NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

12 September 2018

2 hours

Chemistry (9729)

Paper 2 Structured Questions

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

You may use an 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.

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

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:

Question	1	2	3	4	5	Total
Marks	19	20	10	7	19	75

This document consists of **20** printed pages (including this page).

Answer **all** the questions.

1 Glucose oxidase (GOx) is an enzyme found in certain species of insects and fungi that catalyses the oxidation of glucose to gluconic acid.

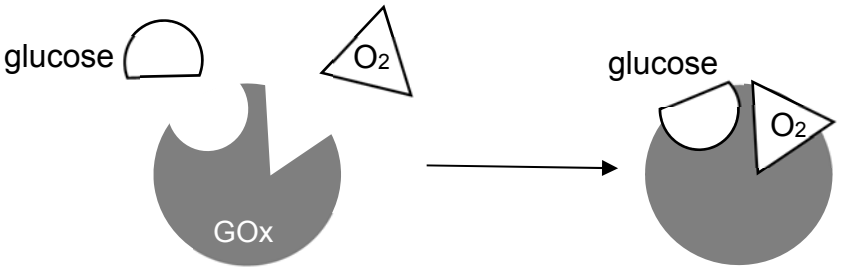
$$\underset{\text{glucose}}{C_6H_{12}O_6} + O_2 + H_2O \xrightarrow{GOx} \underset{\text{gluconic acid}}{C_6H_{12}O_7} + H_2O_2$$

(a) Write two half-equations to show that this is a redox reaction. **[2]**

$C_6H_{12}O_6 + H_2O \rightarrow C_6H_{12}O_7 + 2H^+ + 2e^-$

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

(b) The binding of reactants to GOx can be simplified with a diagram as shown below.



(i) Explain why GOx can be described as a *biological catalyst*. **[2]**

GOx allows certain reactants to bind specifically to it for the conversion into products.

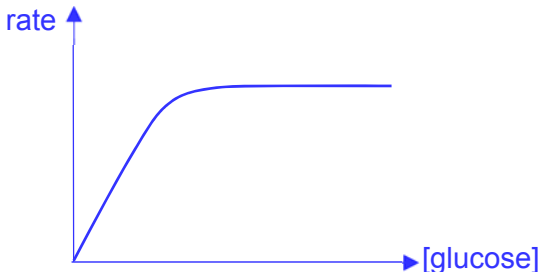
GOx speeds up the rate of reaction by providing an alternative pathway of lower activation energy. OR It is regenerated / remained chemically unchanged at the end of the reaction.

(ii) Based on the diagram above, suggest why the sign of ΔS is negative for the reaction. **[1]**

The 2 reactants and GOx must come together to form one large entity. OR There is a decrease in number of (gaseous) particles.

Hence, the products are less disordered than the reactants.

(iii) Sketch a graph showing how the rate of this GOx-catalysed reaction varies with the concentration of glucose. **[1]**



(c) The overall equation can be re-expressed to show the change in functional group.

$$C_5H_{11}O_5CHO + O_2 + H_2O \longrightarrow C_5H_{11}O_5COOH + H_2O_2$$

glucose — gluconic acid

Calculate the enthalpy change of reaction for the conversion of glucose into gluconic acid. Use relevant data from the *Data Booklet*. **[2]**

Bonds broken in reactant: C–H, ~~C=O~~, O=O, ~~2O–H~~

Bonds formed in product: ~~C=O~~, C–O, O–H + ~~2O–H~~ + O–O

$\Delta H = (410 + 496) - (360 + 460 + 150) = -64.0$ kJ mol^{-1}

(d) Experiments were done to determine the kinetics of the reaction.
In the first investigation, the following reaction mixture was prepared.

