Cambridge International AS & A Level

Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

8601419465

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **October/November 2017**

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.

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.

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

CAMBRIDGE International Examinations

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

1 The compound chlorine dioxide, ClO_2, can be prepared by the reaction shown.

$$NaClO_2 + \tfrac{1}{2}Cl_2 \rightarrow ClO_2 + NaCl$$

(a) Using oxidation numbers, explain why this reaction is a redox reaction.

....

....

.... [2]

(b) The central atom in the molecule of ClO_2 is chlorine.

Draw the 'dot-and-cross' diagram for ClO_2. Show outer electrons only.

[2]

(c) The reaction between ClO_2 and F_2 is shown.

$$2ClO_2 + F_2 \rightarrow 2ClO_2F$$

The rate of the reaction was measured at various concentrations of the two reactants and the following results were obtained.

experiment	$[ClO_2]$ / mol dm^{-3}	$[F_2]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.010	0.060	2.20×10^{-3}
2	0.025	0.060	to be calculated
3	to be calculated	0.040	7.04×10^{-3}

The rate equation is rate = $k[ClO_2][F_2]$.

(i) What is meant by the term *order of reaction* with respect to a particular reagent?

....

.... [1]

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

rate constant, k = ... units .... [2]

(iii) Use the data in the table to calculate

- the initial rate in experiment 2,

initial rate = ... $mol\,dm^{-3}\,s^{-1}$

- $[ClO_2]$ in experiment 3.

$[ClO_2]$ = ... $mol\,dm^{-3}$

[2]

(d) (i) What is meant by the term *rate-determining step*?

....

.... [1]

(ii) The equation for the reaction between ClO_2 and F_2 is shown.

$$2ClO_2 + F_2 \rightarrow 2ClO_2F$$

$$\text{rate} = k[ClO_2][F_2]$$

The mechanism for this reaction has two steps.

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

step 1 ....

step 2 ....

rate-determining step = ...

[2]

(e) By considering the rate equation, explain why the rate increases with increasing temperature.

....

.... [1]

[Total: 13]

2 **(a)** When water is added to magnesium nitride, Mg_3N_2, the products are a white suspension of $Mg(OH)_2$ and an alkaline gas.

(i) Write an equation for this reaction.

.... [1]

(ii) A 2.52 g sample of Mg_3N_2 is added to an excess of water.

Calculate the mass of $Mg(OH)_2$ formed.

mass of $Mg(OH)_2$ = ... g [2]

(b) State and explain how the solubility of the Group 2 hydroxides varies down the group.

....

....

....

....

.... [4]

(c) Magnesium hydroxide is sparingly soluble in water. The concentration of its saturated solution at 298 K is 1.7×10^{-4} mol dm^{-3}.

(i) Write an expression for the solubility product, K_{sp}, of $Mg(OH)_2$.

K_{sp} =

[1]

(ii) Calculate the value of K_{sp} for $Mg(OH)_2$ at 298 K and state its units.

K_{sp} = ... units .... [2]

(d) The temperature at which the Group 2 hydroxides and carbonates start to decompose increases down the group.

Suggest an explanation for this trend in the decomposition temperature of the Group 2 hydroxides.

