Cambridge Assessment International Education
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME	

CENTRE NUMBER						

CANDIDATE NUMBER				

2557393576

CHEMISTRY **9701/41**

Paper 4 A Level Structured Questions **May/June 2019**

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 **20** printed pages.

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[Turn over

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

1 **(a)** Aqueous solutions of copper(II) salts contain the blue-coloured $[Cu(H_2O)_6]^{2+}$ complex ion. Separate portions of this blue solution react with aqueous sodium hydroxide and with concentrated hydrochloric acid.

Give the following information for each of these reactions.

- reaction with aqueous sodium hydroxide

  ionic equation ....

  type of reaction ....

  colour and state of the copper-containing product ....

- reaction with concentrated hydrochloric acid

  ionic equation ....

  type of reaction ....

  colour and state of the copper-containing product ....

[6]

(b) Chloride ions can be identified using aqueous silver nitrate, $AgNO_3(aq)$.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

0.303 g of a chloride of sulfur is completely hydrolysed with water. All the chlorine atoms present in the chloride of sulfur are converted into chloride ions. The solution is diluted to 100.0 cm^3. A 25.00 cm^3 sample of this solution is titrated with 0.0500 mol dm^{-3} $AgNO_3(aq)$. The titration requires 22.40 cm^3 of 0.0500 mol dm^{-3} $AgNO_3(aq)$.

Calculate the empirical formula of the chloride of sulfur. Show all your working.

empirical formula of chloride of sulfur = ... [3]

[Total: 9]

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2 **(a)** Group 2 nitrates decompose when heated.

Write an equation for the decomposition of strontium nitrate.

.... [1]

(b) Describe and explain how the thermal stability of Group 2 nitrates changes with increasing atomic number.

....

....

....

....

.... [3]

(c) The variation in the thermal stability of Group 2 amides is similar to that of Group 2 nitrates.

(i) Suggest whether calcium amide, $Ca(NH_2)_2$, will decompose more or less readily than barium amide, $Ba(NH_2)_2$. Explain your answer.

....

.... [1]

(ii) $Ba(NH_2)_2$ decomposes when heated to form barium nitride, Ba_3N_2, and ammonia as the only products.

Write an equation for this reaction.

.... [1]

(d) $Ba(NH_2)_2$ contains the NH_2^- ion.

Predict the bond angle of NH_2^-. Explain your answer using the qualitative model of electron-pair repulsion.

bond angle ....

explanation ....

....

....

[3]

[Total: 9]

3 Chlorate(V) ions are powerful oxidising agents.

(a) The reduction of chlorate(V) ions, ClO_3^-, with SO_2 forms chlorine dioxide, ClO_2, and sulfate ions, SO_4^{2-}, as the only products.

Construct an equation for this reaction.

.... [1]

(b) **(i)** Chlorine dioxide, ClO_2, disproportionates with hydroxide ions, $OH^-(aq)$, to form a mixture of ClO_2^- and ClO_3^- ions.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

Explain, using this reaction as an example, what is meant by *disproportionation*.

....

.... [1]

(ii) Deduce the ionic half-equations for the reaction in **(b)(i)**.

....

.... [2]

(c) A lithium-iodine electrochemical cell can be used to generate electricity for a heart pacemaker. The cell consists of a lithium electrode and an inert electrode immersed in body fluids. When current flows lithium is oxidised and iodine is reduced.

(i) Use the *Data Booklet* to write half-equations for the reactions taking place at the two electrodes. Hence write the overall equation for when a current flows.

- ....
- ....

overall equation ....

[2]

(ii) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for this cell.

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

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(iii) A current of 2.5×10^{-5} A is drawn from this cell.

