

CANDIDATE
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9701/41

October/November 2020

2 hours

You must answer on the question paper.

You will need: Data booklet

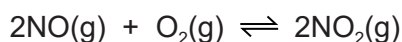
- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction 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.

- 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 **24** pages. Blank pages are indicated.

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

- 1 Nitrogen monoxide, NO, reacts with oxygen to form nitrogen dioxide, NO₂.



The rate equation for the forward reaction is shown.

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

- (a) Complete the following table.

the order of reaction with respect to [NO]	
the order of reaction with respect to [O ₂]	
the overall order of reaction	

[1]

- (b) Two separate experiments are carried out at 30 °C to determine the rate of the forward reaction.

experiment	[NO]/mol dm ⁻³	[O ₂]/mol dm ⁻³	rate/mol dm ⁻³ s ⁻¹
1	0.00300	0.00200	1.51×10^{-4}
2		0.00500	6.05×10^{-5}

- (i) Use the data for experiment 1 to calculate the value of the rate constant, k . State the units of k .

$k = \dots\dots\dots$ units = $\dots\dots\dots$
[2]

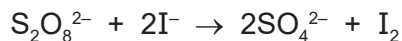
- (ii) Calculate the value of [NO] in experiment 2.

[NO] = $\dots\dots\dots$ mol dm⁻³ [1]

- (c) Define the term *rate-determining step*.

$\dots\dots\dots$ [1]

- (d) Peroxodisulfate ions, $\text{S}_2\text{O}_8^{2-}$, react with iodide ions, I^- .



The rate equation for the reaction in the absence of any catalyst is shown.

$$\text{rate} = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$$

- (i) Suggest equations for a two-step mechanism for this reaction, stating which of the two steps is the rate-determining step.

step 1

step 2

rate-determining step = ...

[2]

- (ii) A large excess of peroxodisulfate ions is mixed with iodide ions. Immediately after mixing, $[\text{I}^-] = 0.00780 \text{ mol dm}^{-3}$. Under the conditions used, the half-life of $[\text{I}^-]$ is 48 seconds.

Calculate the iodide ion concentration 192 seconds after the peroxodisulfate and iodide ions are mixed.

iodide ion concentration = ... mol dm^{-3} [1]

[Total: 8]

- 2 (a) The lattice energies of three ionic compounds are given.

compound	lattice energy / kJ mol^{-1}
LiF(s)	–1022
CaO(s)	–3513
SrO(s)	–3310

- (i) Define the term *lattice energy*.

.....

 [2]

- (ii) Explain why the lattice energy of CaO is more exothermic than the lattice energy of LiF.

.....

 [1]

- (iii) Use the data in the table to estimate approximate values for the lattice energies of magnesium oxide and barium oxide.

$$\Delta H_{\text{latt}} \text{MgO(s)} = \dots\dots\dots \text{kJ mol}^{-1}$$

$$\Delta H_{\text{latt}} \text{BaO(s)} = \dots\dots\dots \text{kJ mol}^{-1}$$

[1]

- (b) (i) Write an equation for the reaction between BaO and H_2O .
 Include state symbols.

..... [1]

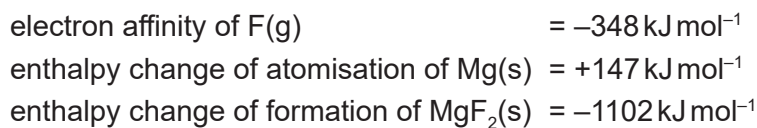
- (ii) State and explain how the solubilities of the hydroxides of the Group 2 elements vary down the group.

.....

 [4]

- (c) Use the following data and relevant data from the *Data Booklet* to calculate a value for the lattice energy of magnesium fluoride, $\text{MgF}_2(\text{s})$.

You might find it helpful to construct an energy cycle.
Show your working.



$$\Delta H_{\text{latt}} \text{MgF}_2(\text{s}) = \dots\dots\dots [3]$$

- (d) (i) Define the term *electron affinity*.

