RIVER VALLEY HIGH SCHOOL
JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME									
CLASS	18J								
CENTRE NUMBER	S					INDEX NUMBER				

H2 CHEMISTRY 9729/02

Paper 2 Structured Questions

18 September 2019

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Answer **all** questions in the space provided.
A Data Booklet is provided. Do NOT write anything on it.

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 2										
Question Number	1	2	3	4	5	6	7	Total (Paper 2)	sf	Units
Marks	/9	/9	/10	/12	/12	/10	/13	/75		
Paper 1		/30		Paper 3		/80		Total		/185

This document consists of **21** printed pages and **3** blank pages.

1 Group 2 metals are also known as alkaline earth metals. The elements have similar properties and appearance. The metals are silvery-white and are reactive at room temperature and pressure.

(a) Ionisation energy of Group 2 varies down the group.

Explain how the 1st ionisation energy of beryllium and barium differs.

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…… **[3]**

(b) The nitrates, carbonates and hydroxides of Group 2 elements can undergo thermal decomposition.

(i) In the thermal decomposition of Group 2 nitrates, oxygen and a brown gas are also produced.

Write a balanced equation, with state symbols, for the decomposition of calcium nitrate.

…… **[1]**

(ii) The nitrates of lead and zinc can undergo thermal decomposition similar to calcium nitrate. The decomposition temperatures of the three nitrates are given in the following table

Table 1.1

Compound	Decomposition temperature /°C
Lead(II) nitrate, $Pb(NO_3)_2$	290
Calcium nitrate, $Ca(NO_3)_2$	132
Zinc nitrate, $Zn(NO_3)_2$	105

Explain, with reference to the *Data Booklet,* the trend in the decomposition temperatures of the metal nitrates in the Table 1.1.

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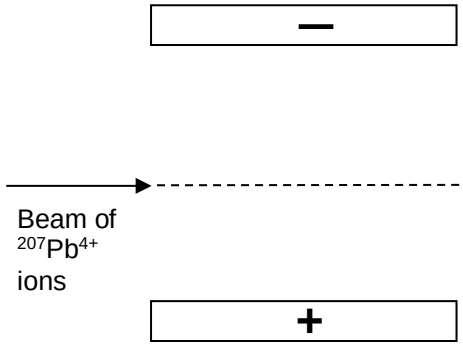
[3]

(c) Lead can exhibit variable oxidation states and its cation can exist either as $^{207}Pb^{2+}$ or $^{207}Pb^{4+}$. **[2]**

Given that the angle of deflection for $^{207}Pb^{2+}$ is 8°, calculate the angle of deflection for $^{207}Pb^{4+}$ and draw a labelled line to the figure below to represent the path of a beam of $^{207}Pb^{4+}$ ions, at high temperature, in an electric field.



[Total: 9]

2 Citric acid ($H_3C_6H_5O_7$) is a naturally occuring weak organic tribasic acid. It is found in a variety of vegetables and fruits. In a typical sample of lemon, the concentration of citric acid is about 0.300 mol dm^{-3}.

Table 2.1

	K_{a1}	K_{a2}	K_{a3}
$H_3C_6H_5O_7$	1.43×10^{-3}	1.74×10^{-5}	3.98×10^{-7}

(a) Calculate the pH of a typical sample of lemon. You may ignore K_{a2} and K_{a3} for this calculation.

[1]

(b) Calculated the pH of solution containing 46.0 g dm^{-3} of $Na_3C_6H_5O_7$.

[3]

(c) **(i)** A buffer solution can resist changes in pH when small amounts of acid or base is added to it. Suggest two conditions necessary to make a good buffer solution.

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[2]

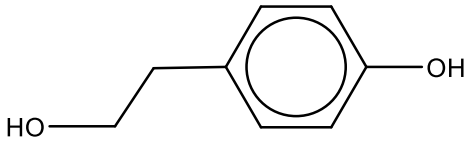
(ii) Calculate the mass of NaOH(s) required to be added to 50 cm^3 of 0.300 mol dm^{-3} citric acid for the preparation of buffer at pH = 6.40.

Clearly identify the acid and salt species in the buffer.

