NAME _____ CLASS **19S**

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2020

CHEMISTRY **9729/02**

Higher 2

Paper 2 Structured Questions

17 September 2020
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a HB pencil for any diagrams, 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.

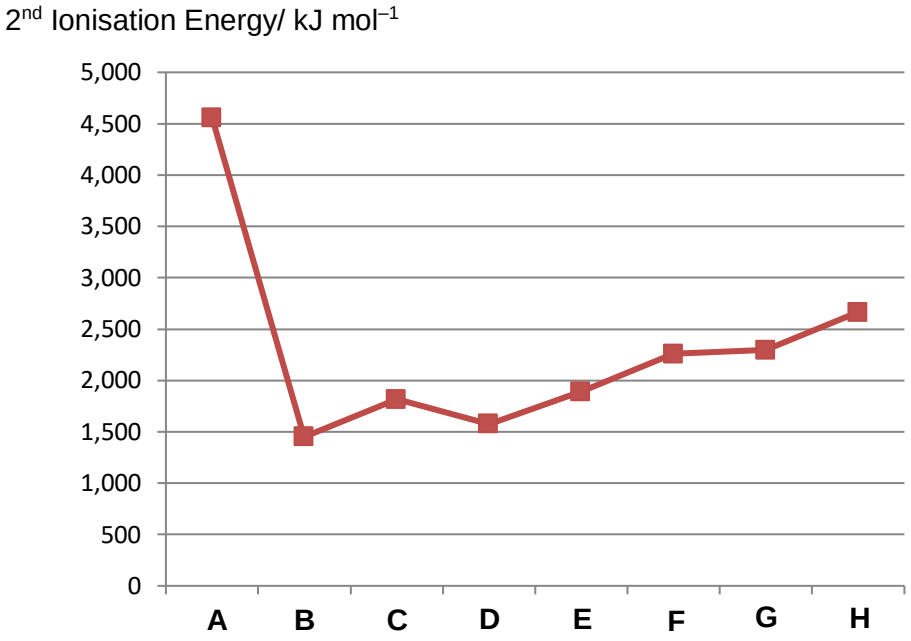
For Examiner's Use		
Paper	**Question**	**Mark**
2	**1**	**/ 13**
	2	**/ 9**
	3	**/ 14**
	4	**/ 12**
	5	**/ 6**
	6	**/ 21**
Penalty (delete accordingly)		
Lack **3sf** in final ans		**–1 / NA**
Missing/wrong **units** in final ans		**–1 / NA**
Total		**/ 75**

This document consists of **21** printed pages.

Answer all the questions in the spaces provided.

1 **(a)** The following graph below shows the **second** ionisation energies of Period 3 elements with consecutive proton number.

For Examiner's Use



(i) Explain why the second ionisation energy generally increases from **B** to **H**.

Across the period, the nuclear charge/ proton number increases and the radius decreases while the shielding effect is relatively constant (due to same number of inner shell electrons).
Hence, increase in effective nuclear charge OR nuclear attraction on the electron to be removed increases and hence, the second IE generally increases.

[2]

(ii) Which of the above elements, **A** to **H**, is aluminium?

Element **C**

[1]

(iii) Explain the following:

- big drop in second ionisation energy from **A** to **B**
- slight drop in second ionisation energy from **C** to **D**

A to **B**: 2nd ionisation energy involves removal of 3s electron from $\mathbf{B}^+$ and removal of 2p electron in $\mathbf{A}^+$. $\mathbf{B}^+$ has 1 more quantum shell with electrons thus the electron to be removed from H^+ is further away from nucleus, hence the nuclear attraction on the electron to be removed is weaker and hence, the 2nd IE of **B** is much lower than that of **A**.

C to **D**: $\mathbf{C}^+$: ns^2 $\mathbf{D}^+$: $ns^2\,np^1$
The n*p* electron removed from $\mathbf{D}^+$ is further away from the nucleus and has a higher energy than the n*s* electron removed from $\mathbf{C}^+$. Thus more energy is required to remove it.

[2]

(b) Among the elements of Group 14, those towards the top, carbon to germanium, have very different properties from those at the bottom, tin and lead. For example, the melting points show a marked change after germanium.

element	C	Si	Ge	Sn	Pb
mp / °C	>3550	1410	937	232	327

Carbon, silicon and germanium each form a solid with the same type of structure.

(i) Explain why the melting points of these elements decrease from carbon to germanium.

Size of atom increases, covalent bonds between atoms become longer and weaker (BE: C – C > Si – Si > Ge –Ge)
Lesser energy required to break the decreasing strength of covalent bonds. [1]

(ii) Carbon and silicon each form a tetrachloride. CCl_4 has no reaction with water; $SiCl_4$ reacts violently with water. Suggest an explanation for the inertness of CCl_4 to water.

CCl_4 has no reaction with water because C atom has no available empty d orbitals to form dative bonds with water molecules.

