Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

8339479569

CHEMISTRY **9701/43**

Paper 4 A Level Structured Questions **October/November 2021**

2 hours

You must answer on the question paper.

You will need: Data booklet

INSTRUCTIONS

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working, use appropriate units and use an appropriate number of significant figures.

INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].

This document has **20** pages. Any blank pages are indicated.

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

1 When dilute sulfuric acid is electrolysed, water is split into hydrogen and oxygen.

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

A current of **x** A is passed through the solution for 14.0 minutes. 462 cm^3 of hydrogen are produced at the cathode, measured under room conditions.

(a) Calculate the number of hydrogen molecules produced during the electrolysis.

number of hydrogen molecules = ... [2]

(b) Calculate the total number of electrons transferred to produce this number of hydrogen molecules.

total number of electrons = ... [1]

(c) Calculate the quantity of charge, in coulombs, of the total number of electrons calculated in **(b)**.

quantity of charge = ... C [1]

(d) Calculate the current, **x**, passed during this experiment.

x = ... A [1]

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(e) The standard entropies, $S^{\ominus}$, of three species are given in the table.

species	$S^{\ominus}$ / J K^{-1} mol^{-1}
$H_2O(l)$	+70
$H_2(g)$	+131
$O_2(g)$	+205

(i) Calculate $\Delta S^{\ominus}$ for the reaction $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$.

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

(ii) $\Delta H^{\ominus}$ for the reaction $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ is +572 kJ mol^{-1}.

Calculate $\Delta G^{\ominus}$ for this reaction at 298 K.

$\Delta G^{\ominus}$ = ... kJ mol^{-1} [2]

(iii) Predict the effect of increasing temperature on the spontaneity of this reaction.
Explain your answer.

.....

..... [1]

[Total: 9]

2 Solution **Y** is hydrochloric acid, HCl(aq). Solution **Z** is aqueous 4-chlorobutanoic acid, Cl(CH_2)$_3$$CO_2$H(aq). The p$K_a$ of Cl(CH_2)$_3$$CO_2$H(aq) is 4.52. The pH of both solutions is 4.00.

(a) (i) Write an expression for the K_a of Cl(CH_2)$_3$$CO_2$H(aq).

K_a =

[1]

(ii) Write a mathematical expression to describe the relationship between K_a and pK_a.

..... [1]

(iii) Calculate [H^+] in solutions **Y** and **Z**.

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

(iv) Calculate the ratio $\frac{\text{[HC}l\text{] dissolved in solution Y}}{\text{[C}l\text{(CH}_2\text{)}_3\text{CO}_2\text{H] dissolved in solution Z}}$.

$\frac{\text{[HC}l\text{] dissolved in solution Y}}{\text{[C}l\text{(CH}_2\text{)}_3\text{CO}_2\text{H] dissolved in solution Z}}$ = ... [2]

(b) A buffer solution of pH 5.00 is produced by adding sodium propanoate to 5.00 g of propanoic acid in 100 cm^3 of distilled water.

Calculate the mass of sodium propanoate that must be used to produce this buffer solution. The K_a of propanoic acid is 1.35×10^{-5} mol dm^{-3}.

[M_r: propanoic acid, 74.0; sodium propanoate, 96.0]

mass of sodium propanoate = ... g [3]

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(c) Some dilute sulfuric acid is mixed with a small sample of the buffer solution described in **(b)**. The final pH of the mixture is close to 1.

Explain this observation.

.....

.....

.....

..... [2]

[Total: 10]

3 **(a)** Define the term *electron affinity*.

.....

..... [2]

(b) Write an equation for the process corresponding to the **second** ionisation energy of calcium. Include state symbols.

..... [1]

Some data relating to calcium and oxygen are listed. Select relevant data from this list for your answers to parts **(c)**, **(d)** and **(e)**.

process	value / kJ mol^{-1}
first ionisation energy of oxygen	+1310
second ionisation energy of oxygen	+3390
first electron affinity of oxygen	–142
second electron affinity of oxygen	+844
enthalpy change for $\frac{1}{2}O_2(g) + 2e^- \rightarrow O^{2-}(g)$	+951
enthalpy change for $Ca(s) \rightarrow Ca^{2+}(g) + 2e^-$	+1933
lattice energy of CaO(s)	–3517

(c) Oxygen exists as O_2 molecules.

Use the data in this question to calculate a value for the bond energy of the O=O bond.
Show all your working.

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

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(d) (i) Suggest why the first electron affinity of oxygen is negative.

.....

..... [1]

(ii) Suggest why the second electron affinity of oxygen is positive.

.....