.....
 [2]

- (ii) The electron affinity of carbon, $\text{C}(\text{g})$, is -120 kJ mol^{-1} .

Suggest an explanation for the difference between the electron affinity of fluorine and the electron affinity of carbon.

.....

 [1]

[Total: 15]

- 3 (a) Identify the substances liberated at the anode and at the cathode during the electrolysis of aqueous sodium sulfate, $\text{Na}_2\text{SO}_4(\text{aq})$.

anode

cathode

[1]

- (b) When molten sodium chloride is electrolysed, chlorine is liberated at the anode and sodium is liberated at the cathode.

A sample of molten sodium chloride is electrolysed for 1.50 hours using a current of 4.50A.

Calculate the volume of chlorine and the mass of sodium that are liberated under room conditions.

volume of chlorine = ... dm^3

mass of sodium = ... g
[4]

- (c) The equation representing the standard electrode potential, E° , for the reduction of $\text{MnO}_4^-(\text{aq})$ to $\text{Mn}^{2+}(\text{aq})$ in acid solution is given.



- (i) Draw a diagram of the apparatus that would be used to measure the E° value of this half-cell. Your diagram should be fully labelled to identify all apparatus, substances and conditions.

[4]

- (ii) Use the *Data Booklet* to identify a substance that could be used to oxidise Mn^{2+} ions to MnO_4^- ions under standard conditions.

Write an equation for the reaction.

.....

 [2]

[Total: 11]

- 4 (a) (i) Give the mathematical expression for each of the terms pH and K_w .

pH = ...

K_w = ...

[2]

- (ii) Calculate the pH of $0.027 \text{ mol dm}^{-3} \text{ NaOH(aq)}$.

pH = ... [1]

- (b) The K_a value of chloric(I) acid, HClO , is $3.72 \times 10^{-8} \text{ mol dm}^{-3}$.

Calculate the pH of $0.010 \text{ mol dm}^{-3} \text{ HClO(aq)}$.

pH = ... [1]

- (c) Water and octan-1-ol form two layers when mixed.

Ethanamide is more soluble in water than it is in octan-1-ol. When 1.00 g of ethanamide is added to 50.0 cm^3 of water and this is then shaken with 50.0 cm^3 of octan-1-ol, it is found that the water layer contains 0.935 g of ethanamide at equilibrium.

- (i) Calculate the partition coefficient, K_{pc} , for ethanamide in water and octan-1-ol.

K_{pc} = ... [1]

- (ii) The 50.0 cm^3 of water containing 0.935 g of ethanamide is then shaken with 100.0 cm^3 of pure octan-1-ol under the same conditions.

Calculate the mass of ethanamide that is dissolved in the 100.0 cm^3 of octan-1-ol at equilibrium.

mass of ethanamide = ... g
[2]

[Total: 7]

- 5 A solution is made by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in an excess of aqueous ammonia. This solution contains the copper complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

(a) (i) Write an expression for the K_{stab} of $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

$$K_{\text{stab}} =$$

[1]

(ii) State the colour of the solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

..... [1]

The solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is heated gently in a fume cupboard so that NH_3 is released. Some NH_3 remains in solution and some forms NH_3 gas. The colour of the solution changes; a precipitate of $\text{Cu}(\text{OH})_2$ forms and is collected.

A sample of $\text{Cu}(\text{OH})_2$ is added to concentrated hydrochloric acid. A reaction takes place forming a coloured copper complex, **Y**.

A sample of $\text{Cu}(\text{OH})_2$ is added to dilute sulfuric acid. A reaction takes place forming a coloured copper complex, **Z**.

$[\text{Cu}(\text{NH}_3)_4]^{2+}$, **Y** and **Z** are different colours.

(b) Suggest an equation for the reaction of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ to form $\text{Cu}(\text{OH})_2$ as the aqueous solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is heated.

..... [1]

(c) Suggest an equation for the reaction of $\text{Cu}(\text{OH})_2$ with concentrated hydrochloric acid, forming **Y**.

..... [2]

(d) Complete the table with the colour and geometry of complex **Y** and the colour, geometry and formula of complex **Z**.

