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NUMBER

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CHEMISTRY

9701/41

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	
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10	
Total	

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

Section A

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

- 1 (a) Calcium has atomic number 20.

Complete the electronic structures for a

calcium atom, $1s^2 2s^2 2p^6$

calcium ion in the +2 oxidation state. $1s^2 2s^2 2p^6$

[1]

- (b) Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, is used in fertilisers and can be prepared by an acid-base reaction.

Write an equation for the preparation of calcium nitrate by an acid-base reaction.

..... [1]

- (c) (i) When anhydrous calcium nitrate is heated strongly, it decomposes to leave a white solid.

Identify this white solid and suggest **another** observation for this reaction.

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- (ii) The ease of thermal decomposition of the Group II nitrates **decreases** down the group.

Explain this trend.

.....

.....

..... [2]

- (d) (i) What is meant by the term *standard enthalpy change of hydration*, $\Delta H_{\text{hyd}}^{\ominus}$?

.....

 [2]

- (ii) Use the following data to calculate the lattice energy, $\Delta H_{\text{latt}}^{\ominus}$, of calcium nitrate, $\text{Ca}(\text{NO}_3)_2(\text{s})$. You may find it helpful to construct an energy cycle.

enthalpy change	value
$\Delta H_{\text{hyd}}^{\ominus} (\text{Ca}^{2+}(\text{g}))$	$-1650 \text{ kJ mol}^{-1}$
$\Delta H_{\text{hyd}}^{\ominus} (\text{NO}_3^{-}(\text{g}))$	-314 kJ mol^{-1}
enthalpy change of solution for $\text{Ca}(\text{NO}_3)_2(\text{s})$	-19 kJ mol^{-1}

$$\Delta H_{\text{latt}}^{\ominus} \text{Ca}(\text{NO}_3)_2(\text{s}) = \dots\dots\dots \text{kJ mol}^{-1} \quad [3]$$

- (e) The standard enthalpy change of hydration for Ba^{2+} , $\Delta H_{\text{hyd}}^{\ominus} (\text{Ba}^{2+}(\text{g}))$, is $-1305 \text{ kJ mol}^{-1}$.

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

.....

 [2]

[Total: 12]

- 2 (a) Complete the table to show the number of **unpaired** electrons in the outer shell of each of the gaseous atoms, Na to Ar.

	Na	Mg	Al	Si	P	S	Cl	Ar
number of unpaired electrons								

[3]

- (b) (i) Complete the table for the reactions of two Period 3 chlorides with water.

Period 3 chloride	observations	pH of solution formed
SiCl_4		
PCl_5		

[3]

- (ii) Write an equation for the reaction between SiCl_4 and H_2O .

..... [1]

[Total: 7]

3 The transition element iron is the most abundant element in the Earth's core.

(a) What is meant by the term *transition element*?

.....
 [1]

(b) In aqueous solution, iron can form complex ions which contain ligands.

(i) Name the *type of bonding* that occurs between a ligand and a transition element.

..... [1]

(ii) Which of the following species can act as a ligand?

Complete the table by placing a tick (✓) in the appropriate column to indicate whether the species can act as a ligand or not.

species	can act as a ligand	cannot act as a ligand
NO_3^-		
BF_3		
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$		
NH_4^+		

[2]

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

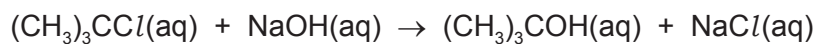
Use this information and the *Data Booklet* to suggest the formula of the manganese species formed in each of the following reactions. State the *type of reaction* taking place in each case.

	formula of manganese species formed	type of reaction
$\text{Mn}^{2+}(\text{aq}) + \text{NaOH}(\text{aq})$		
$\text{Mn}^{2+}(\text{aq}) + \text{concentrated HCl}$		
$\text{Mn}^{2+}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq})$		

[5]

[Total: 9]

- 4 In aqueous solution, 2-chloro-2-methylpropane, $(\text{CH}_3)_3\text{CCl}$, reacts with sodium hydroxide, NaOH . This is a nucleophilic substitution reaction.

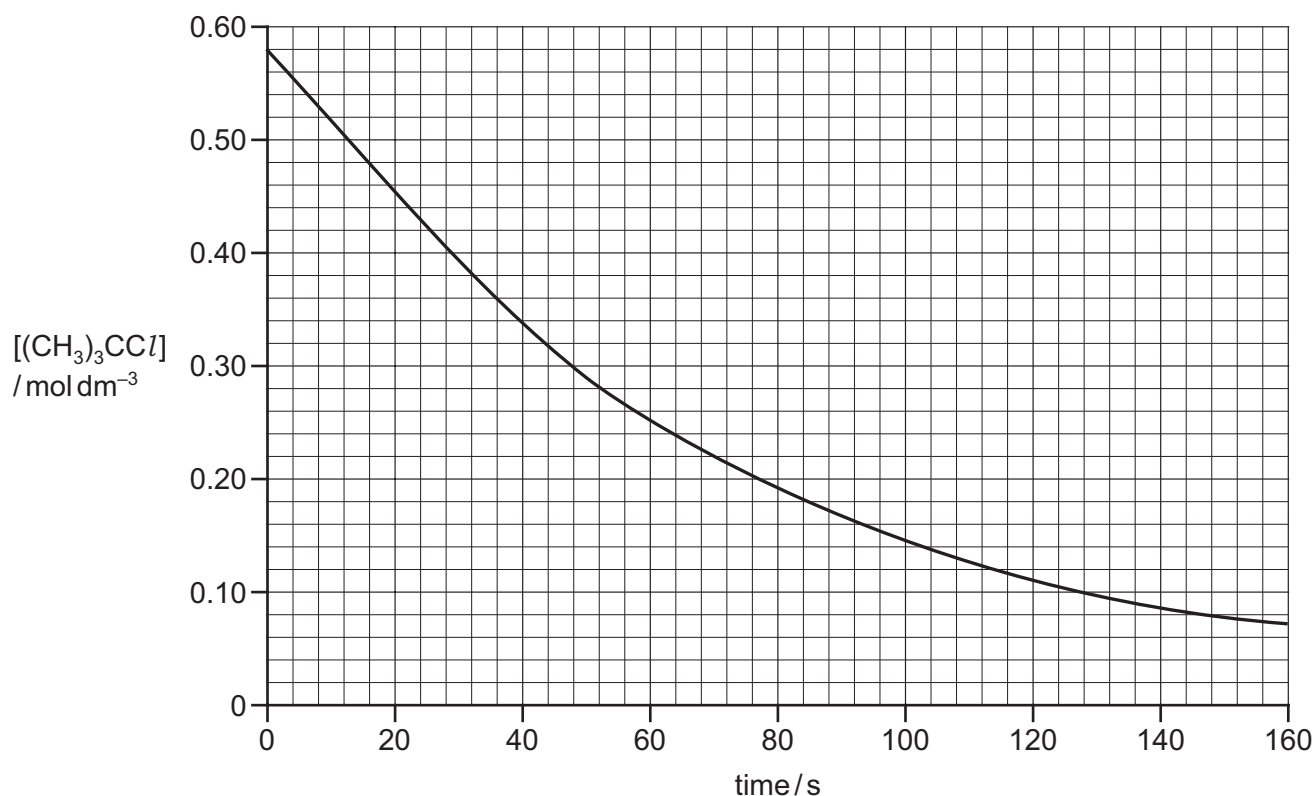


- (a) Show the mechanism for this reaction. Include all necessary curly arrows, lone pairs and relevant dipoles.

