

CANDIDATE
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CHEMISTRY

9701/42

Paper 4 Structured Questions

May/June 2014

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.

Section A

Answer **all** questions.

Section B

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.

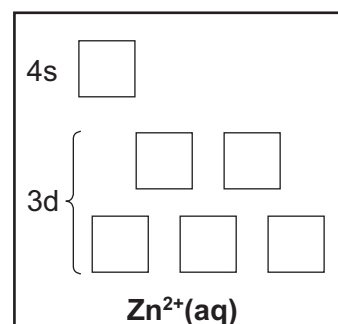
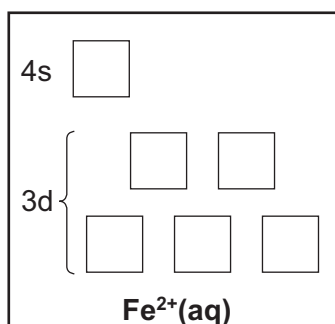
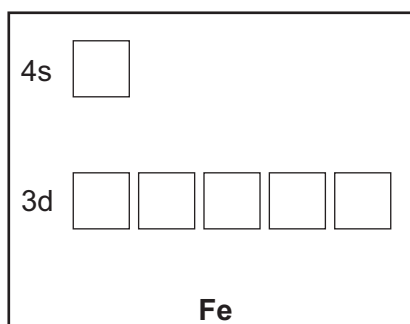
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8	
Total	

This document consists of **19** printed pages and **1** blank page.

Section A

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

- 1 (a) (i) On the diagrams below, show the outer electron arrangements of the atoms and ions indicated. (Use the symbol $\uparrow\downarrow$ to represent a pair of electrons in an orbital.)



- (ii) Use the above diagrams to explain why Fe²⁺(aq) ions are coloured, whereas Zn²⁺(aq) ions are colourless.

.....

.....

.....

.....

[4]

- (b) When concentrated HCl is added to a solution of Cu²⁺(aq) ions, the solution turns yellow.

- (i) State the formula of the species responsible for the yellow colour and name the *type of reaction* that has occurred.

.....

.....

- (ii) Ammonia can react as a base or as a ligand. Describe the colour changes that occur when NH₃(aq) is **gradually** added, with stirring, to the yellow solution, until the NH₃(aq) is in excess. Identify the **three** ions or compounds responsible for the new colours.

.....

.....

.....

.....

.....

.....

[7]

(c) When aqueous solutions of KI and $K_2S_2O_8$ are mixed almost no reaction occurs, but when a few drops of $Fe^{2+}(aq)$ or $Fe^{3+}(aq)$ are added, iodine, $I_2(aq)$, is produced at a steady rate.

(i) Write an equation for the overall reaction.

.....

(ii) State the precise role of the iron ions during this reaction.

.....

(iii) By means of equations or otherwise, explain why the presence of *either* Fe^{2+} or Fe^{3+} is able to speed up the reaction.

.....

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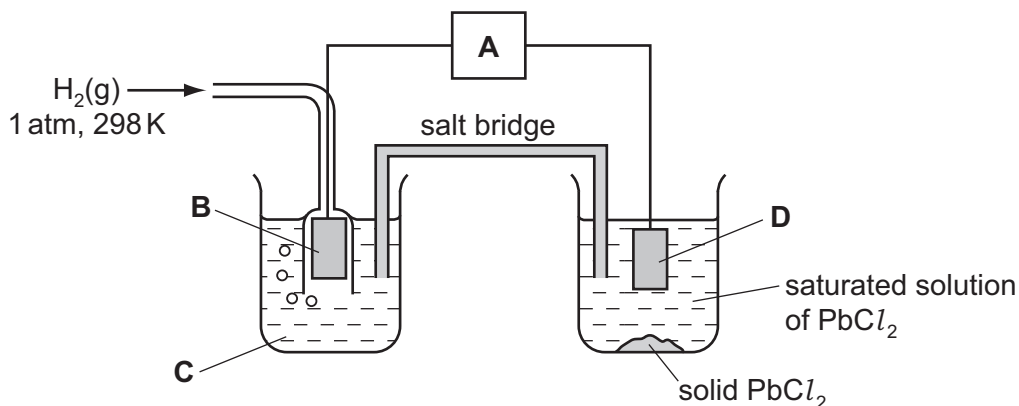
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[3]

[Total: 14]

2 Lead(II) chloride, PbCl_2 , can be used in the manufacture of some types of coloured glass.

PbCl_2 is only sparingly soluble in water. The $[\text{Pb}^{2+}]$ in a saturated solution of PbCl_2 can be estimated by measuring the cell potential, E_{cell} , of the following cell.