..... [1]

(e) Calculate the enthalpy of formation of calcium oxide, CaO(s).

enthalpy of formation = ... $kJ\,mol^{-1}$ [2]

(f) The lattice energy of lithium fluoride, LiF(s), is $-1022\,kJ\,mol^{-1}$.

Identify the factor that causes the lattice energy of calcium oxide to be more exothermic than that of lithium fluoride. Explain why this factor causes the difference in lattice energies.

.....

..... [2]

[Total: 12]

4 Separate samples of 0.02 mol of calcium carbonate and 0.02 mol of barium carbonate are heated until completely decomposed to the metal oxide and carbon dioxide.

(a) State which of these two Group 2 carbonates requires the **higher** temperature before it begins to decompose. Explain your answer.

.....

.....

..... [2]

(b) After decomposition is complete, the 0.02 mol sample of calcium oxide is taken and added to 2.00 dm^3 of water. A solution is formed with no solid present. Dilute sulfuric acid is then added dropwise until a precipitate is seen.

The same procedure is repeated with the 0.02 mol sample of barium oxide, using the same concentration solution of dilute sulfuric acid.

Identify the sample to which **most** sulfuric acid must be added to cause a precipitate to appear.

Explain your answer. You should refer to the solubilities of the precipitates and relevant energy terms in your answer.

.....

.....

.....

..... [3]

(c) (i) Calculate the mass, in g, of CO_2 produced by the decomposition of 0.020 moles of calcium carbonate.

mass of CO_2 = ... g [1]

(ii) Calculate the minimum mass, in g, of propane that would, on complete combustion, produce the same mass of CO_2 calculated in **(c)(i)**.
Give your answer to three significant figures.

mass of propane = ... g [2]

[Total: 8]

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5 **(a)** $[MnCl_4]^{2-}$ is a complex ion.

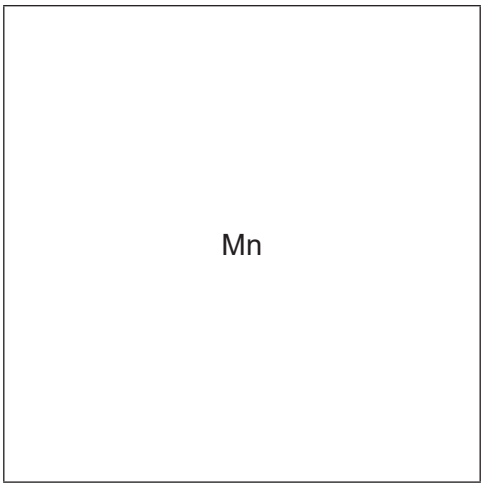
(i) Deduce the oxidation state of manganese in $[MnCl_4]^{2-}$.

oxidation state = ... [1]

(ii) The $[MnCl_4]^{2-}$ complex does **not** contain any 180° bond angles.

Draw a three-dimensional diagram to show the shape of the $[MnCl_4]^{2-}$ complex.

State one bond angle on your diagram.



[2]

(b) A solution of cobalt(II) sulfate contains the complex ion $[Co(H_2O)_6]^{2+}$.

A solution containing $[Co(H_2O)_6]^{2+}$ is reacted separately with an excess of each of NaOH(aq), NH_3(aq) and NaCl(aq).

Write an equation for each of these reactions. State **one** observation that can be made immediately after the reaction, include the colour and state of the cobalt-containing product.

(i) $[Co(H_2O)_6]^{2+}$ and an excess of NaOH(aq)

equation .....

observation .....

[2]

(ii) $[Co(H_2O)_6]^{2+}$ and an excess of NH_3(aq)

equation .....

observation .....

[2]

(iii) $[Co(H_2O)_6]^{2+}$ and an excess of NaCl(aq)

equation .....

observation .....

[2]

(iv) Name the type of reaction that occurs in **(b)(iii)**.

..... [1]

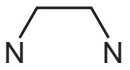
(c) Cobalt forms the complex ion $[Co(NH_3)_2(en)_2]^{2+}$. The abbreviation en is used for the bidentate ligand 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$. The complex ion shows both geometrical and optical isomerism.

(i) Define the term *bidentate ligand*.

.....

..... [2]

(ii) Draw three-dimensional diagrams for the two **optical** isomers of $[Co(NH_3)_2(en)_2]^{2+}$.

Each en ligand can be represented using 

.

Co

Co

[2]

[Total: 14]

6 An excess of sodium iodide is added to a solution of copper(II) sulfate. Iodine and a white precipitate of copper(I) iodide are formed.

(a) Write an equation for the reaction that occurs.

..... [1]

(b) (i) Explain why the copper(II) sulfate solution is coloured.

.....

.....

.....

.....