[3]

The rate of this reaction was investigated using a **large excess** of sodium hydroxide.

- (b) The graph below shows the results of the experiment.



The reaction is first order with respect to $[(\text{CH}_3)_3\text{CCl}]$. This can be confirmed from the graph using half-lives.

- (i) What is meant by the *half-life* of a reaction?

.....
 [1]

- (ii) Calculate the half-life for this reaction. Show all your working and show clearly any construction lines on the graph.

[1]

- (iii) What would be the effect on the half-life of this reaction if the initial concentration of $[(\text{CH}_3)_3\text{CCl}]$ was **doubled**?

..... [1]

- (c) (i) Use the graph in (b) to determine the rate of reaction at 80 s.
 Show all your working.

rate = ... units [2]

The rate equation for this reaction is shown.

$$\text{rate} = k[(\text{CH}_3)_3\text{CCl}]$$

- (ii) Calculate the value of the rate constant, k , for this reaction and give its units.

k = ... units [1]

[Total: 9]

5 X is a metallic element.

- (a) (i) Draw a fully labelled diagram to show how the standard electrode potential, $E^\ominus$, of $X^{2+}(aq)/X(s)$ could be measured.

[4]

- (ii) What are the conditions needed for the value measured to be a **standard** electrode potential?

..... [1]

- (iii) State the charge carriers that transfer current through

the solutions, ... the wire. [1]

(b) An electrochemical cell was set up consisting of an $\text{X}^{2+}(\text{aq})/\text{X}(\text{s})$ half-cell ($E^\ominus = -0.40\text{ V}$) and an $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ half-cell ($E^\ominus = +0.80\text{ V}$).

- (i) Write an equation for the reaction that would take place if the electrodes of this cell were connected by a wire.

..... [1]

When the current was allowed to pass for a period of time,

- the Ag electrode gained 1.30 g in mass,
- the electrode made of metal **X** lost 0.67 g in mass.

- (ii) Calculate the A_r of metal **X**; hence suggest an identity for **X**.
Show all your working. Use of the *Data Booklet* is relevant to this question.

$A_r =$

X is [4]

[Total: 11]

6 Boron forms many useful compounds.

- (a) The compound diborane, B_2H_6 , can be used as a rocket fuel.
It can be prepared by the reaction of boron trifluoride, BF_3 , with sodium borohydride, $NaBH_4$.

Balance this equation.



[1]

- (b) Primary and secondary alcohols can be formed by the reaction of carbonyl compounds with $NaBH_4$, which is a source of hydride ions, H^- .

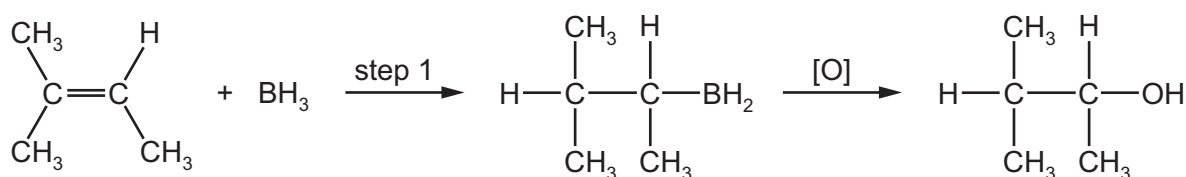
Complete the mechanism for the reaction of butanone with hydride ions, H^- , and draw the intermediate in the box. Include all necessary curly arrows and relevant dipoles.



[3]

- (c) Borane, BH_3 , is used to synthesise alcohols from alkenes.
The reaction occurs in two steps.

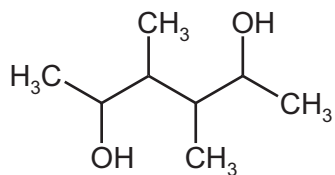
The BH_2 group from BH_3 bonds to the **least** substituted carbon atom of the double bond, and the remaining H from BH_3 bonds to the other carbon.



- (i) Suggest the *type of reaction* in step 1.

..... [1]

- (ii) The diol **Y** can be prepared by the same method.



Y

Draw the structure of the **diene** which could be used to prepare diol **Y**.

[1]

- (d) Benzene, C_6H_6 , and borazine, $B_3N_3H_6$, have planar, cyclic structures.

- (i) Describe the structure of and bonding in benzene, C_6H_6 .

.....

.....

.....

.....

.....

.....

..... [3]

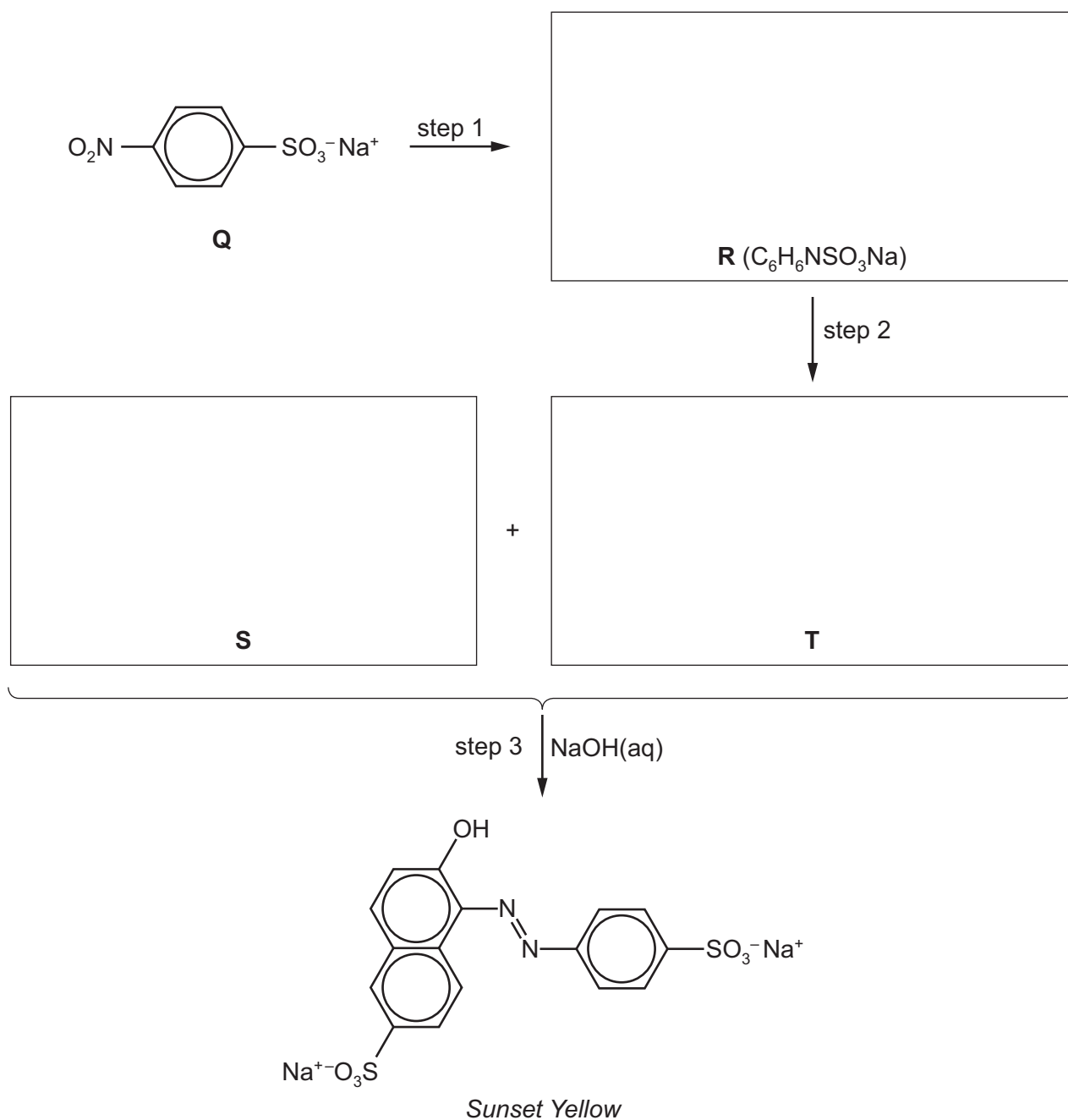
- (ii) In borazine, $B_3N_3H_6$, the boron and nitrogen atoms alternate around the ring. Each ring atom has a single hydrogen atom bonded to it.
All boron-nitrogen bonds in borazine are 0.144 nm in length, whereas in simple compounds B–N and B=N bond lengths are 0.154 nm and 0.136 nm respectively.

