

CANDIDATE
NAME

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CENTRE
NUMBER

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CANDIDATE
NUMBER

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CHEMISTRY

9701/41

Paper 4 Structured Questions

October/November 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.

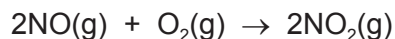
For Examiner's Use	
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Total	

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

Section A

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

- 1 (a) The oxidation of nitrogen(II) oxide is shown in the equation.



The initial rate of this reaction was measured, starting with different concentrations of the two reactants. The following results were obtained.

experiment number	[NO] / mol dm ⁻³	[O ₂] / mol dm ⁻³	initial rate / mol dm ⁻³ s ⁻¹
1	0.032	0.012	4.08×10^{-3}
2	0.032	0.024	8.15×10^{-3}
3	0.064	0.024	3.28×10^{-2}
4	0.096	0.036	

- (i) Use the data in the table to determine the order with respect to each reactant. Show your reasoning.

.....

.....

.....

.....

- (ii) Calculate the initial rate in experiment 4. Give your answer to **two** significant figures.

initial rate = ... mol dm⁻³ s⁻¹

- (iii) Write the rate equation for this reaction.

.....

- (iv) Use the results of experiment 1 to calculate the rate constant, k , for this reaction. Include the units of k .

rate constant, k = ... units

[6]

(b) (i) On the following axes

- draw two Boltzmann distribution curves, at two different temperatures, T_1 and T_2 ($T_2 > T_1$),
- label the curves and the axes.



(ii) State and explain, using your diagram, the effect of increasing temperature on the rate of reaction.

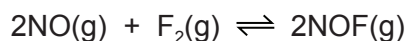
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[5]

(c) The compound nitrosyl fluoride, NOF, can be formed by the following reaction.



The rate is first order with respect to NO and F_2 .
The reaction mechanism has **two** steps.

Suggest equations for the two steps of this mechanism, stating which is the rate determining slower step.

.....

.....

..... [2]

[Total: 13]

- 2 (a) Complete the electron configurations for Ni and Ni^{2+} .

		3d					4s
Ni	[Ar]	↑↓					
Ni ²⁺	[Ar]	↑↓					

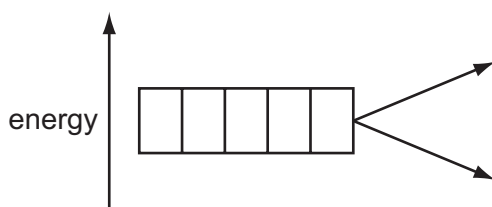
[2]

- (b) The presence of electrons in d orbitals is responsible for the colours of transition element compounds.

- (i) The d orbitals in an isolated transition metal atom or ion are all at the same energy level. What term is used to describe orbitals that are at the same energy level?

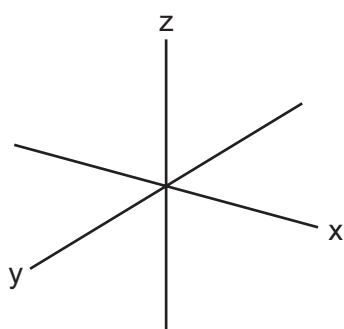
.....

- (ii) Complete the diagram to show the splitting of the d orbital energy levels in an octahedral complex ion.

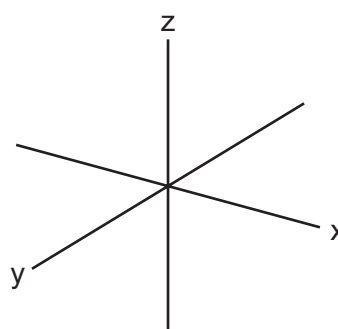


- (iii) On the axes below, sketch the shapes of one d orbital from the lower energy level and one d orbital from the higher energy level.

lower energy level



higher energy level



[4]

- (c) The octahedral complex $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green. Explain the origin of the colour of this complex.

.....

.....

.....

.....

..... [3]

- (d) When $\text{NH}_3(\text{aq})$ is added to the green solution containing $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, a grey-green precipitate, **A**, is formed. This precipitate dissolves in an excess of $\text{NH}_3(\text{aq})$ to give a blue-violet solution, **B**. Suggest formulae for **A** and **B** and write equations for the two reactions producing **A** and **B**.

.....

.....

.....

..... [4]

[Total: 13]

- 3 (a) Natural phosphorus consists of one isotope, ^{31}P . Chlorine exists naturally as two isotopes, ^{35}Cl and ^{37}Cl , in the relative abundance ratio of 3 : 1.

- (i) The mass spectrum of PCl_3 contains several peaks corresponding to a number of molecular fragments.

Suggest the isotopic composition of the fragments with the following mass numbers.

mass number	isotopic composition
101	
103	
105	

- (ii) Predict the relative ratios of the peak heights of the three peaks corresponding to these fragments.

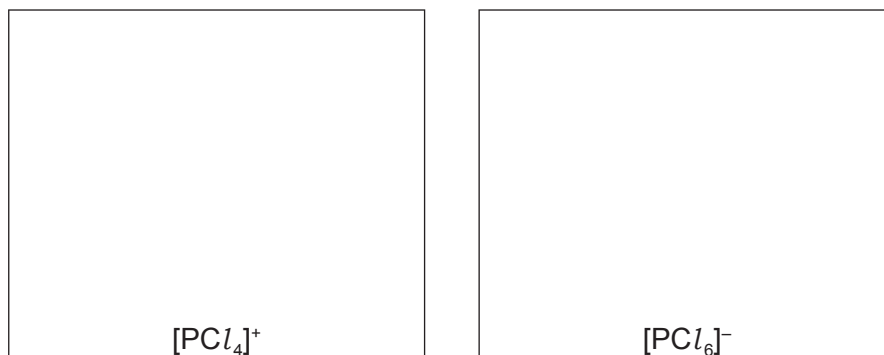
..... [4]

- (b) Phosphorus reacts with chlorine to form a variety of chlorides.
 PCl_5 is an example of a compound that exists as two structures depending on the conditions.



- (i) Draw a 'dot-and-cross' diagram to show the bonding in PCl_5 . Show the outer electrons only.

- (ii) Draw diagrams to suggest the shapes of $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$.



[3]

- (c) (i) Phosphorus(III) oxide, P_4O_6 , contains no P–P or O–O bonds. In the P_4O_6 molecule, all oxygen atoms are divalent and all phosphorus atoms are trivalent.

Sketch a structure for P_4O_6 .

- (ii) P_4O_6 can act as a ligand.

What is meant by the term *ligand*?

.....

[2]

- (d) Phosphate ions in water can be removed by adding a solution containing $\text{Ca}^{2+}(\text{aq})$ ions, which form a precipitate of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$.

- (i) Write an expression for the K_{sp} of $\text{Ca}_3(\text{PO}_4)_2$.

$K_{\text{sp}} =$

- (ii) The solubility of $\text{Ca}_3(\text{PO}_4)_2$ is $2.50 \times 10^{-6} \text{ mol dm}^{-3}$ at 298 K.

Calculate the solubility product, K_{sp} , of $\text{Ca}_3(\text{PO}_4)_2$ at this temperature. Include the units.

$K_{\text{sp}} =$ units

[4]

(e) (i) What is meant by the term *lattice energy*?

.....

.....

(ii) Explain why the lattice energy of calcium phosphate is **less** exothermic than that of magnesium phosphate.

.....

.....

[3]

[Total: 16]

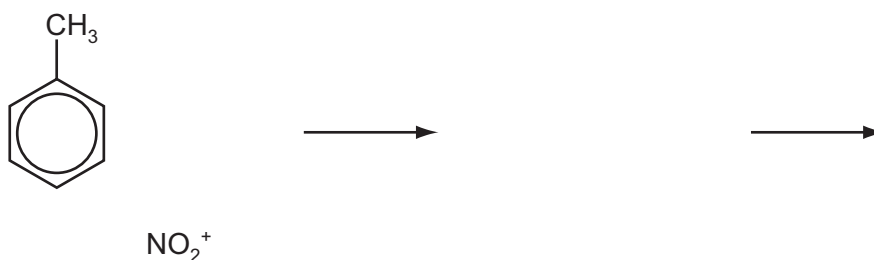
Question 4 starts on the next page.

- 4 (a) Methylbenzene undergoes electrophilic substitution with nitronium ions, NO_2^+ . Nitronium ions are generated by the reaction between concentrated sulfuric acid and concentrated nitric acid.

(i) Construct an equation for the formation of nitronium ions, NO_2^+ , by this method.

.....

(ii) Complete the scheme to show the mechanism for this reaction. Use curly arrows to show the movement of electron pairs.



[4]

(b) (i) Describe and explain the relative acidities of chloroethanoic acid and ethanoic acid.

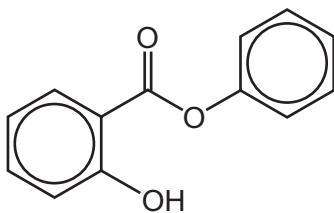
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(ii) Describe and explain the relative acidities of phenol and ethanol.