initial [glucose] = 5.00×10^{-3} mol dm^{-3}

initial [GOx] = 1.00×10^{-2} mol dm^{-3}

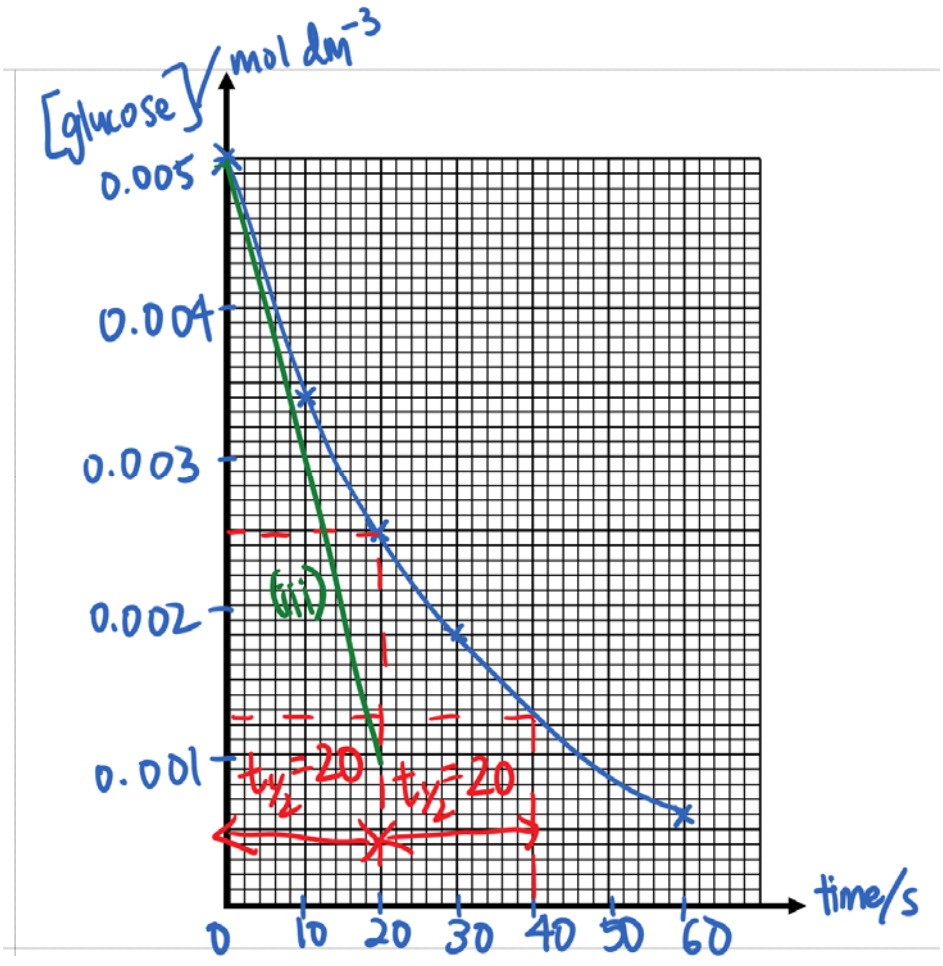
initial [O_2] = 1.00×10^{-2} mol dm^{-3}

The following results in **Table 1** were obtained.

Table 1

t/s	[glucose] / mol dm^{-3}
0	5.00 x 10^{-3}
10	3.40 x 10^{-3}
20	2.50 x 10^{-3}
30	1.80 x 10^{-3}
60	6.00 x 10^{-4}

(i) To determine the order of reaction with respect to [glucose], use these data to plot a suitable graph on the grid below.



[2]

Guidelines for scale:

x-axis: *t*/s, 1 big square = 20s

y-axis: [glucose] / mol dm^{-3}, 1 big square = 1.0 X 10^{-3} mol dm^{-3}

(ii) Hence, deduce the order of reaction with respect to [glucose], showing all your working and drawing clearly on your graph. **[2]**

Show two $t_{1/2}$ clearly on the graph.

Since $t_{1/2}$ is (approximately) constant at 20s, the reaction is first order with respect to [glucose].

In the second and third investigations, the concentrations of oxygen and GOx were changed, but the initial [glucose] was kept the same as before. The following results in **Table 2** were obtained.

Table 2

Investigation	**Initial [O_2] (mol dm^{-3})**	**Initial [GOx] (mol dm^{-3})**	**Initial rate (mol dm^{-3} s^{-1})**
1	1.00 x 10^{-2}	1.00 x 10^{-2}	**Y**
2	5.00 x 10^{-3}	1.00 x 10^{-2}	2.00 x 10^{-4}
3	5.00 x 10^{-3}	2.50 x 10^{-3}	5.00 x 10^{-5}

(iii) Use your graph in **(d)(i)** to determine the initial rate **Y**, showing all your working and drawing clearly on your graph. Hence, use the information in **Table 2** to determine the orders of reaction with respect to [O_2] and [GOx]. Explain your reasoning. **[3]**

Y = $\frac{(5.0 \times 10^{-3} - 1.0 \times 10^{-3})}{20} = 2.00 \times 10^{-4}$

Using investigation 1 and 2, when [O_2] is halved, the initial rate remains the same. Hence, the reaction is zero order with respect to [O_2].

Using investigation 2 and 3, when [GOx] decreases 4 times, the initial rate decreases 4 times. Hence, the reaction is first order with respect to [GOx].

(e) GOx can be used in a biosensor to convert glucose present in body fluids into gluconic acid. The amount of hydrogen peroxide produced is then reduced electrochemically to determine the amount of glucose present.