Suggest and draw the structure of borazine.

[1]

[Total: 10]

- 7 (a) *Sunset Yellow* is a yellow colouring agent used in food and drinks, which can be made by the following route.
 In step 3 of this synthesis, a phenol-like compound, **S**, reacts with intermediate **T** made from amine **R**.
 Assume that the $\text{SO}_3^- \text{Na}^+$ group does not react.



(i) Suggest structures for compounds **R**, **S** and **T** and draw them in the boxes above. [3]

(ii) Suggest reagents and conditions for

step 1, ...

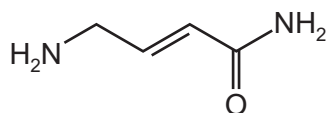
step 2.

[3]

(iii) What type of organic salt is formed in step 2?

..... [1]

(b) Compound **W** has the following structure.



(i) How many σ and π bonds are present in a molecule of **W**?

σ bonds π bonds [2]

(ii) The products of the reactions of **W** with cold HCl and with $\text{CH}_3\text{CH}_2\text{Br}$ are soluble in water but **not** in organic solvents.

Complete the table for these reactions of **W**.

reagent	structure of product (molecular formula given)	type of reaction
HCl	$(\text{C}_4\text{H}_9\text{N}_2\text{OCl})$	
$\text{CH}_3\text{CH}_2\text{Br}$	$(\text{C}_6\text{H}_{13}\text{N}_2\text{BrO})$	

[3]

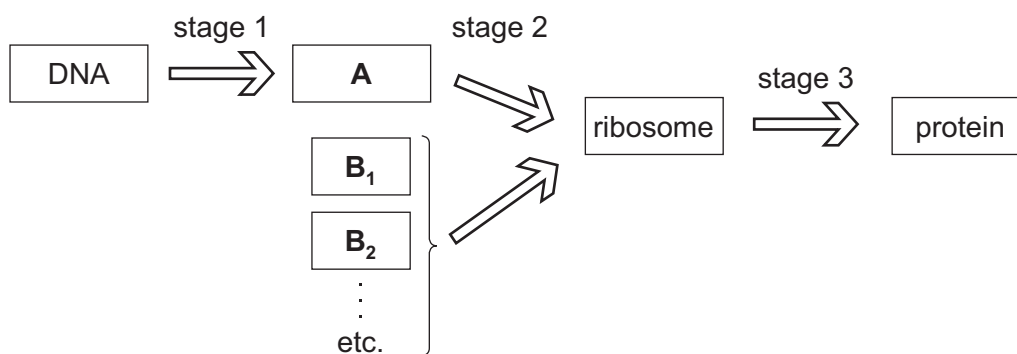
[Total: 12]

Section B

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

- 8 (a) The sequence of bases in DNA is a code for the order of amino acids in the primary structure of proteins.

The diagram represents the stages involved in the formation of a protein from DNA.



- (i) Identify the biochemical structures, **A** and **B₁**, **B₂** etc.

biochemical structure	identity
A	
B₁ , B₂ etc.	

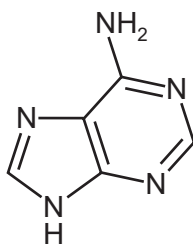
[2]

- (ii) Name the biochemical processes involved in stages 1 and 3.

process	name of biochemical process
stage 1	
stage 3	

[1]

(b) Adenine is an integral part of DNA.



adenine

(i) State the molecular formula of adenine.

..... [1]

(ii) Identify the three **other** nitrogenous bases in DNA.

..... [1]

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

What type of bonding exists between the

phosphate and sugar groups within a DNA strand, ...

different bases on the two strands?

[2]

(c) The breakdown of adenosine triphosphate, ATP, provides the energy for many cellular reactions.



What *type of chemical reaction* is this?

..... [1]

(d) X-ray crystallography can be useful in obtaining information about the structures of large organic molecules, such as ATP. The technique involves X-rays interacting with the electrons within the molecule.

(i) Which element in the molecule of ATP will interact most strongly with the X-ray beam?

..... [1]

(ii) Explain why X-ray crystallography will **not** detect hydrogen atoms.

.....

..... [1]

[Total: 10]

- 9 (a) Some metals are essential to biochemical processes.

Complete the following table naming one metal in each case.

biochemical process	metal
haemoglobin in oxygen transport	
transmission of nerve impulses	
enzyme cofactor	

[2]

- (b) Enzymes are a special type of protein molecule that catalyse biochemical reactions.

Explain briefly the mechanism by which an enzyme breaks down a substrate molecule.

.....

.....

.....

.....

..... [3]

- (c) Disulfide bonds play an important role in the stability of some proteins such as the keratin in human hair.

The amino acid involved in the formation of a disulfide bond is cysteine, $\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{CO}_2\text{H}$.

- (i) At which level of protein structure (primary, secondary, tertiary) are disulfide bonds formed?

..... [1]

- (ii) Use a functional group in cysteine to show how disulfide bonds are formed.

[1]

- (iii) What type of chemical reaction is this?

..... [1]

(d) The NMR spectrum of cysteine, $\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{CO}_2\text{H}$, shows five absorptions.

After shaking a solution of cysteine with a few drops of D_2O , the NMR spectrum shows **only two** absorptions, **E** and **F**, shown below.



(i) Identify the **two** types of protons responsible for the absorptions **E** and **F**.

E

F

[1]

(ii) State and explain the splitting patterns of the absorptions **E** and **F**.

E

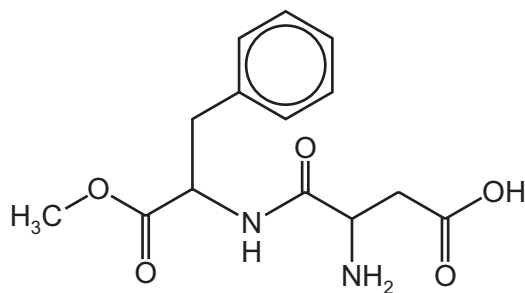
.....