(a) In the spaces below, identify what the four letters **A-D** in the above diagram represent.

A **B**

C **D**

[4]

(b) In a saturated solution of PbCl_2 , $[\text{PbCl}_2(\text{aq})] = 3.5 \times 10^{-2} \text{ mol dm}^{-3}$.

(i) The E° for the Pb^{2+}/Pb electrode is -0.13 V . Predict the potential of the right-hand electrode in the diagram above. Indicate this by placing a tick in the appropriate box in the table below.

electrode potential / V	place one tick only in this column
-0.17	
-0.13	
-0.09	
0.00	

Explain your answer.

.....

.....

(ii) Write an expression for the solubility product, K_{sp} , of $PbCl_2$.

.....

(iii) Calculate the value of K_{sp} , including units.

$K_{sp} = \dots\dots\dots$ units $\dots\dots\dots$ [5]

(c) The behaviours of $PbCl_2$ and $SnCl_2$ towards reducing agents are similar, but their behaviours towards oxidising agents are very different.

(i) Illustrate this comparison by quoting and comparing relevant E° values for the two metals and their ions. Explain what the relative E° values mean in terms of the ease of oxidation or reduction of these compounds.

.....

(ii) Writing a balanced molecular or ionic equation in each case, suggest a reagent to carry out each of the following reactions.

the reduction of $PbCl_2$

.....

the oxidation of $SnCl_2$

.....

[5]

(d) (i) Write an equation to represent the lattice energy of PbCl_2 . Show state symbols.

.....

(ii) Use the following data, together with appropriate data from the *Data Booklet*, to calculate a value for the lattice energy of PbCl_2 .

electron affinity of chlorine	=	-349 kJ mol^{-1}
enthalpy change of atomisation of lead	=	$+195 \text{ kJ mol}^{-1}$
enthalpy change of formation of $\text{PbCl}_2(\text{s})$	=	-359 kJ mol^{-1}

lattice energy = kJ mol^{-1}

(iii) How might the lattice energy of PbCl_2 compare to that of PbBr_2 ? Explain your answer.

.....

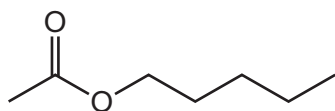
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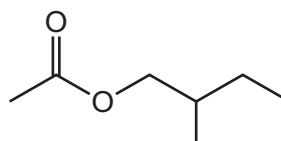
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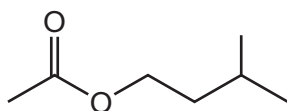
- 3 The following four isomeric esters with the molecular formula $C_7H_{14}O_2$ are used as artificial flavours in drinks and sweets to give a pear, banana or plum taste to foodstuffs.



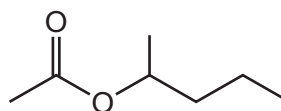
A



B



C



D

- (a) In each of the spaces below, write one or more of the letters **A-D**, as appropriate.

- (i) Which of these compounds can exist as optical isomers?

.....

- (ii) On hydrolysis, which of these compounds produce(s) a secondary alcohol?

.....

[3]

- (b) The hydrolysis of all these compounds produces ethanoic acid, CH_3CO_2H , as one of the products.

State the reagents and conditions needed for this hydrolysis.

..... [1]

(c) The acid dissociation constant, K_a , of ethanoic acid is $1.75 \times 10^{-5} \text{ mol dm}^{-3}$.

(i) Explain why this value of K_a is

- much larger than that of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$,

.....
.....

- smaller than that of chloroethanoic acid, $\text{ClCH}_2\text{CO}_2\text{H}$.

.....
.....

(ii) Calculate the pH of a $0.100 \text{ mol dm}^{-3}$ solution of ethanoic acid.