[3]

[Total: 9]

3 Olives are commonly used in foods and production of edible oils. In their natural state, olives contain organic compounds like tyrosol that make them unpalatable to people.



tyrosol

In order for olives to be made edible, their natural bitterness has to be removed in a process known as debittering. This is done by soaking olives in brine, followed by sodium hydroxide solution, which will react with tyrosol and extracted.

(a) (i) Write an equation for the reaction between tyrosol and sodium hydroxide.

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[1]

(ii) State the different types of interaction that the product in **(a)(i)** will have with water molecules.

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..... **[2]**

(iii) After treatment, tyrosol can be converted back to its original form. Outline a simple chemical test that could be carried out to check for the presence of tyrosol.

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..... **[2]**

(iv) For this debittering process to be effective, the sodium hydroxide solution has to be changed frequently.

Suggest, using ideas behind Le Chatelier's principle, why the sodium hydroxide solution has to changed in order to remove tyrosol.

You may find it useful to use the equation $[T]_{olive} \rightleftharpoons [T]_{NaOH}$ where [T] refers to the concentration of tyrosol.

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..... **[2]**

(b) (i) When tyrosol is heated with ethanoic acid with concentrated H_2SO_4, compound **D** is formed.

When bromine water is added to tyrosol, a brominated tyrosol, **E**, is formed.

Suggest a structure for compound **D** and **E**.

D	**E**

[2]

(ii) Explain how the acidity of brominated tyrosol might differ from that of tyrosol.

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..... **[1]**

[Total: 10]

4 $SOCl_2$ and S_2Cl_2 are chlorine and sulfur containing compounds.

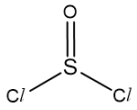
(a) Draw the dot-and-cross diagram of S_2Cl_2 and state its bond angle.

[2]

(b) The dipole moments and boiling points for $SOCl_2$ and S_2Cl_2 are shown in the table below.

The larger the dipole moment in Debye (*D*), the greater the difference in electrical charge in a species.

Table 4.1

Compound	M_r	Boiling point / ^oC	Net dipole moment / *D*
	119	74.6	1.44
S_2Cl_2	135.2	137.1	1.60

With reference to their structures and bonding and the information above, account for the large difference in their boiling points.

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[3]

(c) $SOCl_2$ is used in organic synthesis.

The following Synthetic Route A shows how a carboxylic acid can be converted into an amine.

Synthetic Route A

$$CH_3CO_2H \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{\text{Step 2}} CH_3CONH_2 \xrightarrow{\text{Step 3}} CH_3CH_2NH_2$$

(i) State the reagents and conditions for Steps 2 and 3.

Step 2 ……..

Step 3 ……..

[2]

(ii) Angelic acid, $C_5H_8O_2$, is a natural product isolated from the roots of the angelica plant.

- Angelic acid reacts with H_2 + Ni to form **T**, $C_5H_{10}O_2$.
- **T** undergoes the above Synthetic Route A to form the amine **U**, $C_5H_{13}N$.
- **U** can also be made by reacting 1-bromo-2-methylbutane with ammonia.

Both angelic acid and **T** can exhibit stereoisomerism.

Suggest structures for angelic acid, **T** and **U**.

angelic acid	**T**
U	

[3]

(iii) State the types of stereoisomerism shown by angelic acid and **T**.

angelic acid ……..

T …….. **[2]**

[Total: 12]

5 *Use of the Data Booklet and the information about the various oxidation states of vanadium from Table 5.1 are relevant to this question.*

Table 5.1

Example of Species	Oxidation State of Vanadium	Solution Colour	Wavelength / nm
V^{2+}	+2	violet	400
V^{3+}	+3	green	515
VO^{2+}	+4	blue	460
VO_2^{+}	+5	yellow	580

(a) In a solution containing $V^{2+}(aq)$, water molecules act as ligands that bind to the vanadium cation in an octahedral arrangement and cause the 3d subshell in V^{2+} to split into two different energies. As a result, a solution of $V^{2+}(aq)$ appears violet.

(i) Explain why a solution of $V^{2+}(aq)$ is coloured.

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……... **[2]**

(ii) Given that the energy of light is inversely proportional to its wavelength, deduce which of the two solutions, $V^{2+}(aq)$ or $V^{3+}(aq)$, has a larger 3d-subshell splitting.

