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CHEMISTRY

9701/43

Paper 4 Structured Questions

October/November 2015

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.

For Examiner's Use	
1	
2	
3	
4	
5	
6	
7	
8	
9	
Total	

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

Section A

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

- 1 (a) The dissolving of an ionic compound in water is accompanied by an energy change, the enthalpy change of solution, ΔH_{sol} .



Describe, in terms of bond breaking and bond making, what happens to the solid ionic lattice when an ionic compound dissolves in water.

.....

 [2]

- (b) (i) What is meant by the term *enthalpy change of solution*, ΔH_{sol} ?

.....
 [1]

- (ii) Use the following data to calculate the standard enthalpy change of hydration, $\Delta H_{\text{hyd}}^{\ominus}$, of chloride ions, $\text{Cl}^{-}(\text{g})$.
 You may find it helpful to construct an energy cycle.

enthalpy change	value
$\Delta H_{\text{hyd}}^{\ominus} (\text{Mg}^{2+}(\text{g}))$	$-1925 \text{ kJ mol}^{-1}$
lattice energy of $\text{MgCl}_2(\text{s})$	$-2524 \text{ kJ mol}^{-1}$
enthalpy change of solution for $\text{MgCl}_2(\text{s})$	-155 kJ mol^{-1}

$$\Delta H_{\text{hyd}}^{\ominus} (\text{Cl}^{-}(\text{g})) = \dots\dots\dots \text{ kJ mol}^{-1} \quad [2]$$

- (iii) The enthalpy change of hydration for Na^+ , $\Delta H_{\text{hyd}}^{\ominus}(\text{Na}^+(\text{g}))$, is -410 kJ mol^{-1} .

Suggest an explanation for why the $\Delta H_{\text{hyd}}^{\ominus}$ of the Na^+ ion is **less** exothermic than the $\Delta H_{\text{hyd}}^{\ominus}$ of the Mg^{2+} ion.

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

- (c) Describe and explain how the solubility of the Group II sulfates varies down the group.

.....
.....
.....
.....
.....
.....
..... [4]

[Total: 11]

- 2 (a) Cobalt is a transition element and forms compounds with oxidation numbers +2 and +3.

Complete the electronic structures for

a cobalt atom, $1s^2 2s^2 2p^6$

cobalt in the +3 oxidation state. $1s^2 2s^2 2p^6$

[2]

- (b) (i) In an aqueous solution of cobalt(II) sulfate the cobalt forms complex ions.

What is meant by the term *complex ion*?

.....

..... [1]

- (ii) State **two** chemical properties of cobalt, other than the formation of complexes, that are **not** shown by a typical s-block element.

.....

..... [2]

- (c) Cobalt(II) ions, $\text{Co}^{2+}(\text{aq})$, show some chemical properties similar to those of copper(II) ions, $\text{Cu}^{2+}(\text{aq})$.

Use this information and the *Data Booklet* to suggest the formula of the cobalt species formed in each of the following reactions. State the *type of reaction* taking place in each case.

	formula of cobalt species formed	type of reaction
$\text{Co}^{2+}(\text{aq}) + \text{an excess of } \text{NH}_3(\text{aq})$		
$\text{Co}^{2+}(\text{aq}) + \text{OH}^-(\text{aq})$		
$\text{Co}^{2+}(\text{aq}) + \text{S}_2\text{O}_8^{2-}(\text{aq})$		

[5]

- (d) Some transition elements are present in superconductors. These are materials that conduct electricity with little or no resistance.

Compound **Q** is a superconductor and contains 13.4% yttrium, 41.2% barium, 28.6% copper and 16.8% oxygen by mass.

- (i) Show that the empirical formula of **Q** is $\text{YBa}_2\text{Cu}_3\text{O}_7$. Show all your working.

[1]

- (ii) The table shows the oxidation numbers of yttrium, barium and oxygen in **Q**.

element	oxidation number
yttrium	+3
barium	+2
oxygen	-2

Calculate the **average** oxidation number of copper in **Q**.

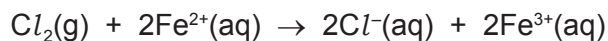
[1]

- (iii) Hence deduce the oxidation number of **each** of the **three** copper atoms in **Q**.