..... [4]

(ii) Suggest why the precipitate of copper(I) iodide is white.

.....

..... [1]

(c) Use suitable $E^{\ominus}$ values from the *Data Booklet* to predict whether iodide ions can reduce Cu^{2+} to Cu^{+} under standard conditions. Explain your answer.

.....

.....

..... [2]

(d) An excess of sodium iodide is added to copper(II) sulfate solution. Copper(I) iodide forms as a precipitate. After precipitation, $[Cu^{+}]$ is much lower than $1.0\,mol\,dm^{-3}$.

Use this information and your answer to **(c)** to explain how the relevant electrode potentials change and hence why I^{-} ions can reduce Cu^{2+} ions.

.....

.....

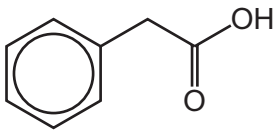
.....

.....

..... [2]

[Total: 10]

7 The structure of phenylethanoic acid is shown.



(a) Give the number of different peaks in the carbon-13 (^{13}C) NMR spectrum of phenylethanoic acid.

number of peaks = ... [1]

(b) Phenylethanoic acid, ethanol and phenol can all behave as acids.

Compare and explain the relative acidities of these three compounds.

..... > ..... > .....
most acidic least acidic

.....

.....

.....

.....

..... [4]

(c) Phenylethanoic acid can be synthesised using benzene as the starting material.

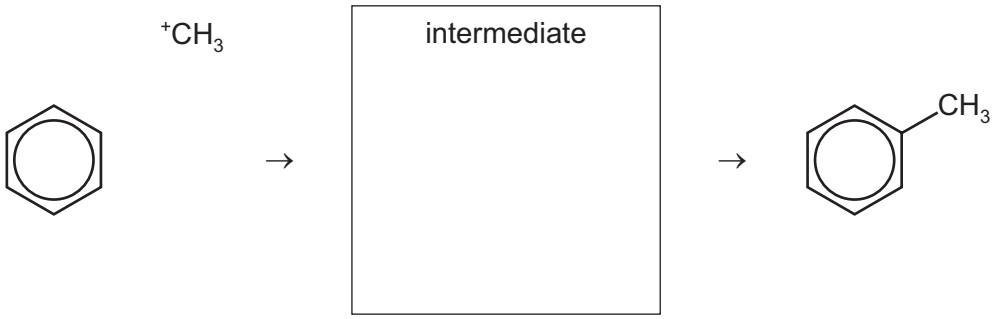
In the first stage of this synthesis, benzene reacts with chloromethane in the presence of an $AlCl_3$ catalyst to form methylbenzene.

Chloromethane reacts with $AlCl_3$ to form two ions. One of these is the carbocation $^+CH_3$.

(i) Write an equation for the reaction between chloromethane and $AlCl_3$.

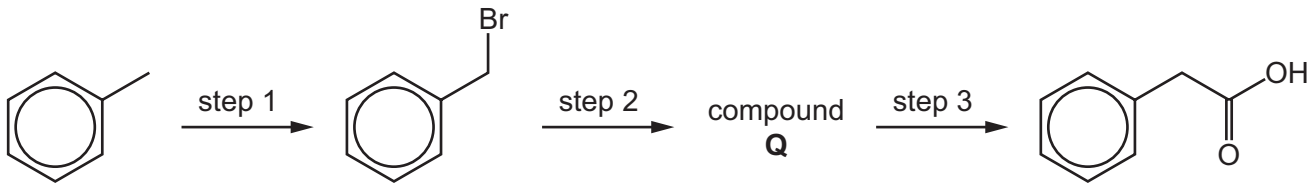
..... [1]

(ii) Draw the mechanism of the reaction between benzene and $^+CH_3$. Include all relevant curly arrows, charges and the structure of the intermediate.



[3]

(d) A three-step synthesis of phenylethanoic acid from methylbenzene is shown.



(i) State reagents and conditions for step 1.

..... [1]

(ii) Suggest the structure of compound **Q**.

[1]

(iii) State reagents and conditions for steps 2 and 3.

step 2 .....

step 3 .....

[2]

(iv) Draw the structure of an organic by-product that forms in step 1.

[1]

[Total: 14]

8 Phenylamine, $C_6H_5NH_2$, and ethylamine, $C_2H_5NH_2$, can be distinguished by adding aqueous bromine.

(a) State what is seen when aqueous bromine is added to phenylamine.

.....

..... [2]

(b) Suggest what is seen when aqueous bromine is added to ethylamine.

..... [1]

(c) Draw the structure of the organic product formed when an excess of aqueous bromine is added to phenylamine.

[1]

(d) Name the product you have drawn in **(c)**.