[4]

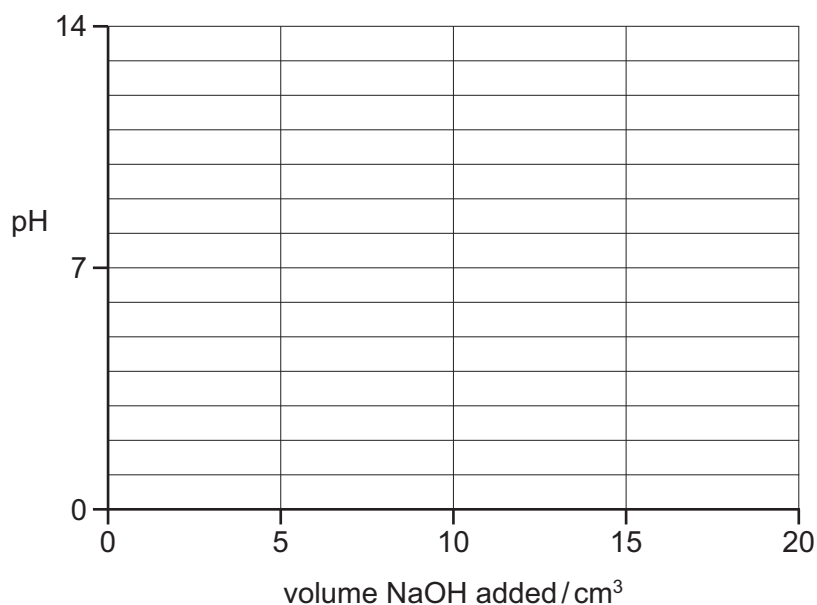
(d) 20.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ NaOH were slowly added to a 10.0 cm^3 sample of $0.100 \text{ mol dm}^{-3}$ ethanoic acid, and the pH was measured throughout the addition.

(i) Calculate the number of moles of NaOH remaining at the end of the addition.

(ii) Calculate the $[\text{OH}^-]$ at the end of the addition.

(iii) Using the expression $K_w = [\text{H}^+][\text{OH}^-]$ and your value in (ii), calculate $[\text{H}^+]$ and the pH of the solution at the end of the addition.

- (iv) On the following axes, sketch how the pH will change during the addition of a total of 20.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ NaOH. Mark clearly where the end point occurs.



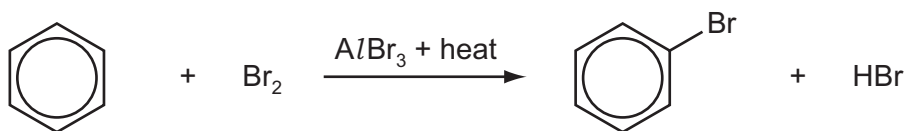
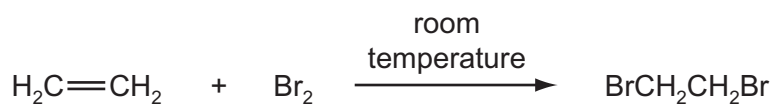
- (v) From the following list of indicators, put a tick in the box by the side of the indicator you consider most suitable for this titration.

indicator	pH at which colour changes	place one tick only in this column
malachite green	0 - 1	
thymol blue	1 - 2	
bromophenol blue	3 - 4	
thymolphthalein	9 - 10	

[7]

[Total: 15]

4 Both ethene and benzene react with bromine.



(a) What *type of reaction* is the reaction of bromine with

(i) ethene,

.....

(ii) benzene?

.....

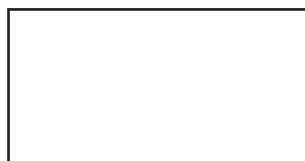
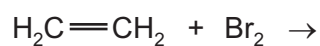
[1]

(b) Write an equation to show the formation of the electrophile during the reaction between bromine and benzene.

..... [1]

(c) Each of these reactions involves an intermediate.

(i) Draw the structure of the intermediate in each reaction.



(ii) Suggest why the product of the reaction between bromine and benzene, bromobenzene, is still unsaturated.