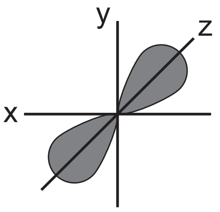
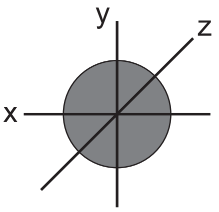
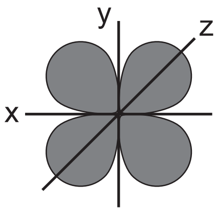
Calculate the time taken for 0.10 g of lithium electrode to be used up. Assume the current remains constant throughout this period.

time = ... s [3]

[Total: 10]

4 **(a)** Sketches of the shapes of some atomic orbitals are shown.

Identify the type of orbital, s, p, or d.

shape of orbital			
type of orbital			

[1]

(b) Cadmium forms the two ions, Cd_2^{2+} and Cd^{2+}. The electronic configuration of cadmium in these ions is shown.

- [Kr] $4d^{10}5s^1$
- [Kr] $4d^{10}$

Use this information to explain why cadmium is **not** a transition element.

....

.... [1]

(c) Methylamine, CH_3NH_2, is a monodentate ligand.

(i) State what is meant by the term *monodentate* in this context.

....

.... [1]

In the presence of aqueous methylamine, $[Cd(H_2O)_6]^{2+}$ reacts to form a mixture of two isomeric octahedral complexes.

equilibrium **1** $[Cd(H_2O)_6]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 4H_2O \quad \Delta H_r^{\ominus} = -57\,kJ\,mol^{-1}$

(ii) Complete the three-dimensional diagrams to show the isomers of $[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}$.

Use L to represent CH_3NH_2 in your diagrams.

[2]

(d) (i) State what is meant by the term *stability constant*.

....

.... [1]

(ii) Complete the table by placing **one** tick (✓) in each row to suggest how increasing temperature will affect K_{stab} and the equilibrium concentration of the cadmium complex, $[[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}]$, for equilibrium **1**. Explain your answer.

	decreases	no change	increases
K_{stab}			
$[[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}]$			

explanation ....

....

[2]

$EDTA^{4-}$ is a polydentate ligand. When a solution of $EDTA^{4-}$ is added to $[Cd(H_2O)_6]^{2+}$ a new complex $[CdEDTA]^{2-}$ is formed.

The values for the stability constants for two Cd^{2+} complexes are shown.

	K_{stab}
$[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}$	4.0×10^{6}
$[CdEDTA]^{2-}$	4.0×10^{16}

(iii) A solution containing equal numbers of moles of CH_3NH_2 and EDTA is added to $[Cd(H_2O)_6]^{2+}$.

Predict which complex is formed in the larger amount. Explain your answer.

....

.... [1]

(e) Methylamine is a Brønsted-Lowry base.

Write an equation showing how methylamine dissolves in water to give an alkaline solution.

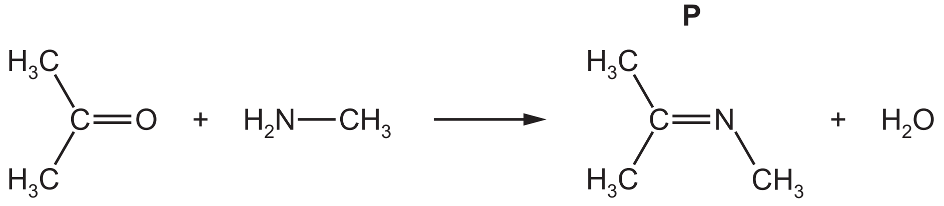
.... [1]

(f) Methylamine is a useful reagent in organic chemistry.

(i) Write an equation for the reaction of ethanoyl chloride with methylamine.

.... [2]

(ii) Methylamine also reacts with propanone to form compound **P** as shown.



Deduce the *type of reaction* shown here.

.... [1]

[Total: 13]

5 **(a)** Chlorate(I) ions undergo the following reaction under aqueous conditions.

$$2NH_3 + ClO^- \rightarrow N_2H_4 + Cl^- + H_2O$$

A series of experiments was carried out at different concentrations of ClO^- and NH_3.