A 0.1 cm^3 of blood sample from a patient was tested to diagnose if he was at risk of diabetes. The diagnosis is based on the concentration of glucose in the blood.

Condition	**[glucose] in blood (x 10^{-3} mol dm^{-3})**
Normal	less than 5.6
Pre-diabetes	5.6 − 6.9
Diabetes	More than 6.9

The biosensor gave a current of 1.01 mA for 1 min. (1000 mA = 1A)

(i) Calculate the number of moles of hydrogen peroxide produced. Hence, diagnose the condition of the patient. **[3]**

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

Amt of charge = $1.01 \times 10^{-3} \times 60 = 0.0606$ C

Amt of e^- = $0.0606 / 96500 = 6.2798 \times 10^{-7}$ mol

Amt of H_2O_2 = $6.2798 \times 10^{-7} / 2 = 3.14 \times 10^{-7}$ mol (3sf)

Amt of glucose = amt of H_2O_2 = 3.14×10^{-7} mol

[glucose] = $3.14 \times 10^{-7} / (0.1 \times 10^{-3}) = 3.14 \times 10^{-3}$ mol dm^{-3}

The patient is normal.

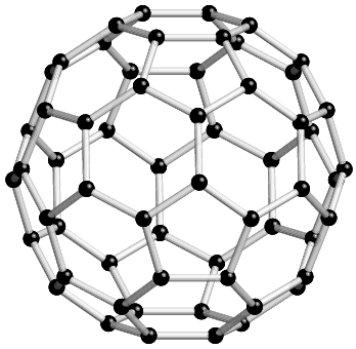
(ii) Before the test, the blood sample has to be treated to remove some components present. Suggest why a treated blood sample was necessary for the biosensor to give an accurate reading. **[1]**

The blood has to be treated to remove some components that can be reduced or oxidised by the biosensor or GOx .

[Total: 19]

2 This question deals with carbon and silicon which are both elements in Group 14.

(a) C_{60} and diamond are allotropes of carbon. C_{60} is a simple covalent molecule while diamond is a giant covalent molecule. State the type of bonding and describe the lattice structure of solid C_{60}.



C_{60}

[2]

Type of bonding: Within each C_{60} molecule, there is strong covalent bonds between carbon atoms.

Describe lattice structure: C_{60} exists as a regular lattice of simple covalent molecules with instantaneous dipole-induced dipole interactions between C_{60} molecules.

(b) 0.144 g of C_{60} was placed in a 100 cm^3 container of hydrogen gas at 20 °C and 1.00×10^5 Pa.

The reaction occurred as shown in the equation.

$$C_{60}\,(s) + xH_2\,(g) \rightarrow C_{60}H_{2x}\,(s)$$

When all the C_{60} had reacted, the pressure was found to be 2.21×10^4 Pa at the same temperature.

(i) Calculate the amount, in moles, of C_{60} that reacted. **[1]**

Amount of $C_{60} = 0.144 / 720 = 2 \times 10^{-4}$

(ii) Calculate the amount, in moles, of hydrogen gas that reacted with C_{60}. **[2]**

$pV = nRT$

$\therefore \Delta n = (p1 - p2)V / RT$

$\Delta n = (1.00 \times 10^5 - 2.21 \times 10^4).100 \times 10^{-6} / 8.31 \times 293 = 0.00320$ mol

(iii) Use your answers from **(i)** and **(ii)** to deduce the molecular formula of the hydrocarbon, $C_{60}H_{2x}$. **[2]**

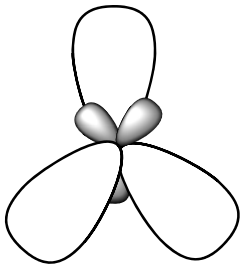
$C_{60}:H_2 = 2.00 \times 10^{-4} : 0.00320 = 1:16$

$X = 16$

$C_{60}H_{32}$

(c) (i) Graphite is another allotrope of carbon. State the type of hybridisation and draw the arrangement of the hybrid orbitals about each C atom. **[2]**

sp^2



(ii) Graphite is a good conductor of electricity. Explain, with reference to orbital overlap, how graphite has a high electrical conductivity. **[2]**

The unhybridised p orbitals on each carbon are overlapping sideways.
This side–on overlap results in the formation of a π-electron cloud.
The π electrons are delocalised and account for the high electrical conductivity of graphite.

(c) (iii) The values for the enthalpy change of combustion of graphite and diamond are given in the table below.

Substance	**Enthalpy change of combustion / kJ mol^{-1}**
Graphite	−394
Diamond	−396

The products of the combustion reactions of graphite and diamond are carbon dioxide and water.

