Cambridge International AS & A Level

Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

0516596213

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **February/March 2016**

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.

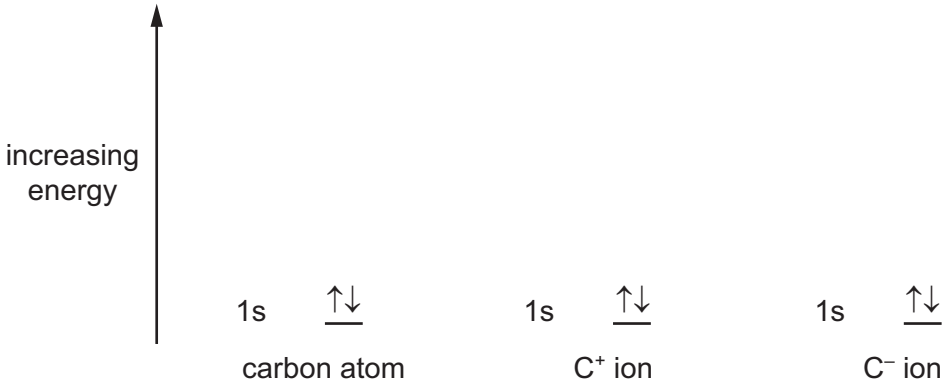
This document consists of **19** printed pages and **1** blank page.

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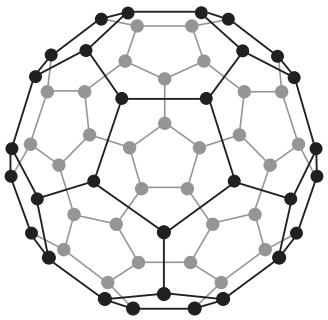
Answer **all** the questions in the spaces provided.

1 **(a)** Complete the diagrams to show the energies of the electrons in a carbon atom, a C^+ ion and a C^- ion.



[2]

(b) One of the simple molecular allotropes of carbon is buckminsterfullerene, C_{60}.



buckminsterfullerene

(i) What is the hybridisation of the carbon atoms in C_{60}?

..... [1]

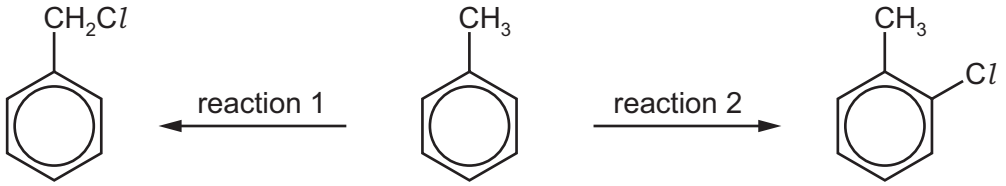
(ii) C_{60} reacts with an excess of hydrogen to form a single product, $C_{60}H_x$.

Using your answer to **(i)**, suggest a suitable value for *x*.

..... [1]

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(c) Methylbenzene can undergo different reactions to form the products shown below.



methylbenzene

(i) Give the reagents and conditions for these two reactions.

reaction 1 .....

reaction 2 .....

[2]

(ii) Name the mechanism of reaction 1.

..... [1]

(iii) Draw the structure of the product obtained if reaction 1 is carried out using an excess of chlorine.

[1]

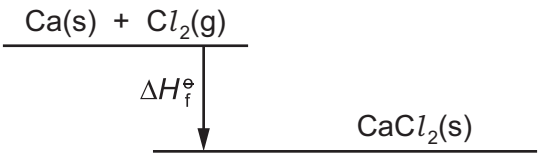
[Total: 8]

2 **(a)** Calcium metal reacts with chlorine gas to form calcium chloride, $CaCl_2$.

(i) Write an equation, including state symbols, to represent the lattice energy of calcium chloride, $CaCl_2$.

..... [1]

(ii) Complete a fully labelled Born-Haber cycle that could be used to calculate the lattice energy, $\Delta H^{\ominus}_{latt}$, for calcium chloride.



[2]

(iii) Use your answer to **(ii)** and the following data, together with relevant data from the *Data Booklet*, to calculate a value for $\Delta H^{\ominus}_{latt}$ for calcium chloride.

standard enthalpy change of formation of $CaCl_2$(s), $\Delta H^{\ominus}_f$	–796 kJ mol^{-1}
standard enthalpy change of atomisation of Ca(s), $\Delta H^{\ominus}_{at}$	+178 kJ mol^{-1}
electron affinity of chlorine atoms	–349 kJ mol^{-1}

$\Delta H^{\ominus}_{latt}$ = ... kJ mol^{-1} [3]

(b) Entropy is a measure of the disorder of a system.