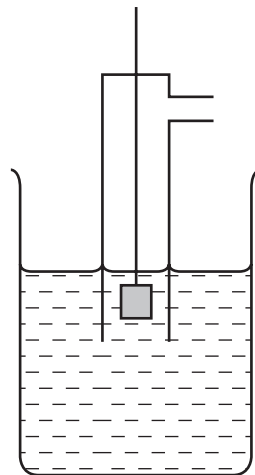
[1]

[Total: 13]

- 3 Chlorine gas and iron(II) ions react together in aqueous solution as shown.



- (a) (i) Complete and label the diagram to show how the standard cell potential, $E^{\ominus}_{\text{cell}}$, for the above reaction could be measured at standard conditions.



[4]

- (ii) Use the *Data Booklet* to calculate the $E^{\ominus}_{\text{cell}}$ for this reaction.

[1]

- (b) What colour change would you see when chlorine gas is bubbled through a solution containing $\text{Fe}^{2+}(\text{aq})$ ions until the reaction is complete?

..... [1]

- (c) Predict the effect, if any, of **decreasing** the concentration of $\text{Cl}^{-}(\text{aq})$ on the magnitude of the cell potential in (a)(ii). Explain your answer.

.....

.....

..... [2]

- (d) (i) A fuel cell is an electrochemical cell that can be used to generate electrical energy.

In the **alkaline** hydrogen-oxygen fuel cell, $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ are passed over two inert electrodes immersed in an alkaline solution.

Write the half-equations for the reactions taking place at each of these electrodes.

hydrogen electrode

oxygen electrode

[2]

- (ii) Construct an equation for the overall reaction.

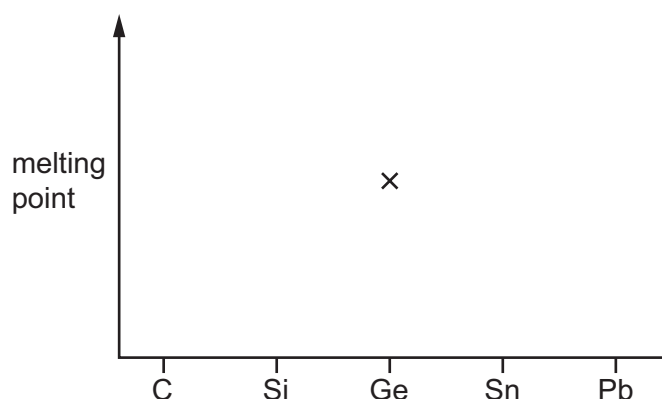
..... [1]

- (iii) Suggest **one** possible advantage of using a hydrogen-oxygen fuel cell over a conventional 'simple cell' battery.

..... [1]

[Total: 12]

- 4 (a) (i) On the grid below, sketch the trend in the melting points of the Group IV elements. The point for germanium has already been shown.



[1]

- (ii) Suggest an explanation of this trend in terms of structure and bonding of the Group IV elements.

.....

 [1]

- (b) GeO_2 , SnO_2 and PbO_2 are amphoteric oxides.

- (i) What is meant by the term *amphoteric*?

.....
 [1]

- (ii) Construct an equation for the reaction of SnO_2 with NaOH .

.....
 [1]

- (c) (i) By quoting information from the *Data Booklet* explain why the reaction between $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ ions and acidified $\text{Sn}^{2+}(\text{aq})$ ions is feasible.

.....

 [1]

- (ii) Construct an equation for the reaction in (c)(i) and give any relevant observations.

equation

observations

..... [2]

- (d) (i) On heating, germanium(II) oxide disproportionates to form germanium(IV) oxide and germanium.

Describe, using this reaction as an example, what is meant by a *disproportionation reaction*.

.....

.....

..... [1]

- (ii) Some of the reactions of cyanogen, NC–CN, are similar to those of chlorine, Cl–Cl. On treatment with **cold**, aqueous sodium hydroxide, cyanogen disproportionates in a similar manner to chlorine.

Complete the equation for this reaction.



- (iii) Draw a 'dot-and-cross' diagram for NC–CN. Show the outer electrons only.

[1]

- (e) At room temperature, phosphorus atoms form P_4 molecules rather than P_2 molecules.

The phosphorus molecule, P_4 , has a cage-like structure containing only P–P single bonds. All the phosphorus atoms in P_4 are trivalent.

- (i) Suggest a structure for P_4 .

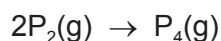
[1]

- (ii) At a temperature of 1200 K P_2 and P_4 exist in equilibrium in the gas phase.