Suggest why the enthalpy change of combustion of graphite is less exothermic than that of diamond. **[1]**

The C-C bonds in graphite are stronger than that in diamond. (or words to the effect, e.g. graphite is energetically more stable than diamond / has lower energy content)

(d) Silicon is another element in Group 14 which shows the same kind of bonding and structure as diamond.

(i) When silicon reacts with magnesium, Mg_2Si forms. Mg_2Si is thought to contain the Si^{4-} ion. Compare and explain the difference between the atomic and anionic radii of silicon. **[2]**

The number of protons in both the atom and its anion is the same, hence **nuclear charge remains constant**. The anion has **more electrons** and hence **valence electrons are less strongly attracted to the nucleus**, resulting in **larger anionic radius in** Si^{4-} when compared to Si.

(ii) Suggest why the second ionisation energy of silicon is lower than that of aluminium. **[2]**

Al^+ : $[Ne]3s^2$

Si^+ : $[Ne]3s^23p^1$

The second electron to be removed from Si is in the p orbital which is further away from the nucleus than the s orbital and it faces additional shielding effect from the 3s electrons. Less energy required to remove it.

(iii) Solid Mg_2Si reacts with dilute hydrochloric acid to form gaseous SiH_4 and a solution of magnesium chloride only. Write an equation, including state symbols, to show the reaction of solid Mg_2Si with dilute hydrochloric acid. **[1]**

$Mg_2Si(s) + 4HCl\ (aq) \rightarrow SiH_4(g) + 2MgCl_2(aq)$

(iv) Describe the reaction, if any, of $NaCl$ and $SiCl_4$ with water, relating any differences to their bonding. Give relevant equations for any reactions and suggest the pH values of each resulting solution. **[3]**

As covalent character of chlorides increases, the more complete the hydrolysis / the more acidic the solution is.

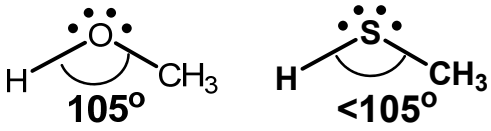
$NaCl$ **dissolves** in water to form a neutral solution of **pH 7**. $SiCl_4$ undergoes complete hydrolysis to form an acidic solution of **pH 2**.

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$

[Total: 20]

3 Hydrocarbons that contain other elements are known as heterocompounds. A special class of heterocompounds are thiols. Thiols are sulfur analogs of alcohols and have the general formula R-SH. Its structure is similar to that of an alcohol, but with sulfur in place of oxygen. One such example is CH_3SH.

(a) State the bond angle about the oxygen atom in CH_3OH and explain if the bond angle is bigger than the bond angle about the sulfur atom in CH_3SH. **[3]**



Both CH_3OH and CH_3SH have 2 bond pairs of electrons and 2 lone pairs of electrons around O and S stoms respectively. In CH_3OH, **oxygen has a greater electronegativity than sulfur** in CH_3SH.

The **bond pair of electrons are more strongly attracted to oxygen**, resulting in **greater repulsion between the bond pairs** in CH_3OH.

Hence, the **H-S-C bond angle in CH_3SH is less than 105°**

(b) Thiols can be converted to produce compounds called disulfides. This type of reaction is common in protein structures where it forms disulfide linkages (**–S–S–**) between two thiols as shown in the following equation:

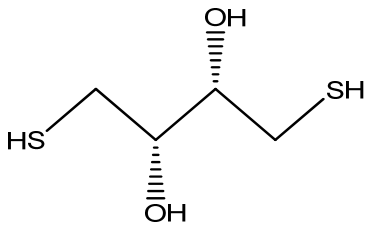
$$2\ RS\text{-}H \rightarrow R\text{-}S\text{-}S\text{-}R + H_2$$

Based on the above equation, suggest two disulfide products that could be formed when $HOCH_2CH_2SH$ and $HOCH_2CH(CH_3)SH$ are reacted.

[1]

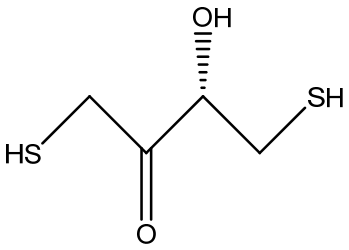
Any two of the three below:
$HOCH_2CH_2S\text{-}SCH_2CH_2OH$,
$HOCH_2CH_2S\text{-}SCH(CH_3)CH_2OH$,
$HOCH_2CH(CH_3)S\text{-}SCH(CH_3)CH_2OH$

(c) Dithiothreitol (**DTT**) is an organic molecule with molecular formula, $C_4S_2O_2H_{10}$. It has both the functional group of an alcohol and a thiol. The structure of **DTT** is given below.