Describe and explain what happens to the entropy of a gas when the temperature is increased.

.....

.....

..... [2]

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(c) The table shows four reactions.

(i) For each reaction, predict the sign of the entropy change, $\Delta S^{\ominus}$. If you predict no entropy change, write 'no change' in the table below. The first one has been done for you.

reaction	sign of $\Delta S^{\ominus}$
$CO(g) + O_2(g) \rightarrow CO_2(g)$	negative
$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$	
$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_5O(s)$	
$NaHCO_3(s) + H^+(aq) \rightarrow Na^+(aq) + CO_2(g) + H_2O(l)$	

[2]

(ii) Explain why the entropy change for the first process is negative.

.....

..... [1]

(d) Calculate the standard entropy change, $\Delta S^{\ominus}$, for this reaction.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Standard entropies, $S^{\ominus}$, in $J\,K^{-1}\,mol^{-1}$ are given.

$N_2(g)$	$H_2(g)$	$NH_3(g)$
+192	+131	+193

$\Delta S^{\ominus}$ ..... $J\,K^{-1}\,mol^{-1}$ [2]

(e) Whether or not a chemical reaction is spontaneous (feasible) can be deduced by calculating the change in free energy, $\Delta G^{\ominus}$, at a given temperature.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

$\Delta H^{\ominus} = +117\,kJ\,mol^{-1}$
$\Delta S^{\ominus} = +175\,J\,K^{-1}\,mol^{-1}$

(i) Calculate the value of $\Delta G^{\ominus}$ at 298 K for the above reaction.

[2]

(ii) Use your answer to **(i)** to explain whether or not this reaction is spontaneous at 298 K.

.....

..... [1]

[Total: 16]

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3 **(a)** Complete the electronic structures of the following species.

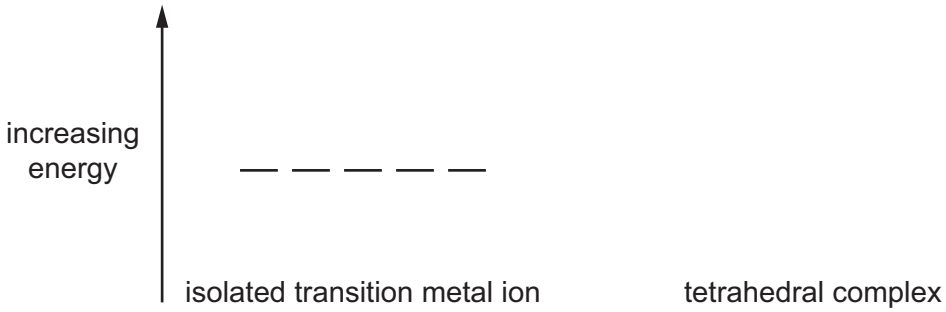
Co [Ar] .....

Co^{2+} [Ar] .....

[2]

(b) In an isolated transition metal atom the five d orbitals have the same energy. When a transition metal ion forms a tetrahedral complex the d orbitals are split into two groups of different energies.

Complete an orbital energy diagram to show this, indicating the number of orbitals in each group.



[1]

(c) Cobalt(II) forms a six co-ordinate complex containing three water molecules and three chloride ions.

(i) Write the formula of this complex showing the overall charge, if appropriate.

..... [1]

(ii) Explain, with the aid of diagrams, how many isomers of the complex in **(i)** exist.

[2]

(d) Platinum(II) forms a four co-ordinate complex containing two ammonia molecules and two chloride ions.

(i) Write the formula of this complex showing the overall charge, if appropriate.

..... [1]

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(ii) This complex exists as two isomers.

Draw the structure of these isomers and give their names.

.....	.....

[3]

(iii) One of the isomers in **(ii)** is an important anticancer drug.

State which isomer this is and explain why this isomer is effective.

isomer .....

reason .....

.....

.....

.....

[2]

(e) Transition metal ions often exist as hexa-aqua complexes in aqueous solution. The reactions which involve ligand exchange are reversible.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

(i) Write an expression for the stability constant, K_{stab}, for this equilibrium. Give its units.

K_{stab} =

units = ...

[2]

(ii) The numerical value for K_{stab} for this equilibrium at 298 K is 1.20×10^{13}.

Explain how this value relates to the relative stabilities of the two complexes.

.....

