Cambridge International AS & A Level

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Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME

CENTRE NUMBER | | | | | |

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7021618830

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **October/November 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 **19** printed pages and **1** blank page.

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[Turn over

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

1 An electrochemical cell is constructed using two half-cells.

- a Br_2/Br^- half-cell
- an Mn^{3+}/Mn^{2+} half-cell

(a) State the material used for the electrode in each half-cell.

Br_2/Br^- half-cell .....

Mn^{3+}/Mn^{2+} half-cell .....
[1]

(b) The cell is operated at 298 K.

The Br_2/Br^- half-cell has standard concentrations.

The Mn^{3+}/Mn^{2+} half-cell has $[Mn^{3+}] = 0.500\,mol\,dm^{-3}$ and $[Mn^{2+}] = 0.100\,mol\,dm^{-3}$.

(i) Use the Nernst equation to calculate the electrode potential, E, of the Mn^{3+}/Mn^{2+} half-cell under these conditions.

E = ... V [2]

(ii) Calculate the E_{cell} under these conditions.

E_{cell} = ... V [1]

(iii) Write an equation for the overall cell reaction that occurs.

..... [2]

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(c) An aqueous solution of copper(II) sulfate is electrolysed using copper electrodes. A current of 1.50 A is passed for 3.00 hours. 5.09 g of copper is deposited on the cathode.

The charge on one electron is -1.60×10^{-19} C.

The relative atomic mass of copper is 63.5.

Use these data to calculate an experimentally determined value for the Avogadro constant, *L*. Give your answer to **three** significant figures.

L = ... mol^{-1} [5]

(d) Explain why magnesium metal cannot be obtained by the electrolysis of dilute aqueous magnesium sulfate. Your answer should include data from the *Data Booklet*.

.....

.....

.....

..... [2]

[Total: 13]

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[Turn over

2 **(a)** Explain what is meant by the following terms.

half-life of a reaction .....

.....

rate-determining step .....

.....
[2]

(b) The reaction between hydroxide ions and bromomethane is first order with respect to $[OH^-]$ and first order with respect to $[CH_3Br]$.

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$

Suggest a practical method that would confirm that the reaction is first order with respect to $[OH^-]$.

- Your method should include details of measurements that would be taken in order to calculate the rate of the reaction.
- You should include a method of presenting the results to show that the reaction is first order with respect to $[OH^-]$.

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.....

..... [4]

(c) The hydrolysis of methyl ethanoate, $CH_3CO_2CH_3$, by hydroxide ions, OH^-, is first order with respect to $[CH_3CO_2CH_3]$ and also first order with respect to $[OH^-]$.

In a particular experiment,

- $[CH_3CO_2CH_3] = 0.100\,mol\,dm^{-3}$
- $[OH^-] = 0.100\,mol\,dm^{-3}$
- rate of reaction = $2.06 \times 10^{-3}\,mol\,dm^{-3}\,s^{-1}$.

Write a rate equation for this reaction and calculate the value of the rate constant, *k*, under these conditions. State the units of *k*.

rate = ...

k = ... units = ...
[3]

[Total: 9]

3 Ammonium chloride, $NH_4Cl(s)$, dissolves in water to form an acidic solution. This is due to the dissociation of the ammonium ions.

$$NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$$

(a) The ammonium ion is a weak acid. The pH of a 0.300 mol dm^{-3} solution of ammonium chloride is 4.89 under standard conditions.

(i) Calculate the $[H^+]$ in a 0.300 mol dm^{-3} solution of ammonium chloride.

$[H^+]$ = ... mol dm^{-3} [1]

(ii) Calculate the value of pK_a of the ammonium ion.

pK_a = ... [2]

(b) A buffer solution can be made by mixing ammonium chloride with ammonia solution.

(i) Explain, with the aid of an equation, how this solution can behave as a buffer when a small amount of a strong acid is added.

.....

..... [1]

(ii) Explain, with the aid of an equation, how this solution can behave as a buffer when a small amount of a strong base is added.

.....

..... [1]

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(c) (i) Use the value of K_w to calculate $[H^+]$ in pure water under standard conditions.

Show your working.

$[H^+]$ = ... $mol\,dm^{-3}$ [1]

(ii) The pH of pure water at 50 °C is 6.64.