The table shows the results obtained.

experiment	$[ClO^-]$ / mol dm^{-3}	$[NH_3]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.200	0.100	0.256
2	0.400	0.200	2.05
3	0.400	0.400	8.20

(i) Use the data in the table to determine the order with respect to each reactant, ClO^- and NH_3.

Show your reasoning.

....

....

....

....

....

.... [2]

(ii) Write the rate equation for this reaction.

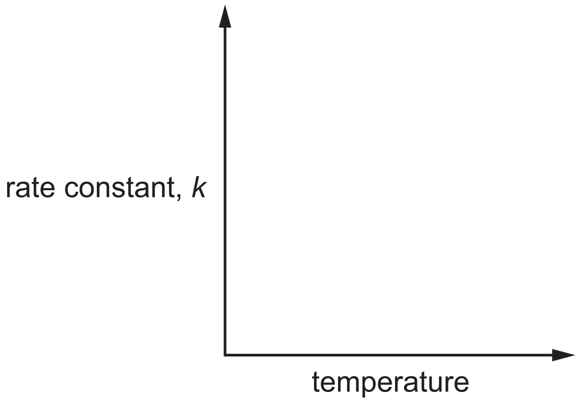
rate = ... [1]

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

k = ...

units = ...
[2]

(iv) On the axes sketch a graph to show how the value of *k* changes as temperature is increased.



[1]

(b) In another experiment, the reaction between chlorate(I) ions and iodide ions in aqueous alkali was investigated.

A solution of iodide ions in aqueous alkali was added to a large excess of chlorate(I) ions and $[I^-]$ was measured at regular intervals.

(i) Describe how the results of this experiment can be used to confirm that the reaction is first-order with respect to $[I^-]$.

....

....

.... [2]

A three-step mechanism for this reaction is shown.

step 1 $ClO^- + H_2O \rightarrow HClO + OH^-$

step 2 $I^- + HClO \rightarrow HIO + Cl^-$

step 3 $HIO + OH^- \rightarrow H_2O + IO^-$

(ii) Use this mechanism to deduce the overall equation for this reaction.

.... [1]

(iii) Identify a step that involves a redox reaction. Explain your answer.

....

.... [1]

[Total: 10]

6 **(a)** Complete the table by placing **one** tick (✓) in each row to indicate the sign of each type of energy change under standard conditions.

energy change	always positive	always negative	either negative or positive
bond energy			
enthalpy change of formation			

[1]

(b) Explain what is meant by the term *enthalpy change of atomisation*.

....

.... [1]

(c) The overall reaction for the atomisation of liquid bromine molecules, $Br_2(l)$, is shown.

$$Br_2(l) \rightarrow 2Br(g)$$

This happens via a two-step process.

- Construct a **labelled** energy cycle to represent this atomisation process, including state symbols.
- Use your cycle and relevant data from the *Data Booklet* to calculate the enthalpy change of vaporisation of $Br_2(l)$, $\Delta H^{\ominus}_{vap}$.
  The enthalpy change of atomisation of bromine, ΔH_{at}, = +112 kJ mol^{-1}.

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

(d) Suggest how the $\Delta H^{\ominus}_{vap}$ of iodine, $I_2(l)$, would compare to that of bromine, $Br_2(l)$. Explain your answer.

....

.... [1]

(e) **(i)** Explain what is meant by the term *enthalpy change of hydration*.

....

.... [1]

(ii) Suggest why the enthalpy change of hydration of $Br^-(g)$ is **more** exothermic than that of $I^-(g)$.

....

....

.... [2]

[Total: 9]

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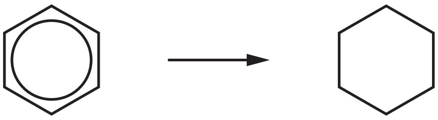
7 **(a)** Benzene can be converted into cyclohexane.