F

..... [2]

[Total: 11]

10 (a) Aspartame is an artificial sweetener that has the structure shown below.

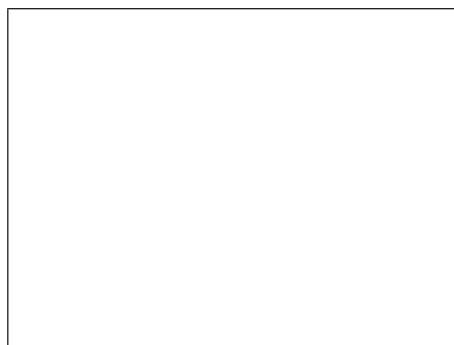
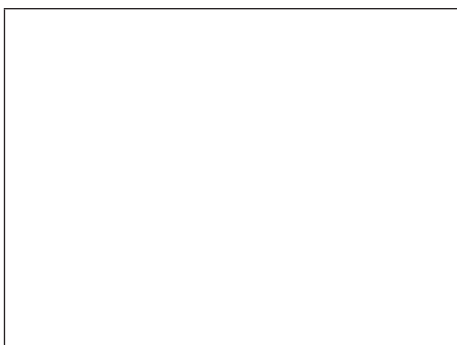


aspartame

- (i) Draw a circle around each chiral centre in aspartame. [1]

In the stomach, aspartame is hydrolysed by acid to form three organic products.

- (ii) On the diagram above, use arrows to indicate the **two** bonds that would be hydrolysed in the stomach. [2]
- (iii) Draw the structures of the **three** products formed after complete acid hydrolysis of aspartame.



[3]

- (b) Aspartame is soluble in water.

By referring to the structure of aspartame, explain why it is soluble in water.

.....

.....

..... [2]

- (c) Recently, nanotechnology has been involved in the development of a new natural sweetener, *Nano Sugar*, extracted from sugar cane.

What is the approximate width of a nanoparticle?

..... [1]

[Total: 9]

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- (b) Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, is used in fertilisers and can be prepared by an acid-base reaction.

Write an equation for the preparation of calcium nitrate by an acid-base reaction.

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- (c) (i) When anhydrous calcium nitrate is heated strongly, it decomposes to leave a white solid.

Identify this white solid and suggest **another** observation for this reaction.

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- (ii) The ease of thermal decomposition of the Group II nitrates **decreases** down the group.

Explain this trend.

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.....

..... [2]

- (d) (i) What is meant by the term *standard enthalpy change of hydration*, $\Delta H_{\text{hyd}}^{\ominus}$?

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- (ii) Use the following data to calculate the lattice energy, $\Delta H_{\text{latt}}^{\ominus}$, of calcium nitrate, $\text{Ca}(\text{NO}_3)_2(\text{s})$. You may find it helpful to construct an energy cycle.

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- (e) The standard enthalpy change of hydration for Ba^{2+} , $\Delta H_{\text{hyd}}^{\ominus} (\text{Ba}^{2+}(\text{g}))$, is $-1305 \text{ kJ mol}^{-1}$.

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

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 [2]

[Total: 12]

- 2 (a) Complete the table to show the number of **unpaired** electrons in the outer shell of each of the gaseous atoms, Na to Ar.

	Na	Mg	Al	Si	P	S	Cl	Ar
number of unpaired electrons								

[3]

- (b) (i) Complete the table for the reactions of two Period 3 chlorides with water.

Period 3 chloride	observations	pH of solution formed
SiCl_4		
PCl_5		

[3]

- (ii) Write an equation for the reaction between SiCl_4 and H_2O .

..... [1]

[Total: 7]

3 The transition element iron is the most abundant element in the Earth's core.

(a) What is meant by the term *transition element*?

.....
 [1]

(b) In aqueous solution, iron can form complex ions which contain ligands.

(i) Name the *type of bonding* that occurs between a ligand and a transition element.

..... [1]

(ii) Which of the following species can act as a ligand?

Complete the table by placing a tick (✓) in the appropriate column to indicate whether the species can act as a ligand or not.

species	can act as a ligand	cannot act as a ligand
NO_3^-		
BF_3		
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$		
NH_4^+		

[2]

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

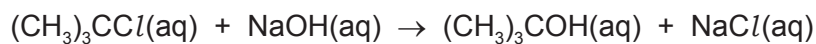
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$\text{Mn}^{2+}(\text{aq}) + \text{concentrated HCl}$		
$\text{Mn}^{2+}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq})$		

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[Total: 9]

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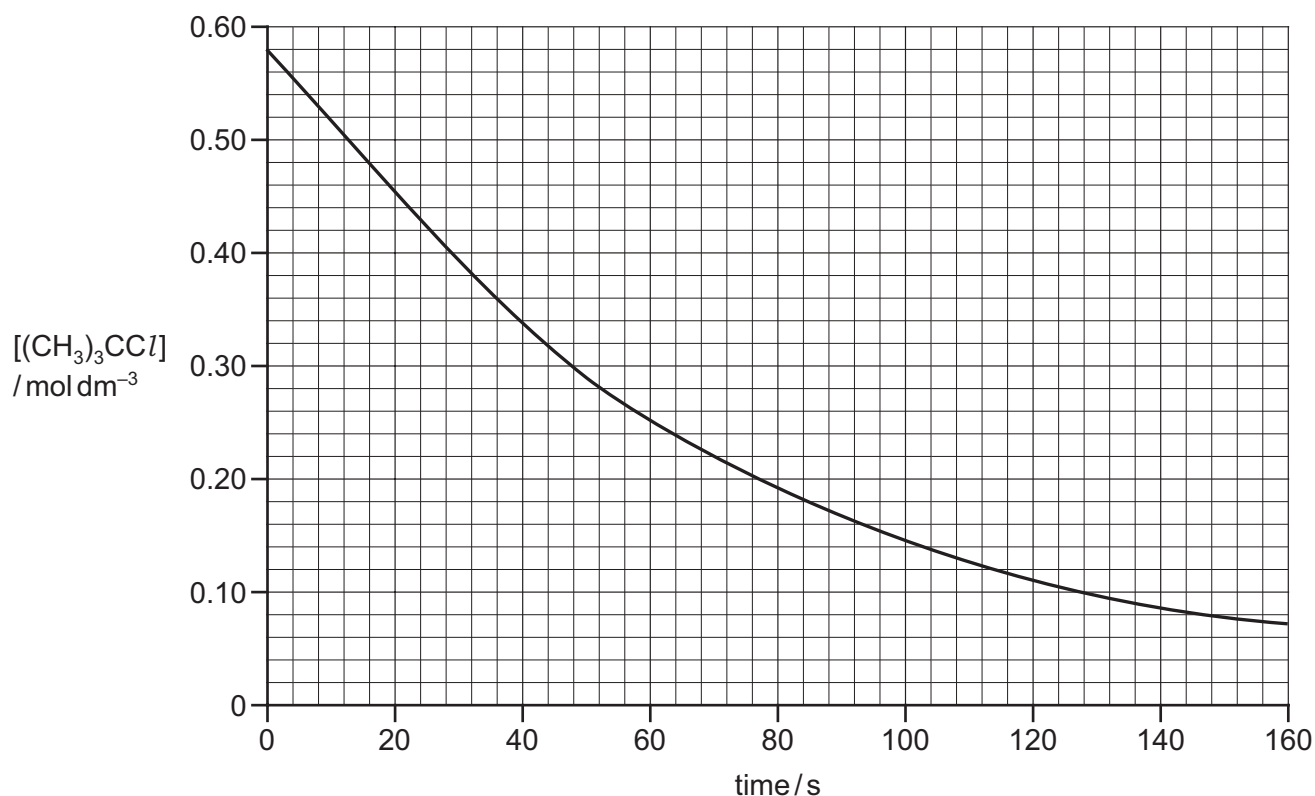


- (a) Show the mechanism for this reaction. Include all necessary curly arrows, lone pairs and relevant dipoles.