Calculate the numerical value of K_w at 50 °C.

K_w = ... [2]

[Total: 8]

4 The table shows some standard entropy data.

substance	standard entropy, $S^\ominus$ / $J\,K^{-1}\,mol^{-1}$
$PbO_2(s)$	77
PbO(s)	69
$O_2(g)$	205

Lead(IV) oxide, PbO_2, decomposes to lead(II) oxide, PbO, and oxygen when heated.

$$2PbO_2(s) \rightarrow 2PbO(s) + O_2(g) \qquad \Delta H^\ominus = +118\,kJ\,mol^{-1}$$

(a) Use the data to calculate the value of $\Delta S^\ominus$ for this reaction.

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

(b) Use the value of $\Delta H^\ominus$ and your answer to **(a)** to calculate the temperature at which this reaction becomes feasible.

T = ... K [3]

(c) Solid lead(II) oxide can be made by heating lead metal in air.

Predict the **sign** of the standard entropy change of this reaction. Explain your answer.

.....

..... [1]

[Total: 6]

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5 **(a)** Describe fully what would be seen when magnesium and strontium are heated separately in oxygen.

magnesium .....

strontium .....
[2]

(b) **(i)** Write an equation for each of the following processes. Include state symbols.

calcium is burned in air

.....

calcium carbonate is heated strongly

.....
[2]

(ii) Calcium hydroxide is formed when water is added to calcium oxide. Calcium hydroxide and calcium carbonate are both used in agriculture.

Describe the main benefit of adding calcium hydroxide or calcium carbonate to soil.

.....

..... [1]

(iii) Explain why the Group 2 hydroxides become more soluble down the group.

.....

.....

.....

..... [3]

(c) Describe the observations, if any, that you would make when:

- a few drops of NaOH(aq) are added to $BaCl_2$(aq)

.....

- a few drops of H_2SO_4(aq) are added to $BaCl_2$(aq).

.....
[2]

(d) Describe and explain how the thermal stability of the Group 2 carbonates varies down the group.

.....

.....

.....

.....

..... [3]

[Total: 13]

6 Many copper compounds, such as $CuSO_4$ and $Cu(NO_3)_2$ contain Cu^{2+} ions. Aqueous solutions of this ion contain the $[Cu(H_2O)_6]^{2+}$ complex ion, in which water behaves as a monodentate ligand.

(a) Explain what is meant by the term *monodentate ligand*.

.....

..... [1]

(b) Copper(II) sulfate solution, $CuSO_4(aq)$, undergoes visible changes with certain reagents.

Complete the table below.

reagent added to a solution of $CuSO_4(aq)$	observations	formula of the copper(II) compound or complex ion that is formed
a few drops of $NH_3(aq)$		
an excess of $NH_3(aq)$		
an excess of NaOH(aq)		
an excess of concentrated HC*l*(aq)		

[4]

(c) When water is added to concentrated aqueous cobalt(II) chloride the colour of the solution changes from blue to pink. Explain this observation.

No equation is needed, but you should include reference to electron movement between orbitals in your answer.

.....

.....

.....

.....

.....

.....

.....

.....

..... [3]

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[Turn over

(d) When chlorine gas is bubbled into $FeSO_4(aq)$ the colour of the solution changes from pale green to yellow.

Use data from the *Data Booklet* to explain this observation. Include an equation in your answer.

Reference to electron movement between orbitals is not needed.

.....

.....

..... [2]

(e) If a solution of chloride ions is added to a solution containing $[Fe(H_2O)_6]^{3+}$ an equilibrium is established.

$$[Fe(H_2O)_6]^{3+} + 4Cl^- \rightleftharpoons [FeCl_4]^- + 6H_2O$$

(i) Write an expression for the stability constant of $[FeCl_4]^-$, K_{stab}.

K_{stab} =

[1]

(ii) For the above equilibrium the numerical value of K_{stab} = 0.080.

Calculate the concentration of $[Fe(H_2O)_6]^{3+}$ in a solution in which the concentration of Cl^- is 2.0 mol dm^{-3} and the concentration of $[FeCl_4]^-$ is 0.10 mol dm^{-3}.