	Y	Z
colour of complex		
geometry of complex		
formula of complex		

[2]

(e) Explain why complexes **Y** and **Z** are coloured and why their colours are different.

.....

.....

.....

.....

.....

.....

.....

..... [5]

[Total: 12]

- 6 (a) When $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3(\text{aq})$ is added to a solution containing $\text{Ag}^+(\text{aq})$ ions, a linear complex, **P**, is formed. $\text{S}_2\text{O}_3^{2-}$ ions are present in **P** as monodentate ligands.

(i) Define the term *monodentate ligand*.

.....
 [2]

(ii) Give the formula of **P**, including its charge.

..... [1]

- (b) When $1.0 \text{ mol dm}^{-3} \text{ NaCN}(\text{aq})$ is added to a solution of **P**, a mixture which includes a second linear complex, **Q**, is formed. In this mixture the concentration of **Q** is much greater than the concentration of **P**.

(i) Write an equation for the reaction that occurs when $\text{NaCN}(\text{aq})$ is added to a solution of **P**.

..... [1]

(ii) Suggest a reason why the concentration of **Q** is much greater than the concentration of **P** in the mixture.

.....

 [1]

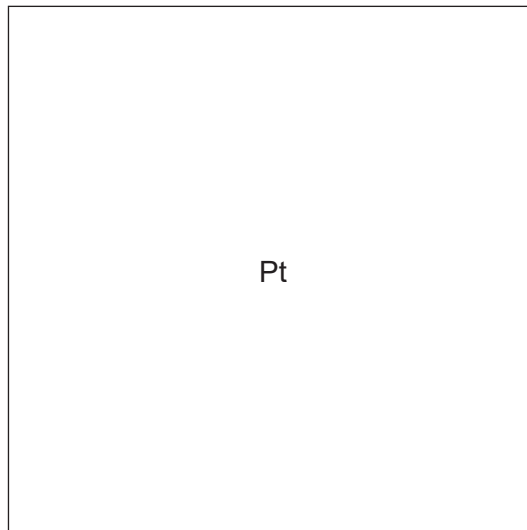
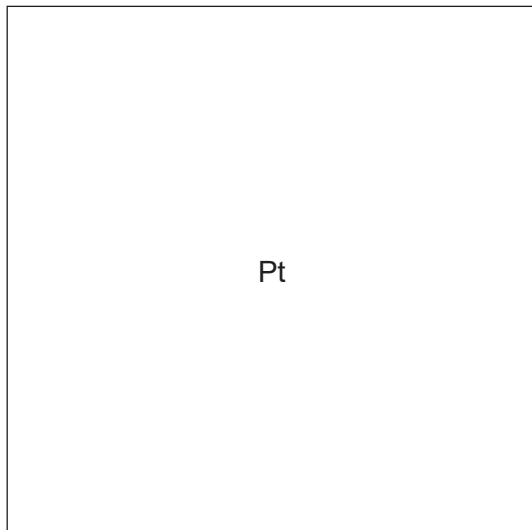
(iii) Name the type of reaction in which **P** forms **Q**.

..... [1]

(c) Platinum forms a complex ion with the formula $[\text{Pt}(\text{CN})_2\text{Cl}_2]^{2-}$. In this complex ion the carbon atom of each CN^- ligand bonds to the platinum ion. This complex shows stereoisomerism.

(i) There are only two isomers of this complex.

Draw structures of these two isomers in the boxes below.



[1]

(ii) Describe the geometry of $[\text{Pt}(\text{CN})_2\text{Cl}_2]^{2-}$.

..... [1]

(iii) Name the type of stereoisomerism shown by $[\text{Pt}(\text{CN})_2\text{Cl}_2]^{2-}$.