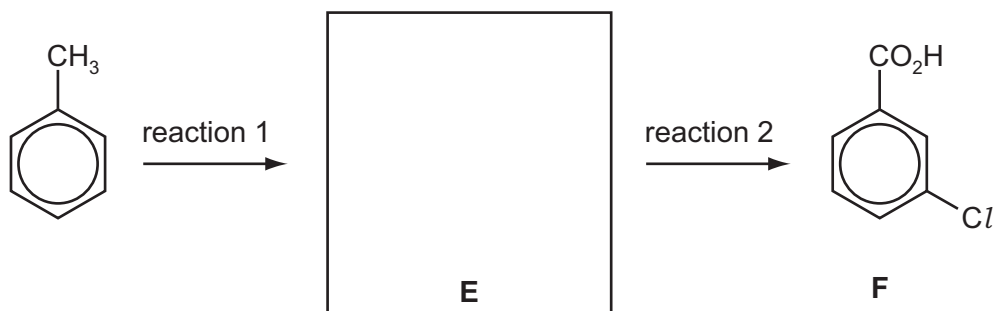
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[3]

- (d) When methylbenzene is nitrated, 4-nitromethylbenzene is formed, but when benzoic acid is nitrated, 3-nitrobenzoic acid is produced.

Consider the following synthesis of 3-chlorobenzoic acid, **F**, from methylbenzene. Use the information given above to suggest

- the structure of the intermediate **E**,
- the reagents and conditions needed for reactions 1 and 2.



reagents and conditions for reaction 1

.....

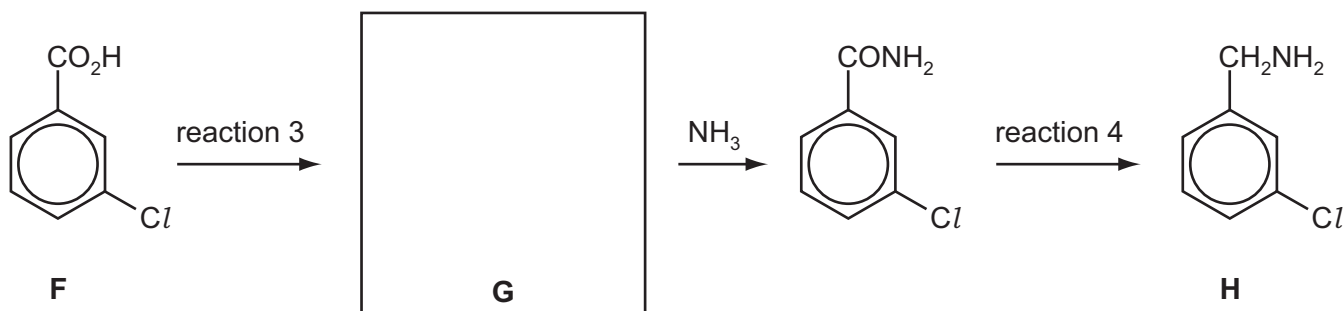
reagents and conditions for reaction 2

.....

[3]

- (e) Consider the following synthesis of 3-chlorophenylmethanamine, **H**, from **F**. Suggest

- the structure of the intermediate **G**,
- the reagents for reactions 3 and 4.



reagents for reaction 3

.....

reagents for reaction 4

.....

[3]

[Total: 11]

- 5 Although now remembered for his music, the Russian composer Alexander Borodin was a chemist. He is credited with the discovery of the *aldol reaction*, a product of which is compound **J**. **J** shows the following properties:

- its molecular formula is $C_4H_8O_2$,
- it is neutral,
- it reacts with sodium metal,
- it reacts with Fehling's solution,
- it does not react with aqueous bromine.

(a) Suggest which functional groups are responsible for the reactions with

(i) sodium,

.....

(ii) Fehling's solution.

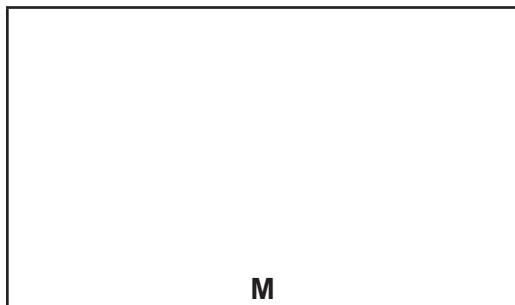
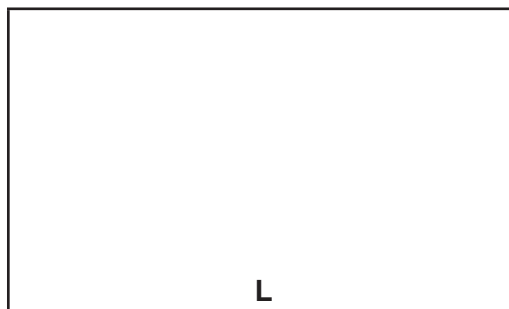
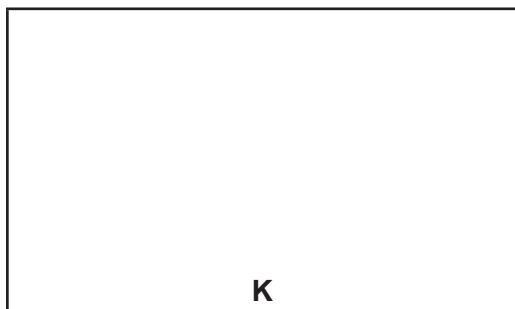
.....