Si atom in $SiCl_4$ has available low-lying empty d-orbitals, which can accept lone pair of electrons from water molecules, allowing dative bond formation between H_2O and Si before the Si – Cl bond needs to be broken. [1]

(c) The chalcogens are Group 16 elements which form compounds with carbon. The properties of some of these compounds, along with CO_2, are given in Table 1 below.

Table 1

compound	**structure**	**dipole moment**	**boiling point / °C**
CO_2	O=C=O	0	sublimes
CS_2	S=C=S	0	46
COS	S=C=O	0.71	–50
COSe	Se=C=O	0.73	–22

(i) Explain, in terms of structure and bonding, the difference in the boiling point of CS_2 and COS.

Both CS_2 and COS have simple molecular or simple covalent structures. CS_2 has a larger number of electrons (or larger electron cloud) to be polarised than COS.

More energy is required to overcome the stronger instantaneous dipole-induced dipole interactions between CS_2 molecules than the permanent dipole-dipole interactions between COS molecules.

Hence, CS_2 has a higher boiling point.

[2]

(ii) Explain why

- CO_2 has no overall dipole moment.
- COSe has a greater dipole moment than COS.

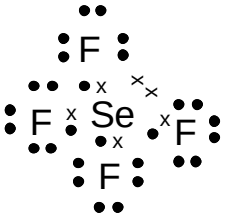
- CO_2 is linear and hence the dipole moments of C=O bonds cancel out.

- C=S bond is more polar than C=Se since S is more electronegative than Se. There is smaller difference between the dipole moment of C=O and C=S than that between C=O and C=Se.

[2]

(d) Chalcogens also form compounds with halogens known as chalcohalides. One such compound is selenium tetrafluoride, SeF_4, which is used as a fluorinating reagent in organic syntheses.

Draw a 'dot-and-cross' diagram showing the electrons (outer shell only) in a SeF_4 molecule. Use the VSEPR (valence shell electron pair repulsion) theory to predict its shape**.**



SeF_4 has 4 bond pairs, 1 lone pair, which gives a see-saw shape.

[2]
[Total:13]

2 **(a)** The key reaction during the Contact process for the manufacture of sulfuric acid is as follows.

For Examiner's Use

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

A mixture of SO_2 and O_2 in a 2 :1 molar ratio was introduced into a sealed vessel and heated to 450K.

At equilibrium it was found that the total pressure was 4.2 atm, and the mole fraction of O_2 was 0.0476.

(i) Write an expression for the equilibrium constant, K_p for this reaction.

$$K_p = \frac{\left(p_{SO_3}\right)^2}{\left(p_{SO_2}\right)^2\left(p_{O_2}\right)}$$

[1]

(ii) Calculate the equilibrium partial pressures of O_2**,** SO_2 and SO_3.

	$2SO_2(g)$	$O_2(g)$	$\rightleftharpoons$	$2SO_3(g)$
Initial amount/ mol	2	1		0
Change amt/ mol	-2x	-x		+2x
Eqm amt /mol	2-2x	1-x		2x
Ratio:	2 :	1		

[2]

Let n_T be the total amount of gaseous particles present.

equilibrium amount of SO_2 = 2 x eqm amount of O_2

$= 2 \times 0.19n_T = 0.38n_T$

$\therefore$ equilibrium amount of $SO_3 = n_T - 0.38n_T - 0.19n_T = 0.43_T$

Using $p_A = \frac{n_A}{n_T} \times p_T$ where $\frac{n_A}{n_T}$ is the mole fraction of A in a gaseous mixture,

	$2SO_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2SO_3(g)$
Eqm pressure/ atm	0.0952(4.2)		0.0476(4.2)		0.857(4.2)
	0.400 (✓)		0.200 (✓)		3.60(✓)

(iii) Calculate the value of K_p for the reaction at 450K.

[1]

$$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 (p_{O_2})} = \frac{(3.6)^2}{(0.4)^2 (0.2)} = 405 \text{ atm}^{-1}$$

(iv) Explain clearly the effect on the yield of SO_3, when the volume of reaction mixture is reduced.

When volume is reduced, total pressure is increased. By LCP, eqm should shift to decrease pressure by favouring the side with fewer moles of gas. [2]
to the right side thus equilibrium position shift to the right and yield of SO_3 increases.

(b) Due to the importance of the Contact process, the spontaneity of the reaction has been studied extensively.

(i) Predict the sign of the entropy change for the Contact process reaction. Explain your answer clearly.

Entropy change is negative.

The amount/ number of moles of gaseous particles decreases as the reaction proceeds since more moles of gaseous reactants react to form less moles of gaseous products. Hence, the degree of disorderliness decreases. [2]

(ii) The enthalpy change for the Contact process is exothermic. Hence, using the answer in **(b)(i)**, explain why this reaction is only spontaneous at low temperature.

By $\Delta G = \Delta H - T\Delta S$ [1]

The reaction is energetically feasible when ΔG is negative. As $T\Delta S$ *is negative,* $-T\Delta S$ *is positive. If* ΔH *is negative,* ΔG is negative occurs only when temperature is low $|T\Delta S| < |\Delta H|$.