..... [1]

[Total: 9]

7 Phenol, $\text{C}_6\text{H}_5\text{OH}$, is a weak acid.

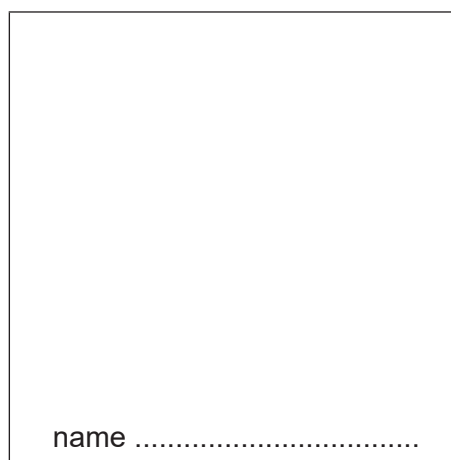
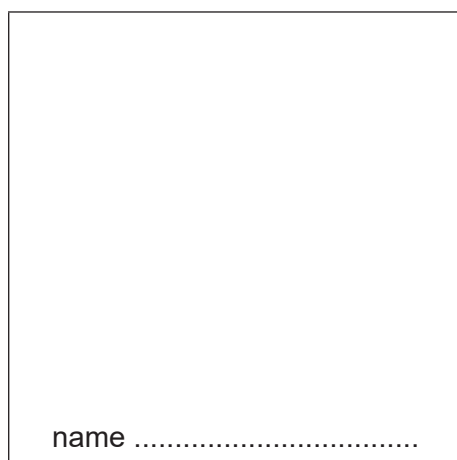
(a) Phenol can be made from phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$.

Give the reagents and conditions for this reaction.

.....
..... [2]

(b) Phenol reacts with dilute aqueous nitric acid under room conditions to give a mixture of two isomeric products with molecular formula $\text{C}_6\text{H}_5\text{NO}_3$.

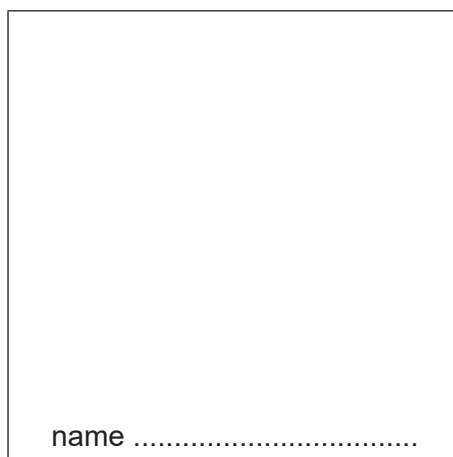
Use the *Data Booklet* to draw the structural formulae of these two products in the boxes and name each product.



[2]

(c) Phenol reacts with an excess of aqueous bromine.

(i) Draw and name the organic product of this reaction in the box.



[2]

- (ii) Describe **two** visual observations that can be made when phenol reacts with an excess of aqueous bromine.

observation 1

observation 2

[1]

- (d) Write an equation for a neutralisation reaction in which phenol behaves as an acid.

..... [1]

- (e) Water, phenol and ethanol can all behave as acids.

Place these three compounds in order of acidity, starting with the **most** acidic.
Explain your answer.

..... > >
most acidic least acidic

.....
.....
.....
.....
.....
.....

[3]

[Total: 11]

8 Benzene, C_6H_6 , can be obtained from crude oil.

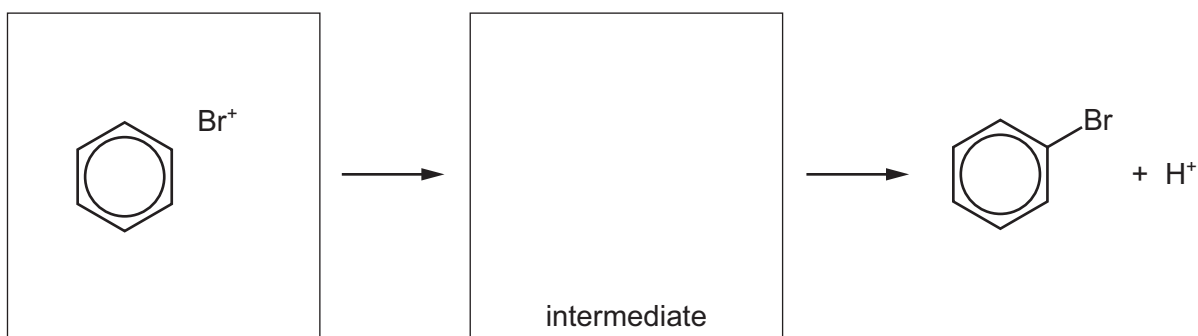
(a) Benzene reacts with bromine, in the presence of a suitable catalyst, forming bromobenzene as one product.

