Cambridge International AS & A Level

Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME	
CENTRE NUMBER	
CANDIDATE NUMBER	

1505297911

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2017**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.
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.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.
You may lose marks if you do not show your working or if you do not use appropriate units.
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.

This document consists of **20** printed pages.

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Answer **all** the questions in the spaces provided.

1 **(a)** **(i)** Describe and explain the variation in the thermal stabilities of the carbonates of the Group 2 elements.

.....

.....

.....

.....

..... [3]

(ii) Suggest and explain a reason why sodium carbonate is more stable to heat than magnesium carbonate.

.....

.....

..... [1]

(b) Sodium hydrogencarbonate, $NaHCO_3$, and potassium hydrogencarbonate, $KHCO_3$, decompose on heating to produce gases and the solid metal carbonate.

(i) Write an equation for the decomposition of $KHCO_3$.

..... [1]

(ii) Predict which of $NaHCO_3$ or $KHCO_3$ will decompose at the **lower** temperature. Explain your answer.

.....

..... [1]

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(c) (i) Use the data in the table below, and relevant data from the *Data Booklet*, to calculate the lattice energy, $\Delta H^{\ominus}_{latt}$, of potassium oxide, $K_2O(s)$.

energy change	value / kJ mol^{-1}
enthalpy change of atomisation of potassium, $\Delta H^{\ominus}_{at}$ K(s)	+89
electron affinity of O(g)	–141
electron affinity of O^-(g)	+798
enthalpy change of formation of potassium oxide, $\Delta H^{\ominus}_{f}$ $K_2O(s)$	–361

$\Delta H^{\ominus}_{latt}$ = ... kJ mol^{-1} [3]

(ii) State whether the lattice energy of Na_2O would be more negative, less negative or the same as that of K_2O. Give reasons for your answer.

.....

..... [1]

[Total: 10]

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[Turn over

2 **(a)** Complete the table to show how **both** $AgNO_3(aq)$ and $NH_3(aq)$ could be used to distinguish between solutions of NaC*l*(aq) and NaI(aq).

test performed	observation with NaC*l*	observation with NaI

[2]

Important information for this question

- In this question (pr) means 'a solution in propanone'.
- Sodium iodide is soluble in propanone giving $Na^+(pr)$ and $I^-(pr)$.
- Sodium chloride is insoluble in propanone.

The reaction between 2-chlorobutane and sodium iodide in propanone is shown.

$$CH_3CH_2CHClCH_3(pr) + Na^+(pr) + I^-(pr) \rightarrow CH_3CH_2CHICH_3(pr) + NaCl(s)$$

The rate of this reaction can be investigated by measuring the electrical conductivity of the reaction mixture. The electrical conductivity changes as the reaction progresses due to the precipitation of the NaC*l* produced.

(b) **(i)** Suggest how the electrical conductivity will change as the reaction proceeds. Explain your answer.

.....

..... [1]

(ii) Describe a suitable method for studying the rate of this reaction at a temperature of 40 °C, using the following.

- an electrical conductance meter which measures the electrical conductivity of solutions
- solutions of known concentrations of 2-chlorobutane in propanone and sodium iodide in propanone
- stopclock
- access to standard laboratory equipment

.....

.....

.....

.....

.....

.....

.....

..... [3]

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(c) The rate of this reaction was measured at different initial concentrations of the two reagents. The table shows the results obtained.

experiment	$[CH_3CH_2CHClCH_3]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	relative rate
1	0.06	0.03	3
2	0.10	0.03	5
3	0.06	0.05	5
4	0.08	0.04	to be calculated

(i) Deduce the order of reaction with respect to each of $[CH_3CH_2CHClCH_3]$ and $[I^-]$. Explain your reasoning.

order with respect to $[CH_3CH_2CHClCH_3]$ .....

.....

order with respect to $[I^-]$ .....

.....
[2]

(ii) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = ... mol dm^{-3} s^{-1}

units of *k* = ...
[1]

(iii) Calculate the relative rate for experiment 4.

relative rate for experiment 4 = ... [1]

(d) (i) Suggest the mechanism for the reaction of 2-chlorobutane with iodide ions. Draw out the steps involved, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structure of any transition state or intermediate

[3]

(ii) This reaction was carried out using a single optical isomer of 2-chlorobutane.

Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

.....

..... [1]

(e) (i) State the number of peaks that would be seen in the carbon-13 NMR spectrum of $CH_3CH_2CHClCH_3$.

..... [1]

(ii) There are two isomers of $CH_3CH_2CHClCH_3$ that have **fewer** peaks in their carbon-13 NMR spectra than $CH_3CH_2CHClCH_3$.