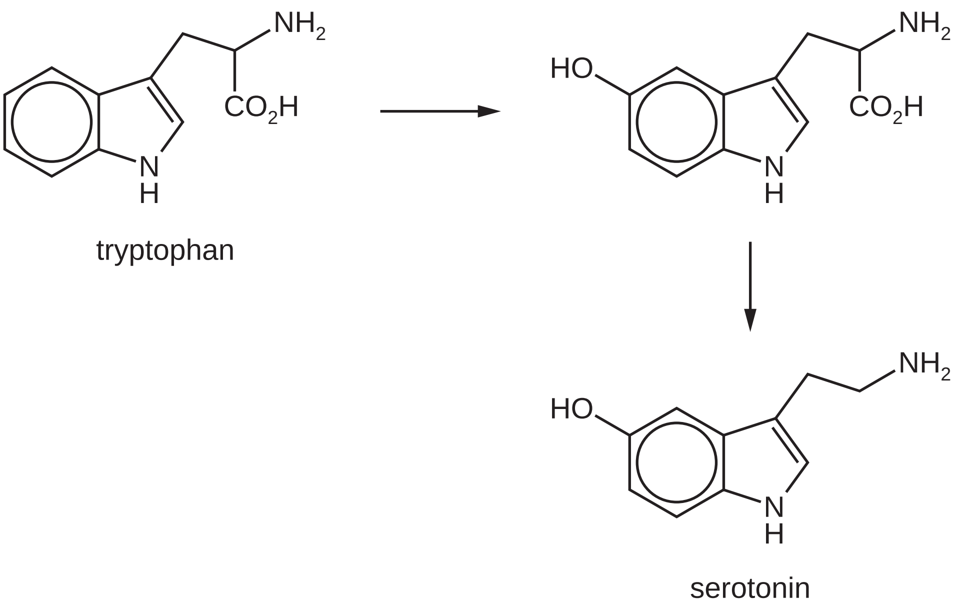
....

....

.... [2]

[Total: 12]

3 Serotonin can be synthesised from the amino acid tryptophan in two steps.



(a) **(i)** In a buffer solution at pH 5.9, a sample of tryptophan does **not** move during electrophoresis.

Draw the structures of the ions formed by tryptophan at pH 1.0 and pH 5.9.

pH 1.0	pH 5.9

[2]

(ii) Tryptophan can combine with valine to form a dipeptide.

Use the *Data Booklet* to draw the structure of this dipeptide.

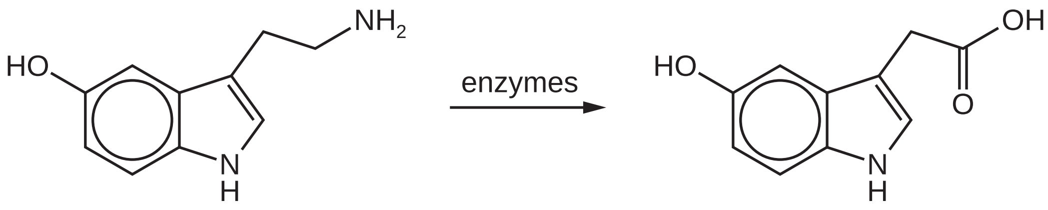
[2]

(b) Complete the following table to show the structures of the products formed and the *type of reaction* occurring when **serotonin** reacts with the four reagents in separate reactions.

reagent	structure of product	*type of reaction*
Na		
excess $Br_2(aq)$		
excess CH_3COCl		
excess H_2 / Pt catalyst		

[8]

(c) Serotonin is converted by enzymes in the liver to compound **M**.



serotonin　　　　**M**

(i) By reference to the *Data Booklet*, suggest how the infra-red spectrum of **M** would differ from that of serotonin.

....

.... [1]

(ii) The proton NMR spectrum of **M** dissolved in $CDCl_3$ shows eight peaks due to the eight different types of proton present in the molecule.

The proton NMR spectrum of **M** dissolved in D_2O was recorded.

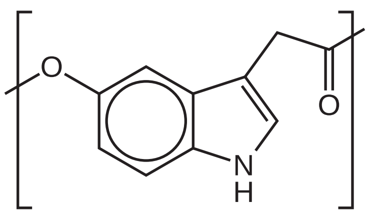
Predict the number of peaks that would be seen in the proton NMR spectrum of **M** in D_2O. Explain your answer.

number of peaks ....

explanation ....

....
[2]

(d) Compound **M** can be polymerised under certain conditions to form polymer **N**, shown.



N

Polymer **N** is biodegradable, unlike polyethene which is not.

Explain why **N** is biodegradable.

....

.... [1]

[Total: 16]

4 An electrochemical cell consists of a half-cell containing V^{3+}(aq) and V^{2+}(aq) ions and another half-cell containing VO_2^{+}(aq) and VO^{2+}(aq) ions.

(a) (i) Use data from the *Data Booklet* to calculate a value for the $E^{\ominus}_{cell}$.