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……... **[2]**

(b) Frost-Ebsworth diagrams are the most common graphical method of representing redox relationships for species of a given element in different oxidation states.

In a Frost-Ebsworth diagram, values of $-\Delta G$ /F for the formation of M(N) from M(0), where N is the oxidation state, are plotted with increasing oxidation states.

From the relationship:

$$\Delta G = -nFE$$

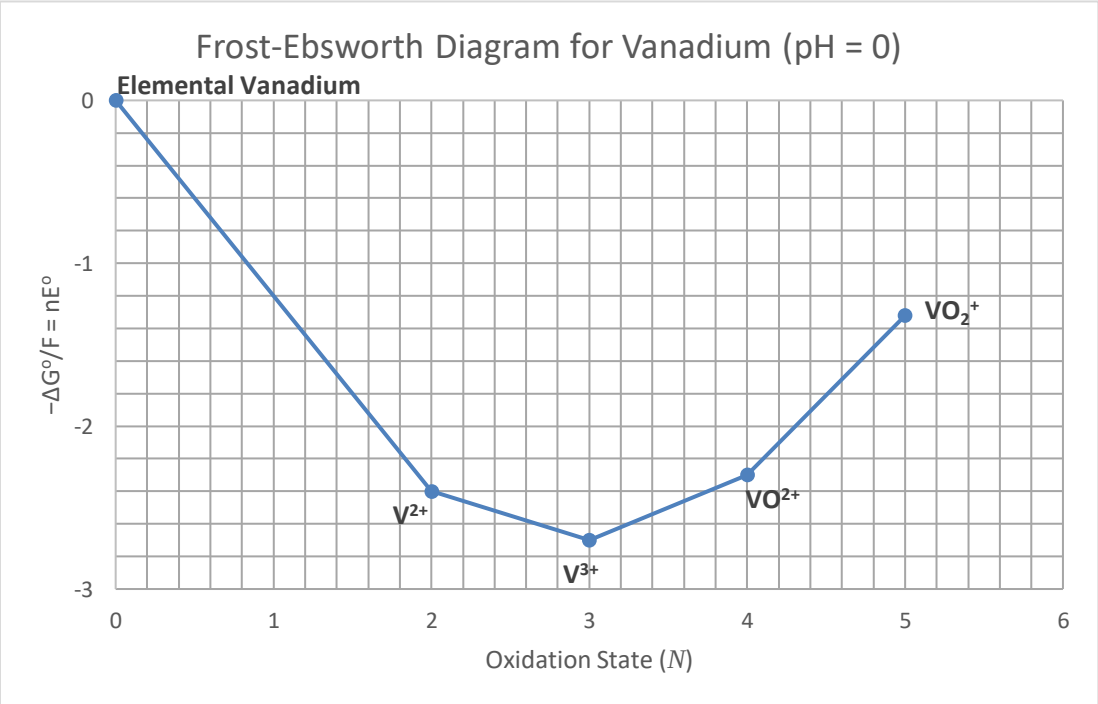
where n is the number of moles of electrons transferred during the redox reaction, it follows that $-\Delta G$ /F = nE , hence a Frost-Ebsworth diagram is essentially a plot of nE against oxidation states.

The ΔG for elements in their standard states is taken as zero.

The gradient of the line drawn between any two points on the plot corresponds to the E of the corresponding redox couple.

A Frost-Ebsworth diagram for vanadium in aqueous solution of pH 0 (i.e. $[H^+]$ = 1 mol dm^{-3}) is shown below.

Fig. 5.1



(i) Fill in the blanks below the y-coordinates of the plotted points for V^{3+} and VO^{2+} to 1 decimal place.

V^{3+} : (3 , ……)

VO^{2+}: (4 , ……) **[1]**

(ii) For the V^{2+}/V redox couple, the coordinates for V^{2+} is (2, −2.40).

For the VO_2^+/VO^{2+} redox couple, the coordinates for VO_2^+ is (5, −1.32).

Calculate the E value for the VO_2^+/V^{2+} redox couple.

[1]

(iii) Suggest the significance of V^{3+} being the lowest point on the Frost-Ebsworth diagram.