.....

[3]

(c) Phenyl 2-hydroxybenzoate is an antiseptic.



phenyl 2-hydroxybenzoate

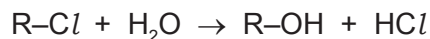
Complete the following table about the reactions of phenyl 2-hydroxybenzoate with the three reagents.

reagent	structure of product(s)		type of reaction
Na			
excess $\text{Br}_2(\text{aq})$			
excess hot $\text{NaOH}(\text{aq})$			

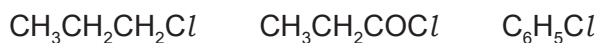
[6]

[Total: 13]

- 5 (a) Organohalogen compounds can undergo hydrolysis.



State the relative rates of hydrolysis of the following compounds.



Explain your answer.

.....

.....

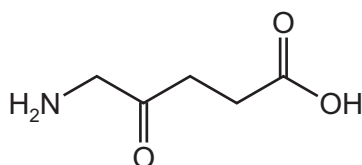
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..... [3]

- (b) Aminolaevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.



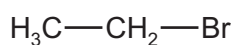
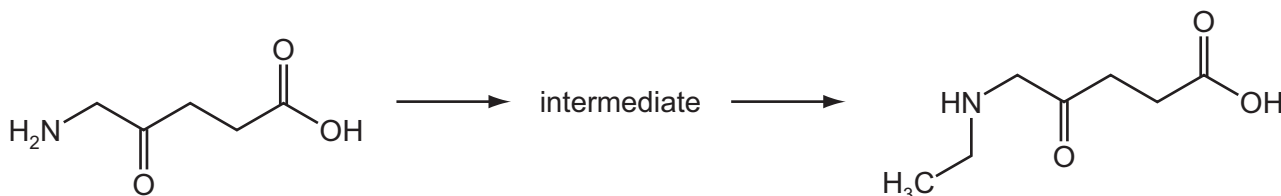
aminolaevulinic acid

Name the **three** functional groups in aminolaevulinic acid.

..... [2]

- (c) Aminolaevulinic acid reacts readily with bromoethane.

- (i) Show the mechanism of the **first step** of this reaction on the diagram. Include all necessary curly arrows, lone pairs and relevant dipoles.



(ii) Name the mechanism in (c)(i).

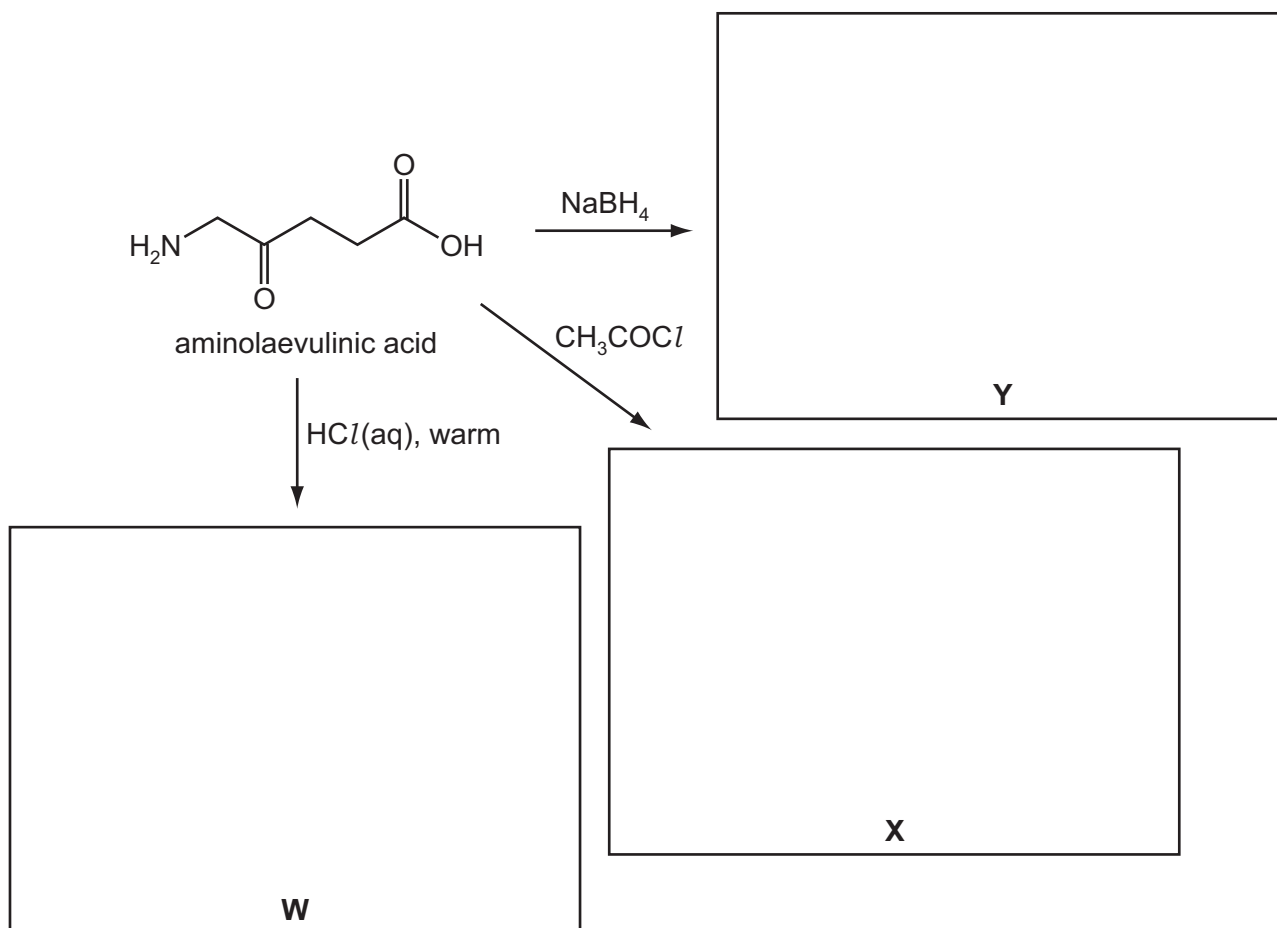
.....

(iii) Identify the non-organic product formed in this reaction.

.....

[5]

(d) Three reactions of aminolaevulinic acid are shown. Draw the structures of the products **W**, **X** and **Y** in the boxes below.



[3]

(e) Aminolaevulinic acid can undergo polymerisation.

Draw the structure of the polymer showing **two** repeat units. The linkages between the monomer units should be shown fully displayed.

[2]

[Total: 15]

Section B

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

- 6 (a) A mixture of amino acids can be separated by electrophoresis. During an electrophoresis experiment,

- different amino acids move in different directions,
- different amino acids move at different speeds,
- some amino acids do not move at all.

Explain these observations.

.....

.....

.....

..... [3]

- (b) (i) A mixture of amino acids can also be separated by thin-layer chromatography. Identify the mobile and the stationary phases in this type of chromatography.

mobile phase

stationary phase

- (ii) What is the process by which thin-layer chromatography can separate a mixture?

..... [3]

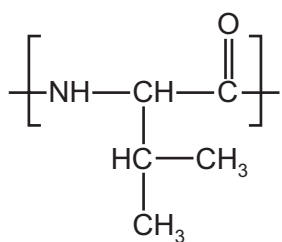
- (c) State **three** structural features of DNA.

.....

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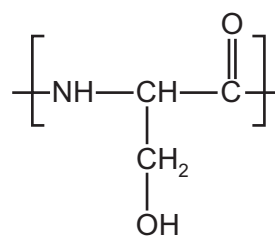
..... [3]

- (d) Some diseases are caused by a mutation in the DNA base sequence which results in one amino acid being replaced by another during protein synthesis. Suggest what changes in the interactions that form the tertiary structure would result from a mutation that replaced a valine residue with a serine residue.



val

replaced by



ser

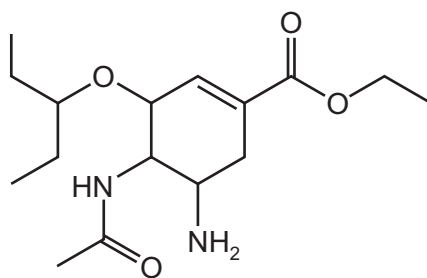
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..... [2]

[Total: 11]

- 7 (a) Oseltamivir is an antiviral drug that slows the spread of the influenza (flu) virus.



oseltamivir

Circle **two** bonds, each in a different functional group, that could be easily hydrolysed in the body. [2]

- (b) Oseltamivir is a chiral drug. This drug is usually taken as a single optical isomer rather than as a mixture of isomers.

Suggest **one** benefit of taking a drug in this way.