(i) Give the name or formula of the other product of this reaction.

..... [1]

(ii) In the presence of the catalyst, bromine can be considered to form the electrophile Br^+ .

Complete the mechanism by which benzene reacts with Br^+ , using curly arrows to show the movement of electron pairs.

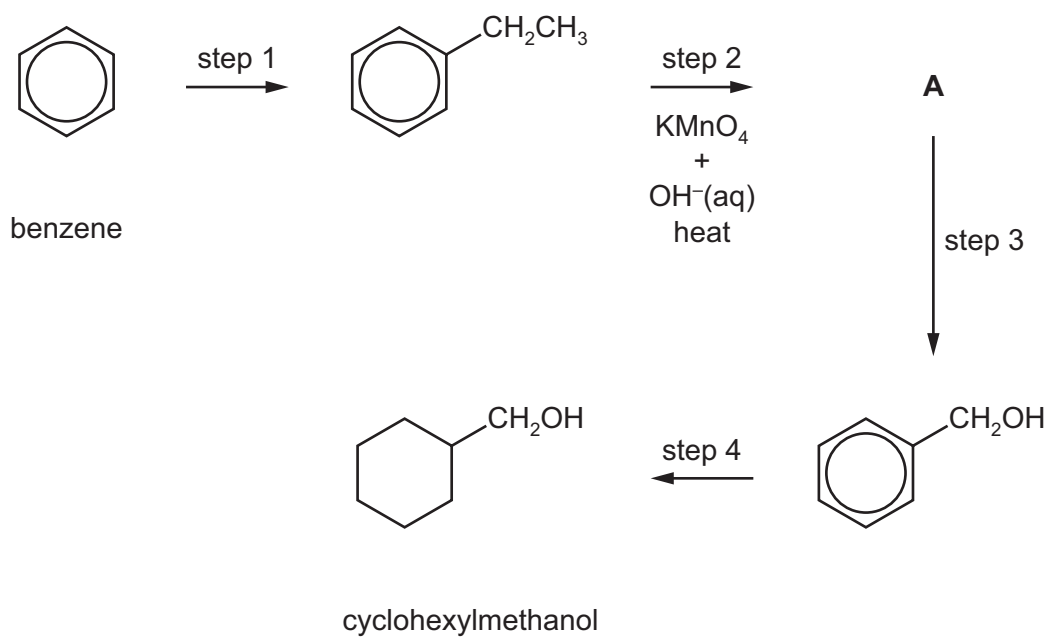


[2]

(iii) Name this mechanism.

..... [1]

- (b) Benzene can be used as a starting material in the synthesis of cyclohexylmethanol, $\text{C}_6\text{H}_{11}\text{CH}_2\text{OH}$, as outlined below.



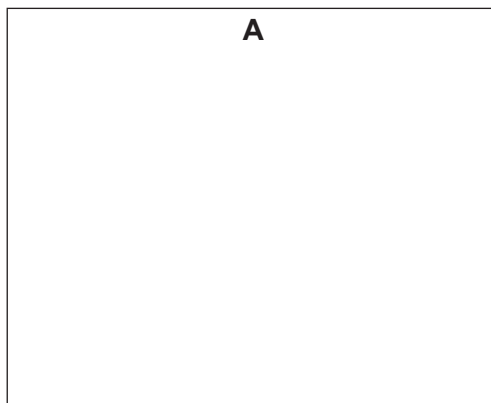
- (i) Identify a suitable reagent and a suitable catalyst for step 1.

reagent

catalyst

[2]

- (ii) Draw the structure of **A**.