(i) For this reaction name the type of reaction and identify the reagent and conditions needed.

type of reaction ....

reagent and conditions ....

[2]

(ii) State the bond angles in benzene and cyclohexane.

bond angle in benzene .... bond angle in cyclohexane ....

Explain your answers.

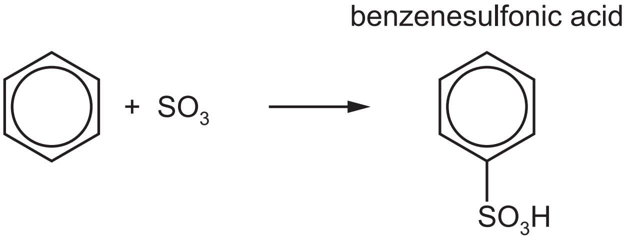
....

....

....

[2]

(b) When benzene reacts with SO_3, benzenesulfonic acid is produced.



The mechanism of this reaction is similar to that of the nitration of benzene. Concentrated H_2SO_4 is used in an initial step to generate the SO_3H^+ electrophile as shown.

$$SO_3 + H_2SO_4 \rightarrow SO_3H^+ + HSO_4^-$$

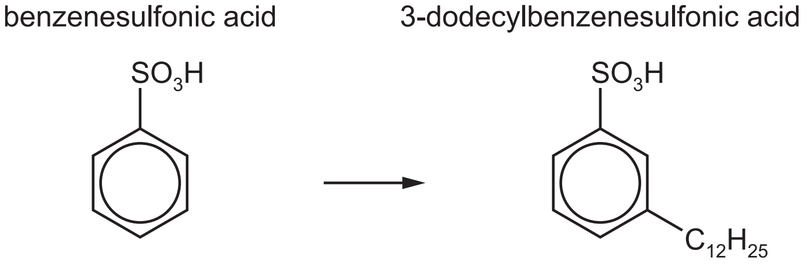
(i) Draw a mechanism for the reaction of benzene with SO_3H^+ ions. Include all necessary curly arrows and charges.

[3]

(ii) Write an equation to show how the H_2SO_4 catalyst is reformed.

.... [1]

(c) 3-dodecylbenzenesulfonic acid can be prepared from benzenesulfonic acid.



Suggest the reagents and conditions and name the mechanism for this reaction.

reagents and conditions ....

mechanism ....
[2]

(d) When concentrated sulfuric acid is added to water, dissociation takes place in two stages.

stage 1 $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

stage 2 $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ $K_{a2} = 1.0 \times 10^{-2}\,\text{mol dm}^{-3}$

K_{a2} is the acid dissociation constant for stage 2.

(i) Write the expression for the acid dissociation constant K_{a2}.

K_{a2} =

[1]

(ii) H_2SO_4 is considered a strong acid whereas HSO_4^- is considered a weak acid.

Suggest how the magnitude of the acid dissociation constant for stage 1 compares to K_{a2}.

.... [1]

(e) Benzoic acid, $C_6H_5CO_2H$, is a weak acid. A solution of 0.0250 mol dm^{-3} benzoic acid has a pH of 2.90.

Calculate the K_a of benzoic acid.

K_a = ... mol dm^{-3}
[2]

[Total: 14]

8 **(a)** The mass spectrum of compound **X**, $C_5H_{10}O_2$, is recorded.

The peak heights of the M and M+1 peaks are 22.65 and 1.25 respectively.

(i) Use these data to show that there are five carbon atoms present in one molecule of **X**.

Show your working.

[1]

(ii) The mass spectrum has a peak at *m*/*e* = 57.

Complete the equation to show the fragmentation of **X** to produce this peak.

$[C_5H_{10}O_2]^+ \rightarrow$ .... + ...