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 [1]

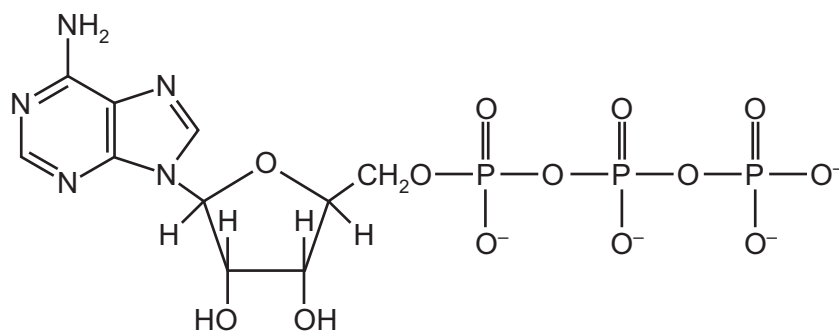
- (c) Oseltamivir is a competitive inhibitor of an enzyme produced by the flu virus.

Explain the meaning of the term *competitive inhibitor* and state how its action could be overcome.

.....

 [3]

(d) ATP plays an important role in metabolic reactions in living organisms.



ATP

What is the function of ATP in living organisms?

.....

..... [1]

[Total: 7]

- 8 **T** is a saturated alcohol. It was analysed by mass spectroscopy and NMR spectroscopy. In the mass spectrum, the molecular ion peak, M , was at an m/e value of 74 and the ratio of the heights of the M and $M+1$ peaks was 20.4 : 0.9.

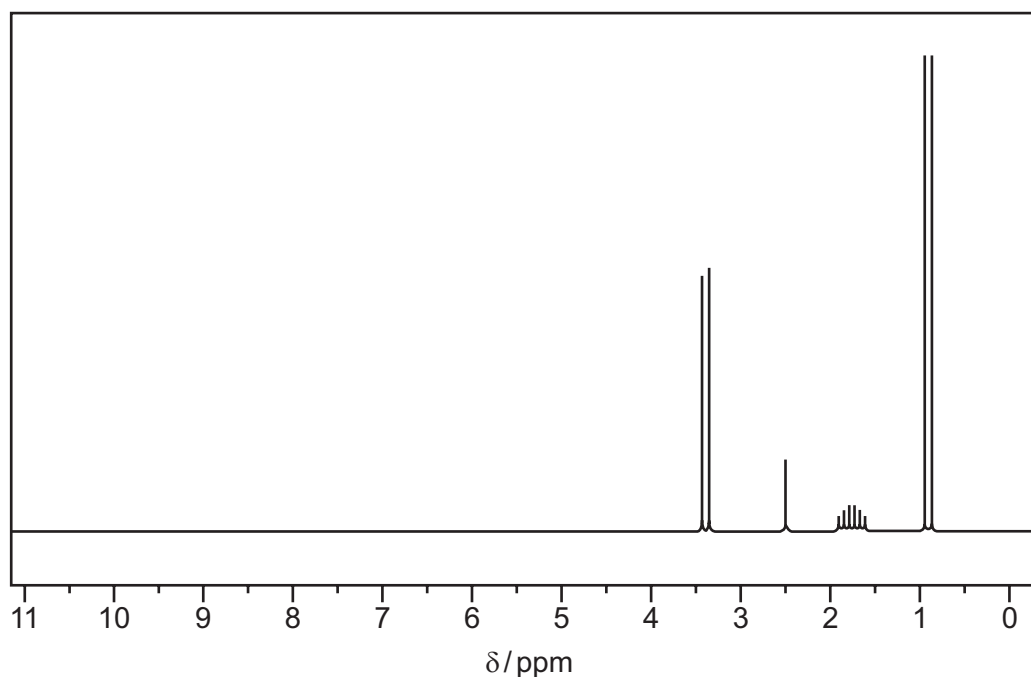
(a) (i) Use the ratio of the heights of the M and $M+1$ peaks to calculate the number of carbon atoms in a molecule of **T**.

(ii) What is the molecular formula of **T**?

molecular formula = ...

[3]

- (b) The NMR spectrum of **T** given below shows four absorptions. The absorption at 1.8 ppm is a multiplet and that at 2.5 ppm is a singlet.



(i) Use this information and your answer to (a)(ii) to deduce the structure of **T**.



- (ii) Describe and explain which type of proton is responsible for each of the absorptions.

.....

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- (iii) The absorption at 1.8 ppm is a multiplet and that at 2.5 is a singlet.
State and explain the splitting patterns of the other absorptions, at 0.9 and 3.4 ppm.

.....

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.....

- (iv) Describe and explain how the NMR spectrum of **T** dissolved in D₂O would differ from the one shown.

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[9]

[Total: 12]

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CHEMISTRY

9701/42

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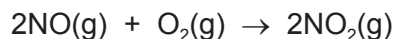
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Section A

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

- 1 (a) The oxidation of nitrogen(II) oxide is shown in the equation.



The initial rate of this reaction was measured, starting with different concentrations of the two reactants. The following results were obtained.

experiment number	[NO] / mol dm ⁻³	[O ₂] / mol dm ⁻³	initial rate / mol dm ⁻³ s ⁻¹
1	0.032	0.012	4.08×10^{-3}
2	0.032	0.024	8.15×10^{-3}
3	0.064	0.024	3.28×10^{-2}
4	0.096	0.036	

- (i) Use the data in the table to determine the order with respect to each reactant. Show your reasoning.

.....

.....

.....

.....

- (ii) Calculate the initial rate in experiment 4. Give your answer to **two** significant figures.

initial rate = ... mol dm⁻³ s⁻¹

- (iii) Write the rate equation for this reaction.

.....

- (iv) Use the results of experiment 1 to calculate the rate constant, k , for this reaction. Include the units of k .

rate constant, k = ... units

[6]

(b) (i) On the following axes

- draw two Boltzmann distribution curves, at two different temperatures, T_1 and T_2 ($T_2 > T_1$),
- label the curves and the axes.



(ii) State and explain, using your diagram, the effect of increasing temperature on the rate of reaction.

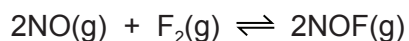
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[5]

(c) The compound nitrosyl fluoride, NOF, can be formed by the following reaction.



The rate is first order with respect to NO and F_2 .
The reaction mechanism has **two** steps.

Suggest equations for the two steps of this mechanism, stating which is the rate determining slower step.

.....

.....

..... [2]

[Total: 13]

- 2 (a) Complete the electron configurations for Ni and Ni²⁺.

		3d					4s
Ni	[Ar]	↑↓					
Ni ²⁺	[Ar]	↑↓					

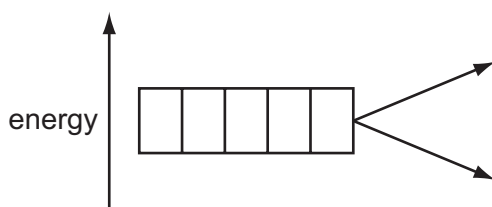
[2]

- (b) The presence of electrons in d orbitals is responsible for the colours of transition element compounds.

- (i) The d orbitals in an isolated transition metal atom or ion are all at the same energy level. What term is used to describe orbitals that are at the same energy level?

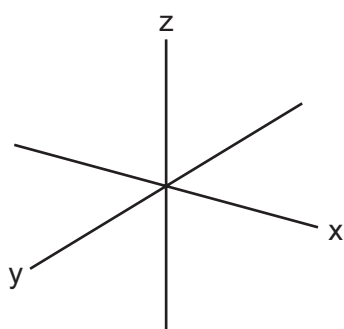
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- (ii) Complete the diagram to show the splitting of the d orbital energy levels in an octahedral complex ion.

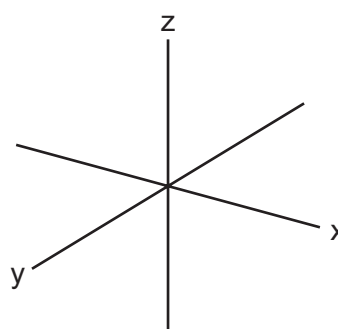


- (iii) On the axes below, sketch the shapes of one d orbital from the lower energy level and one d orbital from the higher energy level.

lower energy level



higher energy level



[4]

- (c) The octahedral complex $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green. Explain the origin of the colour of this complex.

.....

.....

.....

.....

..... [3]

- (d) When $\text{NH}_3(\text{aq})$ is added to the green solution containing $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, a grey-green precipitate, **A**, is formed. This precipitate dissolves in an excess of $\text{NH}_3(\text{aq})$ to give a blue-violet solution, **B**. Suggest formulae for **A** and **B** and write equations for the two reactions producing **A** and **B**.

.....

.....

.....

..... [4]

[Total: 13]

- 3 (a) Natural phosphorus consists of one isotope, ^{31}P . Chlorine exists naturally as two isotopes, ^{35}Cl and ^{37}Cl , in the relative abundance ratio of 3 : 1.

- (i) The mass spectrum of PCl_3 contains several peaks corresponding to a number of molecular fragments.