DTT can be oxidised under suitable conditions to form product **X** with molecular formula, $C_4S_2O_2H_8$.

(i) Draw the structural formula of product **X**. **[1]**



(ii) Product **X** can then undergo nucleophilic addition with hydrogen cyanide under suitable conditions.

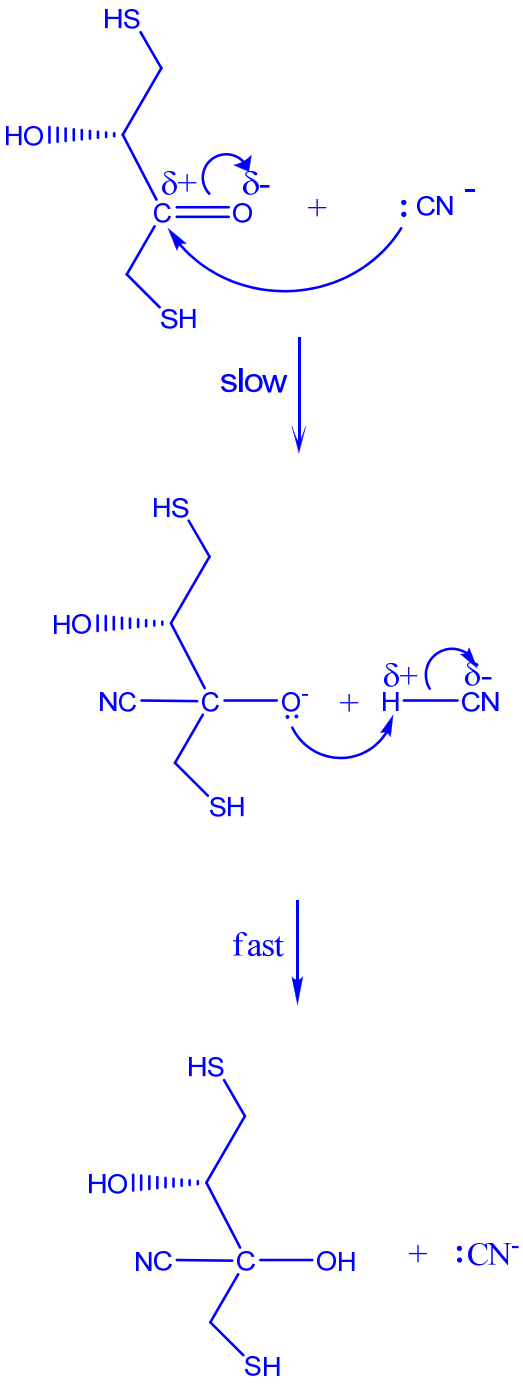
Suggest the conditions for this reaction to take place and hence, describe the mechanism of the reaction, In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows. **[3]**

Conditions: Trace amount of NaOH (aq) or NaCN (aq), 10 – 20 °C

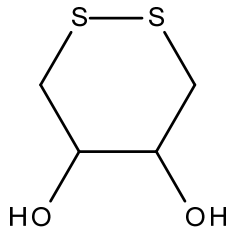
$NaOH + HCN \rightarrow Na^+ + CN^- + H_2O$

OR

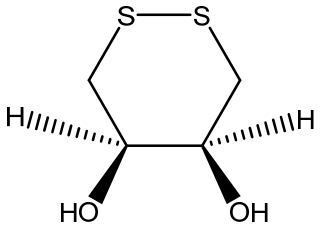
$NaCN \rightarrow Na^+ + CN^-$


HS
HO
δ+
δ-
C
O
+
: CN -
SH
slow
HS
HO
NC
C
O-
+
δ+
δ-
H
CN
SH
fast
HS
HO
NC
C
OH
+
:CN-
SH

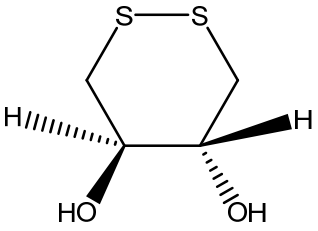
(d) **DTT** can be oxidised to form a stable six-membered ring with an internal disulfide bond as shown in the following structure.



The oxidised form of **DTT** has a restricted rotation about the C-C bond with the two –OH groups hence enabling it to exhibit cis-trans isomerism.
Draw the cis-trans isomers of the oxidised form of **DTT**. **[2]**



cis



trans

[Total: 10]

4 Iron salts, usually iron(II) sulfate, catalyses the decomposition of aqueous hydrogen peroxide to water and oxygen. The reaction mechanism involves OH and HO_2 free radicals. The reaction mechanism is given below.

