Cambridge International A Level

Cambridge International Examinations
Cambridge International Advanced Level

CANDIDATE NAME	
CENTRE NUMBER	
CANDIDATE NUMBER	

3272601861

CHEMISTRY **9701/42**

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	
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8	
Total	

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

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CAMBRIDGE International Examinations

Section A

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

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

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

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.

.....

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.....

.....

(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]

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(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.

.....

.....

.....

[5]

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

$$2NO(g) + F_2(g) \rightleftharpoons 2NOF(g)$$

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.

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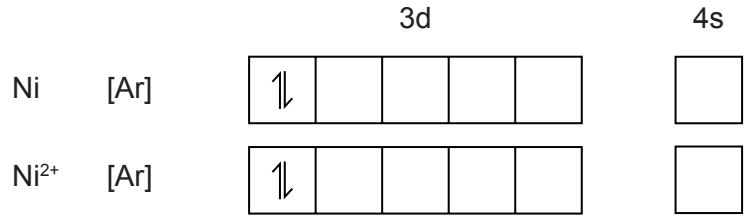
..... [2]

[Total: 13]

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



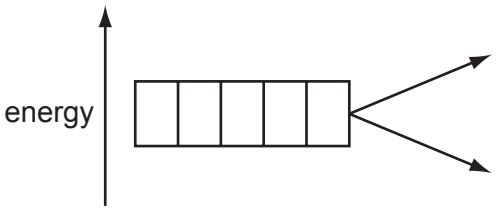
[2]

(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?

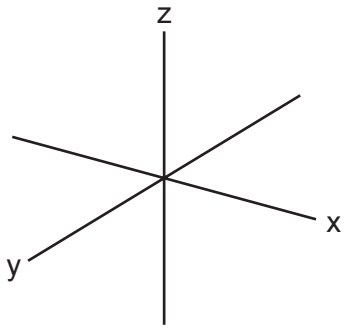
.....

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

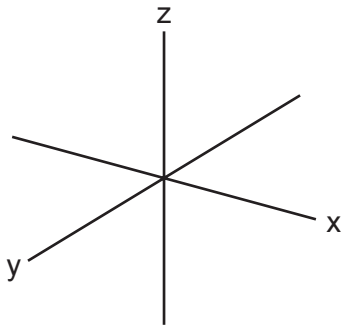


(iii) On the axes below, sketch the shapes of one d orbital from the lower energy level and one d orbital from the higher energy level.

lower energy level



higher energy level



[4]

(c) The octahedral complex $[Ni(H_2O)_6]^{2+}$ is green. Explain the origin of the colour of this complex.

.....

.....

.....

.....

..... [3]

(d) When $NH_3(aq)$ is added to the green solution containing $[Ni(H_2O)_6]^{2+}$, a grey-green precipitate, **A**, is formed. This precipitate dissolves in an excess of $NH_3(aq)$ 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.

$$2PCl_5(g) \rightleftharpoons [PCl_4]^+[PCl_6]^-(s)$$

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

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(ii) Draw diagrams to suggest the shapes of $[PCl_4]^+$ and $[PCl_6]^-$.

$[PCl_4]^+$ $[PCl_6]^-$

[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 $Ca^{2+}(aq)$ ions, which form a precipitate of calcium phosphate, $Ca_3(PO_4)_2$.

(i) Write an expression for the K_{sp} of $Ca_3(PO_4)_2$.

K_{sp} =

(ii) The solubility of $Ca_3(PO_4)_2$ is 2.50×10^{-6} mol dm^{-3} at 298 K.

Calculate the solubility product, K_{sp}, of $Ca_3(PO_4)_2$ at this temperature. Include the units.

K_{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]

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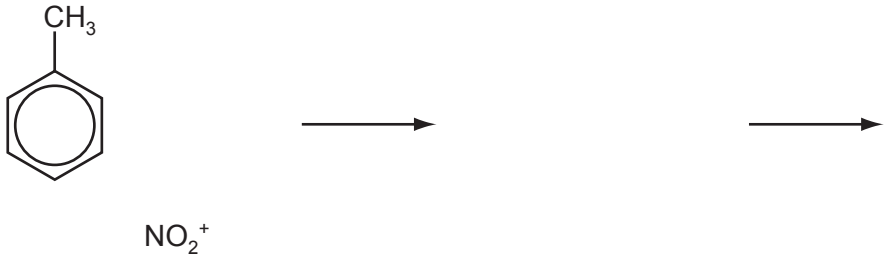
Question 4 starts on the next page.

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.

.....

.....

.....

[3]

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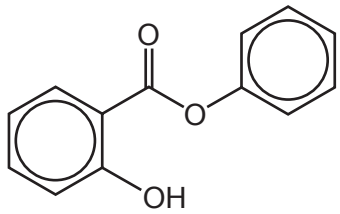
(c) Phenyl 2-hydroxybenzoate is an antiseptic.