P_2 molecules contain the $P \equiv P$ bond.

The average bond energy of P–P is 198 kJ mol^{-1} while that of $P \equiv P$ is 489 kJ mol^{-1} .

Use the above bond energies to calculate the enthalpy change, ΔH , for the following reaction.



[2]

- (f) When phosphorus(V) chloride, PCl_5 , is reacted with ammonium chloride, NH_4Cl , hydrogen chloride gas, HCl , is released and a product with the molecular formula $P_3N_3Cl_6$ is formed.

- (i) Construct an equation for this reaction.

..... [1]

- (ii) $P_3N_3Cl_6$ has a cyclic structure containing alternating phosphorus and nitrogen atoms in the ring system. All the nitrogen atoms are trivalent and all the phosphorus atoms are pentavalent.

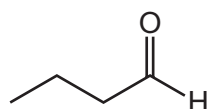
Suggest a structure for $P_3N_3Cl_6$.

[1]

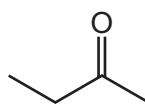
[Total: 15]

TURN OVER FOR QUESTION 5.

- 5 (a) A student carries out some reactions with separate samples of butanal and butanone.



butanal



butanone

The following results are obtained with reagents **L**, **M** and **N**.
(✓ means a reaction takes place.)

reagent	butanal	butanone
L	✓	✓
M	✓	no reaction
N	no reaction	✓

- (i) Suggest a possible identity for each reagent **L**, **M** and **N**.

L

M

N

[3]

- (ii) Give the structure of the organic product formed when **M** reacts with butanal.

[1]

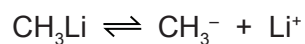
- (iii) What is observed when **N** reacts with butanone?

..... [1]

- (iv) What *type of reaction* is occurring when **N** reacts with butanone?

..... [1]

- (b) The organolithium compound methyl lithium, CH_3Li , can act as a source of CH_3^- ions.



The CH_3^- ion can act as a nucleophile.

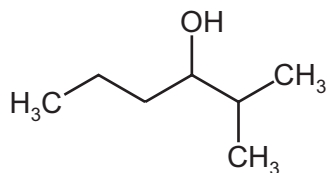
The reaction between methyl lithium and carbonyl compounds can be used to make alcohols.

- (i) Suggest a mechanism for the reaction of butanal with CH_3^- ions. Include all necessary curly arrows, lone pairs and relevant dipoles.



[3]

- (ii) A chemist decides to prepare the following organic compound **G** from butanal.

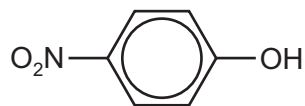
**G**

Draw the structure of the **organolithium** reagent which could be used to prepare **G** from butanal.

[1]

[Total: 10]

- 6 4-nitrophenol can be converted into a range of useful organic products.



4-nitrophenol

- (a) 4-nitrophenol can react with three different reagents.

Complete the table by:

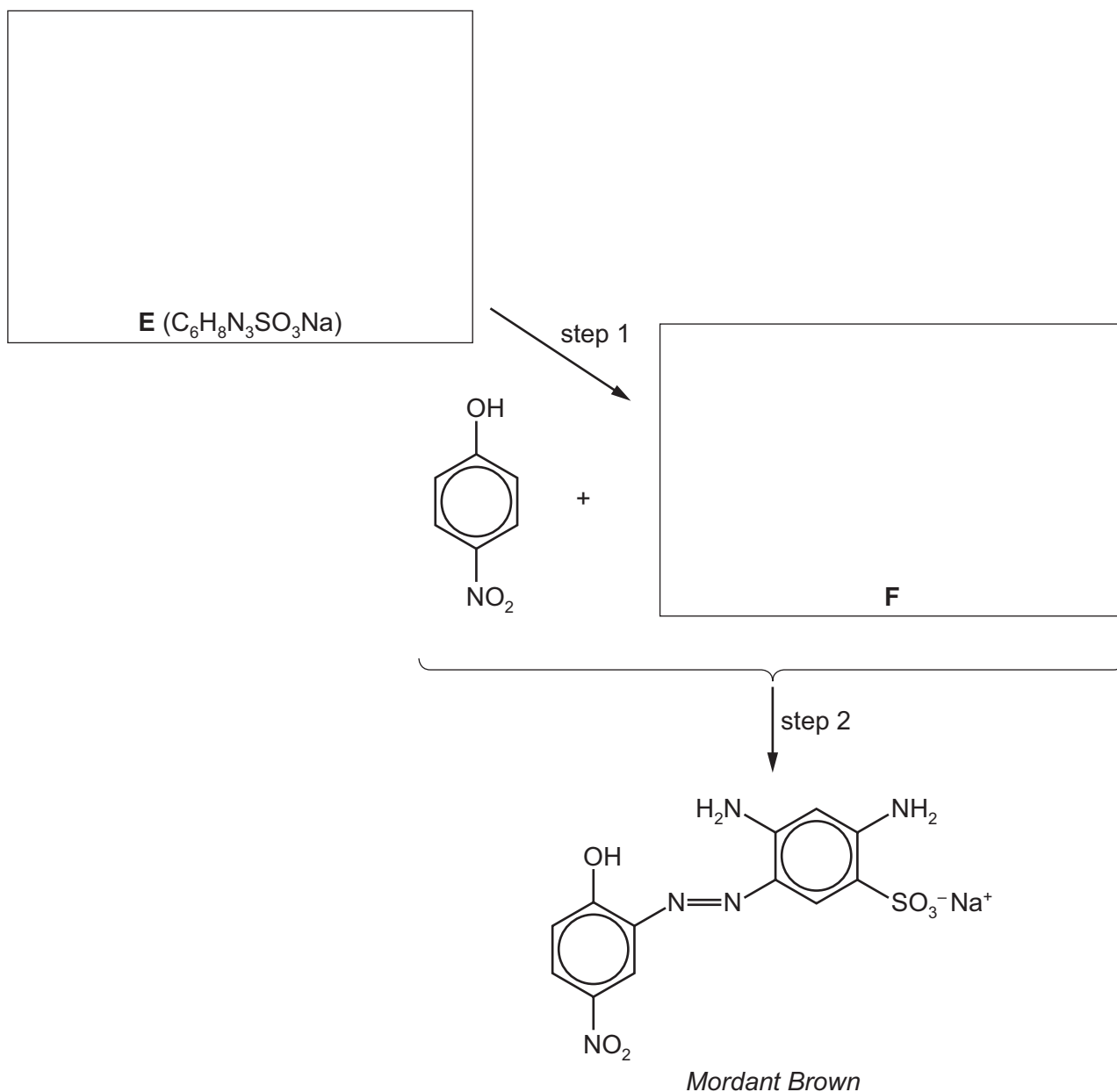
- drawing the structures of the organic products formed,
- identifying the non-organic products formed.

reagent	organic product structure	identity of non-organic product
Na(s)		
Br ₂ (aq)		
CH ₃ COCl(l)		

[4]

- (b) 4-nitrophenol can also be used in the synthesis of the dye *Mordant Brown* by the following route.

In step 2 of this synthesis, 4-nitrophenol reacts with intermediate **F** made from amine **E**. Assume that the $\text{SO}_3^- \text{Na}^+$ group does not react.



- (i) Suggest structures for compounds **E** and **F** and draw them in the boxes above. [2]
- (ii) Suggest reagents and conditions for
- step 1,
- step 2. [3]

[Total: 9]

Section B

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

7 DNA is an important biochemical molecule.

(a) DNA has a double helical structure that consists of two strands linked together.

Draw a **block diagram** of DNA showing **two** repeat units in each strand.
Label all the components, showing and labelling the bonds between the strands.

[5]

(b) Genetic information is stored in DNA.

Outline the main steps in the replication of DNA.

.....

.....

.....

..... [2]

- (c) DNA fingerprinting is based on the fact that all humans (apart from genetically identical twins) have different DNA base sequences. This is regularly used to help investigate serious crimes.
- (i) The first stage of DNA fingerprinting requires a sample of DNA to be broken down into shorter fragments.

What could be used to carry out this fragmentation?