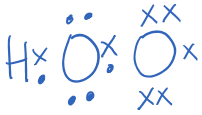
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+$$

(a) Define *free radical*. **[1]**

Free radical is an atom or group of atoms having an **unpaired / single / lone / odd electron**.

(b) Draw the dot-and-cross diagram for HO_2 free radical. **[1]**

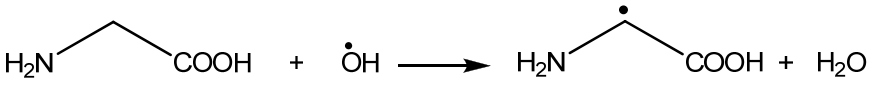


(c) State the type of catalysis that takes place between iron(II) sulfate and hydrogen peroxide and state the property of iron(II) sulfate that allows it to carry out its function as a catalyst in the above decomposition reaction. **[2]**

Homogeneous catalysis.

Iron can exist in **variable oxidation states**.

(d) OH radicals can modify amino acids. They behave similarly to chlorine radicals by abstracting a hydrogen in the propagation step of free radical substitution mechanisms. This is represented using glycine as shown below.

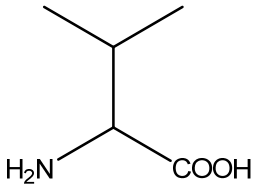


glycine

(i) Suggest why the rate of propagation is slower when glycine exists as an anion. **[1]**

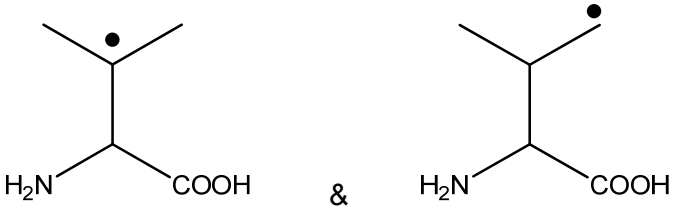
When glycine exists as an anion, the negatively-charged ion and electron on the OH radical will **repel** one another.

(ii) Valine is another amino acid that can react with OH radicals. The structure of valine is as shown below.



valine

Valine reacts with OH radicals to form three radical products, of which two are shown below.

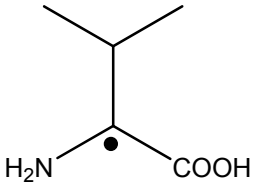


Product A **Product B**

Suggest a reason why product **A** is more stable. **[1]**

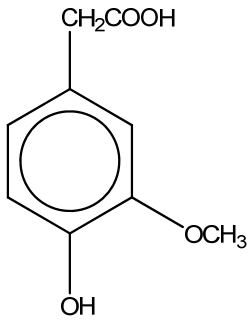
There are more **electron-donating alkyl groups in A** to stabilise the electron deficiency on the carbon with the radical.

(iii) Draw the structural formula of the third radical product for the above reaction in **(ii)**. **[1]**

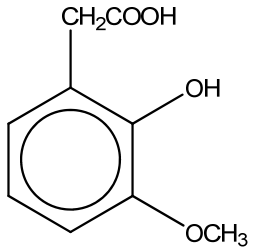


[Total: 7]

5 (a) The concentration of hydrogen peroxide can be determined by fluorescence reaction between homovanillic acid (HVA) and hydrogen peroxide. HVA can be found in urine and can be found to exist in two constitutional forms as shown below.



HVA - I



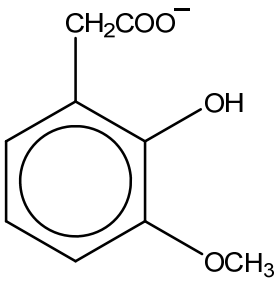
HVA-II

(i) There are two pK_a values associated with **HVA - I**: 3.7 and 5.3. Explain the difference in the pK_a values. **[2]**

The negative charge delocalises over the O-C-O bond of the carboxylate ion, while the negative charge delocalises into the benzene ring of the phenoxide ion. However the resonance effect is greater for carboxylate ion / carboxylate ion is more stable, hence carboxylic acid is a stronger acid / carboxylic acid has a lower pKa.

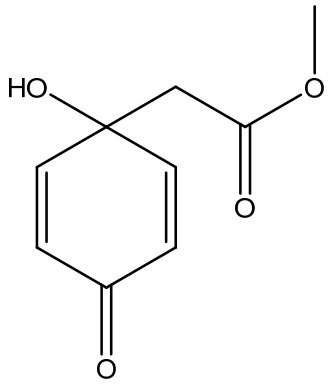
(ii) Draw the structural formula of the monoanion produced from the first dissociation of **HVA – II**.