[1]

(iii) Identify suitable reagents for steps 3 and 4.

step 3

step 4

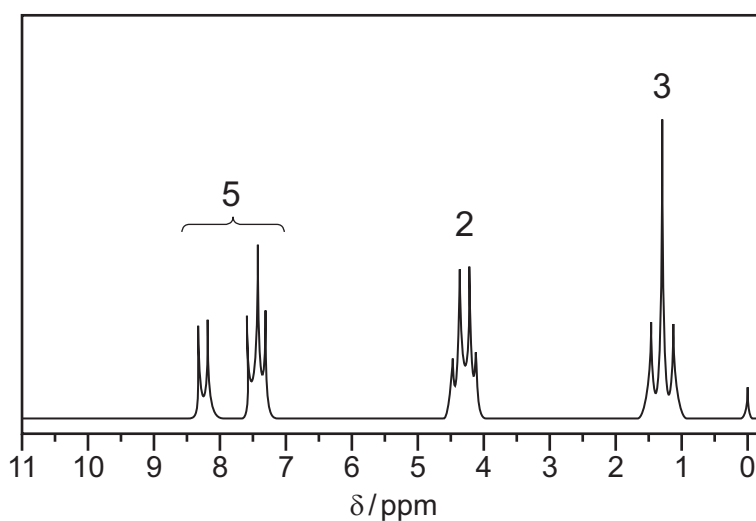
[2]

(iv) Deduce the number of peaks in the carbon-13 NMR spectrum of cyclohexylmethanol.

..... [1]

[Total: 10]

- 9 The proton NMR spectrum of compound **E** in the solvent CDCl_3 is shown. The molecular formula of compound **E** is $\text{C}_9\text{H}_{10}\text{O}_2$.



- (a) Explain why CDCl_3 is used as a solvent instead of CHCl_3 .

..... [1]

- (b) Explain why TMS is added to give the small peak at chemical shift $\delta = 0$.

..... [1]

- (c) Compound **E** is hydrolysed by hot NaOH(aq) , giving two organic products only. One of these products is ethanol.

Name the functional group in compound **E** that is hydrolysed by hot NaOH(aq) .

..... [1]

- (d) (i) Describe and explain the splitting patterns of the peaks at $\delta = 1.4$ and $\delta = 4.3$.

splitting pattern at $\delta = 1.4$

reason for splitting pattern at $\delta = 1.4$

splitting pattern at $\delta = 4.3$

reason for splitting pattern at $\delta = 4.3$

[2]

- (ii) Each molecule of compound **E** contains five protons which give rise to the peaks between $\delta = 7.0$ and $\delta = 8.5$.

Identify the functional group in compound **E** which contains these protons.

..... [1]

(iii) Give the structural formula of compound **E**.

[1]

(e) The mass spectrum of compound **E** includes fragment ions with m/e values of 29 and 77.

Give the formulae of these fragment ions.

fragment ion with $m/e = 29$

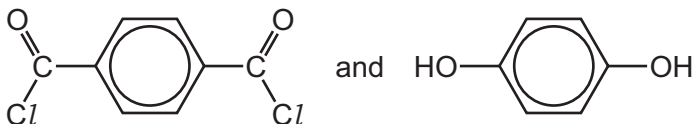
fragment ion with $m/e = 77$

[2]

[Total: 9]

- 10 (a) The table shows three pairs of monomers that are capable of polymerisation.

Complete the table by identifying each type of polymerisation.

pair of monomers	type of polymerisation
$\text{HOCH}_2\text{CH}_2\text{OH}$ and $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$	
	
CH_3CHCF_2 and CH_3CHCH_2	

[1]

- (b) 2-aminopropanoic acid, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, can polymerise under suitable conditions. No other monomer is involved in this reaction.

- (i) Draw a section of the polymer chain formed including **three** monomer residues. Clearly identify **one** repeat unit on your diagram.

[3]

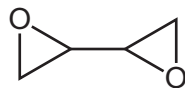
- (ii) 2-aminopropanoic acid, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, exists as two stereoisomers.