[3]

The rate of this reaction was investigated using a **large excess** of sodium hydroxide.

- (b) The graph below shows the results of the experiment.



The reaction is first order with respect to $[(\text{CH}_3)_3\text{CCl}]$. This can be confirmed from the graph using half-lives.

- (i) What is meant by the *half-life* of a reaction?

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 [1]

- (ii) Calculate the half-life for this reaction. Show all your working and show clearly any construction lines on the graph.

[1]

- (iii) What would be the effect on the half-life of this reaction if the initial concentration of $[(\text{CH}_3)_3\text{CCl}]$ was **doubled**?

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- (c) (i) Use the graph in (b) to determine the rate of reaction at 80 s.
 Show all your working.

rate = ... units [2]

The rate equation for this reaction is shown.



- (ii) Calculate the value of the rate constant, k , for this reaction and give its units.

k = ... units [1]

[Total: 9]

5 X is a metallic element.

- (a) (i) Draw a fully labelled diagram to show how the standard electrode potential, $E^\ominus$, of $X^{2+}(aq)/X(s)$ could be measured.

[4]

- (ii) What are the conditions needed for the value measured to be a **standard** electrode potential?

..... [1]

- (iii) State the charge carriers that transfer current through

the solutions, ... the wire. [1]

(b) An electrochemical cell was set up consisting of an $\text{X}^{2+}(\text{aq})/\text{X}(\text{s})$ half-cell ($E^\ominus = -0.40\text{ V}$) and an $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ half-cell ($E^\ominus = +0.80\text{ V}$).

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When the current was allowed to pass for a period of time,

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- (ii) Calculate the A_r of metal **X**; hence suggest an identity for **X**.
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$A_r =$

X is [4]

[Total: 11]

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[1]

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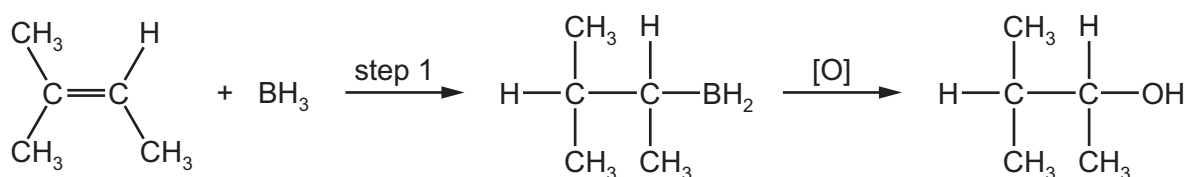
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[3]

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The reaction occurs in two steps.

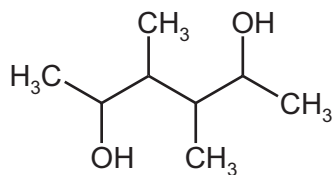
The BH_2 group from BH_3 bonds to the **least** substituted carbon atom of the double bond, and the remaining H from BH_3 bonds to the other carbon.



- (i) Suggest the *type of reaction* in step 1.

..... [1]

- (ii) The diol **Y** can be prepared by the same method.



Y

Draw the structure of the **diene** which could be used to prepare diol **Y**.

[1]

- (d) Benzene, C_6H_6 , and borazine, $B_3N_3H_6$, have planar, cyclic structures.

- (i) Describe the structure of and bonding in benzene, C_6H_6 .

.....

.....

.....

.....

.....

.....

..... [3]

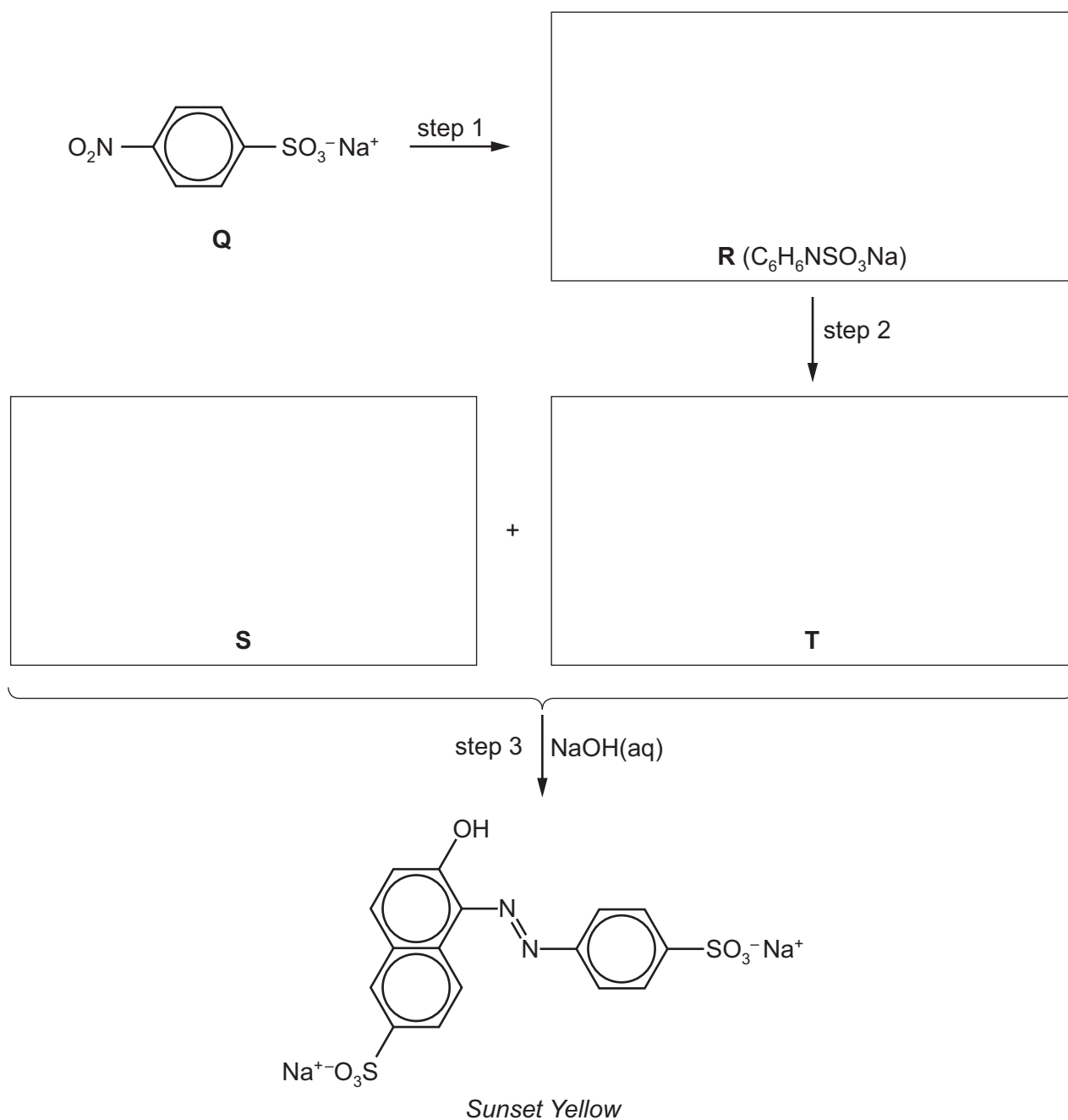
- (ii) In borazine, $B_3N_3H_6$, the boron and nitrogen atoms alternate around the ring. Each ring atom has a single hydrogen atom bonded to it.
All boron-nitrogen bonds in borazine are 0.144 nm in length, whereas in simple compounds B–N and B=N bond lengths are 0.154 nm and 0.136 nm respectively.