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 $Br_2(aq)$			
excess hot NaOH(aq)			

[6]

[Total: 13]

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[Turn over

5 **(a)** Organohalogen compounds can undergo hydrolysis.

$$R\text{–}Cl + H_2O \rightarrow R\text{–}OH + HCl$$

State the relative rates of hydrolysis of the following compounds.

$CH_3CH_2CH_2Cl$ CH_3CH_2COCl C_6H_5Cl

Explain your answer.

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.....

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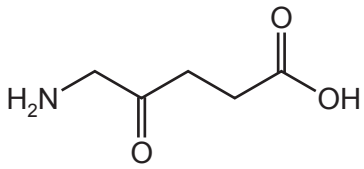
.....

..... [3]

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



aminolaevulinic acid

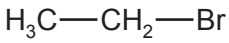
Name the **three** functional groups in aminolaevulinic acid.

..... [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)**.

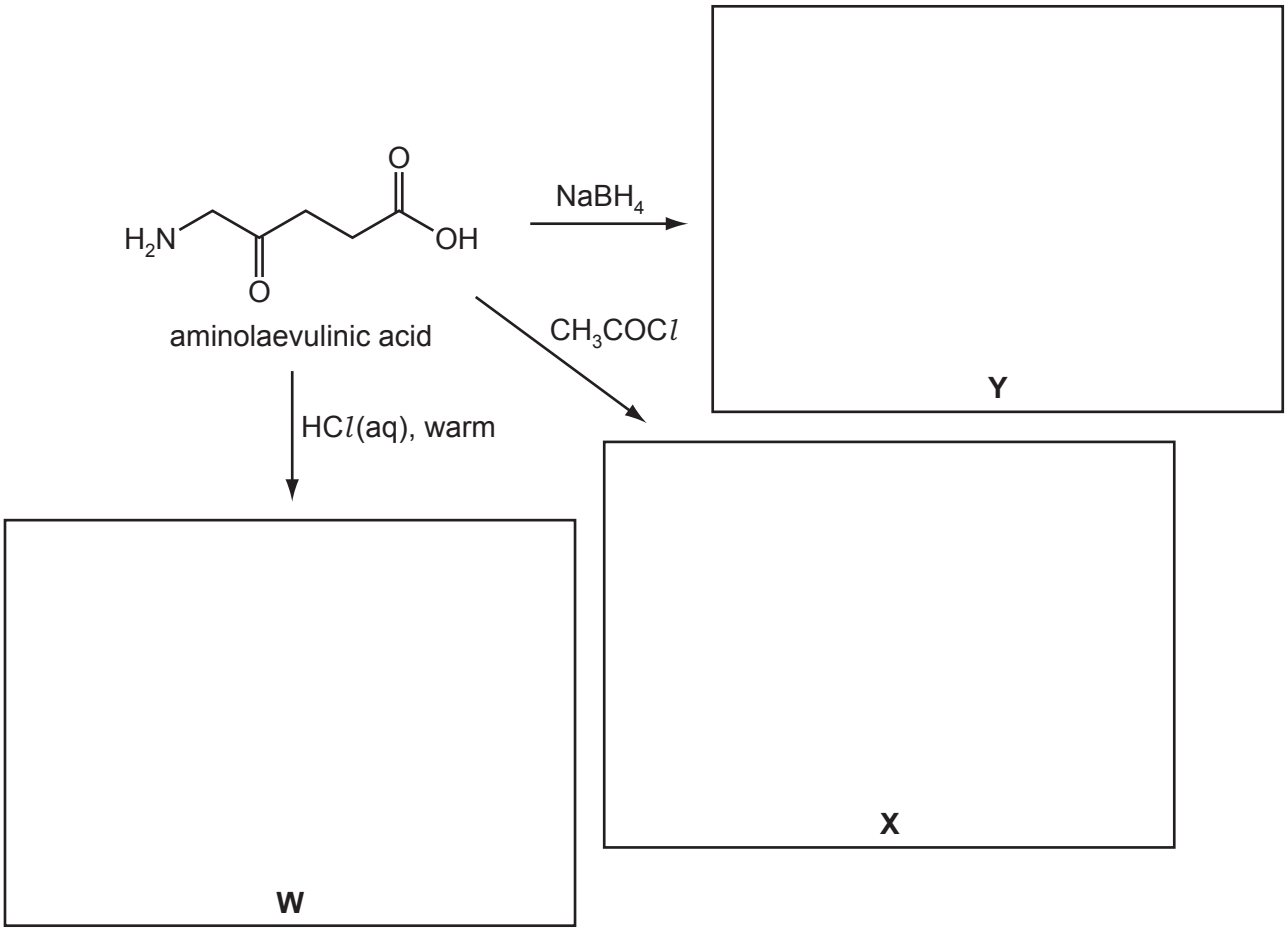
.....