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[1]

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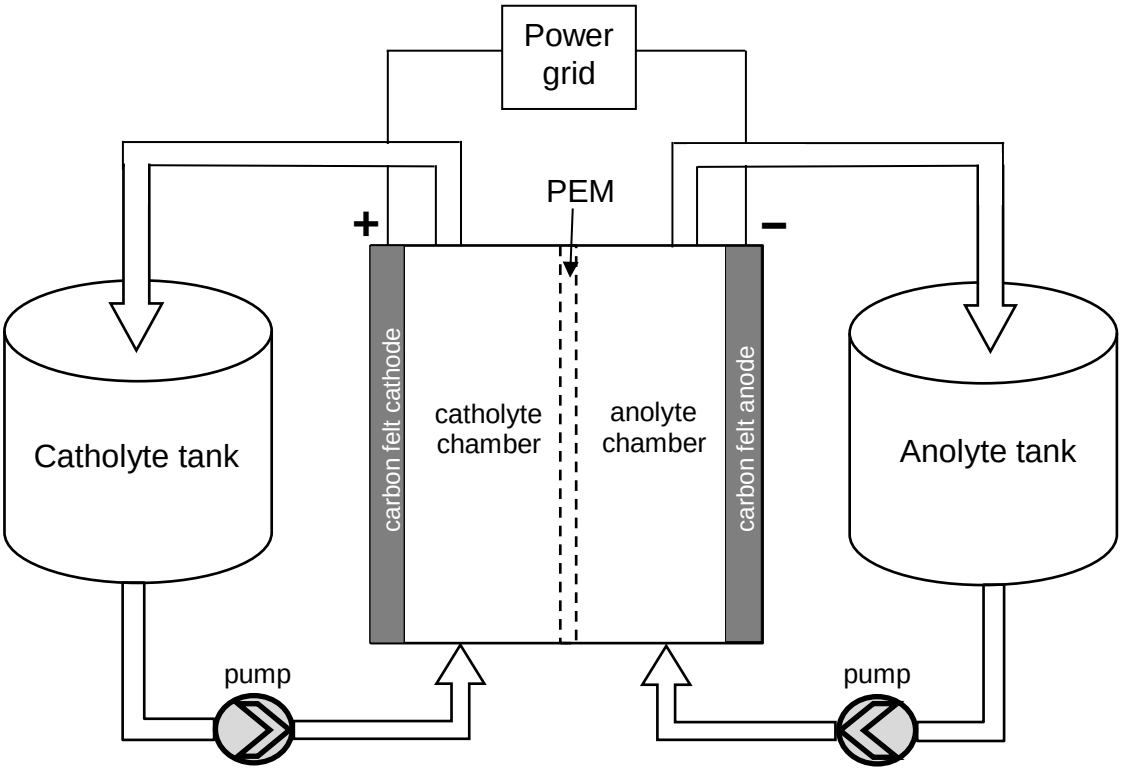
A recent exciting development in the energy storage industry is the vanadium redox flow battery (VRFB), a rechargeable electrochemical cell that employs aqueous vanadium ions in various oxidation states to store chemical potential energy. A 20-year-long cycle life and high energy efficiency are its key advantages, giving rise to its potential to power up cities in the near future.

A schematic diagram of a VRFB, during the discharge phase, is shown below, with the flow of the electrolytes in the connecting pipes shown in block arrows.

Fig. 5.2



Key Characteristics of the VRFB

1. The battery comprises of 2 electrolytes, a catholyte and an anolyte, that flow through the respective half-cells from separate storage tanks. Each electrolyte contains a redox couple, i.e. 2 vanadium species, dissolved in sulfuric acid.
2. The species in each redox couple differs from each other by **one oxidation state**.
3. These electrolytes are separated by a proton exchange membrane (PEM) whereby protons can migrate across to maintain electrical neutrality in the cell.
4. The predominant colours of the electrolytes flowing through the four connecting tubes are **all different**, based on the colours given in Table 5.1.

(c) **(i)** The e.m.f. of a single VRFB is 1.26 V.

With reference to the given information above and the *Data Booklet*, write down the relevant vanadium redox couples present in the catholyte and anolyte chambers in the schematic diagram above.

Catholyte chamber: …….

Anolyte chamber: ……. **[2]**

(ii) Hence or otherwise, construct the overall equation of the redox process in the VRFB.