..... [1]

[Total: 15]

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4 **(a)** Ethanal, CH_3CHO, dimerises in alkaline solution according to the following equation.

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$$

The initial rate of this reaction was measured, starting with different concentrations of CH_3CHO and OH^-. The following results were obtained.

$[CH_3CHO]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	initial rate of reaction (relative values)
0.10	0.015	1
0.20	0.015	2
0.40	0.030	8

(i) Deduce the order of the reaction with respect to CH_3CHO.

..... [1]

(ii) Deduce the order of the reaction with respect to OH^-.

..... [1]

(iii) State the overall rate equation for this reaction.

rate = ... [1]

(iv) State the units for the rate constant, *k*.

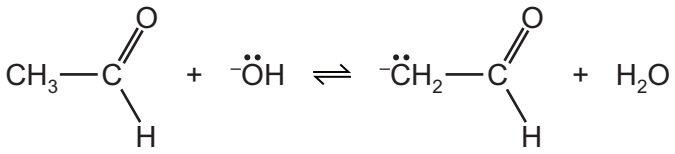
..... [1]

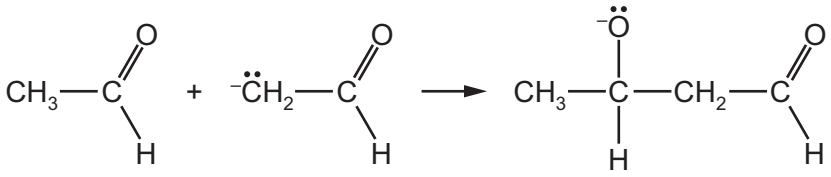
(v) Calculate the initial rate of reaction (relative value) for a reaction where the $[CH_3CHO]$ is 0.30 mol dm^{-3} and $[OH^-]$ is 0.030 mol dm^{-3}.

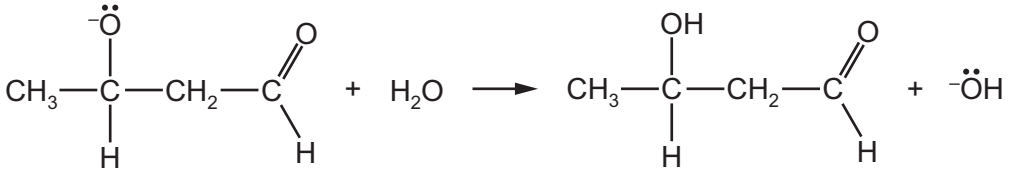
[1]

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(b) (i) A three-step mechanism has been proposed for the reaction in **(a)**.

step 1 

step 2 

step 3 

Using your rate equation in **(iii)**, predict which is the rate-determining step.
Explain your answer.

rate-determining step .....

explanation .....

.....

[2]

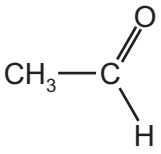
(ii) Describe the chemical behaviour of CH_3CHO in step 1.

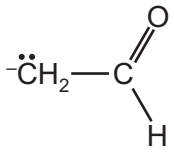
..... [1]

(c) Name the mechanism occurring in steps 2 and 3.

..... [1]

(d) Using the diagram below, show the mechanism for step 2 showing the relevant curly arrows and dipoles.



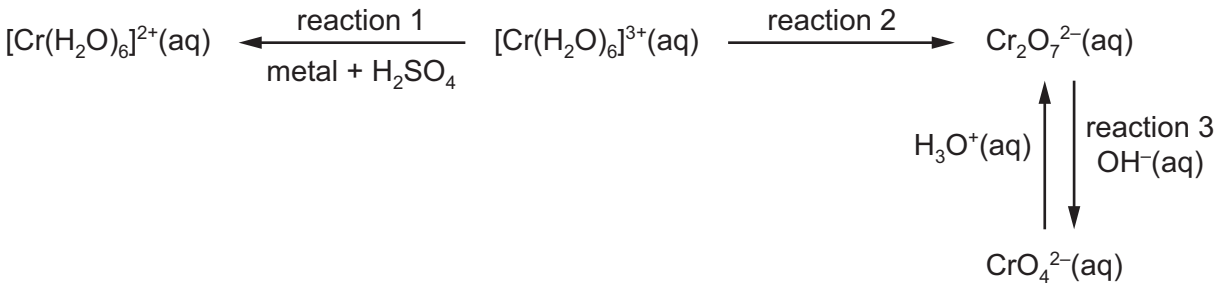


[2]

[Total: 11]

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5 Some reactions of chromium ions are shown below.