(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]

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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]

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(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 ser

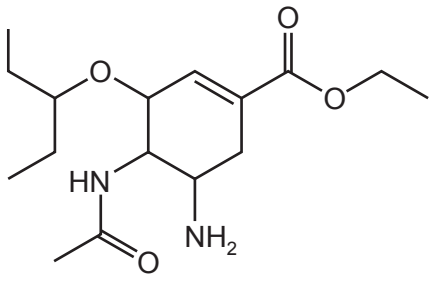
.....

.....

..... [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.

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..... [3]

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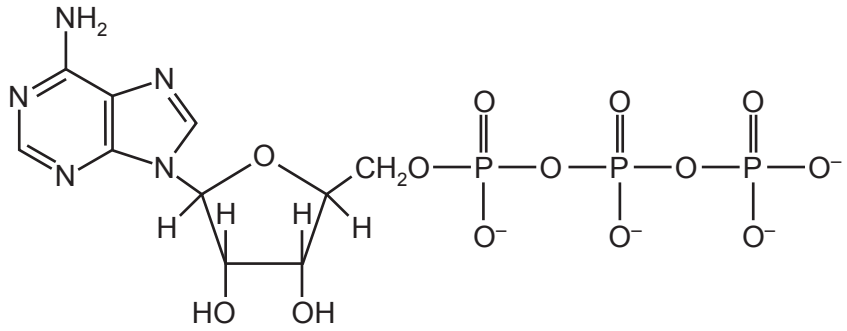
(d) ATP plays an important role in metabolic reactions in living organisms.



ATP

What is the function of ATP in living organisms?

.....

..... [1]

[Total: 7]

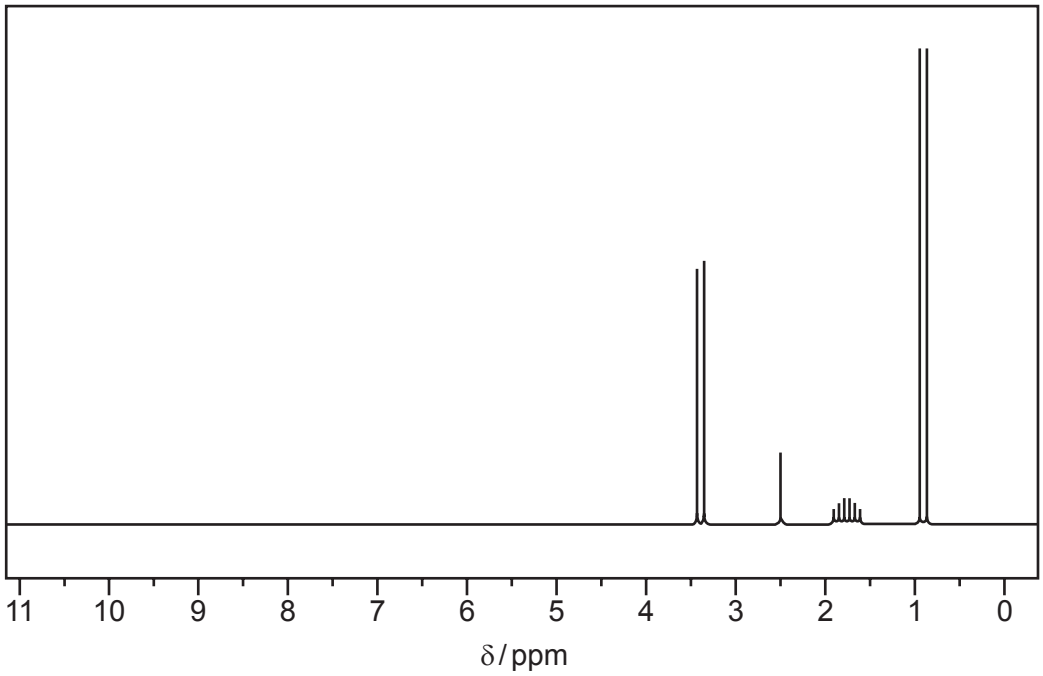
8 **T** is a saturated alcohol. It was analysed by mass spectroscopy and NMR spectroscopy.
In the mass spectrum, the molecular ion peak, M, was at an m/e value of 74 and the ratio of the heights of the M and M+1 peaks was 20.4 : 0.9.

(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**.

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.

.....

.....

.....

(iv) Describe and explain how the NMR spectrum of **T** dissolved in D_2O would differ from the one shown.

.....

.....

.....

[9]

[Total: 12]

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