[Total:9]

For Examiner's Use

3 **(a)** A sample of ground copper powder was contaminated with zinc powder. Treatment of the sample with an excess of hydrochloric acid produced 126 cm^3 of hydrogen gas, measured at a temperature of 300K and a pressure of 1.00×10^5 Pa, by the reaction shown.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

The remaining copper was then reacted with acidified potassium manganate(VII), forming a blue solution containing $Cu^{2+}(aq)$. It was found that 24.00cm^3 of 0.2 mol dm^{-3} of potassium manganate(VII) was required for complete oxidation of the copper.

(i) Calculate the mass of zinc present in the sample.

amount of H_2 formed in reaction 1 $= \dfrac{(1.00 \times 10^5)(126 \times 10^{-6})}{8.31 \times 300}$

$= 5.054 \times 10^{-3}$ mol (4 s.f)

From reaction 1, since $1Zn \equiv 1H_2$,

mass of Zn in sample = $(5.05 \times 10^{-3}) \times 65.4 = 0.331$ g (3s.f) (ecf)

[2]

(ii) Write a balanced **ionic** equation for the reaction between acidified MnO_4^- and Cu. Hence, calculate the percentage by mass of copper present in the sample

$5Cu(s) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 5Cu^{2+}(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$

From reaction 2, since $5Cu \equiv 2MnO_4^-$ (means 5 mol copper reacted with 2 mol manganate)

amount of Cu in sample = $\dfrac{5}{2} \times \left(\dfrac{24.00}{1000} \text{ x } 0.2\right) = 0.012$ mol

mass of Cu in sample = $0.012 \times 63.5 = 0.762$ g

[2]

% by mass of Cu in original sample = $\dfrac{0.762}{0.762 + 0.331} \times$ **100 %**

= 69.7 % (ecf based on students' mol ratio)

(b) Zinc and copper can react to form zinc(II) sulfide, ZnS, and copper (II) sulfide, CuS, both of which are used as semi-conductors.

The values of the solubility products of ZnS and CuS are given below.

K_{sp} (ZnS) = 1.6 x 10^{-24}

K_{sp} (CuS) = 6.3 x 10^{-36}

(i) Write an expression for K_{sp} for ZnS, giving its units.

[1]

K_{sp} for ZnS = $[Zn^{2+}][S^{2-}]$ mol^2 dm^{-6}

(ii) Calculate the solubility of ZnS in mol dm^{-3}.

Let the solubility of ZnS be s mol dm^{-3}

$ZnS(s) + aq \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq)$

Eqm [ ]/ $moldm^{-3}$ s s

$K_{sp}(ZnS) = [Zn^{2+}]_{eqm}[S^{2-}]_{eqm} = (s)(s) = 1.6 \times 10^{-24}$

$s = 1.26 \times 10^{-12}$ mol dm^{-3} [1]

(iii) An experiment was carried out by a chemist in the laboratory involving these two sulfides. Solid ZnS was shaken with water thoroughly. The remaining solid was filtered off, leaving a saturated solution. Drops of aqueous copper nitrate was added to the saturated solution, until CuS just precipitated.

Determine the concentration of Cu^{2+} when CuS just precipitated.

In saturated solution of ZnS, $[S^{2-}] = s = 1.26 \times 10^{-12}$ mol dm^{-3} [1]

When CuS just precipitates; IP (CuS) = K_{sp} (CuS)

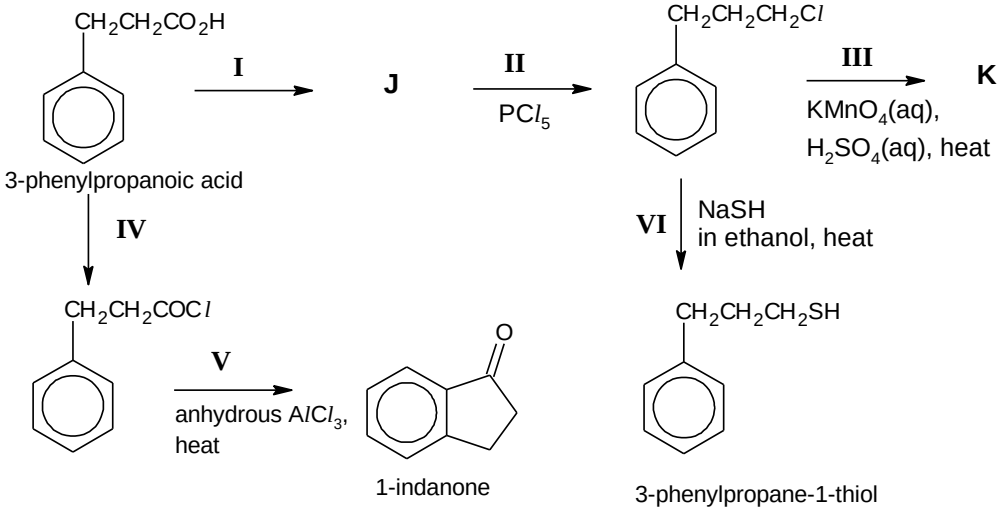
$[Cu^{2+}][S^{2-}] = 6.3 \times 10^{-36}$

$[Cu^{2+}](1.26 \times 10^{-12}) = 6.3 \times 10^{-36}$

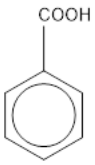
$[Cu^{2+}] = 5.00 \times 10^{-24}$ mol dm^{-3} (3.s.f)

(c) The flow-scheme below outlines the routes from 3-phenylpropanoic acid to form 3-phenylpropane-1-thiol and 1-indanone.