Suggest and draw the structure of borazine.

[1]

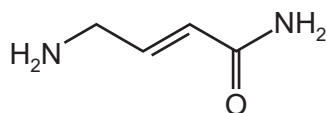
[Total: 10]

- 7 (a) *Sunset Yellow* is a yellow colouring agent used in food and drinks, which can be made by the following route.
 In step 3 of this synthesis, a phenol-like compound, **S**, reacts with intermediate **T** made from amine **R**.
 Assume that the $\text{SO}_3^- \text{Na}^+$ group does not react.



- (i) Suggest structures for compounds **R**, **S** and **T** and draw them in the boxes above. [3]
- (ii) Suggest reagents and conditions for
 step 1, ...
 step 2. [3]
- (iii) What type of organic salt is formed in step 2?
 [1]

(b) Compound **W** has the following structure.



(i) How many σ and π bonds are present in a molecule of **W**?

σ bonds π bonds [2]

(ii) The products of the reactions of **W** with cold HCl and with $\text{CH}_3\text{CH}_2\text{Br}$ are soluble in water but **not** in organic solvents.

Complete the table for these reactions of **W**.

reagent	structure of product (molecular formula given)	type of reaction
HCl	$(\text{C}_4\text{H}_9\text{N}_2\text{OCl})$	
$\text{CH}_3\text{CH}_2\text{Br}$	$(\text{C}_6\text{H}_{13}\text{N}_2\text{BrO})$	

[3]

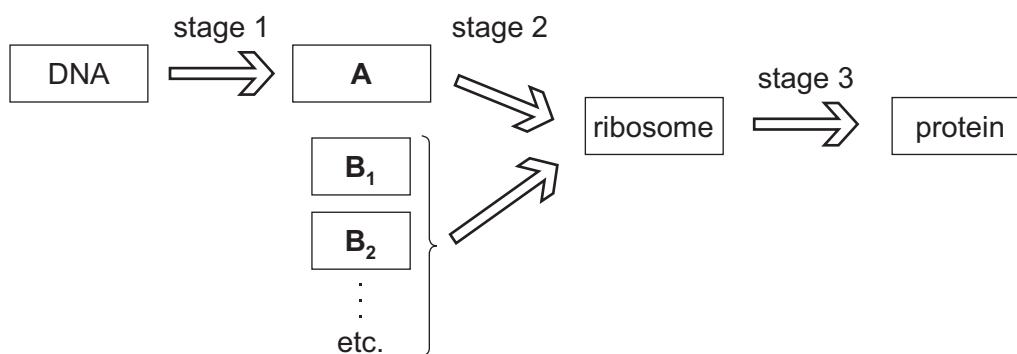
[Total: 12]

Section B

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

- 8 (a) The sequence of bases in DNA is a code for the order of amino acids in the primary structure of proteins.

The diagram represents the stages involved in the formation of a protein from DNA.



- (i) Identify the biochemical structures, **A** and **B₁**, **B₂** etc.

biochemical structure	identity
A	
B₁ , B₂ etc.	

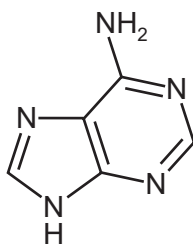
[2]

- (ii) Name the biochemical processes involved in stages 1 and 3.

process	name of biochemical process
stage 1	
stage 3	

[1]

(b) Adenine is an integral part of DNA.



adenine

(i) State the molecular formula of adenine.

..... [1]

(ii) Identify the three **other** nitrogenous bases in DNA.

..... [1]

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

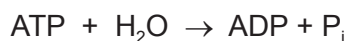
What type of bonding exists between the

phosphate and sugar groups within a DNA strand, ...

different bases on the two strands?

[2]

(c) The breakdown of adenosine triphosphate, ATP, provides the energy for many cellular reactions.



What *type of chemical reaction* is this?

..... [1]

(d) X-ray crystallography can be useful in obtaining information about the structures of large organic molecules, such as ATP. The technique involves X-rays interacting with the electrons within the molecule.

(i) Which element in the molecule of ATP will interact most strongly with the X-ray beam?

..... [1]

(ii) Explain why X-ray crystallography will **not** detect hydrogen atoms.

.....

..... [1]

[Total: 10]

- 9 (a) Some metals are essential to biochemical processes.

Complete the following table naming one metal in each case.

biochemical process	metal
haemoglobin in oxygen transport	
transmission of nerve impulses	
enzyme cofactor	

[2]

- (b) Enzymes are a special type of protein molecule that catalyse biochemical reactions.

Explain briefly the mechanism by which an enzyme breaks down a substrate molecule.

.....

.....

.....

.....

..... [3]

- (c) Disulfide bonds play an important role in the stability of some proteins such as the keratin in human hair.

The amino acid involved in the formation of a disulfide bond is cysteine, $\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{CO}_2\text{H}$.

- (i) At which level of protein structure (primary, secondary, tertiary) are disulfide bonds formed?

..... [1]

- (ii) Use a functional group in cysteine to show how disulfide bonds are formed.

[1]

- (iii) What *type of chemical reaction* is this?

..... [1]

(d) The NMR spectrum of cysteine, $\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{CO}_2\text{H}$, shows five absorptions.

After shaking a solution of cysteine with a few drops of D_2O , the NMR spectrum shows **only two** absorptions, **E** and **F**, shown below.



(i) Identify the **two** types of protons responsible for the absorptions **E** and **F**.

E

F

[1]

(ii) State and explain the splitting patterns of the absorptions **E** and **F**.

E

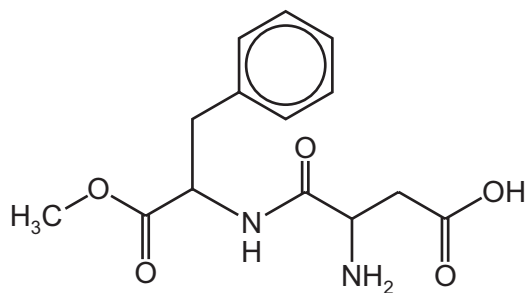
.....

F

..... [2]

[Total: 11]

10 (a) Aspartame is an artificial sweetener that has the structure shown below.