Draw the structures of the isomers and state the number of peaks for each isomer.

isomer 1

number of peaks = ...

isomer 2

number of peaks = ...

[3]

[Total: 18]

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Question 3 starts on the next page.

3 **(a)** In a molecule of $SOCl_2$ the sulfur atom has four bonds.

Draw a 'dot-and-cross' diagram of $SOCl_2$. Show the outer shell electrons only.

[2]

(b) When $SOCl_2$ is reacted with a carboxylic acid to produce an acyl chloride, two acidic gases are formed.

$$SOCl_2(l) + RCO_2H(l) \rightarrow RCOCl(l) + SO_2(g) + HCl(g)$$

A 1.00 g sample of a carboxylic acid RCO_2H was treated in this way, and the gases were absorbed in 60.0 cm^3 of 0.500 mol dm^{-3} NaOH(aq), an excess.

(i) Write equations for the reactions between

NaOH and HCl, ...

NaOH and SO_2. .....
[2]

The excess NaOH was titrated with 0.500 mol dm^{-3} $H^+(aq)$. It required 10.8 cm^3 of the $H^+(aq)$ solution to reach the end-point.

(ii) Calculate the total number of moles of NaOH that reacted with the SO_2 and HCl.

moles of NaOH = ... [2]

(iii) Calculate the number of moles of RCO_2H that produced the SO_2 and HCl.

moles of RCO_2H = ... [1]

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(iv) Hence calculate the M_r of the carboxylic acid, RCO_2H.

M_r RCO_2H = ... [1]

(v) The R group contains carbon and hydrogen only.

Suggest the molecular formula of RCO_2H.

..... [1]

(c) The following synthetic route shows how a carboxylic acid can be converted into an amine.

$$CH_3CO_2H \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{\text{step 3}} CH_3CH_2NH_2$$

(i) Suggest a reagent for step 3.

..... [1]

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 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** exist as stereoisomers.

(ii) Suggest structures for angelic acid, **T** and **U**.

angelic acid	**T**	**U**

[3]

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

angelic acid .....

compound **T** .....
[1]

[Total: 14]

4 **(a)** A number of isomers with the formula $Cr(H_2O)_6Cl_3$ exist. Their general formula is $[Cr(H_2O)_{6-n}Cl_n]Cl_{3-n}.nH_2O$.
Each isomer contains a six co-ordinated Cr(III) ion in an octahedral complex.
Water molecules not directly bonded with the Cr atom are held in the crystal lattice as water of crystallisation.
The Cr–Cl bond is not easily broken and so chloride bonded with the Cr(III) ion in the complex does not react.

1.00 g samples of three of the isomers, **A**, **B** and **C**, were dissolved in separate samples of water. An excess of $AgNO_3(aq)$ was added to each and the mass of AgCl(s) formed was measured.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

The number of moles of AgCl(s) formed was calculated. The table shows the results.

isomer	moles of AgCl formed from 1.00 g of isomer
A	3.75×10^{-3}
B	7.50×10^{-3}
C	1.13×10^{-2}

(i) Calculate the M_r of $Cr(H_2O)_6Cl_3$.

M_r $Cr(H_2O)_6Cl_3$ = ... [1]

(ii) Use the data in the table above to calculate the value of n for each of the isomers, **A**, **B** and **C**. Complete the table below with the values of n and the molecular formula of each isomer, in the style of the general formula given above.

Show your working for at least one calculation of n.

isomer	n	molecular formula
A		
B		
C		

[2]

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(b) Two isomers have the same shape and their formula is $Ni(R_3P)_2(CN)_2$, where $R = CH_3$. Only one of these isomers has a dipole moment.

(i) Name the *type of isomerism* shown by $Ni(R_3P)_2(CN)_2$.

..... [1]

(ii) Draw structures of these two isomers.

isomer 1

isomer 2

[1]

(iii) State which isomer has a dipole moment. Explain your answer.

.....

..... [1]

[Total: 6]

5 **(a)** 1,2-diaminoethane, *en*, $H_2NCH_2CH_2NH_2$, is a bidentate ligand.

(i) What is meant by the terms *bidentate* and *ligand*?

bidentate .....

ligand .....