3-phenylpropane-1-thiol and 1-indanone are both used to synthesise inhibitors used to treat rheumatoid arthritis and Alzheimer's disease.



(i) Draw the structure of Compound **K**. [1]



Compound K: _____

(ii) Give the reagents and conditions for step **I**.

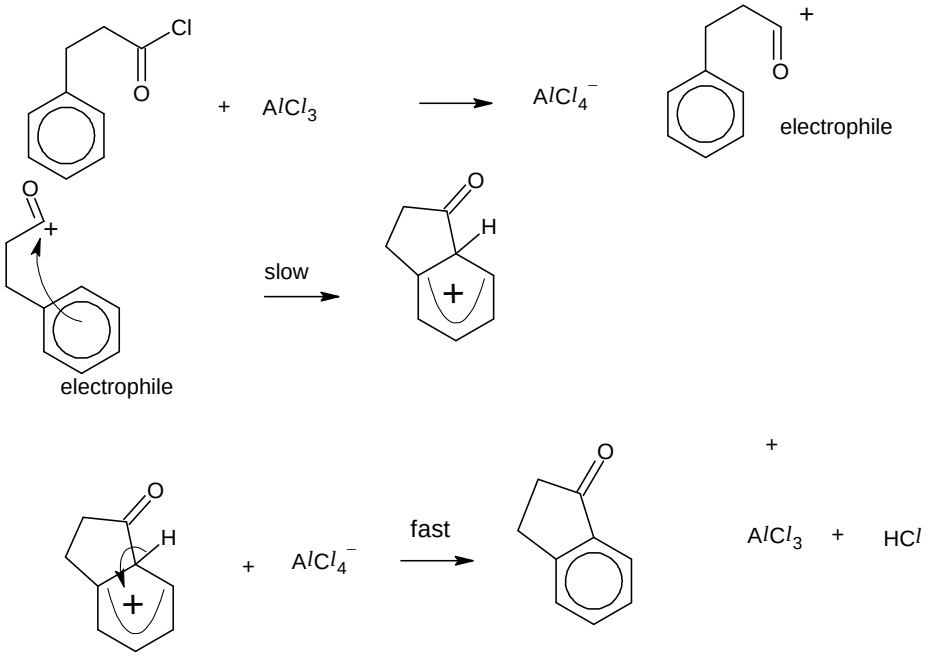
Step I : $LiAlH_4$ in dry ether [1]

(iii) Suggest the role of SH^- ion in step **VI.** [1]

nucleophile

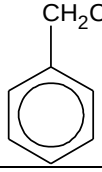
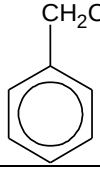
(iv) Name and draw the mechanism for step **V**. [3]

Electrophilic substitution



(v) Suggest a reason why the pK_a of 3-phenylpropane-1-thiol is lower than that of 3-phenylpropan-1-ol in Table 3 below.

Table 3

Name	**Structure**	**pK_a**
3-phenylpropane-1-thiol	$CH_2CH_2CH_2SH$ 	10.2
3-phenylpropan-1-ol	$CH_2CH_2CH_2OH$ 	16.9

[1]

S-H bond is longer and weaker than O-H so it breaks more easily to release H^+.

[Total:13]

For Examiner's Use

4 **(a)** Copper is purified by electrolysis. When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with iron and silver as minor impurities. It contained no other metal. In order to purify it, this alloy was made the anode of an electrolysis cell, with a pure copper cathode and aqueous $CuSO_4$ as electrolyte.
After some time, copper was coated at the cathode and metal **X** was found at the bottom of anode.

(i) Write equations to show the reactions that have occurred at the anode and cathode. [2]

Anode: $Cu \rightarrow Cu^{2+} + 2e$ **(Full forward arrow)**
($Fe \rightarrow Fe^{2+} + 2e$ or $Fe \rightarrow Fe^{3+} + 3e$)

Cathode: $Cu^{2+} + 2e \rightarrow Cu$ **(Full forward arrow)**

[2]

(ii) Identify metal **X**.

X is Ag.

(iii) Given the following information,
surface area of cathode before electrolysis = 30 cm^2
density of copper = 8.96 g cm^{-3}

Calculate the minimum time, in hours, needed to coat a layer of 0.2 mm of pure copper on the cathode if a current of 3.0 A was used. [2]

Mass of pure copper coated = 0.02 x 30 x 8.96 = 5.376 g
no. of mol of Cu deposited = mass/63.5 = 0.08466

no. of moles of e = 2 x 0.08466 = 0.1693
Qty of charge = 0.1693 x 96500 C = 16339.65 C
t = Q/I = 16339.65 / 3.0 = 5446.55 s = 1.51 hrs

[2]

(b) Four different constitutional (structural) isomers, **L**, **M**, **N** and **P**, with molecular formula of C_8H_8NOCl, were tested in order to identify them.
Table 4 shows the results of the tests carried out on the four isomers.