Hence, explain why the first pK_a value of **HVA – II** is much lower than the first pK_a value of **HVA – I.** **[2]**



The **monoanion formed from HVA-II is more stable than the monoanion from HVA-I** as it is able to **form intramolecular hydrogen bonding / ion-dipole interactions.**

An isomer of HVA is jacaranone which is used in cancer treatments. Its structure is given below.



jacaranone

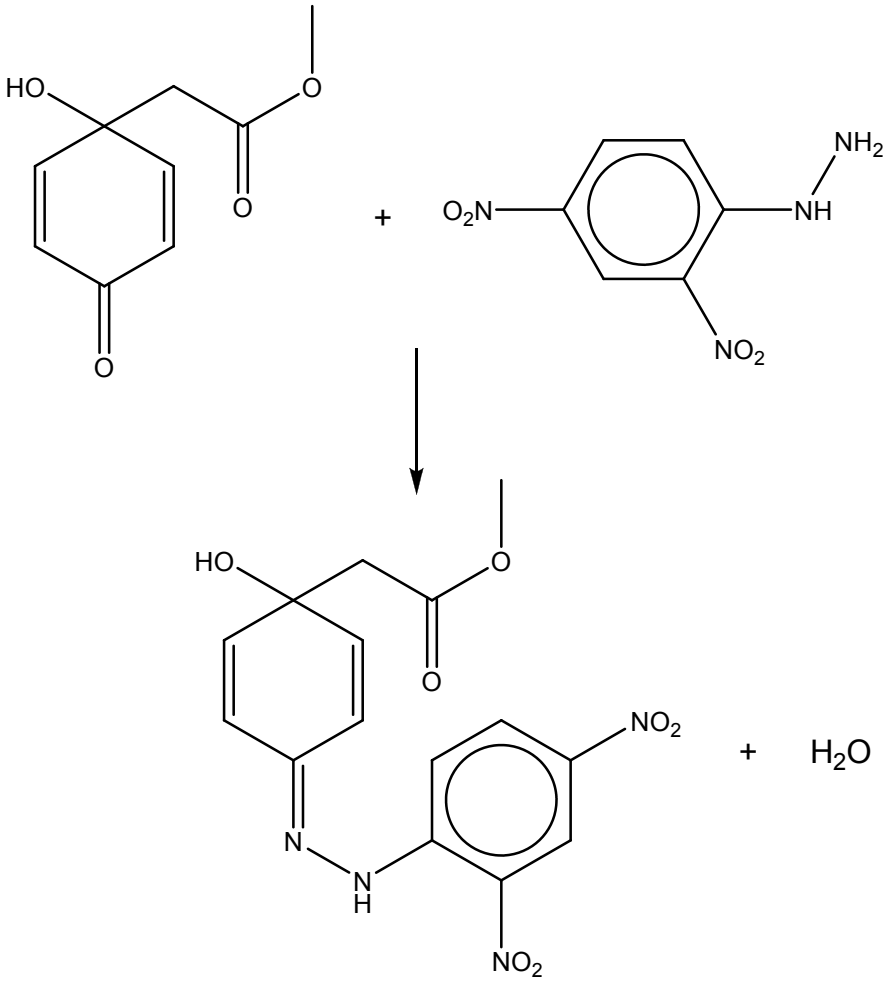
(iii) Identify the functional groups present in jacaranone. **[2]**

Tertiary alcohol, ester, alkene, ketone

(iv) Suggest a simple chemical test which could distinguish between **HVA - I** and jacaranone. Write the balanced equation for the positive test. **[3]**

Add **2,4-dinitrophenylhydrazine** to each compound separately and warm.

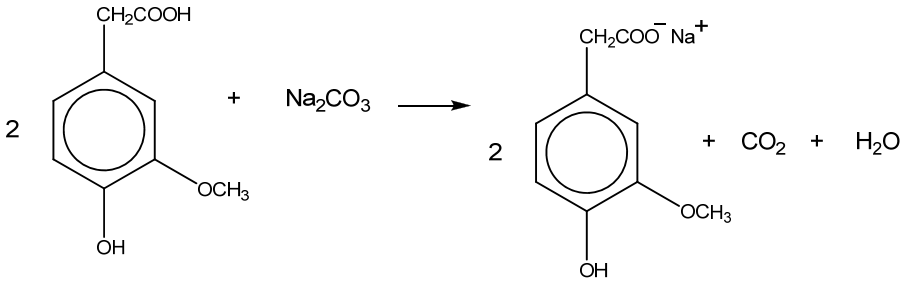
Orange ppt seen with jacaranone.