$E^{\ominus}_{cell}$ = ... V [1]

(ii) Write the ionic equation for the cell reaction.

.... [1]

(iii) Draw a fully labelled diagram of the apparatus you could use to measure the potential of this cell. Include the necessary chemicals.

[4]

(b) Use data from the *Data Booklet* to predict whether a reaction might take place when the following pairs of aqueous solutions are mixed. If a reaction occurs, write an equation for it and calculate the $E^{\ominus}_{cell}$.

- V^{2+}(aq) and Sn^{4+}(aq)

Does a reaction occur? ....

equation ....

$E^{\ominus}_{cell}$ ....

- VO^{2+}(aq) and Fe^{3+}(aq)

Does a reaction occur? ....

equation ....

$E^{\ominus}_{cell}$ ....

[3]

[Total: 9]

5 **(a)** The arrangement of the anions around a cation is called the geometry of the cation; e.g. in $[CuCl_4]^{2-}$ the geometry of copper is tetrahedral and the co-ordination number of copper is 4.

The geometry of a cation in an ionic compound can be predicted from the ratio of the ionic radii of the cation and anion involved.

$\frac{\text{cation radius}}{\text{anion radius}}$	geometry of cation
0.155–0.225	trigonal planar
0.225–0.414	tetrahedral
0.414–0.732	octahedral

Use data from the *Data Booklet* to predict the geometry of, and hence the co-ordination number of, the cation for

- sodium chloride, NaC*l*,

geometry of Na^+ = ... co-ordination number of Na^+ = ...

- magnesium chloride, $MgCl_2$.

geometry of Mg^{2+} = ... co-ordination number of Mg^{2+} = ...
[2]

(b) Magnesium(I) chloride, MgC*l*, is an unstable compound and readily decomposes as shown.

$$2MgCl(s) \rightarrow Mg(s) + MgCl_2(s)$$

Use the following data to calculate the enthalpy change of this reaction.

$\Delta H_f^{\ominus}$ MgCl(s) = –106 kJ mol^{-1}
$\Delta H_f^{\ominus}$ $MgCl_2$(s) = –642 kJ mol^{-1}

enthalpy change = ... kJ mol^{-1} [1]

(c) **(i)** The equation for which ΔH is the lattice energy for MgCl is shown.

$$Mg^{+}(g) + Cl^{-}(g) \rightarrow MgCl(s)$$

Use the equation, the following data, and relevant data from the *Data Booklet* to calculate a value for the lattice energy of MgCl. You might find it helpful to construct an energy cycle.

electron affinity of Cl(g) = –349 kJ mol^{-1}
enthalpy change of atomisation of Mg(s) = +147 kJ mol^{-1}
enthalpy change of formation of MgCl(s) = –106 kJ mol^{-1}

lattice energy MgCl = ... kJ mol^{-1} [3]

(ii) Suggest how the lattice energies of $MgCl_2$ and NaCl will compare to that of MgCl. Explain your answers.

$MgCl_2$ and MgCl ....

....

NaCl and MgCl..

....
[3]

(d) Define the term *electron affinity*.

....

.... [2]

[Total: 11]

6 **(a)** Define the term *transition metal complex*.

....

.... [1]

(b) Platinum can form the compound $[Pt(NH_3)_4Cl_2][PtCl_4]$.

State the co-ordination numbers and the oxidation numbers of the platinum in the two ions of this compound.

	co-ordination number	oxidation number
$[Pt(NH_3)_4Cl_2]^{2+}$		
$[PtCl_4]^{2-}$		

[2]

(c) Draw three-dimensional diagrams to show the structures of the two isomers of $[Pt(NH_3)_4Cl_2]^{2+}$.

[2]

(d) Solutions of the compounds $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$ can be distinguished from each other by a simple chemical test. Assume that any species bonded to the platinum ion does not react in this test.

Complete the table with a test that could be used to positively identify each compound. Give details of expected observations with each compound.

test	observation with $[Pt(NH_3)_4Cl_2]Br_2$	observation with $[Pt(NH_3)_4Br_2]Cl_2$

[2]

(e) In this question you should consider geometrical and optical isomerism.