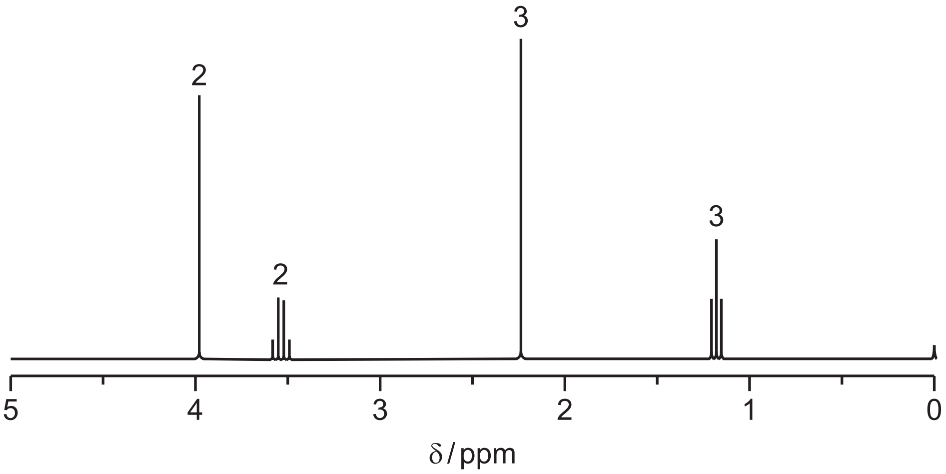
[2]

(b) State the use of TMS and $CDCl_3$ in NMR spectroscopy.

- TMS ....
- $CDCl_3$ ....

[1]

(c) The proton NMR spectrum of compound **X**, $C_5H_{10}O_2$, is shown.



(i) By considering both the relative peak areas and their δ values, use the *Data Booklet* to

- deduce the part of the molecule that produces the peak at δ 2.2,

....

- deduce the part of the molecule that produces the peaks at δ 1.2 and δ 3.5,

....

- deduce the part of the molecule that produces the peak at δ 4.0.

....
[3]

(ii) When reacted with aqueous alkaline iodine, **X** produces a yellow precipitate.

Use this information and your answers to **(c)(i)** to suggest a structure for **X**.

[1]

(d) Compound **W** is an ester with the molecular formula $C_5H_{10}O_2$.

The proton NMR spectrum of **W** contains only **two** peaks.

The relative areas of these two peaks are in the ratio 9 : 1.

Suggest a structure for this ester, **W**.

[1]

(e) Compound **V** is a carboxylic acid which contains a chiral centre. It also has the molecular formula $C_5H_{10}O_2$.

(i) Explain what is meant by the term *chiral centre*.

....

.... [1]

(ii) Suggest a structure for **V**.

[1]

[Total: 11]

9 **(a)** Organochlorine compounds can undergo hydrolysis.

$$R–Cl + H_2O \rightarrow R–OH + HCl$$

State and explain the relative rates of hydrolysis of the following compounds.

CH_3CH_2Cl CH_3COCl C_6H_5Cl

....

....

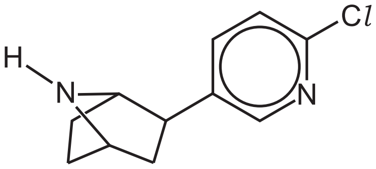
....

....

.... [3]

(b) Epibatidine is a naturally occurring organochlorine compound.

epibatidine



(i) Epibatidine is a weak base.

State what is meant by the term *weak base*.

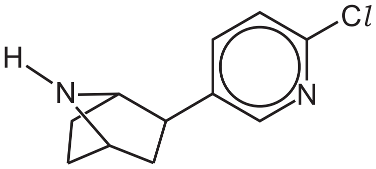
....

.... [1]

A molecule of epibatidine contains two nitrogen atoms, both of which can act as a base.

(ii) Epibatidine reacts with HCl(aq).