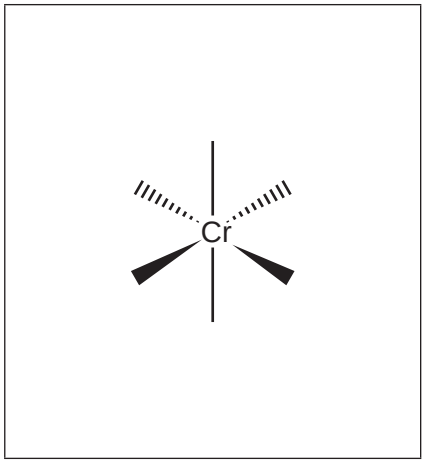
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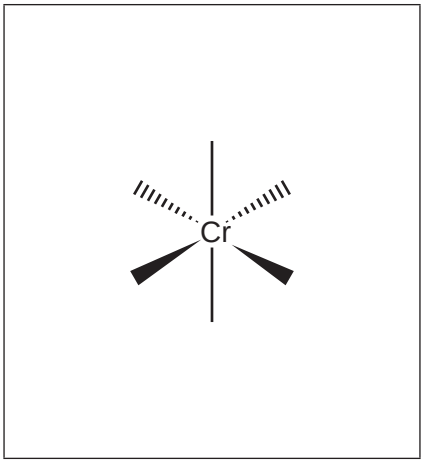
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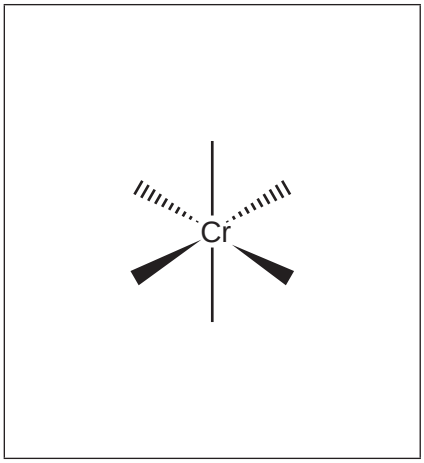
(ii) There are three isomeric complex ions with the formula $[Cr(en)_2Cl_2]^+$.

Complete the three-dimensional diagrams of the isomers in the boxes.

You may use  to represent *en*.







[3]

(b) Copper forms complexes with NH_3 and *en* according to equlibria 1 and 2.

equilibrium 1 $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$

equilibrium 2 $Cu^{2+}(aq) + 2en(aq) \rightleftharpoons [Cu(en)_2]^{2+}(aq)$

(i) Write the expressions for the stability constants, K_{stab1} and K_{stab2}, for equilibria 1 and 2. Include units in your answers.

K_{stab1} =

units = ...

K_{stab2} =

units = ...

[3]

(ii) An equilibrium is set up when both *en* and NH_3 ligands are added to a solution containing $Cu^{2+}(aq)$ as shown in equilibrium 3.

equilibrium 3 $[Cu(NH_3)_4]^{2+}(aq) + 2en(aq) \rightleftharpoons [Cu(en)_2]^{2+}(aq) + 4NH_3(aq)$

Write an expression for the equilibrium constant, K_{eq3}, in terms of K_{stab1} and K_{stab2}.

K_{eq3} = ... [1]

(iii) The numerical values for these stability constants are shown.

$$K_{stab1} = 1.2 \times 10^{13} \qquad K_{stab2} = 5.3 \times 10^{19}$$

Calculate the value of K_{eq3} stating its units.

K_{eq3} = ... unit = ...
[2]

(c) $\Delta S^{\ominus}$ values for equilibria 1 and 2 differ greatly, as can be seen in the table. All values are at a temperature of 298 K.

equilibrium	$\Delta H^{\ominus}$ / kJ mol^{-1}	$\Delta S^{\ominus}$ / J K^{-1} mol^{-1}	$\Delta G^{\ominus}$ / kJ mol^{-1}
1	–92	–60	–74
2	–100	+40	

(i) Explain why $\Delta S^{\ominus}_{eq2}$ is so different from $\Delta S^{\ominus}_{eq1}$.

.....

..... [1]

(ii) Calculate $\Delta G^{\ominus}_{eq2}$ at 298 K.

$\Delta G^{\ominus}_{eq2}$ = ... kJ mol^{-1}
[2]

(iii) What conclusion can be made about the relative feasibility of equilibria 1 and 2?

Explain your answer.

..... [1]

(iv) Using data from the table, suggest a value of $\Delta H^{\ominus}$ for equilibrium 3.

..... [1]

(v) State the *type of reaction* that is occurring in equilibrium 2.

..... [1]

[Total: 17]

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[Turn over

6 The table lists some organic acids and their pK_a values.

acid	formula	pK_a
ethanoic acid	CH_3CO_2H	4.76
chloroethanoic acid	$Cl CH_2CO_2H$	2.86
aminoethanoic acid (glycine)	$H_2NCH_2CO_2H$	9.87

(a) (i) State the relationship between pK_a and the strength of an acid.