..... [1]

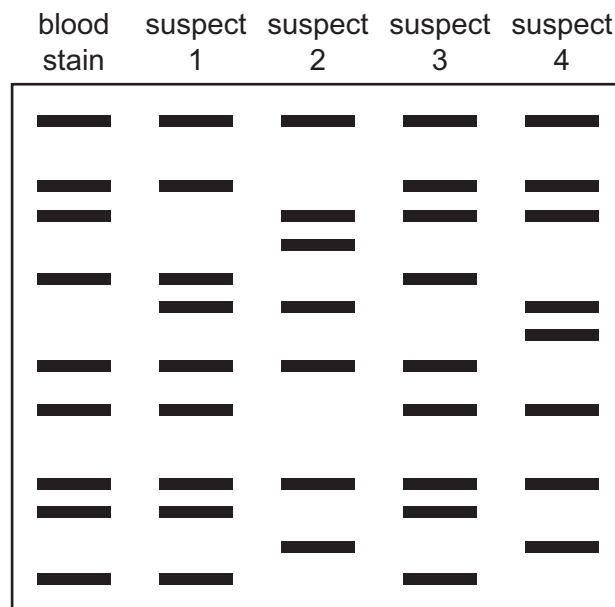
- (ii) Name the analytical technique used to separate these short fragments.

..... [1]

- (iii) After the fragments have been separated, what could the DNA fingerprint be treated with to reveal the position of the bands?

..... [1]

- (iv) A sample of blood, thought to be from the suspect, was found at a crime scene. The DNA of the blood sample, and that of four possible suspects, was analysed.



Based on this evidence, **circle** the suspect who should be arrested.

suspect 1

suspect 2

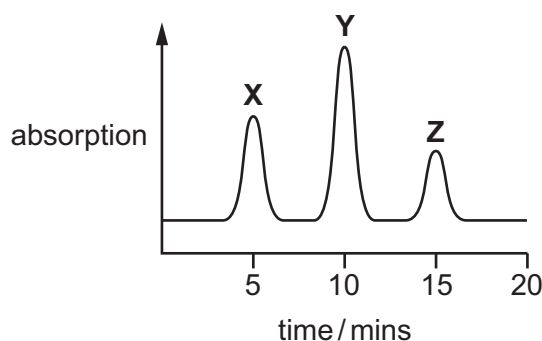
suspect 3

suspect 4

[1]

[Total: 11]

- 8 (a) A mixture of volatile organic compounds **X**, **Y** and **Z** can be separated in a gas chromatograph. Their identities can be confirmed by measuring their different retention times and comparing to known values.
A gas chromatogram is shown.



- (i) Suggest what is meant by the term *retention time*.

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

- (ii) Give an example of a carrier gas used in gas chromatography.

..... [1]

- (iii) **Z** spends the longest time in the chromatography column.

Suggest why this might be the case.

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

- (iv) Explain a possible limitation of gas/liquid chromatography in separating two esters such as ethyl methanoate, $\text{HCO}_2\text{CH}_2\text{CH}_3$, and methyl ethanoate, $\text{CH}_3\text{CO}_2\text{CH}_3$.

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

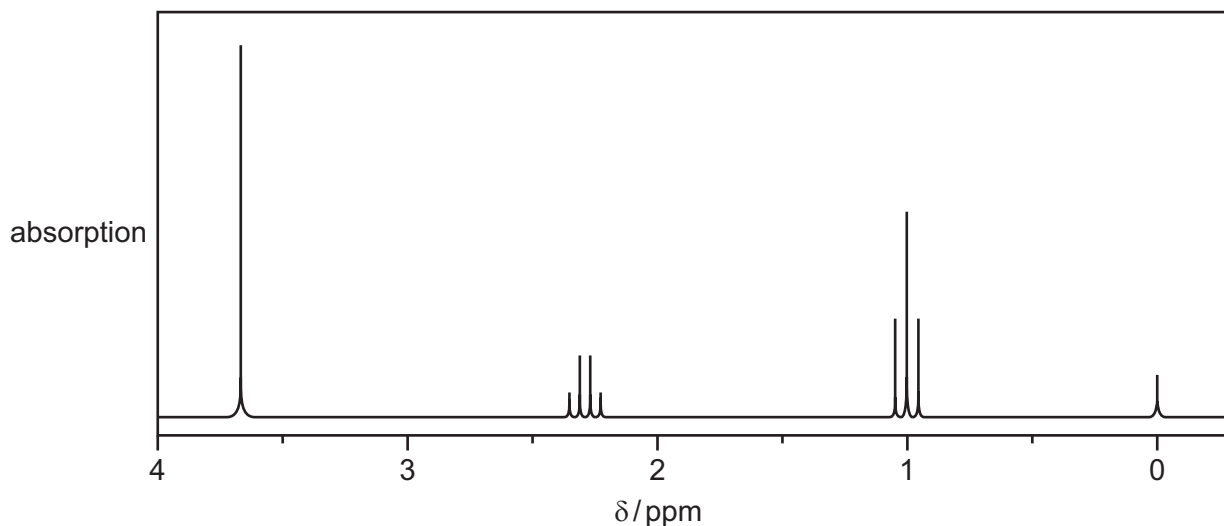
- (v) A student works out the areas underneath the three peaks in the chromatogram.

peak	X	Y	Z
area / mm^2	22	38	16

Assuming the areas underneath the peaks are proportional to the masses of the respective components, what percentage of the original mixture was made up of the organic compound, **X**?