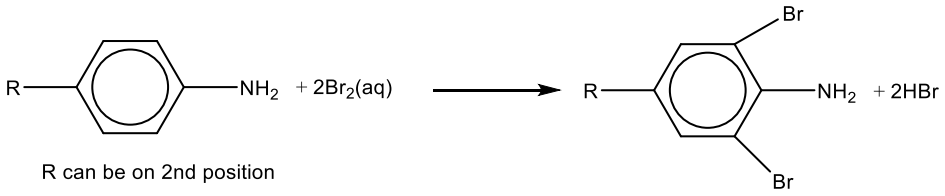
Table 4

	2,4-DNPH	reaction with drops of water	Tollens' reagent	reaction with warm $AgNO_3$(aq)	Fehling's reagent
L	no precipitate	fumes which turn damp litmus paper blue to red	no silver mirror	white ppt formed immediately	no precipitate
M	orange precipitate	no change	silver mirror	white ppt formed after some time	no precipitate
N	orange precipitate	no change	silver mirror	no ppt	no precipitate
P	orange precipitate	no change	silver mirror	white ppt formed after some time	brick red precipitate

(i) All four isomers decolourised orange aqueous bromine with white precipitate formed. One mole of each isomer reacts with two moles of aqueous bromine.

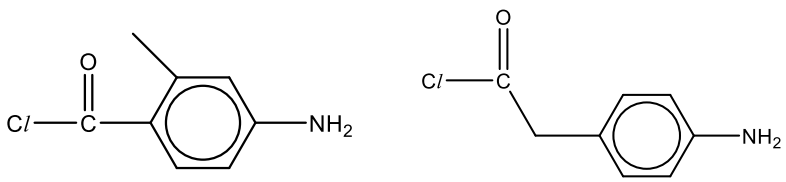
None of the four isomers **L**, **M**, **N** and **P** reacts with sodium metal.

Write an equation to show the reaction of functional group of **one** of the isomers, **L**, **M**, **N** or **P**, with aqueous bromine. You may use R to represent the rest of the molecule.



[1]

(ii) Draw the structure of **L**.

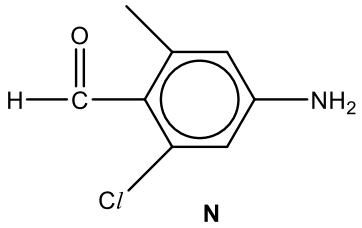


L or **L** [1]

(iii) Explain the difference in observations when **M** and **N** react separately with warm $AgNO_3$(aq). Hence, deduce the structure of **N**.

No white ppt of AgC*l* forms when N reacts with $AgNO_3$, means C*l* is bonded to aromatic ring/ halogenoarene in **N**.
Either

C-C*l* has partial double bond character in N
OR
lone pair of electrons on C*l* delocalised into the p orbital of benzene C, C-C*l* bond is very strong, not able to undergo nucleophilic subsitution by H_2O.



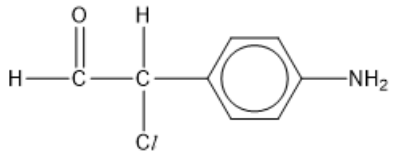
N

[2]

(iv) Compound **P** contains a chiral centre. Draw the structure of compound **P** and explain the chemistry of the reactions that **P** undergoes.

Name of reactions	Deduction
P undergoes oxidation**(✓)** with Fehling's & (or) Tollens' to give ppt.	**P** contains aliphatic aldehyde **(✓)** **(any aldehyde except benzaldehyde)**
P undergoes nucleophilic substitution**(✓)** with $AgNO_3$(aq) to give white ppt of AgC*l* *Note: aq water is the nucleophile*	**P** contains alkyl chloride/halide/ halogenoalkane**(✓)**
P undergoes condensation**(✓)** with 2,4-DNPH to give orange ppt	**P** contains aldehyde (or ketone)**(✓)**.

[3]



P

[Total:12]

5 Many classes of organic compounds can undergo oxidation with potassium manganate (VIII). The structures of these organic compounds can then be elucidated though careful analysis of the oxidation products.

The following equation would enable you to deduce the structure of the **sweet-smelling** organic compound **R**, which contains **alkene** functional groups.

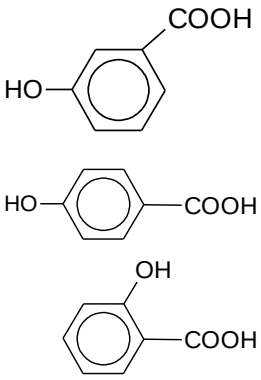
$$\underset{(C_{14}H_{16}O_2)}{\mathbf{R}} \xrightarrow[KMnO_4]{\text{hot acidified}} \underset{(C_7H_6O_3)}{\mathbf{S}} + \underset{(C_2H_4O_2)}{\mathbf{T}} + \underset{(C_3H_6O)}{\mathbf{U}} + 2CO_2$$

(a) The following statements describe the reactions of compounds **S** and **T**.