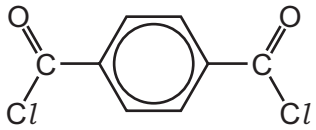
concentration of $[Fe(H_2O)_6]^{3+}$ = ... mol dm^{-3} [1]

[Total: 12]

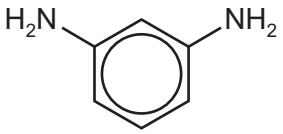
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7 **(a)** A polymer, **P**, can be made from the monomers benzene-1,4-dioyl chloride and benzene-1,3-diamine.

benzene-1,4-dioyl chloride



benzene-1,3-diamine



(i) Draw a section of the polymer chain of **P**. Your structure should include two repeat units.

P

[2]

(ii) Place **one** tick in the table to describe polymer **P** and its method of polymerisation.

type of polymer	type of polymerisation	
	addition	condensation
polyalkene		
polyamide		
polyester		

[1]

(iii) State whether or not polymer **P** is biodegradable. Give a reason for your answer.

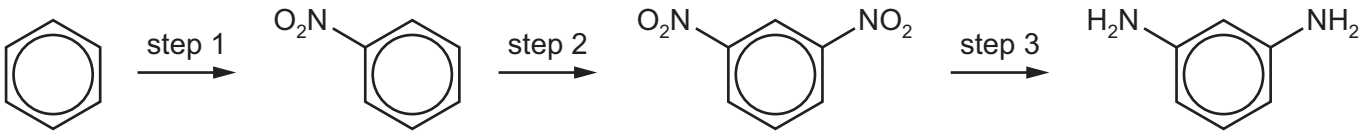
.....

..... [1]

(iv) State a suitable reagent to produce benzene-1,4-dioyl chloride from benzene-1,4-dicarboxylic acid.

..... [1]

(v) Benzene-1,3-diamine can be made from benzene using the reaction sequence shown.



State the reagents used for steps 1 and 3.

step 1 .....

step 3 .....

[2]

(b) Proteins are natural polymers. A protein is said to have a primary, secondary and tertiary structure.

(i) Describe what is meant by each of these terms.

primary structure .....

.....

secondary structure .....

.....

tertiary structure .....

.....

[3]

(ii) Name the forces or bonds responsible for holding together the primary structure of a protein molecule.

..... [1]

(iii) Name the forces or bonds responsible for the stabilisation of the secondary structure of a protein molecule, and identify the groups of atoms within the protein molecule that are held together by these forces or bonds.

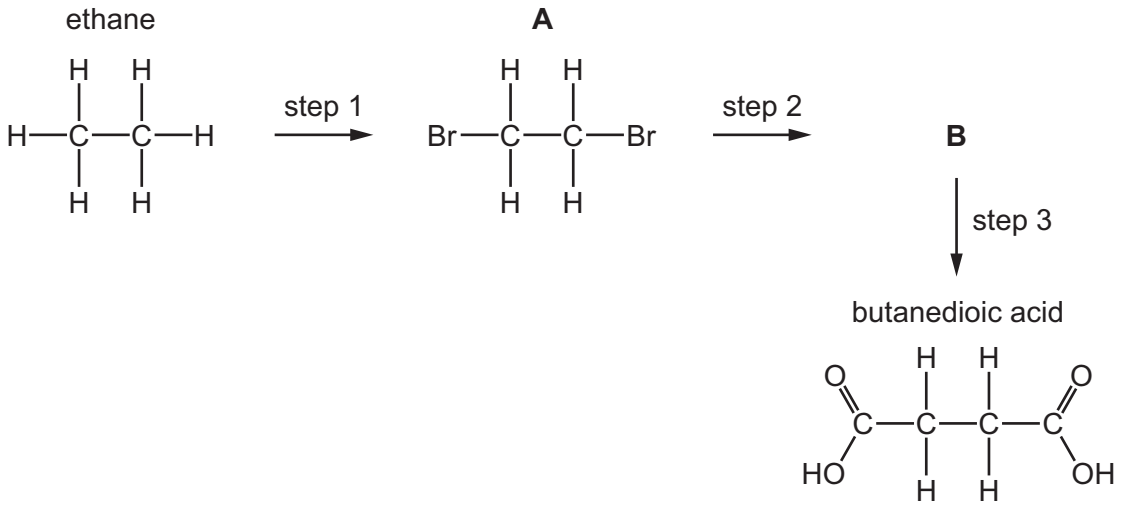
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..... [2]

[Total: 13]

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8 Butanedioic acid can be made in a three-step synthesis using ethane as the starting material.