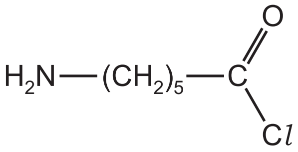
Complete the structure to suggest the product formed in this reaction.



[1]

(c) Polyamides, such as nylon-6, can be prepared from a monomer that contains both an amine and an acyl chloride functional group.

nylon-6 monomer



(i) When the nylon-6 monomer is hydrolysed, bonds are broken and formed.

By considering the two steps in the mechanism of the reaction, complete the table by placing **one** tick (✓) in each row to indicate the types of bonds broken and formed during the mechanism.

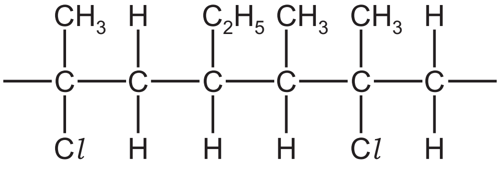
	σ bonds only	π bonds only	both σ and π bonds
bonds broken			
bonds formed			

[1]

(ii) Draw **two** repeat units of nylon-6. The amide bond should be shown fully displayed.

[2]

(d) An addition polymer made from two different alkene monomers is called a co-polymer. A section of a polyalkene co-polymer is shown.



$$-C(CH_3)(Cl)-CH_2-CH(C_2H_5)-CH(CH_3)-C(CH_3)(Cl)-CH_2-$$

Draw the structure of the **two** alkene monomers which produce this co-polymer.

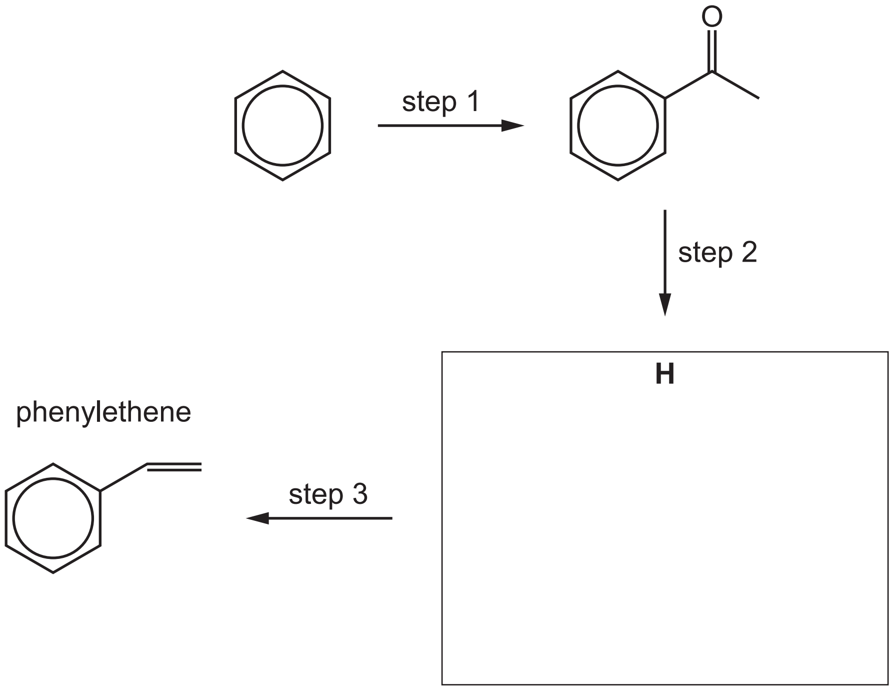
[2]

(e) Explain why polyamides normally biodegrade more readily than polyalkenes.

....

.... [1]

(f) The alkene phenylethene can be prepared from benzene in three steps.



(i) Deduce the identity of compound **H** and draw its structure in the box. [1]

(ii) Suggest reagents and conditions for each of the steps 1–3.

step 1 ....

step 2 ....

step 3 ....

[3]

[Total: 15]

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