(a) (i) Use the *Data Booklet* to suggest a suitable metal to carry out reaction 1.

..... [1]

(ii) Use $E^{\ominus}$ values to explain your answer to **(i)** by calculating the $E^{\ominus}_{cell}$.

.....

.....

..... [2]

(b) A student suggested that reaction 2 could be carried out using acidified hydrogen peroxide solution.

Use the *Data Booklet* to show whether or not this reaction is feasible.

.....

.....

..... [2]

(c) Explain using oxidation numbers whether or not reaction 3 is a redox reaction.

.....

.....

..... [2]

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(d) The student used an acidified solution of $Cr_2O_7^{2-}(aq)$ to electroplate a steel box with chromium metal.

Calculate how long it would take for a current of 0.125A to deposit 0.0312g of chromium metal.

time = ... [3]

[Total: 10]

6 Two elements, **V** and **W**, are in adjacent groups in the Periodic Table.

V reacts with oxygen to form an acidic gas, **X**. **V** forms an anion with formula $\mathbf{V}O_m^-$.

W reacts with oxygen to form an acidic gas, **Y**. **W** forms an anion with formula $\mathbf{W}O_n^{2-}$.

A solution of $\mathbf{W}O_n^{2-}$ forms a white precipitate with $Ba^{2+}(aq)$ but shows no visible reaction with $Mg^{2+}(aq)$.

(a) Complete the table below.

	identity or value
V	
X	
m	
W	
Y	
n	

[3]

(b) By referring to enthalpy changes, explain why $\mathbf{W}O_n^{2-}$ forms a white precipitate with $Ba^{2+}(aq)$ but shows no visible reaction with Mg^{2+}.

.....

.....

..... [3]

[Total: 6]

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Question 7 starts on the next page.

7 **(a)** **(i)** State and explain the relative acidities of ethanol and phenol.

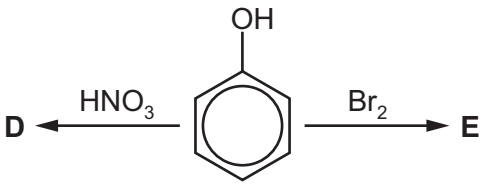
.....

.....

.....

..... [2]

(ii) In the table below, give the reaction conditions for the formation of organic products **D** and **E** and draw their structures.



phenol

reagent	conditions	structure
HNO_3	dilute, 5 °C	**D**
Br_2		**E**

[3]

(iii) Name the mechanism of the reaction forming compound **E**.

..... [1]

(b) **(i)** Phenylamine reacts with aqueous bromine to give compound **F**.

Describe the appearance of compound **F**.

..... [1]

(ii) Phenylamine reacts with nitrous acid to form a diazonium salt.

State the conditions for this reaction.

..... [1]

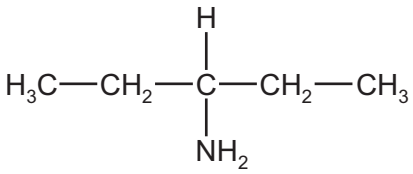
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(iii) The diazonium salt in **(ii)** reacts with an alkaline solution of phenol to produce a coloured compound, **G**.

Draw the structure of **G**.

[2]

(c) Compound **H** is a primary amine which has three peaks in its carbon-13 NMR spectrum.



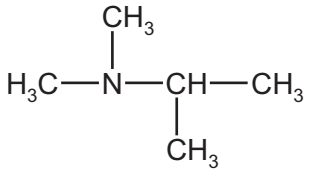
compound **H**

(i) An isomer of **H** is another primary amine **J** which also has three peaks in its carbon-13 NMR spectrum.

Use this information to suggest the structure of **J**.

[1]

(ii) Another isomer of **H** is the tertiary amine **K**. It has three peaks in its proton NMR spectrum. One of the peaks is a doublet.

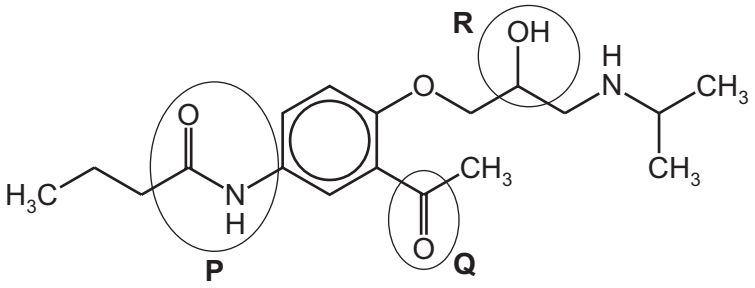


K

Circle the protons responsible for the doublet. [1]

[Total: 12]

8 Acebutolol is a drug that can be used to lower blood pressure.



acebutolol

(a) Give the **full name** of the circled functional groups labelled **P**, **Q** and **R** in acebutolol.