Suggest the isotopic composition of the fragments with the following mass numbers.

mass number	isotopic composition
101	
103	
105	

- (ii) Predict the relative ratios of the peak heights of the three peaks corresponding to these fragments.

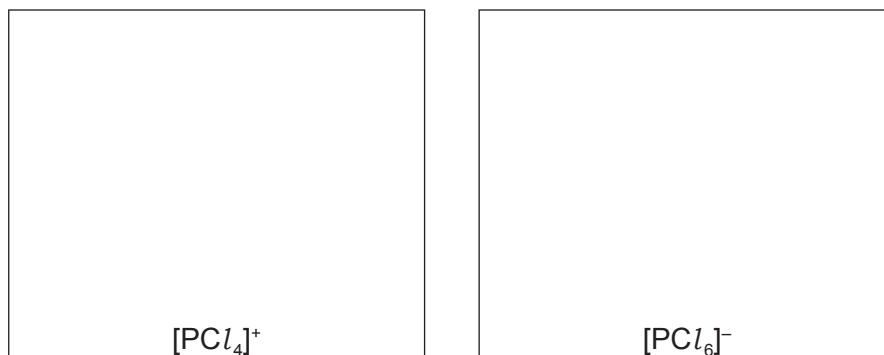
..... [4]

- (b) Phosphorus reacts with chlorine to form a variety of chlorides.
 PCl_5 is an example of a compound that exists as two structures depending on the conditions.



- (i) Draw a 'dot-and-cross' diagram to show the bonding in PCl_5 . Show the outer electrons only.

- (ii) Draw diagrams to suggest the shapes of $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$.



[3]

- (c) (i) Phosphorus(III) oxide, P_4O_6 , contains no P–P or O–O bonds. In the P_4O_6 molecule, all oxygen atoms are divalent and all phosphorus atoms are trivalent.

Sketch a structure for P_4O_6 .

- (ii) P_4O_6 can act as a ligand.

What is meant by the term *ligand*?

.....

[2]

- (d) Phosphate ions in water can be removed by adding a solution containing $\text{Ca}^{2+}(\text{aq})$ ions, which form a precipitate of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$.

- (i) Write an expression for the K_{sp} of $\text{Ca}_3(\text{PO}_4)_2$.

$K_{\text{sp}} =$

- (ii) The solubility of $\text{Ca}_3(\text{PO}_4)_2$ is $2.50 \times 10^{-6} \text{ mol dm}^{-3}$ at 298 K.

Calculate the solubility product, K_{sp} , of $\text{Ca}_3(\text{PO}_4)_2$ at this temperature. Include the units.

$K_{\text{sp}} =$ units

[4]

(e) (i) What is meant by the term *lattice energy*?

.....

.....

(ii) Explain why the lattice energy of calcium phosphate is **less** exothermic than that of magnesium phosphate.

.....

.....

[3]

[Total: 16]

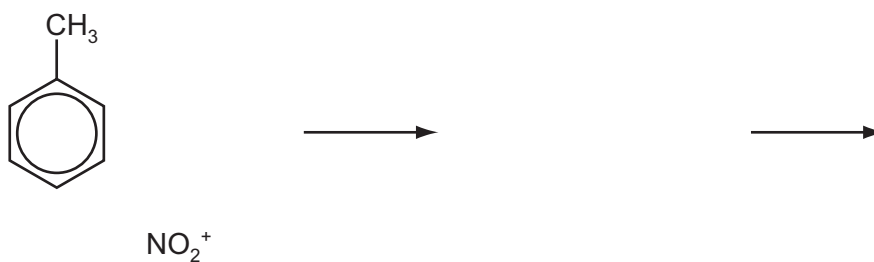
Question 4 starts on the next page.

- 4 (a) Methylbenzene undergoes electrophilic substitution with nitronium ions, NO_2^+ . Nitronium ions are generated by the reaction between concentrated sulfuric acid and concentrated nitric acid.

(i) Construct an equation for the formation of nitronium ions, NO_2^+ , by this method.

.....

(ii) Complete the scheme to show the mechanism for this reaction. Use curly arrows to show the movement of electron pairs.



[4]

(b) (i) Describe and explain the relative acidities of chloroethanoic acid and ethanoic acid.

.....

.....

.....

(ii) Describe and explain the relative acidities of phenol and ethanol.

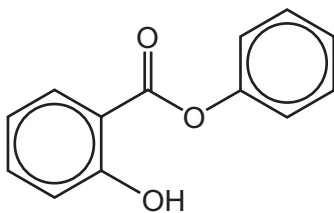
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[3]

(c) Phenyl 2-hydroxybenzoate is an antiseptic.



phenyl 2-hydroxybenzoate

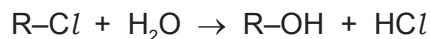
Complete the following table about the reactions of phenyl 2-hydroxybenzoate with the three reagents.

reagent	structure of product(s)		type of reaction
Na			
excess $\text{Br}_2(\text{aq})$			
excess hot $\text{NaOH}(\text{aq})$			

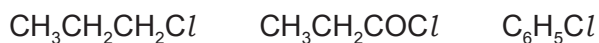
[6]

[Total: 13]

- 5 (a) Organohalogen compounds can undergo hydrolysis.



State the relative rates of hydrolysis of the following compounds.



Explain your answer.

.....

.....

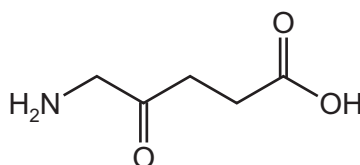
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.....

.....

..... [3]

- (b) Aminolaevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.



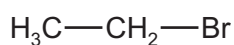
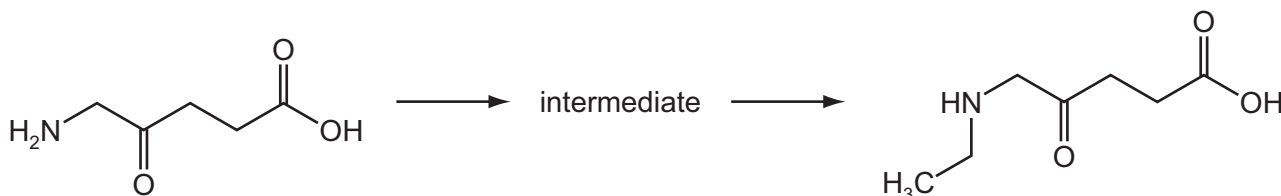
aminolaevulinic acid

Name the **three** functional groups in aminolaevulinic acid.

..... [2]

- (c) Aminolaevulinic acid reacts readily with bromoethane.

- (i) Show the mechanism of the **first step** of this reaction on the diagram. Include all necessary curly arrows, lone pairs and relevant dipoles.



(ii) Name the mechanism in (c)(i).

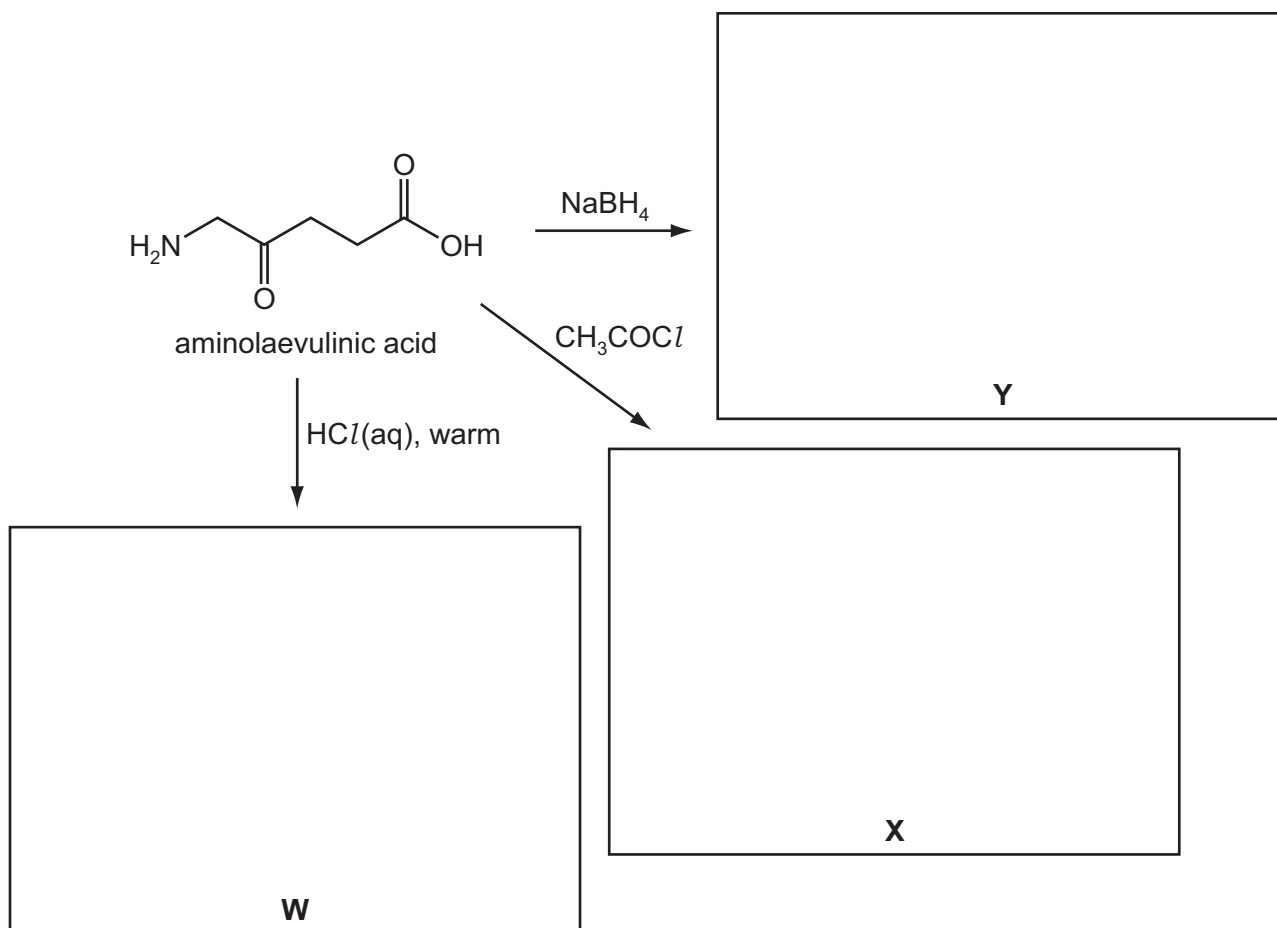
.....