(a) Describe the reagents and conditions needed for step 1.

..... [1]

(b) Name the other product also formed in step 1 which is an isomer of **A**.

..... [1]

(c) Give the structural formula of **B**.

[1]

(d) State the reagents and conditions needed for step 2.

..... [2]

(e) Butanedioic acid cannot be oxidised by a warm, aqueous solution of any commonly used oxidising agents but ethanedioic acid can.

(i) Identify the oxidising agent that could be used to oxidise ethanedioic acid.

..... [1]

(ii) State the product(s) of the reaction in **(e)(i)**.

..... [1]

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[Turn over

(f) Compare and explain the relative acidities of hexanoic acid, hexan-1-ol and phenol.

.....

.....

.....

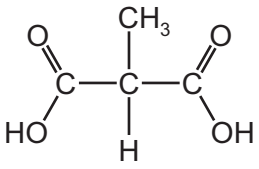
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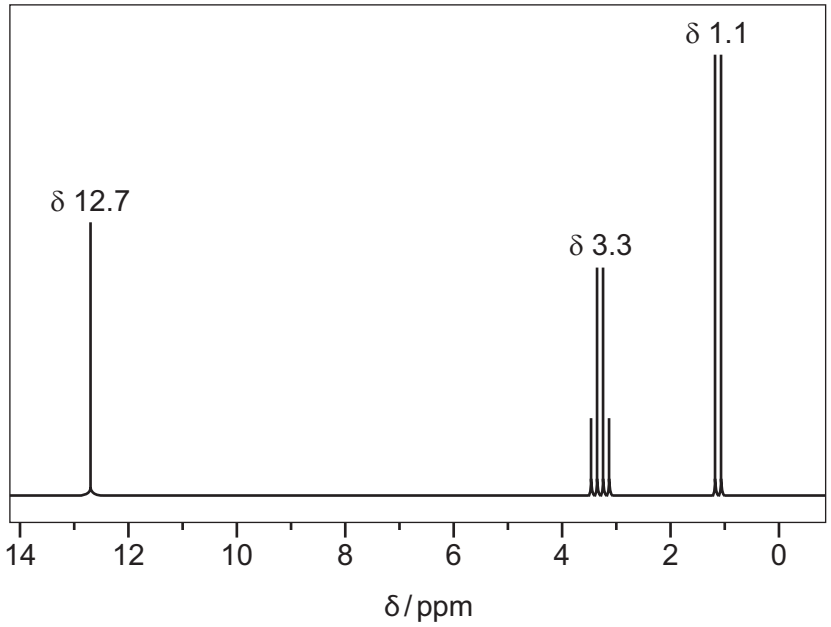
..... [3]

(g) Methylpropanedioic acid is an isomer of butanedioic acid.

methylpropanedioic acid



The proton NMR spectrum of methylpropanedioic acid in CCl_4 is shown.



(i) Identify the protons in the methylpropanedioic acid molecule that are responsible for each area of the proton NMR spectrum.

δ 12.7 .....

δ 3.3 .....

δ 1.1 .....

[2]

(ii) Name the splitting pattern shown at δ 3.3 and explain how it arises.

.....

..... [1]

The carbon-13 NMR spectra of butanedioic acid, $HO_2CCH_2CH_2CO_2H$, and methylpropanedioic acid, $HO_2CCH(CH_3)CO_2H$ are different.

(iii) State the number of peaks

- in the carbon-13 NMR spectrum of butanedioic acid

.....

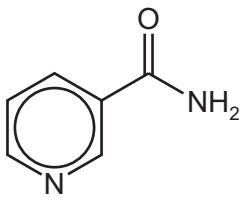
- in the carbon-13 NMR spectrum of methylpropanedioic acid.