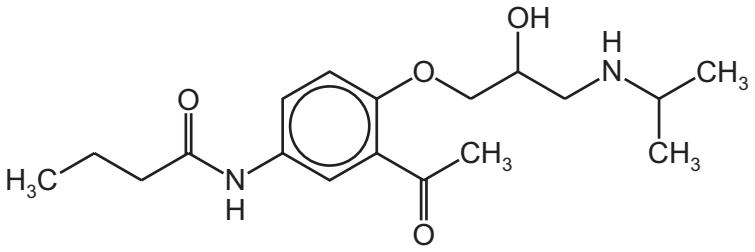
P .....

Q .....

R .....

[3]

(b) On the diagram of acebutolol below, draw a **circle** around any chiral carbon atoms.



[1]

(c) On warming with dilute hydrochloric acid, acebutolol splits to form two molecules.

(i) Draw a line through the bond broken by heating with dilute hydrochloric acid. [1]

(ii) Draw the structure of the **smaller** molecule produced by this reaction.

[1]

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(d) Suggest what would be observed when acebutolol reacts with the following reagents. If no reaction would take place, write 'none' in the table below.

reagent	observation
alkaline iodine solution	
universal indicator solution	
2,4-dinitrophenylhydrazine	
Tollens' reagent	

[3]

(e) Butanoic acid can be reduced to form compound **N**. Compound **N** reacts with sodium.

(i) Suggest a suitable reducing agent for this reaction.

..... [1]

(ii) Draw the **skeletal** formula of the isomer of **N** that exists as a pair of optical isomers.

[1]

(iii) Another isomer of **N** does **not** react with acidified dichromate(VI) solution but does react with sodium.

Draw the structure of this isomer.

[1]

[Total: 12]

9 **(a)** **(i)** Name an example of a synthetic polyester and a synthetic polyamide.

polyester .....

polyamide .....

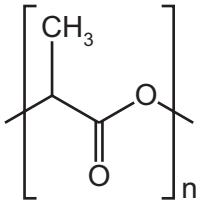
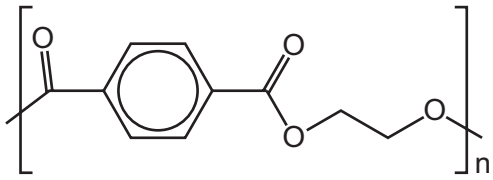
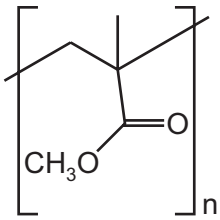
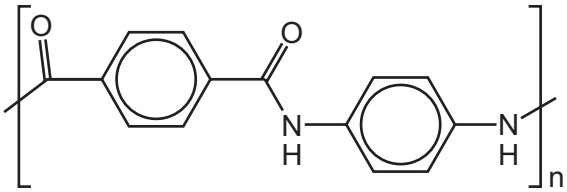
[1]

(ii) Polyesters and polyamides are formed by condensation reactions.

Name a molecule which is commonly eliminated in such reactions.

..... [1]

(b) **(i)** The table shows the repeat units of a number of polymers. Place a tick (✓) against the ones which are biodegradable.

polymer	repeat unit	biodegradable
A		
B		
C		
D		

[2]

(ii) Draw the structures of two monomers used to form polymer **B**.

[2]

(c) A section of polypeptide was hydrolysed and the following amino acids identified.

amino acid	formula
T	$CH_3CH(NH_2)CO_2H$
U	$C_6H_5CH_2CH(NH_2)CO_2H$
V	$H_2N(CH_2)_4CH(NH_2)CO_2H$

(i) Which of the amino acids **T**, **U** or **V** has the highest pH in aqueous solution? Explain why.

amino acid .....

.....

.....

[1]

(ii) State how many different dipeptides could be formed from a reaction mixture consisting of amino acids **T** and **U**.

..... [1]

(iii) Polypeptides contain a high proportion of carbon and hydrogen in their structures, yet many are soluble in water.

By referring to the structure of a polypeptide, explain why.

.....

.....

.....

..... [2]

[Total: 10]

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