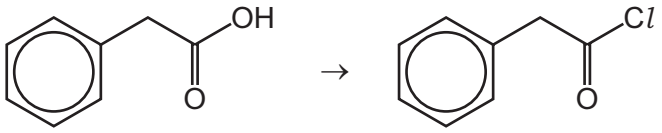
..... [1]

[Total: 5]

9 Compound **T** is made by a three-stage synthesis.

(a) In stage 1, phenylethanoic acid reacts with a suitable reagent to form compound **R**.

phenylethanoic acid **R**

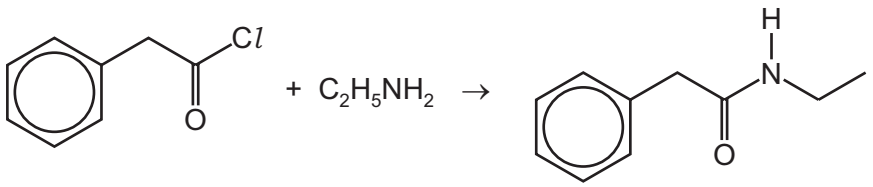
stage 1 

Suggest a suitable reagent for stage 1.

..... [1]

(b) In stage 2, compound **R** reacts with ethylamine to form compound **S**.

R **S**

stage 2 

(i) Name the functional group formed in stage 2.

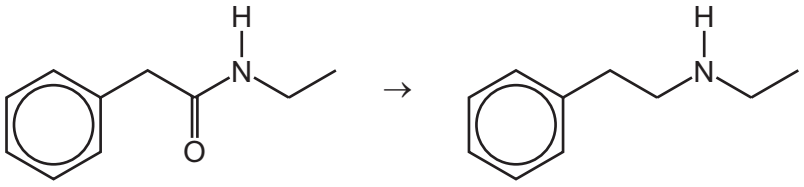
..... [1]

(ii) Identify the other product formed in stage 2.

..... [1]

(c) In stage 3, compound **S** reacts with a suitable reagent to form compound **T**.

S **T**

stage 3 

(i) State the formula of a suitable reagent for stage 3.

..... [1]

(ii) Name the type of reaction that occurs in stage 3.

..... [1]

(d) The relative abundance of the molecular ion peak in the mass spectrum of ethylamine is 62.

(i) Calculate the relative abundance of the M+1 peak in the mass spectrum of ethylamine.

relative abundance = ... [1]

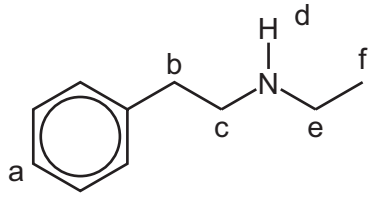
(ii) The mass spectrum of compound **T** contains several fragments. The *m*/*e* values of two of these fragments are 29 and 91.

Draw the structures of the ions responsible for these peaks.

m/*e*	structure of ion
29	
91	

[2]

(e) The proton (^{1}H) NMR spectrum of compound **T** shows hydrogen atoms in different environments. Six of these environments are shown on the structure using letters a, b, c, d, e and f.



Use the letters a, b, c, d, e and f to answer the questions that follow. The questions relate to the proton (^{1}H) NMR spectrum of **T**.

Proton d does not cause splitting of the peaks for protons c or e under the conditions used.

Each answer may be one, or more than one, of the letters a, b, c, d, e and f.

(i) Identify the proton or protons with a chemical shift (δ) in the range 6.0 to 9.0.

..... [1]

(ii) Identify the proton or protons whose peak will disappear if D_2O is added.

..... [1]

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(iii) Identify the proton or protons whose peak is a triplet.

..... [1]

(iv) Identify the proton or protons with the lowest chemical shift (δ).

..... [1]

[Total: 12]

10 Valine (Val) and lysine (Lys) are amino acids. The structures of these amino acids can be found in the *Data Booklet*.

The isoelectric point of an amino acid is the pH at which it exists as a zwitterion. The isoelectric point of valine is 6.0. The isoelectric point of lysine is 9.7.

(a) Draw the structure of valine at pH 6.0.

[1]

(b) A solution of lysine is produced with pH 9.7. Dilute sulfuric acid is added slowly until the pH of the solution is 1.0. The sulfuric acid reacts with lysine to produce different organic ions that are not present in significant concentrations at pH 9.7.

Draw the structures of three of the organic ions that form during the addition of sulfuric acid in the boxes. Draw the organic ion present at pH 1.0 in box C.

A	B	C (pH 1.0)

[3]

(c) Draw the structure of the dipeptide Val-Lys. The peptide bond should be shown fully displayed.

[2]

[Total: 6]

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