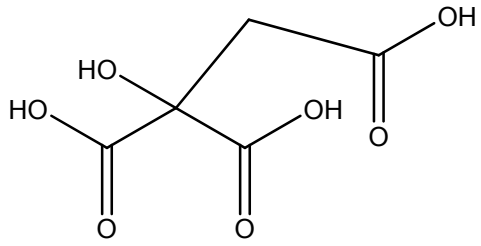
OR

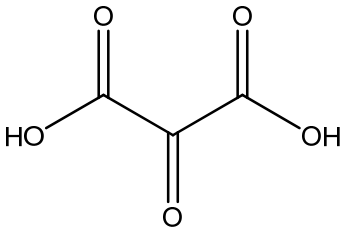
Add **Na_2CO_3** to each compound separately.

Effervescence is seen for HVA-I and gas forms white ppt in limewater.



(v) Draw all the carbon-containing products formed when jacaranone is heated with acidified $KMnO_4$. **[3]**





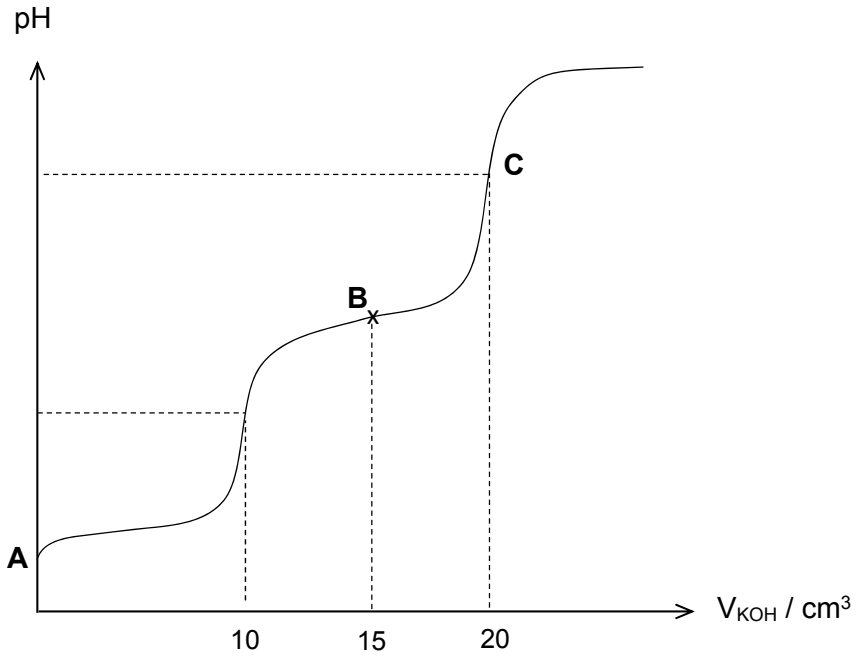
CO_2

(b) **HVA - I**, $C_9H_{10}O_4$, is a weak dibasic acid which dissociates in water as follows:

$$C_9H_{10}O_4 \rightleftharpoons C_9H_9O_4^- + H^+ \qquad pK_{a1} = 3.7$$

$$C_9H_9O_4^- \rightleftharpoons C_9H_8O_4^{2-} + H^+ \qquad pK_{a2} = 5.3$$

A quantitative analysis was performed on a 25.0 cm^3 sample of **HVA - I**. It was titrated against 0.75 mol dm^{-3} of potassium hydroxide. The resulting pH curve was plotted as shown below.



(i) Calculate the concentration of **HVA - I** present in the sample. **[2]**

Amount of KOH = 0.75 x 0.020 = 0.015 mol

Mole ratio of KOH : **HVA - I** = 2 : 1

Amount of **HVA - I** = 0.015 / 2 = 0.0075 mol

[**HVA - I**] = 0.0075 / 0.025 = **0.300** mol dm^{-3}

(ii) Using the first pK_a value, calculate the initial pH at point **A**. **[2]**

$K_a = 10^{-3.7} = 1.995 \times 10^{-4}$

$K_a = [H^+]^2 / [\mathbf{HVA - I}]$

$[H^+] = (1.995 \times 10^{-4} \times 0.300)^{1/2} = 7.736 \times 10^{-3}$ mol dm^{-3}

pH = $-\lg(7.736 \times 10^{-3})$ = **2.11**

(iii) State the pH at point **B** and hence, explain the significance of point **B**. **[2]**

pH = 5.3

It has equal concentrations of salt and acid. OR It has equal ability to remove small amount of H^+ and OH^-. OR Maximum buffer capacity.

(iv) Write an equation to show that pH at point **C** is more than 7. **[1]**

$C_9H_8O_4^{2-} + H_2O \rightleftharpoons C_9H_9O_4^- + OH^-$

[Total: 19]

~ END OF PAPER ~