..... [1]

(ii) State the mathematical relationship between pK_a and the acidity constant K_a.

..... [1]

(iii) Give reasons for why the pK_a value for chloroethanoic acid is **smaller** than that for ethanoic acid.

.....

.....

..... [2]

(b) (i) Use the zwitterionic structure for aminoethanoic acid (glycine) in aqueous solution to write an equation for its dissociation giving $H^+(aq)$ ions.

..... [1]

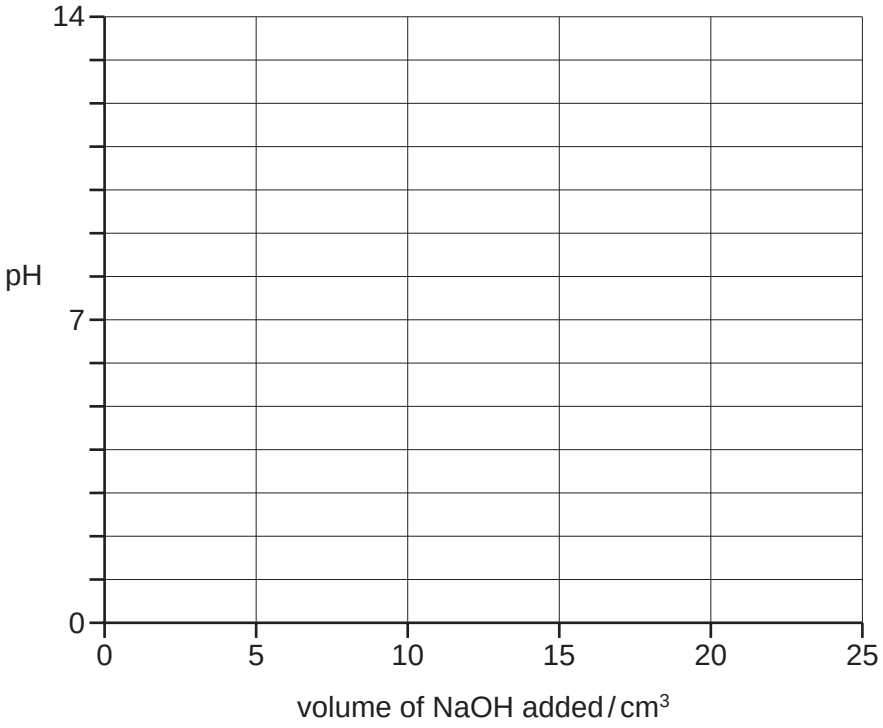
(ii) Calculate the pH of a 0.100 mol dm^{-3} solution of aminoethanoic acid.

pH = ... [2]

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A 10.0 cm^3 sample of 0.100 mol dm^{-3} aminoethanoic acid (glycine) was titrated with 0.100 mol dm^{-3} NaOH. After 20.0 cm^3 of NaOH, an excess, had been added, the pH was found to be 12.5.

(iii) Using the following axes, sketch a graph showing how the pH changes during this titration.



[3]

[Total: 10]

7 Compounds **W**, **X**, **Y** and **Z** are isomers of each other with the molecular formula $C_8H_7Cl O$.
All four isomers contain a benzene ring.
Only **one** of the isomers contains a chiral centre.
The results of six tests carried out on **W**, **X**, **Y** and **Z** are shown in the table.

test		observations with each isomer			
		W	**X**	**Y**	**Z**
1	add cold $AgNO_3(aq)$	white ppt. forms immediately	none	white ppt. forms very slowly	none
2	heat with NaOH(aq), then add dilute HNO_3 + $AgNO_3(aq)$	white ppt.	none	white ppt.	none
3	add NaOH(aq) + $I_2(aq)$	none	pale yellow ppt.	none	none
4	warm with Fehling's solution	none	none	red ppt.	none
5	add cold, dilute, acidified $KMnO_4(aq)$	no change	no change	no change	decolourises
6	add $Br_2(aq)$	no change	no change	no change	decolourises and forms white ppt.

(a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in the four isomers **W**, **X**, **Y** and **Z**.

Complete the table below, identifying the group(s) present in each isomer.

group(s) in compound			
W	**X**	**Y**	**Z**
.....	.....	.....	.....
.....	.....	.....	.....
.....	.....	.....	.....

[5]

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(b) Isomers **W**, **X**, **Y** and **Z** all have the molecular formula C_8H_7ClO.

(i) Use the information in **(a)** to suggest a structure for each of these isomers and draw these in the boxes.