[2]

(b) The result of the bromine test shows a functional group is absent from compound **J**. Suggest the identity of this functional group.

..... [1]

(c) In the boxes below, draw three possible **straight-chain** structures for **J** that fit the above results, and that are structural isomers of each other.



[3]

(d) Compound **J** reacts with alkaline aqueous iodine to give a pale yellow precipitate.

(i) Which functional group does this reaction show that **J** contains?

.....

(ii) Which of your three structures **K**, **L** or **M** contains this group and is therefore **J**?

.....

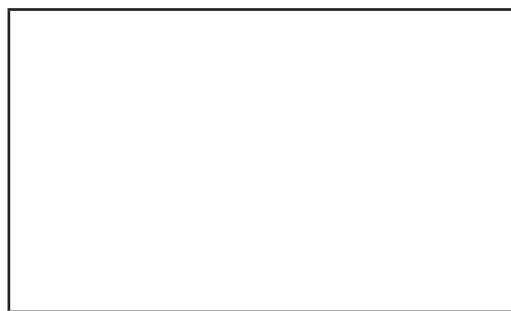
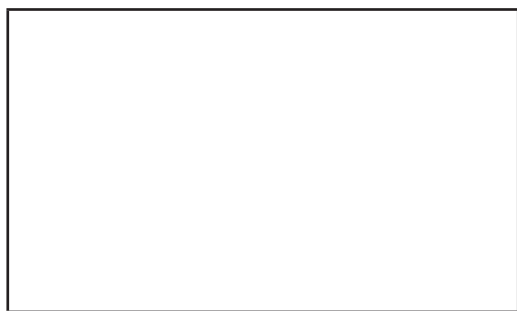
[2]

(e) Compound **J** exists as stereoisomers.

(i) Name the type of stereoisomerism shown by **J**.

.....

(ii) Draw two structures of **J** to illustrate this stereoisomerism.



[2]

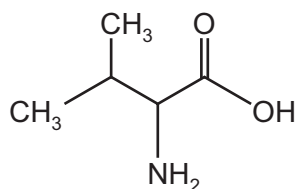
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Section B

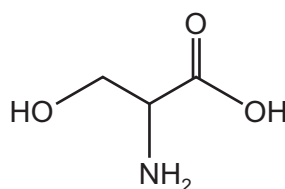
Answer **all** the questions in the spaces provided.

6 This question looks at the formation and breakdown of protein chains in the body.

(a) Proteins are formed from chains of amino acid monomers joined together. The structures of two amino acids, valine and serine are shown.



valine (val)



serine (ser)

(i) Draw the structure of the dipeptide val-ser, showing the peptide bond in displayed form.

(ii) What *type of reaction* has taken place in order to form this dipeptide?

.....

(iii) Identify the other molecule produced in this reaction.

.....

[4]

(b) Both DNA and RNA are involved in protein synthesis.

Complete the table to show **three** differences between the structures of DNA and RNA.

	DNA	RNA
1		
2		
3		

[3]

- (c) In protein synthesis, sections of the DNA are copied by mRNA and this, in turn, is read by the ribosome in order to assemble the amino acids for the new protein chain. Each group of three bases codes for one amino acid, with some amino acids having several codes. The codes are summarised in the table.