.....
[1]

[Total: 14]

9 The structure of nicotinamide is shown.

nicotinamide



(a) The nitrogen atom in the six-membered ring has one electron in an unhybridised p-orbital. This electron becomes delocalised, becoming part of a single delocalised system of electrons. This delocalised system also includes:

- electrons from the carbon atoms in the six-membered ring
- the two electrons in the π bond of the C=O group
- the two electrons in the lone pair on the nitrogen atom of the amide group.

(i) State the number of delocalised electrons in one nicotinamide molecule.

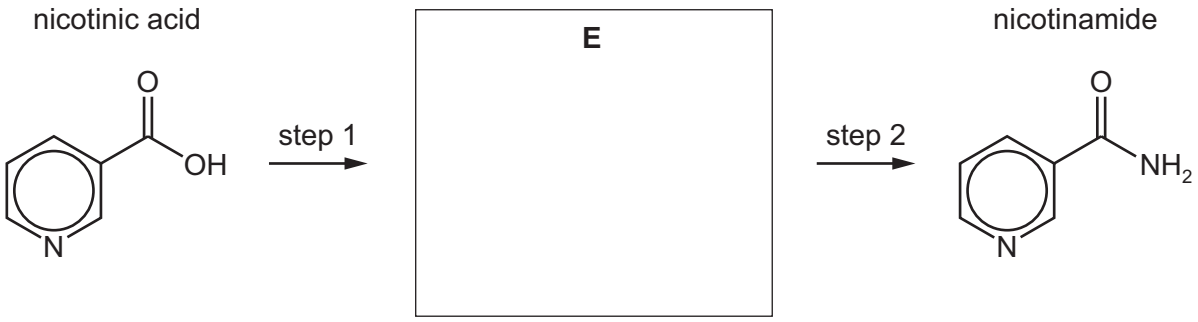
..... [1]

(ii) Predict the H–N–H bond angle in the NH_2 group in nicotinamide.

..... [1]

(b) Nicotinamide can be synthesised from nicotinic acid.

The synthesis involves two steps.



(i) Draw the structural formula of **E** in the box. [1]

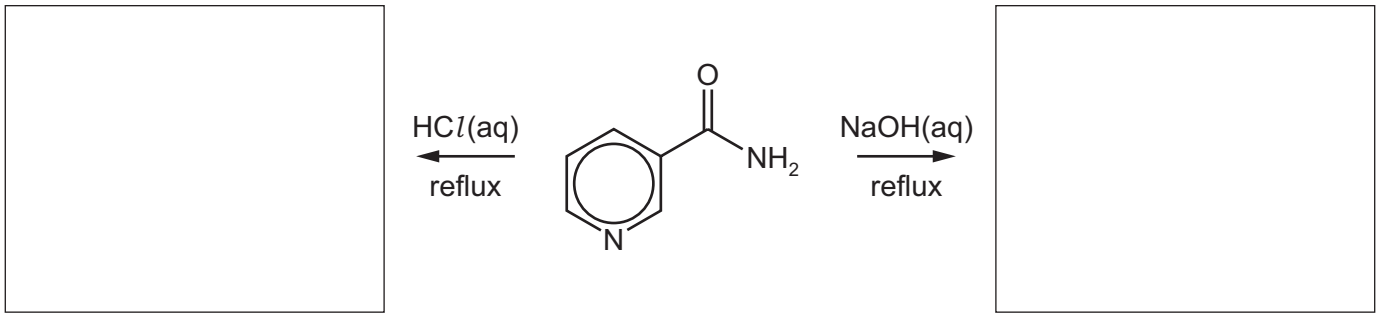
(ii) Give the name or formula of a suitable reagent for step 2.

..... [1]

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(c) Nicotinamide reacts separately with aqueous acid and aqueous alkali. The six-membered ring remains unchanged in these reactions.

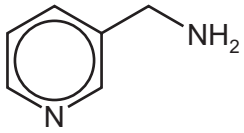
Complete the reaction scheme below to give the structural formula of the organic product of each reaction.



[2]

(d) Nicotinamide can be reduced to compound **X**.

X



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

..... [1]

(ii) Predict and explain the relative basicities of the NH_2 groups in phenylamine, $C_6H_5NH_2$, nicotinamide and compound **X**.

.....

.....

.....

..... [3]

(e) The height of the M peak in a mass spectrum of nicotinamide is 80.

Calculate the expected height of the M+1 peak.

[2]

[Total: 12]

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