(iii) Identify the non-organic product formed in this reaction.

.....

[5]

(d) Three reactions of aminolaevulinic acid are shown. Draw the structures of the products **W**, **X** and **Y** in the boxes below.



[3]

(e) Aminolaevulinic acid can undergo polymerisation.

Draw the structure of the polymer showing **two** repeat units. The linkages between the monomer units should be shown fully displayed.

[2]

[Total: 15]

Section B

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

- 6 (a)** A mixture of amino acids can be separated by electrophoresis. During an electrophoresis experiment,

- different amino acids move in different directions,
- different amino acids move at different speeds,
- some amino acids do not move at all.

Explain these observations.

.....

.....

.....

..... [3]

- (b) (i)** A mixture of amino acids can also be separated by thin-layer chromatography. Identify the mobile and the stationary phases in this type of chromatography.

mobile phase

stationary phase

- (ii)** What is the process by which thin-layer chromatography can separate a mixture?

..... [3]

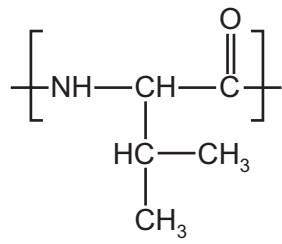
- (c)** State **three** structural features of DNA.

.....

.....

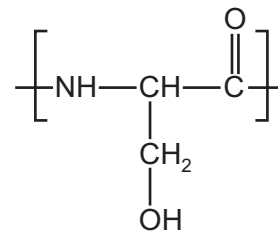
..... [3]

- (d) Some diseases are caused by a mutation in the DNA base sequence which results in one amino acid being replaced by another during protein synthesis. Suggest what changes in the interactions that form the tertiary structure would result from a mutation that replaced a valine residue with a serine residue.



val

replaced by



ser

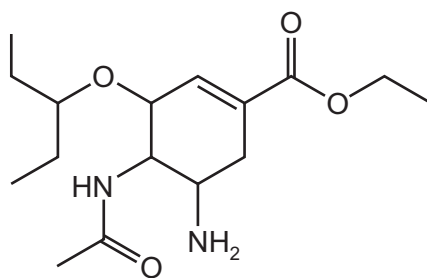
.....

.....

..... [2]

[Total: 11]

- 7 (a) Oseltamivir is an antiviral drug that slows the spread of the influenza (flu) virus.



oseltamivir

Circle **two** bonds, each in a different functional group, that could be easily hydrolysed in the body. [2]

- (b) Oseltamivir is a chiral drug. This drug is usually taken as a single optical isomer rather than as a mixture of isomers.

Suggest **one** benefit of taking a drug in this way.

.....
 [1]

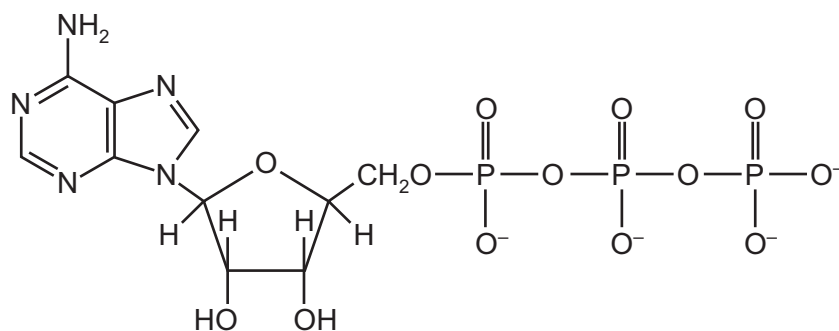
- (c) Oseltamivir is a competitive inhibitor of an enzyme produced by the flu virus.

Explain the meaning of the term *competitive inhibitor* and state how its action could be overcome.

.....

 [3]

(d) ATP plays an important role in metabolic reactions in living organisms.



ATP

What is the function of ATP in living organisms?

.....
 [1]

[Total: 7]

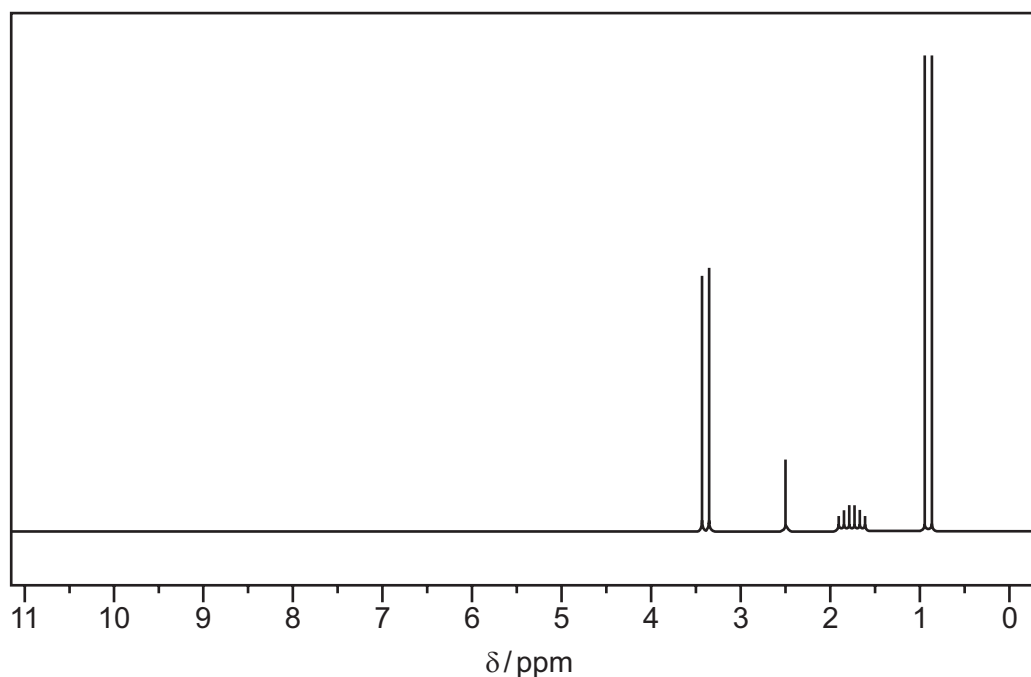
- 8 **T** is a saturated alcohol. It was analysed by mass spectroscopy and NMR spectroscopy. In the mass spectrum, the molecular ion peak, M , was at an m/e value of 74 and the ratio of the heights of the M and $M+1$ peaks was 20.4 : 0.9.

(a) (i) Use the ratio of the heights of the M and $M+1$ peaks to calculate the number of carbon atoms in a molecule of **T**.

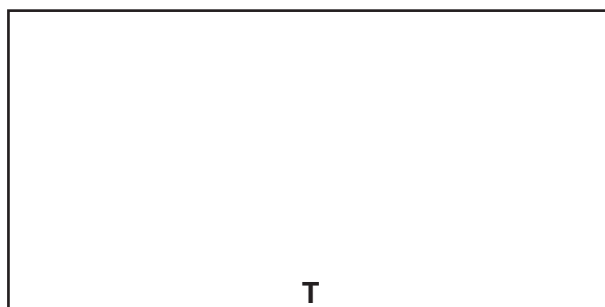
(ii) What is the molecular formula of **T**?

molecular formula = ... [3]

- (b) The NMR spectrum of **T** given below shows four absorptions. The absorption at 1.8 ppm is a multiplet and that at 2.5 ppm is a singlet.