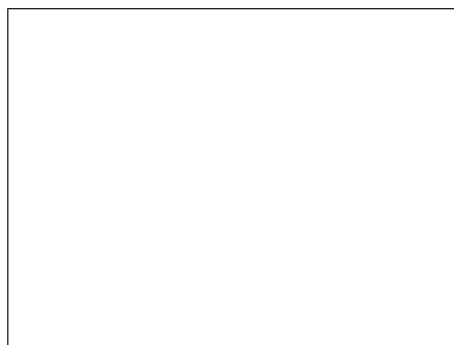
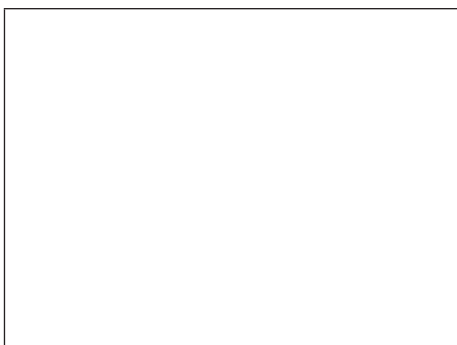


aspartame

- (i) Draw a circle around each chiral centre in aspartame. [1]

In the stomach, aspartame is hydrolysed by acid to form three organic products.

- (ii) On the diagram above, use arrows to indicate the **two** bonds that would be hydrolysed in the stomach. [2]
- (iii) Draw the structures of the **three** products formed after complete acid hydrolysis of aspartame.



[3]

- (b) Aspartame is soluble in water.

By referring to the structure of aspartame, explain why it is soluble in water.

.....

.....

..... [2]

- (c) Recently, nanotechnology has been involved in the development of a new natural sweetener, *Nano Sugar*, extracted from sugar cane.

What is the approximate width of a nanoparticle?

..... [1]

[Total: 9]

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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**.

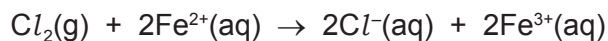
[1]

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

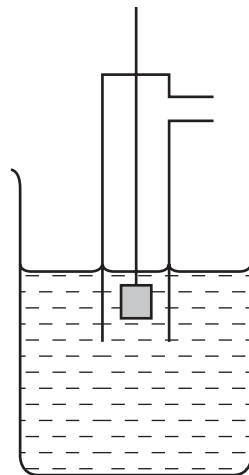
[1]

[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, $E_{\text{cell}}^{\ominus}$, for the above reaction could be measured at standard conditions.



[4]

- (ii) Use the *Data Booklet* to calculate the $E_{\text{cell}}^{\ominus}$ 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.

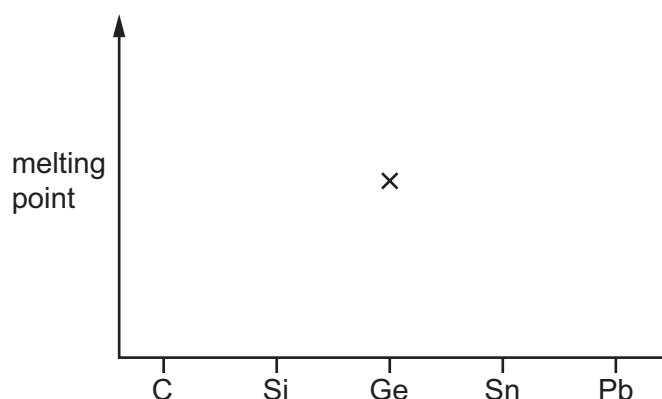
..... [1]

- (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 .

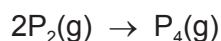
[1]

- (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.

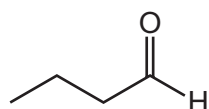
Suggest a structure for $P_3N_3Cl_6$.

[1]

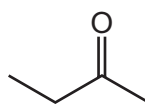
[Total: 15]

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]

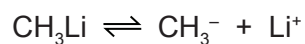
- (iii) What is observed when **N** reacts with butanone?

..... [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.

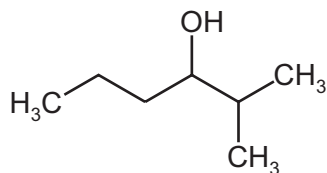
The reaction between methyl lithium and carbonyl compounds can be used to make alcohols.

- (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.

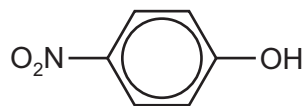
**G**

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:

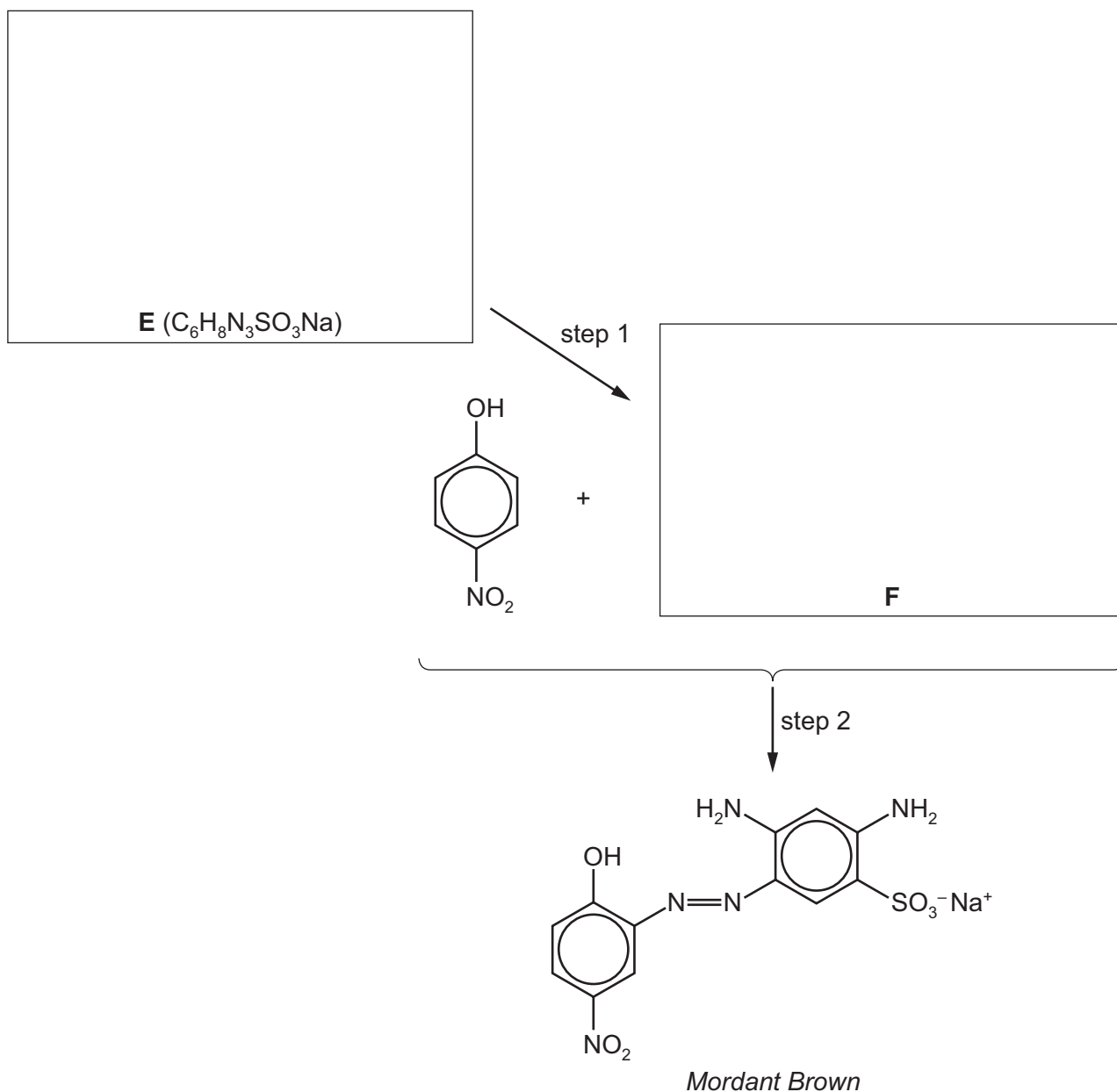
- drawing the structures of the organic products formed,
- identifying the non-organic products formed.