UUU	phe	UCU	ser	UAU	tyr	UGU	cys
UUC	phe	UCC	ser	UAC	tyr	UGC	cys
UUA	leu	UCA	ser	UAA	stop	UGA	stop
UUG	leu	UCG	ser	UAG	stop	UGG	trp
CUU	leu	CCU	pro	CAU	his	CGU	arg
CUC	leu	CCC	pro	CAC	his	CGC	arg
CUA	leu	CCA	pro	CAA	gln	CGA	arg
CUG	leu	CCG	pro	CAG	gln	CGG	arg
AUU	ile	ACU	thr	AAU	asn	AGU	ser
AUC	ile	ACC	thr	AAC	asn	AGC	ser
AUA	ile	ACA	thr	AAA	lys	AGA	arg
AUG	met/ start	ACG	thr	AAG	lys	AGG	arg
GUU	val	GCU	ala	GAU	asp	GGU	gly
GUC	val	GCC	ala	GAC	asp	GGC	gly
GUA	val	GCA	ala	GAA	glu	GGA	gly
GUG	val	GCG	ala	GAG	glu	GGG	gly

In general the amino acid chains start with the code AUG, and end with one of the three 'stop' codes shown in the table.

- (i) Use the abbreviations to show the sequence of amino acids in the peptide for the base sequence shown.

– AUGCUAACACCGGAGUAA –

.....

- (ii) Sometimes an error can occur in the base sequence.

What are these errors called?

.....

- (iii) This type of error can lead to the formation of a protein with a different structure from the original, as in *sickle cell anaemia*. In this case the amino acid glutamic acid (glu) is replaced by valine (val) in the protein as a result of one base being changed in a three base code.

Use the table to suggest the change of base that causes this.

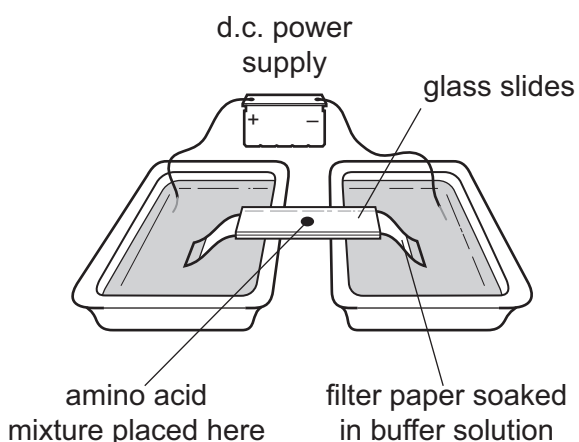
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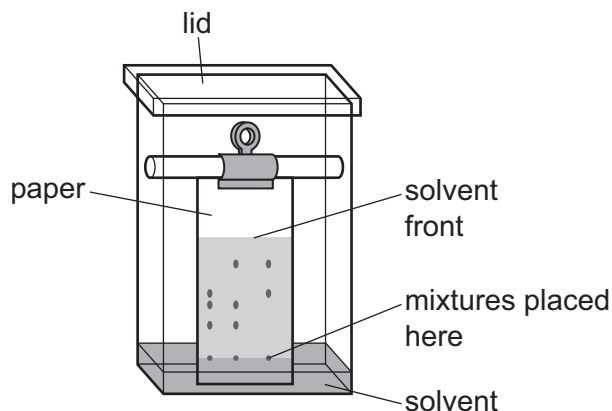
[Total: 10]

7 Modern methods of chemical analysis often rely on the interpretation of data gathered from instrumental techniques.

(a) Electrophoresis and paper chromatography can both be used to separate amino acids from a mixture obtained from polypeptides.



electrophoresis



paper chromatography

In each case, give **one** property of the amino acids that causes their separation.

electrophoresis

.....

paper chromatography

.....

[2]

(b) Amino acids are colourless.

How are the positions of the different amino acids made visible so that measurements can be made?

.....

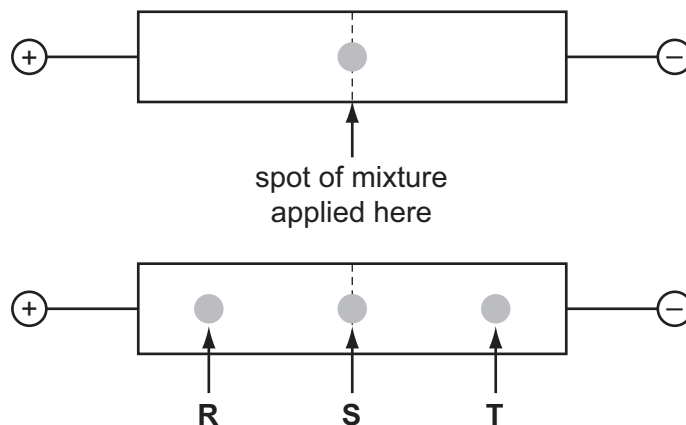
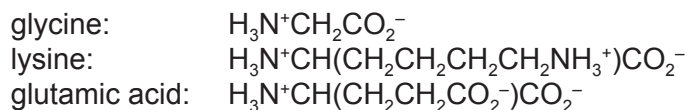
..... [1]