(i) Use this information and your answer to (a)(ii) to deduce the structure of **T**.



- (ii) Describe and explain which type of proton is responsible for each of the absorptions.

.....

.....

.....

.....

- (iii) The absorption at 1.8 ppm is a multiplet and that at 2.5 is a singlet.
State and explain the splitting patterns of the other absorptions, at 0.9 and 3.4 ppm.

.....

.....

.....

- (iv) Describe and explain how the NMR spectrum of **T** dissolved in D₂O would differ from the one shown.

.....

.....

.....

[9]

[Total: 12]

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CHEMISTRY

9701/43

Paper 4 Structured Questions

October/November 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.

For Examiner's Use

1	
2	
3	
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7	
8	
9	
Total	

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



Section A

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

- 1 (a) Chlorine exists naturally as a mixture of two isotopes, ^{35}Cl and ^{37}Cl , in the abundance ratio of 3 : 1.

The mass spectrum of chlorine consists of five peaks.

- (i) Suggest the mass numbers for these five peaks and the identities of the species responsible.

mass number	formula of species

- (ii) Predict the ratios of the abundances of the three species with the highest mass numbers.

ratio of abundances = ...
[4]

- (b) Strontium chloride, SrCl_2 , can be used to produce a red colour in fireworks.

- (i) Draw the 'dot-and-cross' diagram for strontium chloride. Show outer shell electrons only.

- (ii) Use the following data, together with relevant data from the *Data Booklet*, to calculate a value for the lattice energy of strontium chloride. You may find it helpful to construct a Born-Haber cycle.

electron affinity per mole of chlorine atoms	-349 kJ mol^{-1}
standard enthalpy of atomisation of Sr(s)	$+164 \text{ kJ mol}^{-1}$
standard enthalpy of formation of $\text{SrCl}_2(\text{s})$	-830 kJ mol^{-1}

lattice energy = ... kJ mol^{-1}
[5]

- (c) Strontium nitrate, $\text{Sr}(\text{NO}_3)_2$, can also be used to produce a red colour in fireworks.

- (i) Strontium nitrate can easily be prepared from strontium carbonate, SrCO_3 .

Suggest an equation for this preparation of strontium nitrate.

.....

- (ii) Write an equation for the reaction that occurs when strontium nitrate is heated.

.....

[2]

- (d) Describe and explain the trend in the thermal stabilities of the nitrates of the Group II elements.

.....

.....

.....

.....

..... [3]

[Total: 14]

- 2 (a) Bromate(V) ions, BrO_3^- , react with bromide ions in the presence of acid to produce bromine. Write an **ionic** equation for this reaction.

.....
 [2]

- (b) The initial rate of this reaction was measured, starting with different concentrations of the three reactants.

The following results were obtained.

experiment number	$[\text{BrO}_3^-]$ / mol dm^{-3}	$[\text{Br}^-]$ / mol dm^{-3}	$[\text{H}^+]$ / mol dm^{-3}	initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.040	0.020	0.50	2.64×10^{-4}
2	0.040	0.020	1.00	1.06×10^{-3}
3	0.040	0.080	0.50	1.06×10^{-3}
4	0.080	0.020	0.50	5.21×10^{-4}

- (i) Use the data in the table to determine the order with respect to each reactant. Show your reasoning.

.....

- (ii) Write the rate equation for this reaction.

.....

- (iii) Use the results of experiment 1 to calculate the rate constant, k , for this reaction. Include the units of k .

rate constant, k = ... units [6]

[Total: 8]

3 Transition elements have characteristic properties due to their partially-filled d orbitals.

- (a) (i) Which **two** elements in the first row of the d-block have only one electron in the 4s orbital of their neutral atoms?

.....

- (ii) The d orbitals in an isolated transition metal atom or ion are described as being degenerate.

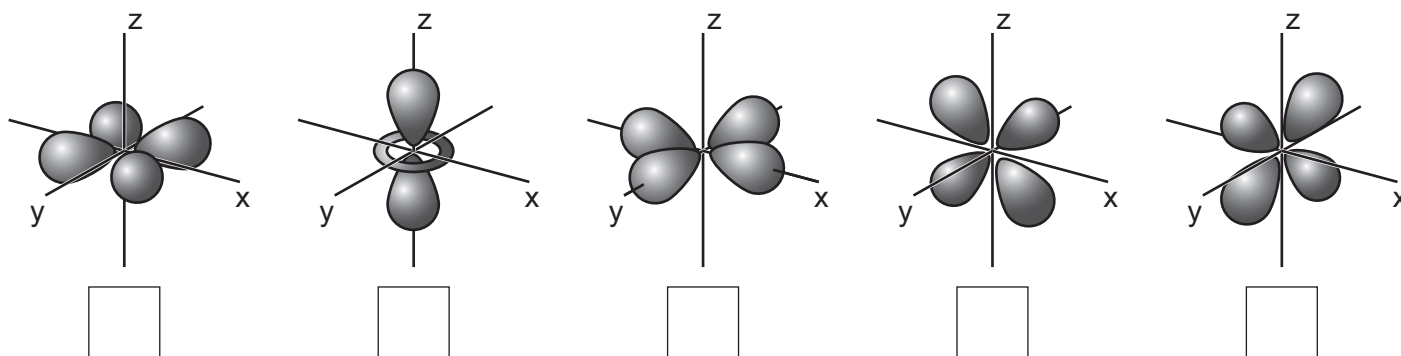
What is meant by the term *degenerate*?

.....

- (iii) Sketches of the shapes of the atomic orbitals from the d subshell are shown.

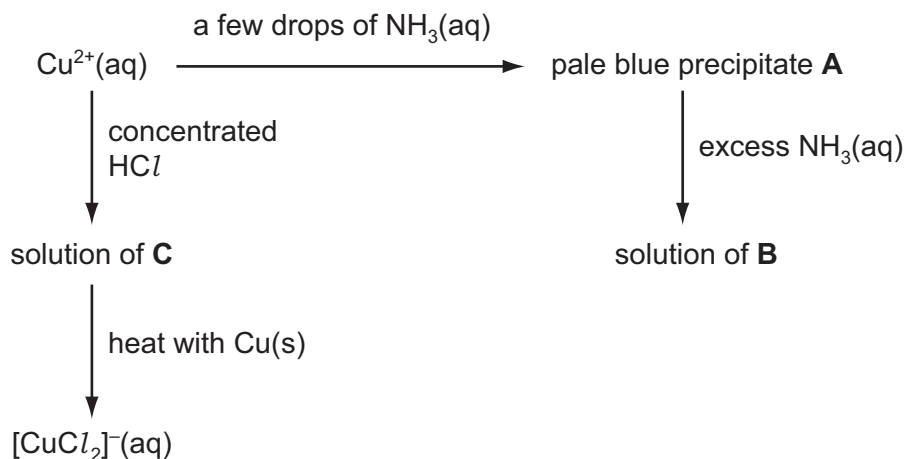
In an octahedral complex, the d orbitals are split into two groups at different energy levels.

On the diagram below, write an 'H' in the box under each of the orbitals at the higher energy level.



[4]

(b) The following scheme shows some reactions of $\text{Cu}^{2+}(\text{aq})$.



(i) Suggest the formula of each of the following.

A

B

C

(ii) State the colour of the following solutions.

solution of **B**

solution of **C**

(iii) Name the type of reaction that occurs when **C** is heated with copper.

.....

Deduce the role of the copper metal in this reaction.

.....

[6]

(c) When the solution containing the complex $[\text{CuCl}_2]^{-}$ is poured into water, a precipitate of CuCl is formed. CuCl is white because it does not absorb visible light.

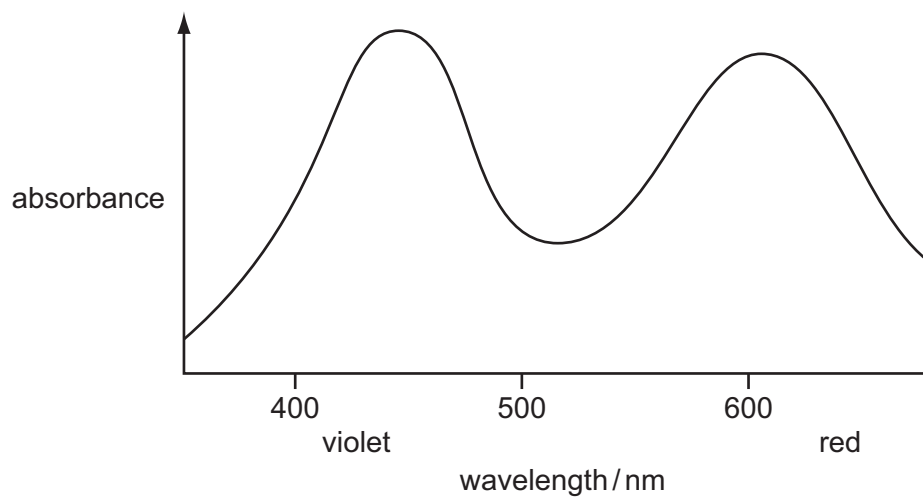
Explain why CuCl does **not** absorb visible light.