- **S** reacts with neutral aqueous FeCl_3(aq) to form a purple colouration.
- Both **S** and **T** effervesce with aqueous sodium carbonate, producing a gas that gives a white precipitate in limewater.

Suggest the structures for compounds **S** and **T**.

S: **T**: CH_3COOH



[2]

accept 1, 3- , 1,2- and 1, 4- disubstitution (any of the 3 structures above for S)

(b) Compound **U** gives yellow crystals when it is warmed with alkaline aqueous iodine.

State the type of reaction occurred. Suggest the structure for compound **U**.

Oxidation / Positive Iodoform Test
U: CH_3COCH_3

[2]

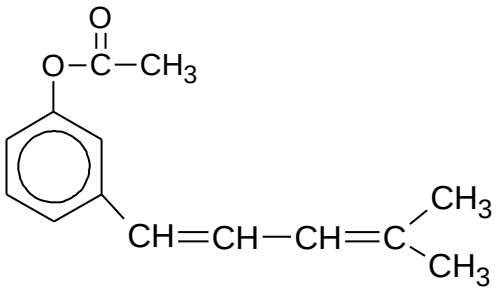
(c) What does the production of 2 mol of carbon dioxide gas reveal about the structure of compound **R**?

Compound **R** must contain a =CH-CH= group OR 2 terminal alkenes or $=CH_2$.

The HOOC-COOH produced or the 2 terminal alkenes can be further oxidised to give CO_2 gas.

[1]

(d) You now have sufficient information to deduce the structure of compound **R**.
Give the structure of **R**.



[1]

accept 1, 3- , 1,2- and 1, 4- disubstitution of the 2 substituents

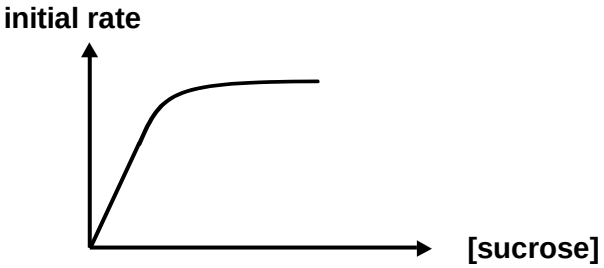
[Total:6]

6 **(a)** Enzymes are special proteins that function as biological catalysts. They speed up the rate of chemical reactions in our body to help support life.

An example is the enzymatic hydrolysis of the complex sugar, sucrose, by the enzyme invertase to form simple sugars, fructose and glucose.

$$\text{sucrose} \xrightarrow{\text{invertase}} \text{fructose + glucose}$$

The graph below shows the initial rate of hydrolysis against [sucrose].



Explain the shape of the graph and determine the order of reaction with respect to [sucrose] when:

- concentration of sucrose is low;
- concentration of sucrose is high.

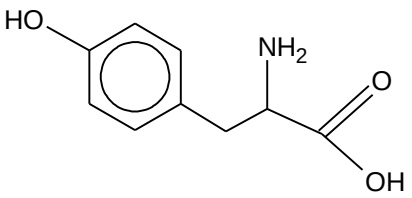
When [sucrose] is low, reaction is first order with respect to [sucrose]. **(✓)**
When [sucrose] is low, rate ∝ [sucrose] OR increasing the concentration of the sucrose also increases the rate of reaction. **(✓)**

When [sucrose] is high, reaction is zero order with respect to [sucrose]. **(✓)**
Due to a limited amount of invertase enzyme molecules present, further increase in [sucrose] will no longer increase the rate as the active sites of the enzymes are saturated/ all in use. **(✓) (either of the underlined phrase/ words with same meaning)**

[2]

(b) Tyrosine is a non-essential amino acid that is present in the structure of almost every protein in the human body. It plays an important role in the production of neurotransmitters, which help nerve cells communicate and influence our mood.

The structure of a Tyrosine molecule is given below.



Some important information of Tyrosine is given below.

- Melting point: 343°C
- The pK_a values associated with the amino acid are 2.20, 9.11 and 10.2.
- For fully protonated Tyrosine, $H_3N^+CH(CH_2C_6H_4OH)CO_2H$, it is known that the phenol group would be the last to lose a proton.

(i) Provide an explanation for the high melting point of Tyrosine amino acid.

Tyrosine exists as zwitterions **(✓)** which are held by strong ionic bonds / electrostatic forces of attraction **(✓)**.

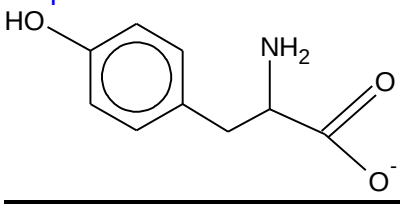
Large amount of energy is required to overcome the strong ionic bonds between the zwitterions.