……. **[1]**

(iii) Once a discharge cycle is completed, the VRFB will be connected to an external power supply to "charge up".

State the direction of proton transfer during the charging cycle.

……. **[1]**

(iv) Suggest a suitable modification to the VRFB to increase the e.m.f without changing the species in the catholyte and anolyte chambers.

……. **[1]**

[Total: 12]

6 When Group 1 metals are heated in an excess of air, alkali metal oxides, peroxides and superoxides are produced. The principal product obtained depends on the metal.

For potassium, its superoxide, KO_2, is formed predominantly.

(a) (i) The enthalpy change of formation of the oxides increases drastically as shown in Table 6.1. Suggest a reason for each of the following:

- $\Delta H_f(O_2^{2-})$ is more endothermic than $\Delta H_f(O_2^{-})$
- $\Delta H_f(O^{2-})$ is more endothermic than that of the other two anions

Table 6.1

	O_2^-	O_2^{2-}	O^{2-}
ΔH_f/ *k*J mol^{-1}	–43.0	553	903

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……... **[2]**

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(ii) Define the term *lattice energy*.

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…….... **[1]**

(iii) Explain how the magnitude of lattice energy changes from KO_2 to K_2O_2 to K_2O.

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…….... **[2]**

(b) Potassium superoxide, KO_2, is a rare yet stable salt of superoxide anion. It is used in rebreathers as it reacts with carbon dioxide exhaled to generate oxygen and potassium carbonate.

Potassium superoxide is stable as long as it is kept dry. Upon contact with water, it hydrolyses extremely quickly to give potassium hydroxide.

Interestingly, the alkaline products from both reactions aforementioned also absorb the exhaled CO_2.

The following table lists the ΔH values of the reactions.

Table 6.2

reaction	ΔH / kJ mol^{-1}
$2KO_2(s) + CO_2(g) \rightarrow K_2CO_3(aq) + \frac{3}{2}O_2(g)$	–219
$2KO_2(s) + H_2O(l) \rightarrow 2KOH(aq) + \frac{3}{2}O_2(g)$	–113
$CO_2(g) + K_2CO_3(aq) + H_2O(l) \rightarrow 2KHCO_3(aq)$	–100
$KOH(aq) + CO_2(g) \rightarrow KHCO_3(aq)$	ΔH_r

Using the data given in Table 6.2, construct a fully labelled energy cycle to determine ΔH_r.

$$2KO_2(s) + H_2O(l) \longrightarrow 2KOH(aq) + \frac{3}{2}O_2(g)$$

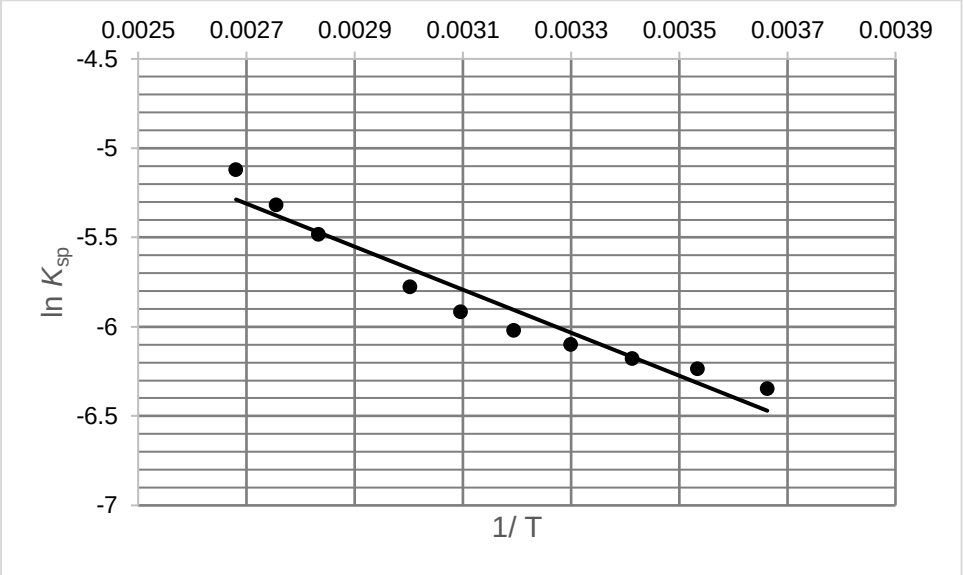
[3]