.....

.....

..... [2]

- (d) The complex ion $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is coloured because it **absorbs** visible light. The absorption spectrum for $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is shown below.

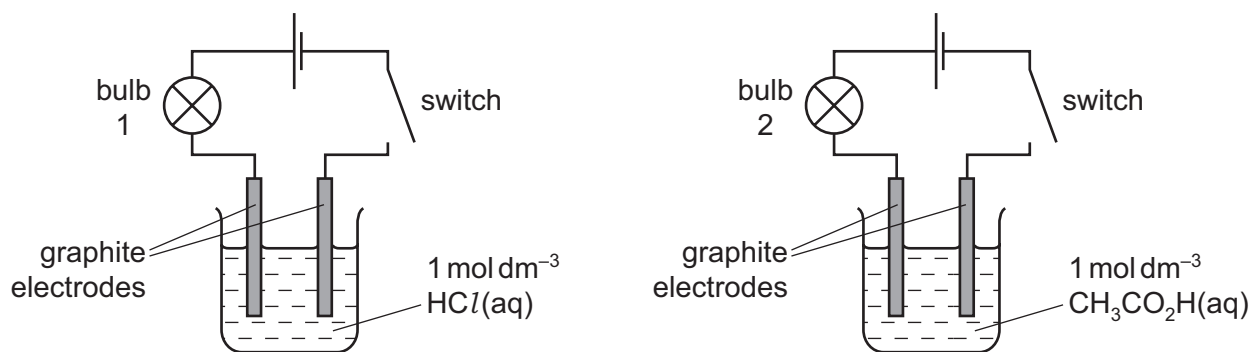


Suggest the colour of this complex ion. Explain your answer.

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

[Total: 14]

- 4 (a) The following circuits were set up using aqueous hydrochloric and aqueous ethanoic acids as electrolytes. Assume that the two circuits were identical apart from the electrolyte.



When the switches were closed, bulb 1 was brighter than bulb 2. Explain why.

.....

 [2]

- (b) (i) State what is meant by a *buffer solution*.

.....

- (ii) Outline how a buffer solution can be prepared from ethanoic acid and a named base.

.....
 [4]

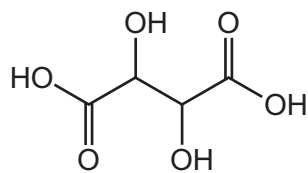
- (c) Amino acids such as alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, can act as a buffer solution. Construct **two** equations to illustrate this.

equation 1

equation 2

[2]

(d) Tartaric acid is present in many plants.



tartaric acid

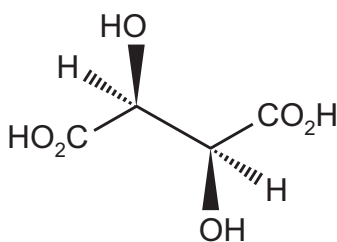
- (i) Tartaric acid has two dissociation constants, K_1 and K_2 , for which the pK_a values are 2.99 and 4.40.

Suggest equations showing the two dissociations that give rise to these pK_a values.

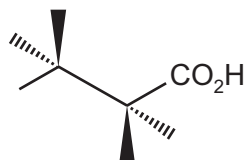
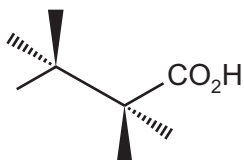
pK_a 2.99

pK_a 4.40

- (ii) One stereoisomer of tartaric acid is shown.



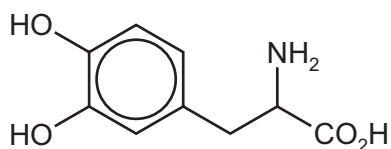
Complete the diagrams showing two other stereoisomers of tartaric acid.



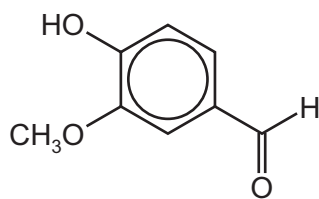
[4]

[Total: 12]

- 5 L-DOPA is used in the treatment of Parkinson's disease. It can be prepared from vanillin.



L-DOPA



vanillin

- (a) L-DOPA and vanillin each contain an aromatic benzene ring.
Describe, with the aid of a diagram, the bonding and shape of a molecule of benzene, C_6H_6 .

.....

.....

.....

.....

.....

..... [5]

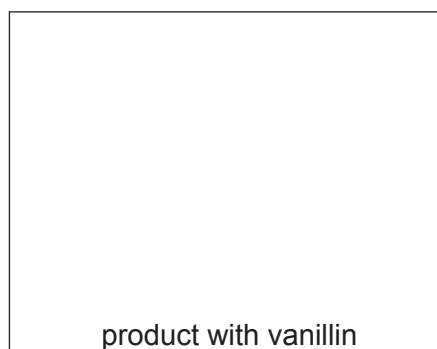
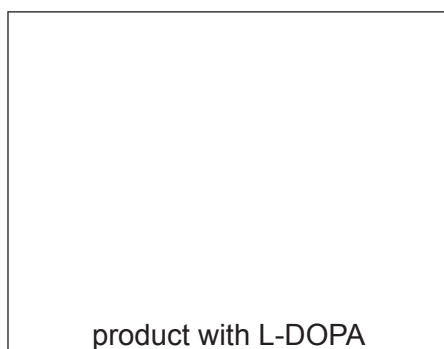
(b) A student carried out some reactions with samples of L-DOPA and vanillin using reagents **X**, **Y** and **Z**.

- Reagent **X** reacted with L-DOPA **and** with vanillin.
- Reagent **Y** reacted with L-DOPA but **not** with vanillin.
- Reagent **Z** reacted with vanillin but **not** with L-DOPA.

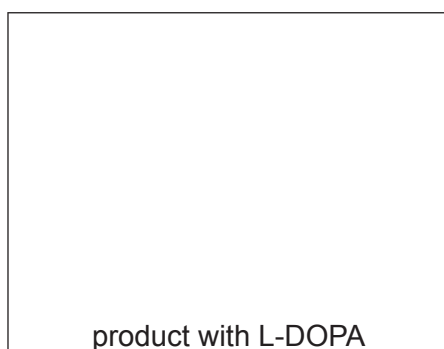
Assume that the $\text{CH}_3\text{O}-$ group in vanillin does not react.

Suggest possible identities of reagents **X**, **Y** and **Z** and give the structures of the organic products that were formed.

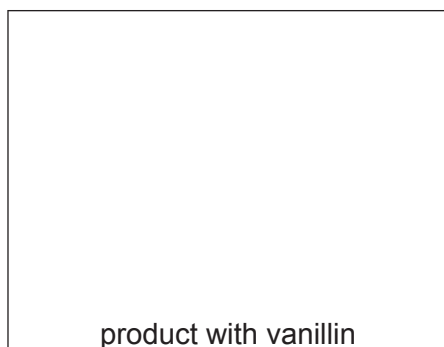
Reagent **X**



Reagent **Y**



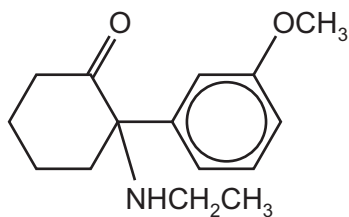
Reagent **Z**



[7]

[Total: 12]

- 6 Methoxetamine is a derivative of the pharmaceutical drug, ketamine.



methoxetamine

- (a) (i) What is the molecular formula of methoxetamine?

.....

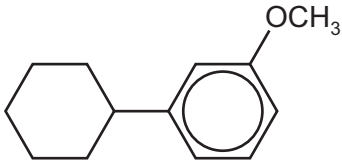
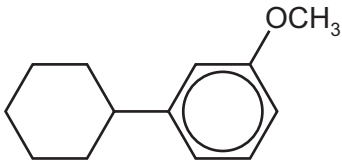
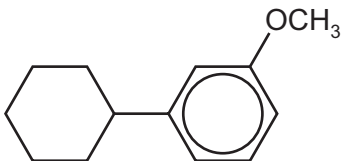
- (ii) On the diagram above, **circle** any chiral centres that are present in methoxetamine.

- (iii) Name **two** functional groups in methoxetamine, in addition to the aryl group.

.....

[4]

- (b) In the table, complete the structure of each of the compounds formed when methoxetamine is reacted with the following reagents. State the type of reaction in each case.

reagent	structure of product	type of reaction
(i) LiAlH_4		
(ii) HCl(aq)		
(iii) CH_3COCl		

[6]

[Total: 10]

Section B

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

- 7 (a) Explain what is meant by the term *partition coefficient*.