[1]

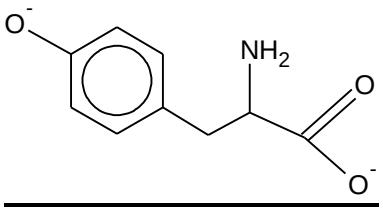
(ii) Give the structures of the major chemical species that would be present in solutions of Tyrosine at various pH values given below:

- pH = 9.5
- pH = 13

- pH = 9.5

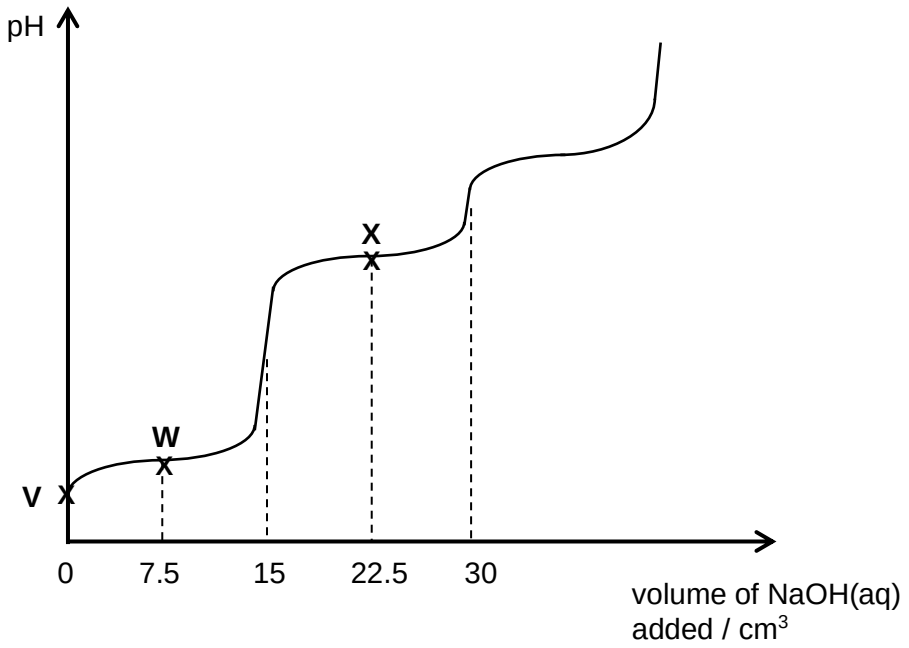


- pH = 13



[2]

(c) The graph below is obtained when a solution containing 0.100 mol dm^{-3} of fully protonated Tyrosine, $H_3N^+CH(CH_2C_6H_4OH)CO_2H$, is titrated with aqueous sodium hydroxide.



(i) Calculate the initial pH at point **V**. (ignore the effects of pK_2 and pK_3 of protonated Tyrosine on the pH)

Species present:
$H_3N^+CH(CH_2C_6H_5OH)$**CO_2H (weak acid)**

Dissociation of **weak acid:**
$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$
$K_a = 10^{-2.20} = x^2 / (0.100 - x) \approx x^2 / (0.100)$
Solving,
$[H_3O^+] = x = 2.512 \times 10^{-2}$ mol dm^{-3}
$pH = -\lg(2.512 \times 10^{-2}) = 1.60$ [1]

(ii) The two major organic species present at point **W** are given below:
$H_3N^+CH(CH_2C_6H_4OH)CO_2H$ and $H_3N^+CH(CH_2C_6H_4OH)CO_2^-$

Write equations to show how these organic species present help to resist pH changes when the following are added separately:

- HC*l* (aq)
- NaOH(aq)

$H_3N^+CH(CH_2C_6H_4OH)CO_2^- + H^+ \rightarrow H_3N^+CH(CH_2C_6H_4OH)CO_2H$

$H_3N^+CH(CH_2C_6H_4OH)CO_2H + OH^- \rightarrow H_3N^+CH(CH_2C_6H_4OH)CO_2^- + H_2O$ [2]

(iii) In light of your answer to **(c)(ii)** or otherwise, state the pH at point **W**.

Acidic Buffer at Maximum Buffer Capacity:
$pH = pK_a = 2.20$ [1]

(iv) From Table 6.1 below, suggest a suitable indicator that you would use to detect the first equivalence point. Briefly explain your choice.