What type of isomerism is shown by the following complexes?
You should answer **geometrical**, **optical**, **both** or **neither**.

octahedral $[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$ ....

square planar $[Ni(CN)_2Cl_2]^{2-}$ ....

tetrahedral $[CuBr_2Cl_2]^{2-}$ .... [3]

(f) Many enzymes contain transition metal complexes.

Describe, with the aid of a suitably labelled diagram, how an enzyme catalyses the breakdown of a substrate molecule.

....

....

....

.... [3]

[Total: 13]

7 **(a)** Calcium carbide, CaC_2, reacts readily with water, forming ethyne, C_2H_2, and a sparingly soluble white ionic compound.

(i) Write an equation for the reaction of CaC_2 with water.

.... [1]

(ii) Draw a 'dot-and-cross' diagram for the carbide ion, C_2^{2-}. Show outer electrons only.

[1]

(b) Ethyne is the simplest member of the alkyne homologous series.

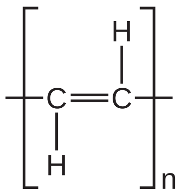
ethyne

Propyne, C_3H_4, and butyne, C_4H_6, are the next two members of the series.

Deduce the general formula for the alkynes.

.... [1]

(c) Ethyne can be polymerised into poly(acetylene), which is a conducting polymer.



poly(acetylene)

(i) Suggest why this polymer conducts electricity.

....

.... [1]

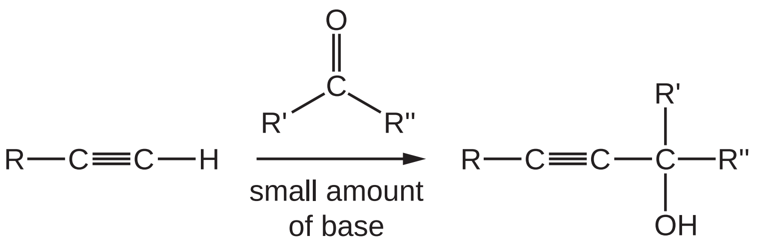
(ii) State the empirical formula of poly(acetylene).

.... [1]

(iii) By reference to a physical or chemical property, suggest **one** advantage of a conducting polymer when compared with metals.

.... [1]

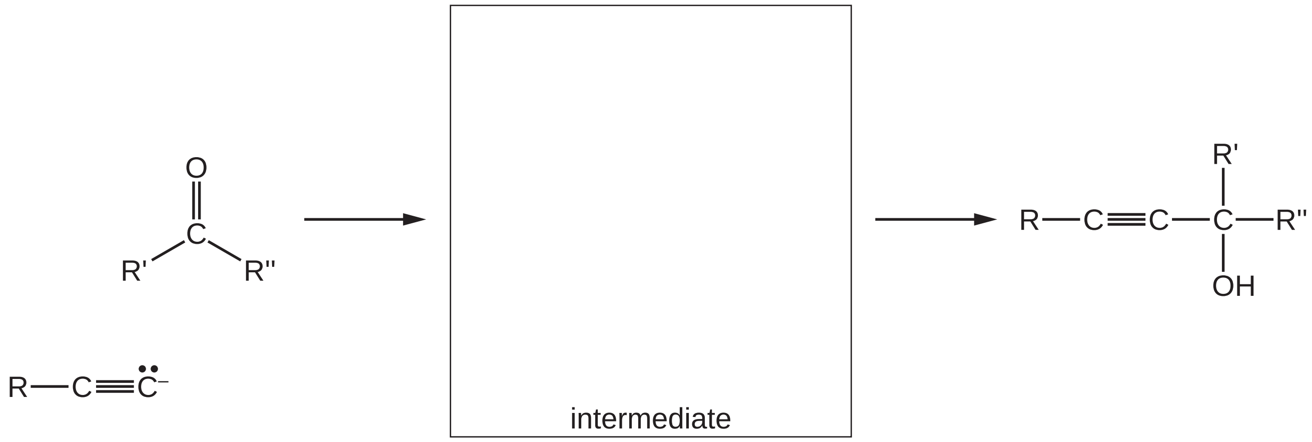
(d) Alkynes can react with carbonyl compounds under basic conditions as shown in reaction 1.



reaction 1

(i) The first step of the mechanism of reaction 1 involves the alkyne anion reacting with the carbonyl compound.