(c) Which **measurements** need to be made in order to identify individual amino acids in paper chromatography?

.....

..... [1]

(d) The diagram shows the results of electrophoresis on a mixture of the amino acids glycine, lysine and glutamic acid at pH 7.0. The structures of the amino acids at pH 7.0 are shown.



Identify the amino acids responsible for the spots labelled **R**, **S** and **T**.

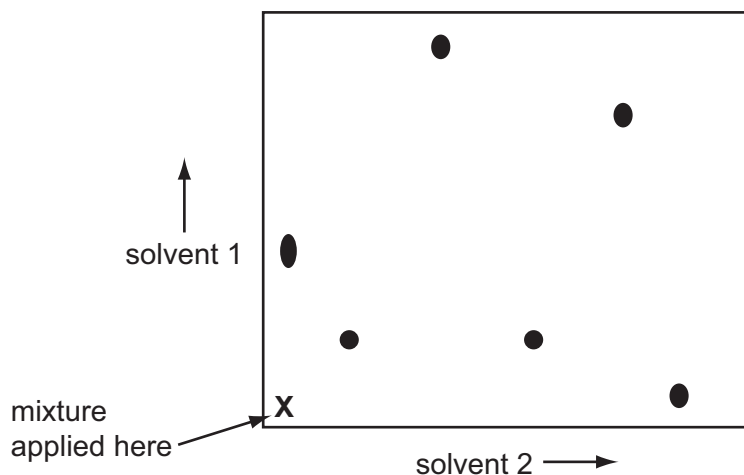
R

S

T

[3]

(e) This diagram shows the results of two-way paper chromatography of a mixture of amino acids.



To answer these questions you need to indicate clearly on the diagram above as directed in the questions.

(i) Put a **U** next to the amino acid that travelled furthest in solvent 2.

(ii) Put a ring around the **two** amino acids that were **not** separated in solvent 1.

(iii) Put a **W** next to the amino acid that was very soluble in **both** solvents.

[3]

[Total: 10]

8 Polymers consist of monomers joined by either addition or condensation reactions.

(a) Name an example of a synthetic addition polymer and a synthetic condensation polymer.

addition polymer

condensation polymer

[2]

(b) Addition polymers are long-term pollutants in the environment but condensation polymers are often biodegradable.

(i) What *type of reaction* occurs when condensation polymers biodegrade?

.....

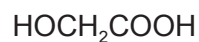
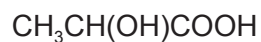
(ii) Identify **two** functional groups that could undergo this type of reaction.

.....

[2]

(c) Petroleum is a non-renewable resource from which a wide range of useful polymers is currently produced. Current polymer research is looking at renewable plant material as a potential source of monomers.

Two monomers obtained from plants are shown.



Draw the displayed formula of the repeat unit of a polymer using **both** monomers.

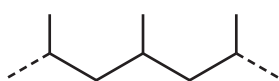
[2]

(d) Monomers obtained from plant sources do not usually form addition polymers. Suggest why this is.

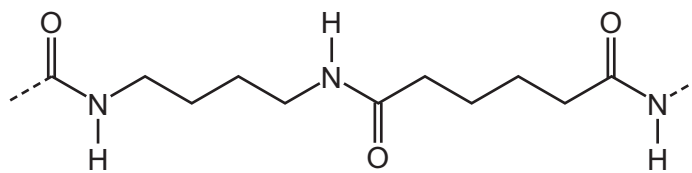
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..... [1]

(e) The diagrams show sections of two polymers **Y** and **Z**.



Y



Z

(i) What would be the main force between the chains in each polymer?

Y

Z

(ii) Which is likely to be the more hydrophilic of these two polymers? Explain your answer.

.....

.....

[3]

[Total: 10]

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