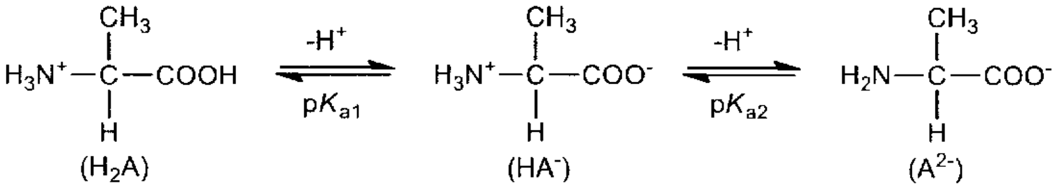
(vi) The student proposed an alternative synthetic route by reacting ethanal directly with HCN and traces of aqueous NaOH. The route will also produce compound **B** as the precursor to protonated alanine.

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]

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



$$H_3N^+-CH(CH_3)-COOH \underset{pK_{a1}}{\overset{-H^+}{\rightleftharpoons}} H_3N^+-CH(CH_3)-COO^- \underset{pK_{a2}}{\overset{-H^+}{\rightleftharpoons}} H_2N-CH(CH_3)-COO^-$$

(H_2A) (HA^-) (A^{2-})

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

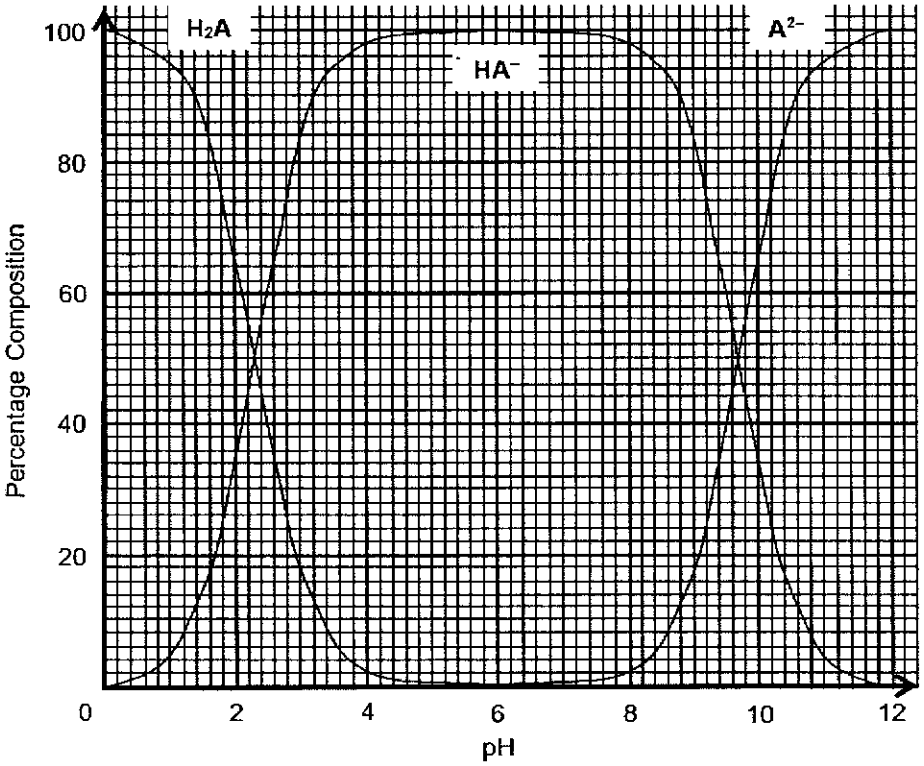


Figure 5.2

(i) State the values of pK_{a1} and pK_{a2} of alanine.

At 1st maximum buffering capacity
where percentage composition of $H_2A = HA^- = 50\%$, $pH = pK_{a1} = 2.30$

At 2nd maximum buffering capacity
Where percentage composition of $HA^- = A^{2-} = 50\%$, $pH = pK_{a2} = 9.70$

[1]

(ii) A buffer of pH 10.0 is prepared by adding solid NaOH to 0.100 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.

At pH 10.0, the mixture contains 34% HA^- and 66% A^{2-}.

Amount of $HA^- = 0.100 \times 34\% = 0.0340$ mol
Amount of $A^{2-} = 0.100 \times 66\% = 0.0660$ mol

$H_2A + OH^- \rightarrow HA^- + H_2O$ --- eqn 1
$HA^- + OH^- \rightarrow A^{2-} + H_2O$ --- eqn 2
Amount of NaOH required for eqn 1 = 0.100 mol
Amount of NaOH required for eqn 2 = 0.0660 mol
Total amount of NaOH required = 0.166 mol
Mass of NaOH required = 0.166 × 40.0 = 6.64 g

[2]

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

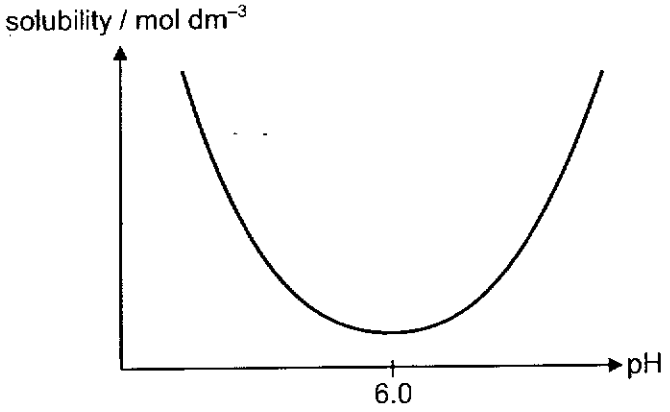


Figure 5.3

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.

At isoelectric point, alanine exist as zwitterions, HA^-. The opposite charges favours attraction between zwitterions. Thus, less ion-dipole interactions can be formed between the zwitterions and water molecules. The energy released from the ion–dipole interactions formed between the zwitterion and water molecules release insufficient energy to overcome the strong electrostatic forces of attractions between the zwitterions and the hydrogen bonds between water molecules. Hence, the solubility of alanine is low at pH 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.

At low and high pH, alanine exist as cation and anion respectively. At low pH, the cations repel each other and at high pH, the anions repel each other. Thus, more ion-dipole interactions can be formed between the ions and water molecules. The energy released from the ion–dipole interactions formed between the ions and water molecules release sufficient energy to overcome the the hydrogen bonding between water molecules. Hence, the solubility of alanine is high at low and high pH.

[2]
[Total: 20]