Complete the first step of the mechanism and draw the intermediate for this reaction. Include all relevant dipoles, charges and curly arrows.

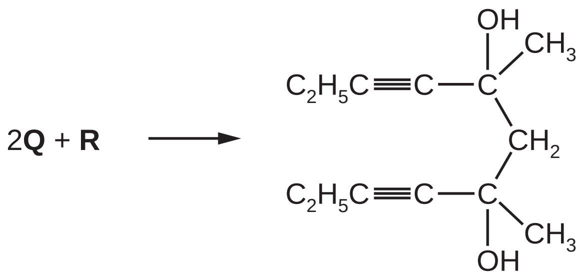


[3]

(ii) Suggest the name of the mechanism in reaction 1.

.... [1]

(iii) An alkyne, **Q**, and a carbonyl compound, **R**, react together to form compound **P** as shown.



P

Use reaction 1 to suggest the structures of **Q** and **R**.

Q

R

[2]

(e) A series of twelve separate experiments is carried out as shown in the table.

Complete the table by writing in **each** box a tick (✓) if a reaction occurs, or a cross (✗) if no reaction occurs.

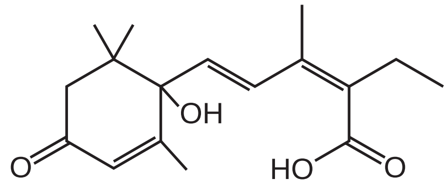
	CH_3CHO	HCO_2H	CH_3COCH_3	HO_2CCO_2H
hot, acidified $MnO_4^-(aq)$				
alkaline $I_2(aq)$				
warm Tollens' reagent				

[4]

[Total: 16]

8 **(a)** Compound **A** can be produced from a plant hormone.

A



(i) Compound **A** shows optical and geometrical isomerism.

On the structure of **A** above,
- draw a **line** through the bond(s) that give rise to geometrical isomerism,
- **circle** all chiral carbon atoms.

[2]

(ii) Give the **names** of four functional groups present in **A**.

....

.... [2]

(iii) A molecule of **A** has 17 carbon atoms.

State the number of carbon atoms that are sp, sp^2 and sp^3 hybridised in **A**.

sp carbons = ... sp^2 carbons = ... sp^3 carbons = ...

[1]

(iv) When **A** is reacted with an excess of hot, concentrated manganate(VII) ions, a mixture of three organic compounds is formed.

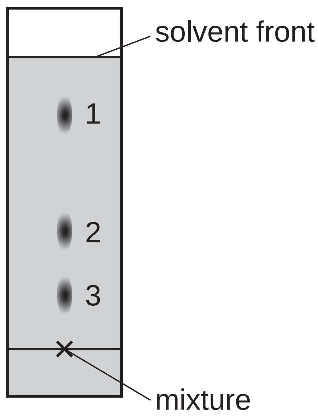
A → **X** ($C_{10}H_{14}O_7$) and **Y** ($C_3H_4O_3$) and **Z** ($C_4H_6O_3$)

Suggest the structures of **Y** and **Z**.

Y ($C_3H_4O_3$)	**Z** ($C_4H_6O_3$)

[2]

(b) A mixture of three different compounds, **J**, **K** and **L**, was analysed by thin layer chromatography using a polar stationary phase and a non-polar mobile phase. The three compounds all have similar molecular masses. The resulting chromatogram is shown.



(i) Identify which spot corresponds to each compound.

compound	spot
J CH_3COCO_2H	
K HO_2CCO_2H	
L $CH_3CH_2COCH_2CH_3$	

[1]

(ii) Explain your answers to **(b)(i)**.

....

.... [1]

(iii) What is meant by the term R_f *value*?

....

.... [1]

[Total: 10]

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