.....
 [2]

- (b) When 20 cm³ of ethoxyethane were shaken with 75 cm³ of an aqueous solution containing 5.00 g of an organic compound, **J**, in 75 cm³ of water, it was found that 2.14 g of **J** were extracted into the ethoxyethane.

Calculate the partition coefficient, $K_{\text{partition}}$, of **J** between ethoxyethane and water.

$K_{\text{partition}} = \dots\dots\dots$ [2]

- (c) In a new experiment

- 10 cm³ of ethoxyethane were shaken with 75 cm³ of an aqueous solution containing 5.00 g of **J** and the layers were separated.
- The aqueous layer was shaken with a second 10 cm³ portion of ethoxyethane and the layers were separated.
- The two organic layers were combined.

Use the value of $K_{\text{partition}}$ you calculated in (b) to calculate the total mass of **J** extracted by this procedure.

total mass of **J** = ... [2]

- (d) Paper chromatography and gas/liquid chromatography both rely on the partition of compounds between mobile and stationary phases.

- (i) Identify the mobile phase in paper chromatography.

.....

- (ii) Suggest what type of liquid is used for the stationary phase in gas/liquid chromatography.

.....

(iii) Both these techniques can be used to separate mixtures.

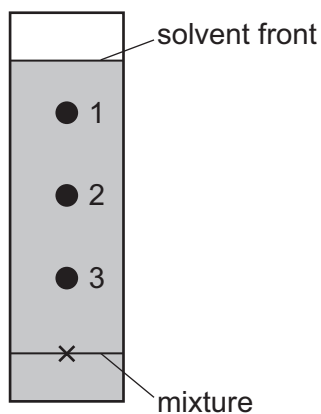
State what you would measure in order to distinguish between the components in the mixture in

1. paper chromatography, ...

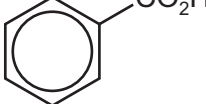
2. gas/liquid chromatography.

[4]

(e) A mixture of three compounds was analysed by paper chromatography using a non-polar solvent. The resulting chromatogram is shown.



Identify which compound is responsible for each spot.

compound	spot
CO_2H 	
CH_2OH 	
CO_2H 	

[1]

[Total: 11]

- 8 (a) Analysis of a sample of DNA showed that 33% of the nitrogenous bases present was guanine. Calculate the percentages of the **other** bases in this sample of DNA.

adenine% cytosine% thymine% [2]

- (b) Many drug molecules are chiral, but are often produced as a mixture of optical isomers.

- (i) Suggest why a larger mass of the mixture is required than of a single optical isomer.

.....
.....

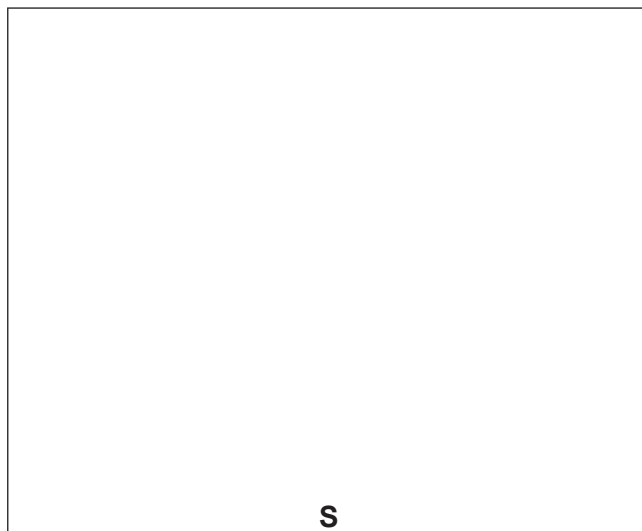
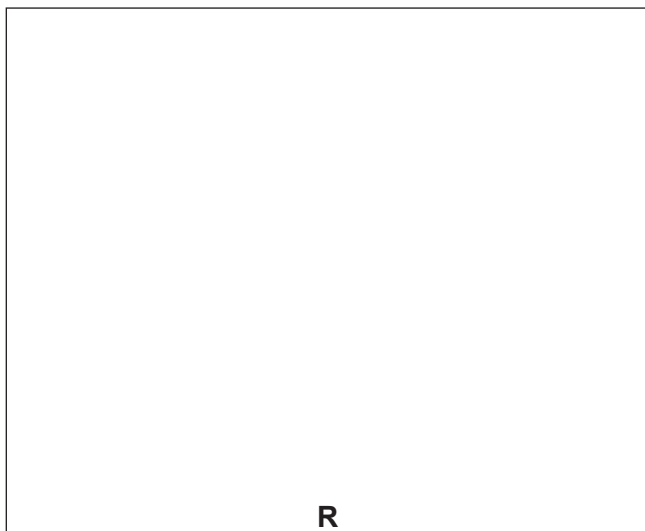
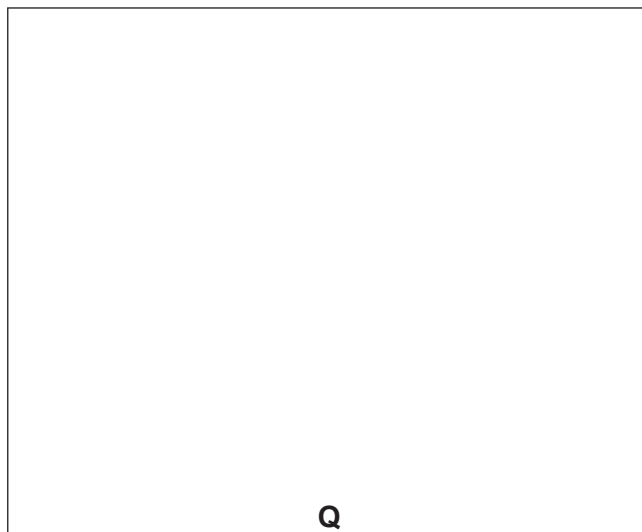
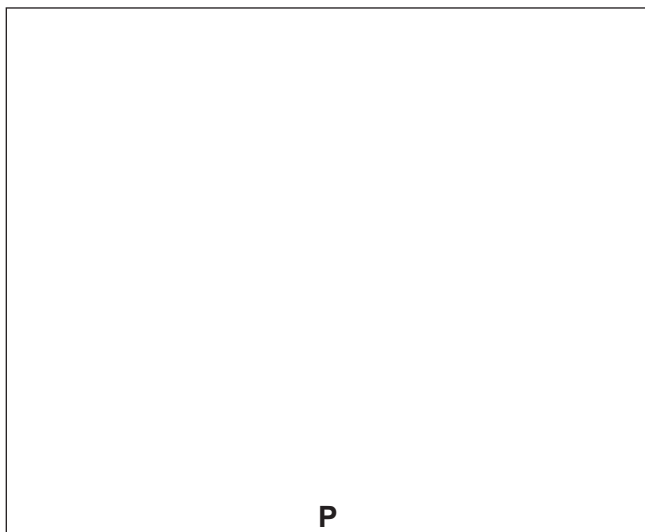
- (ii) Suggest a problem that might arise as a result of taking a mixture of optical isomers.

.....
.....

[2]

(c) There are four structural isomers with the molecular formula $C_5H_{10}O$ that are aldehydes.

(i) Draw the structures of these aldehydes.



(ii) The NMR spectrum of **one** of these isomers contains **four** absorptions. Which isomer **P**, **Q**, **R** or **S** gives this spectrum?

isomer

(iii) Predict the number of absorptions that would be given by each of the other three isomers.

isomer letter (P , Q , R or S)	number of absorptions

[6]

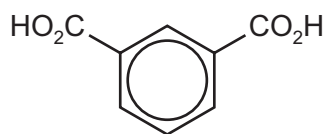
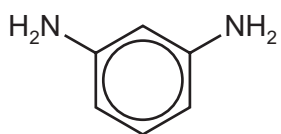
[Total: 10]

- 9 (a) Polymers can be formed by addition or condensation polymerisation. Complete the table.

polymer	method of polymerisation
nylon	
PVC (polychloroethene)	
<i>Terylene</i>	

[1]

- (b) *Nomex* is a polymeric material with excellent flame-resistant properties. It contains a polymer made from the two monomers shown below.



Draw the structure of the polymer showing **two** repeat units. The linkages between monomer units should be shown fully displayed.

[2]

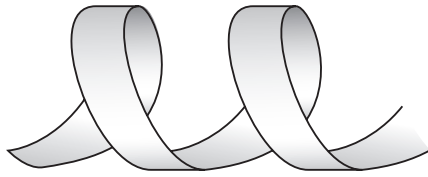
- (c) Proteins are natural polymers. Explain what is meant by the *primary structure* of a protein.

.....

.....

..... [1]

- (d) Use the diagram to show an example of how the α -helix secondary structure in proteins is stabilised.



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

- (e) The tertiary structure of a protein is destroyed during the process of denaturation. Explain how this can occur by

- (i) the addition of alkali,

.....
.....

- (ii) the addition of Hg^{2+} ions,

.....
.....

- (iii) heating to 70°C .

.....
..... [3]

[Total: 9]

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