(c) The relationship between the thermodynamic functions, ΔG_{ppt}, ΔH_{ppt} and ΔS_{ppt} of a reaction and its equilibrium constant is given as follows.

$$\Delta G_{ppt} = \Delta H_{ppt} - T\Delta S_{ppt} = - RT \ln(K_{sp}).$$

An experiment was conducted to determine the entropy change of precipitation of potassium carbonate. The solubility product of potassium carbonate at various specific temperatures were determined and Figure 6.1 shows a plot of ln K_{sp} against 1/T which can be used to obtain ΔS_{ppt}.

Fig. 6.1



(i) Using the graph, determine ΔS_{ppt}.

[1]

(ii) Explain the significance of the sign of ΔS_{ppt} of K_2CO_3.

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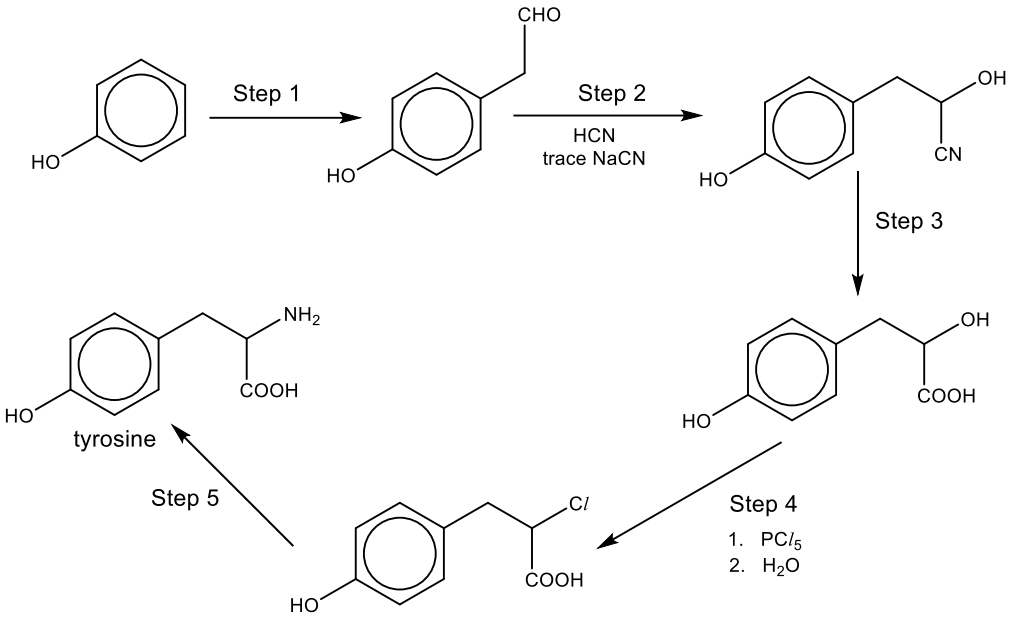
[1]

[Total: 10]

7 **(a)** Tyrosine is a naturally occurring amino acid.

The amino acid tyrosine can be synthesised from phenol by the route shown.



(i) Describe the mechanism in Step 2.

[3]

(ii) State the reagents and conditions for Steps 1, 3 and 5.

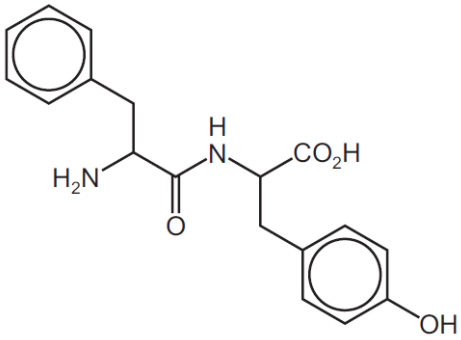
Step 1 ……

Step 3 ……

Step 5 ……

[3]

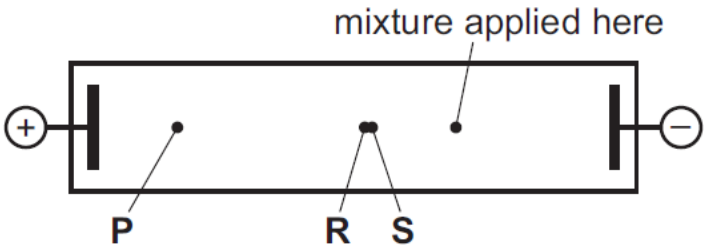
(b) The dipeptide phe-tyr has the following structure.