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]

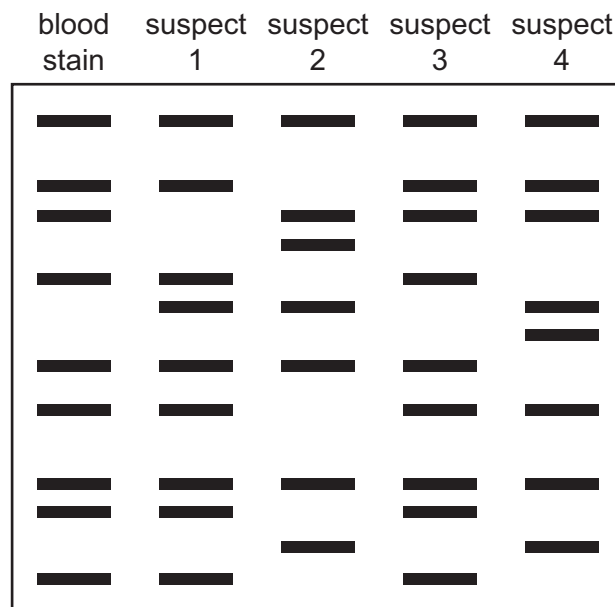
- (ii) Name the analytical technique used to separate these short fragments.

..... [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.



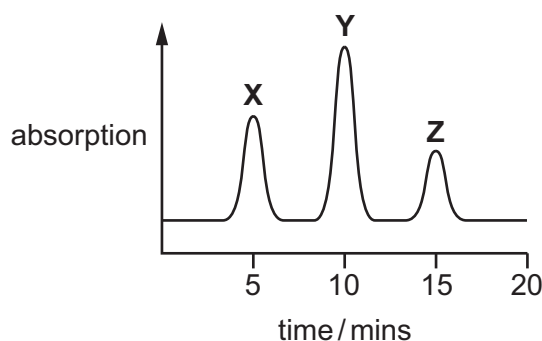
Based on this evidence, **circle** the suspect who should be arrested.

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]

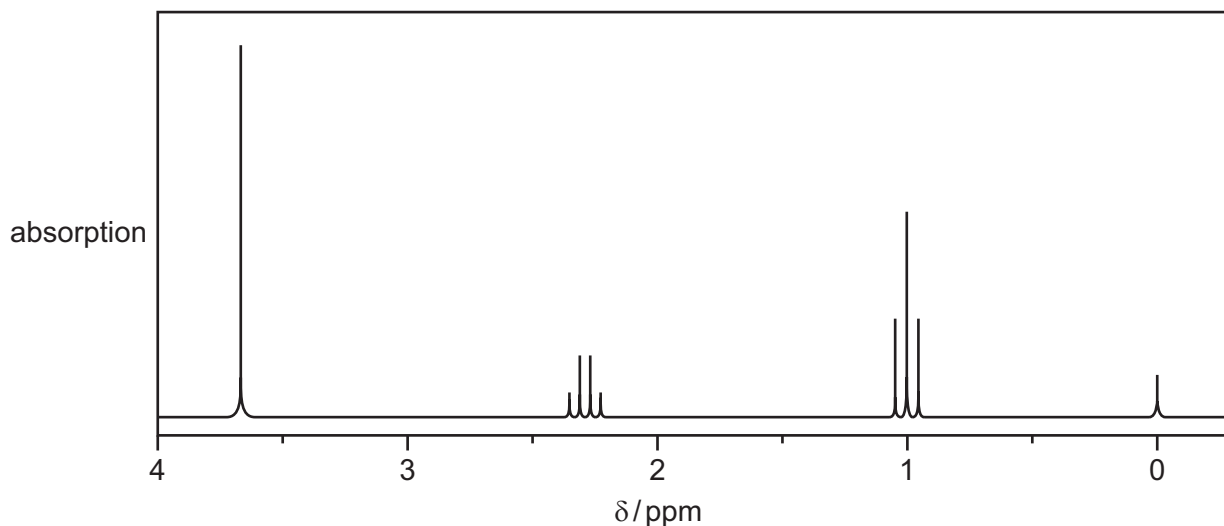
- (v) A student works out the areas underneath the three peaks in the chromatogram.

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]

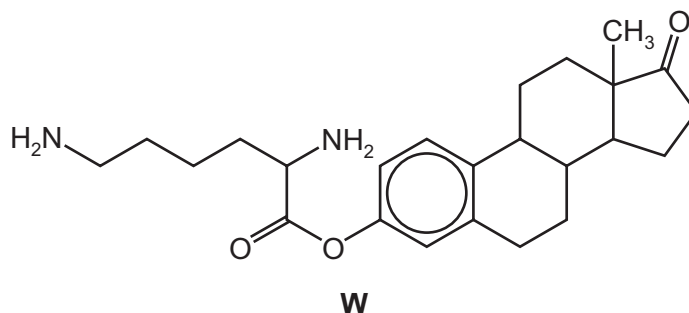
(iii) Use your conclusions to suggest a structure for the ester **Y**.

[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]

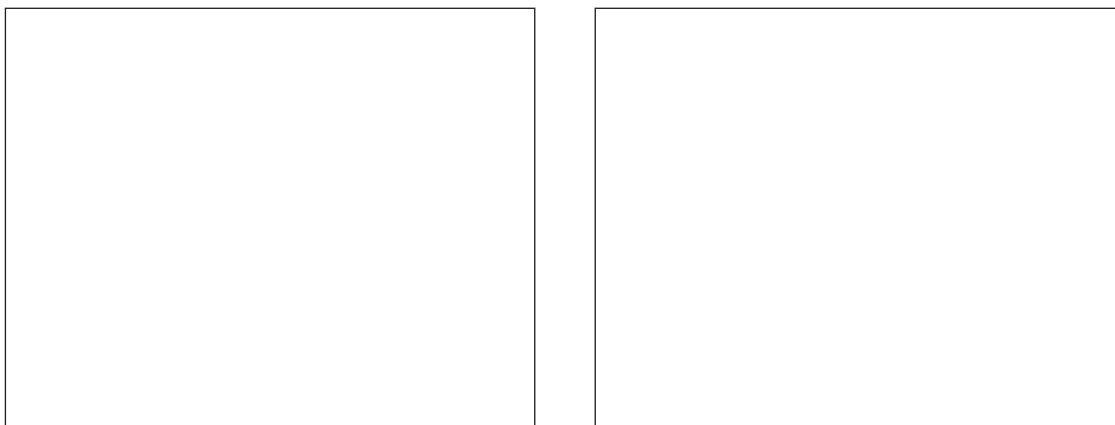
- (b) Compound **W** contains a benzene ring in its structure.

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]