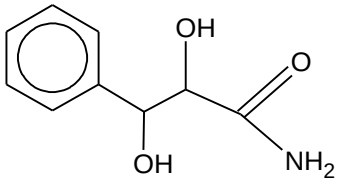
Table 6.1

Indicator	colour (lower pH)	pH range	colour (upper pH)
dichlorofluorescein	colourless	3.5 – 6.6	green
alizarin yellow	yellow	10.0 – 12.1	red

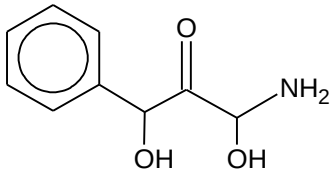
pH at first equivalence point ≈ (2.20+9.11) / 2 = 5.66
(for debrief, no need for student to calculate this)

Indicator: dichlorofluorescein **(✓)**
Reason:
working pH range of indicator lies within the region of rapid pH change **(✓)**
OR equivalence pH lies within working pH range of indicator**(✓)** [1]

(d) The structures of compound **Y** and compound **Z**, $C_9H_{11}NO_3$, which are isomers of Tyrosine, are given below. **Y** and **Z** are used as plant fertilisers.



compound **Y**



compound **Z**

(i) Compare the base strength of the nitrogen-containing functional groups in compound **Y** and compound **Z**. Explain your answer. [2]

Compound **Y** contains an amide (1°) while compound **Z** contains an amine (1°).

The C=O group on the amide is electron-withdrawing or **lone pair of electrons on the N atom of the amide is delocalised into the C=O group**. **(✓)** Hence, the lone pair of electrons on the N atom of the amide will NOT be **(✓)** available for protonation / accept a proton.

Hence the amide functional group in compound **Y** is less basic (neutral) than the amine group in compound **Z**.

Compound **Y** is one of the many chemicals that can be found in a plant fertiliser.

A known mass of the fertiliser was boiled with an excess of dilute potassium hydroxide. NH_3 gas was evolved, which could turn moist red litmus paper blue.

The NH_3 gas was absorbed in water and titrated with dilute sulfuric acid.

The equation for the reaction of compound **Y** with dilute KOH to produce NH_3 is given below.

$C_6H_5CH(OH)CH(OH)CONH_2 + OH^- \rightarrow C_6H_5CH(OH)CH(OH)COO^- + NH_3$

When 1.20 g of a fertiliser was subjected to this treatment, the resulting solution containing the pungent gas required 25.20 cm^3 of 0.100 mol dm^{-3} dilute sulfuric acid for complete reaction.

(ii) Given that the molar mass of **Y** is 181 g mol^{-1}, determine the percentage of compound **Y** in this fertiliser. [2]

$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

Amount of H_2SO_4 = (25.20/1000 x 0.100) = 0.00252 mol
Amount of NH_3 = 0.00252 x 2 = 0.00504 mol = Amount of compound **E**

Mass of compound **E** = 0.00504 x 181 = 0.9122 g
% of compound **E** in the fertiliser = (0.9122 / 1.20) x 100% = 76.0%
(ecf for the 2nd mark to be given if the equation is balanced wrongly)

(e) Due to its high reactivity towards nitrogen gas, lithium nitride is often used as an intermediate to "fix" nitrogen in the production of ammonia-based fertilisers.

$$N_2(g) \xrightarrow{+ Li} Li_3N \xrightarrow{+ H_2O} NH_3 + \text{ compound } \mathbf{U}$$

(i) Construct a balanced equation for the reaction between Li_3N and water, identifying compound **U**.

$Li_3N + 3H_2O \rightarrow NH_3 + 3LiOH$
compound **U**

[1]

(ii) *Use of the Data Booklet is relevant to this part of the question.*
How would you expect the magnitude of the lattice energy of barium oxide, BaO to be compared with that of lithium nitride, Li_3N? Explain your answer.

$|LE| \propto | (q_+ \times q_-) / (r_+ + r_-) |$

- $(q_+ \times q_-)$ for BaO > $(q_+ \times q_-)$ for Li_3N
- $(r_+ + r_-)$ for BaO > $(r_+ + r_-)$ for Li_3N
- $(q_+ \times q_-)$ more significant than $(r_+ + r_-)$
- Magnitude of LE is larger for BaO [1]

[2]

(f) Ammonia, NH_3, reacts with boron trifluoride, BF_3, to form a compound of the formula $H_3N.BF_3$. State and explain if NH_3 and BF_3 are behaving as Lewis acid or Lewis base in this reaction.

NH_3 is acting as Lewis base **(✓)** as it donated electron pair**(✓)** of electrons to B of BF_3

BF_3 is acting as Lewis acid**(✓)** as it accepted electron pair**(✓)**of electrons to from N of NH_3

[2]

(g) (i) Hydrazine (N_2H_4) is a colourless liquid with a slight odour like ammonia. However, the solubility of hydrazine in water is higher than that of ammonia.

Account for the difference in solubility of hydrazine and ammonia in water.

Each hydrazine molecule has two -NH_2 groups, which allow it to form more extensive hydrogen bonds with water molecules than ammonia which release more heat. Hence, hydrazine has a higher solubility than ammonia.

[2]

(ii) Table 6.2 lists the boiling points of hydrazine and hydrogen peroxide. Suggest a reason why the boiling point of H_2O_2 is much higher than that of N_2H_4.

Table 6.2

Compound	Formula	boiling point/ ^oC
N_2H_4	32.0	114
H_2O_2	34.0	150

Stronger hydrogen bonds (✓) between H_2O_2 molecules compared to that between N_2H_4 molecules because the O-H bond is more polar(✓) (accept also: H in H_2O_2 is more delta positive).

[1]

[Total:21]

End of paper