A mixture of this dipeptide (phe-tyr) and its two constituent amino acids (phe and tyr) was subjected to electrophoresis in a buffer at pH 12.

Electrophoresis is a technique commonly used in the lab to separate species like amino acids. The speed of migration of the amino acids depends on their charge and size.

At the end of the experiment the following results were seen. Spots **R** and **S** remained very close together.



(i) Draw the structure of the species responsible for spot **P**.

[1]

(ii) Suggest a simple modification to the electrophoresis setup to increase the separation for spots **R** and **S.**

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……... **[1]**

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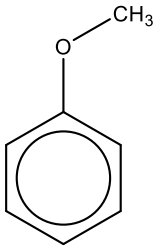
(c) Anisole, or methoxybenzene, is an organic compound with the formula $CH_3OC_6H_5$. It is a colorless liquid with a smell reminiscent of anise seed, and in fact many of its derivatives are found in natural and artificial fragrances. It is an ether and contain the C–O–C functional group.



anisole

Ether can be synthesised via Williamson ether synthesis which involves an alkoxide ion, $R'O^-$, reacting with an alkyl halide, RX.

$$R'O^- + RX \longrightarrow R'OR + X^-$$

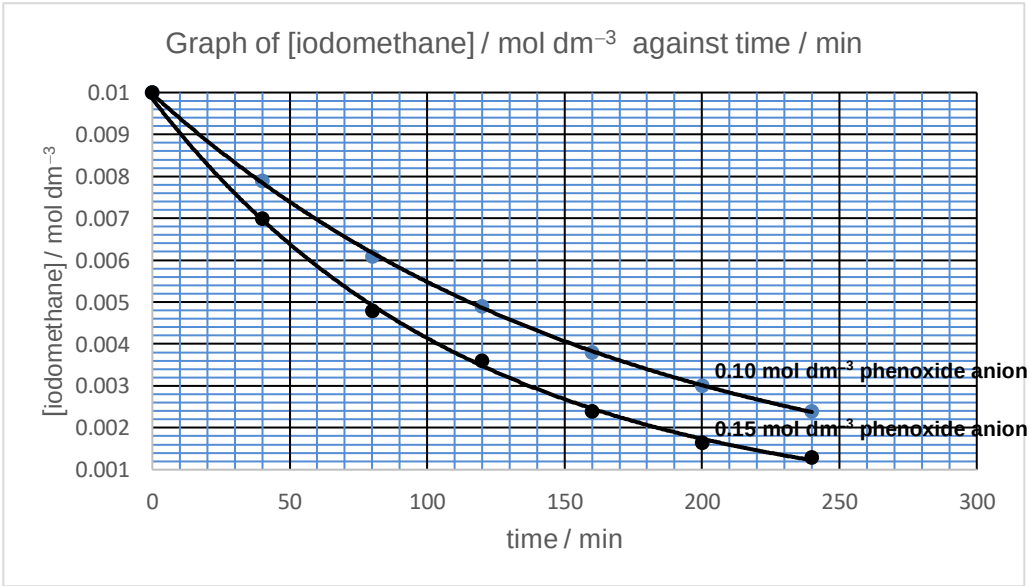
(i) To produce anisole, phenol is first reacted with sodium hydride, NaH, via an acid–base reaction to produce phenoxide ion.

Construct a balanced chemical equation for the reaction between phenol and NaH.

…….. **[1]**

(ii) The following graph shows the experimental findings of a Chemistry undergraduate student when iodomethane is reacted with 2 different concentrations of phenoxide ion.

Fig. 7.1



Using the graph, determine the order of reaction with respect to

- iodomethane
- phenoxide ion

Justify your answer in each case. **[4]**

Order of reaction with respect to iodomethane: ……

Justification: ……

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Order of reaction with respect to phenoxide ion: ……

Justification: ……

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[Total: 13]

~END OF PAPER~

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