W

X

Y

Z

[4]

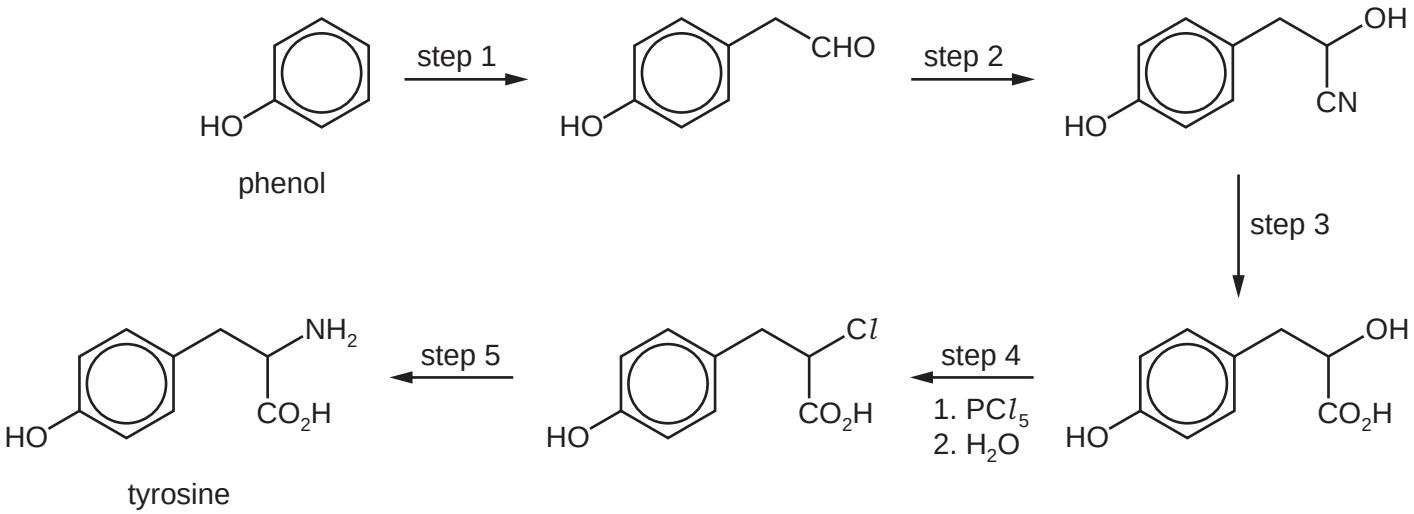
(ii) Draw a **circle** around the chiral centre in **one** of the above structures. [1]

[Total: 10]

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[Turn over

8 **(a)** The amino acid tyrosine can be synthesised from phenol by the route shown.



phenol

tyrosine

(i) Name the mechanism occurring in the following steps.

step 1 .....

step 2 .....

[2]

(ii) What *type of reaction* is occurring in step 3?

..... [1]

(iii) Suggest reagents and conditions for each of the following steps.

step 1 .....

step 2 .....

step 3 .....

step 5 .....

[5]

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(iv) Draw the structures of the products of the reactions of tyrosine with an **excess** of each of the following reagents.

with NaOH(aq)

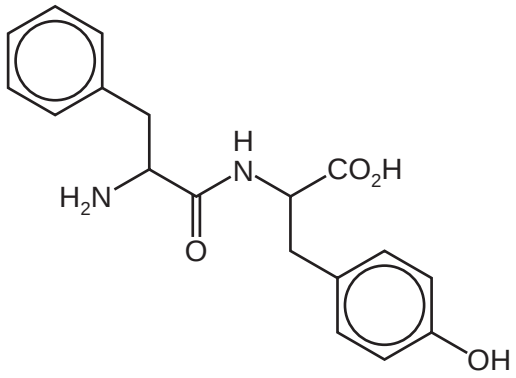
with HCl(aq)

with Br_2(aq)

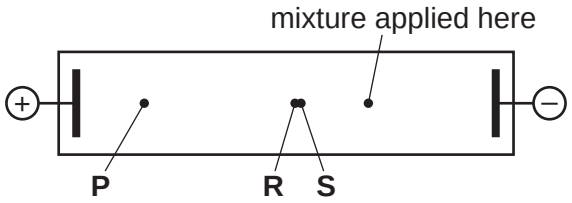
[4]

Question 8 continues on the next page.

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



The three spots are due to the three species phe, tyr and phe-tyr.

(i) Which species is responsible for spot **P**? Explain your answer.

.....

..... [2]

(ii) Suggest why the other two species give spots **R** and **S** that are so close together.

.....

..... [1]

[Total: 15]

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