% of **X** = [1]

(b) The NMR spectrum of **Y** given below shows four absorptions.



(i) What compound is responsible for the absorption at $\delta = 0$?

..... [1]

(ii) Compound **Y** is an ester with the molecular formula $C_4H_8O_2$.

Complete the table for the NMR spectrum of **Y**.

The actual chemical shifts for three absorptions in **Y** and the splitting pattern for the resonance at $\delta = 3.7$ ppm have been given for you.

Use of the *Data Booklet* may be helpful.

chemical shift δ /ppm	type of proton(s)	number of protons	splitting pattern
1.0			
2.3			
3.7			singlet

[4]

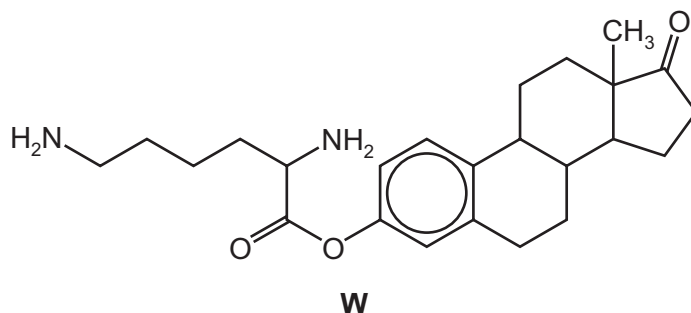
(iii) Use your conclusions to suggest a structure for the ester **Y**.

[1]

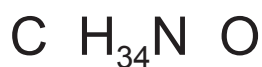
[Total: 11]

- 9 Prodrugs are compounds that are inactive, but are easily converted in the body to the active drug by enzyme hydrolysis.

Compound **W** is a prodrug.



- (a) Complete the molecular formula for **W**.



[1]

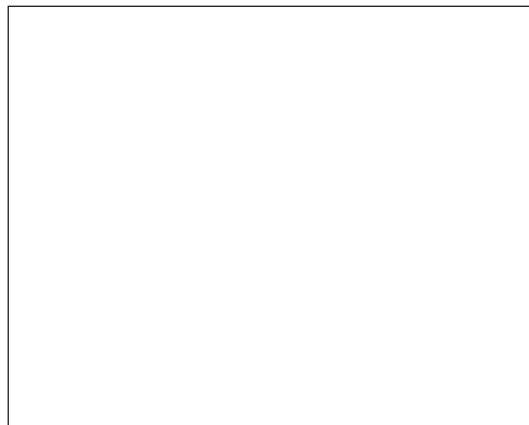
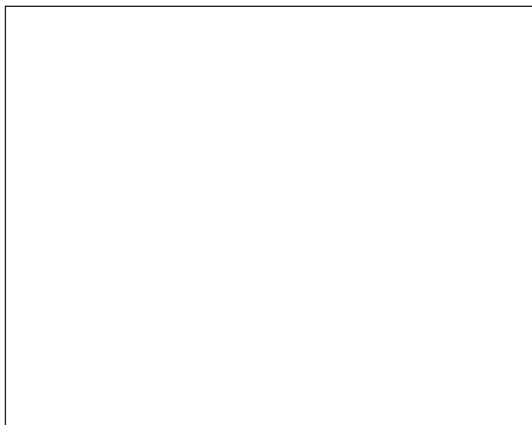
- (b) Compound **W** contains a benzene ring in its structure.

Name **three** other functional groups in **W**.

..... [2]

- (c) (i) On the diagram above, use an arrow to indicate the bond that would be hydrolysed. [1]

(ii) Draw the structures of the likely products of the enzyme hydrolysis of compound **W**.



[2]

- (d) What features of the molecule **W** make it water soluble? Explain your answer.

.....

 [2]

[Total: 8]