Draw three-dimensional diagrams to show the two stereoisomers of 2-aminopropanoic acid. State the type of stereoisomerism shown.

type of stereoisomerism

[2]

(c) The skeletal formula of compound **W** is shown.



When **W** is mixed with a second compound, called a hardener, a polymerisation reaction occurs, producing a non-solvent-based adhesive.

(i) Give the name of this type of non-solvent-based adhesive.

..... [1]

(ii) The hardener is a diamine. A diamine has an alkyl chain with two amine groups which are not bonded to the same carbon atom.

Draw the structural formula of a compound that would make a suitable hardener.

[1]

[Total: 8]

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Cambridge International AS & A Level

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CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

October/November 2020

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.
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- 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 [].

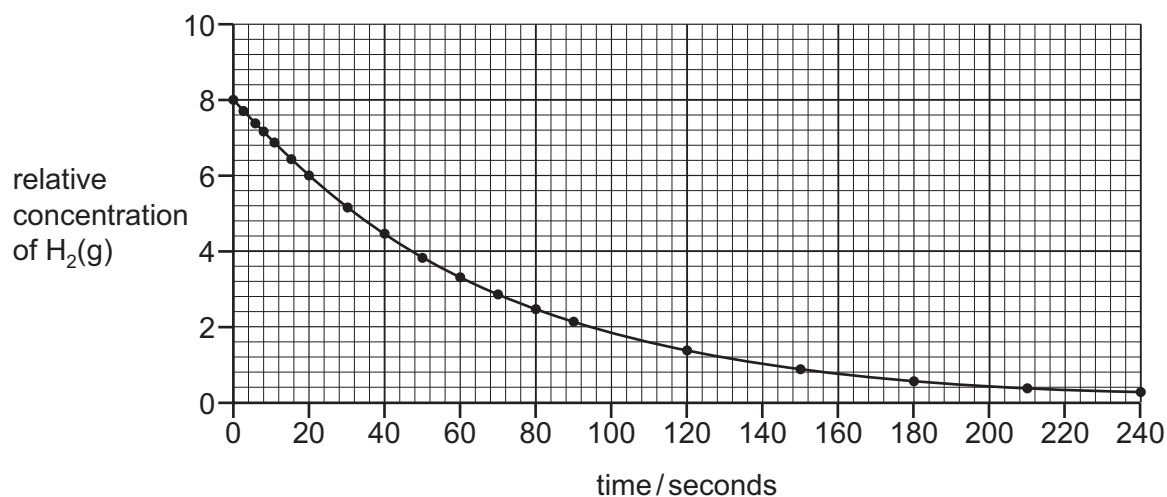
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Answer **all** the questions in the spaces provided.

1 The rate of the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ is studied.

(a) A small amount of $\text{H}_2(\text{g})$ is mixed with a large excess of $\text{I}_2(\text{g})$ at a temperature of 400 K and the reaction is monitored. The graph obtained is shown.



(i) Suggest why a large excess of $\text{I}_2(\text{g})$ is used in this experiment.

..... [1]

(ii) The reaction is first order with respect to $\text{H}_2(\text{g})$.

Use data from the graph to confirm this statement.

.....

.....

.....

..... [2]

- (b) Three separate experiments were carried out at 400 K with different starting concentrations of $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$. The results are shown in the table.

experiment	$[\text{H}_2(\text{g})]/\text{mol dm}^{-3}$	$[\text{I}_2(\text{g})]/\text{mol dm}^{-3}$	rate of reaction $/\text{mol dm}^{-3}\text{s}^{-1}$
1	1.0×10^{-2}	1.0×10^{-2}	2.0×10^{-17}
2	1.0×10^{-1}	1.0×10^{-1}	2.0×10^{-15}
3	5.0×10^{-1}	5.0×10^{-1}	5.0×10^{-14}

- (i) Use the data, and the order of reaction with respect to $\text{H}_2(\text{g})$ given in (a)(ii), to deduce the order of reaction with respect to $\text{I}_2(\text{g})$.

Explain your answer, giving data in support of your explanation.

.....

 [3]

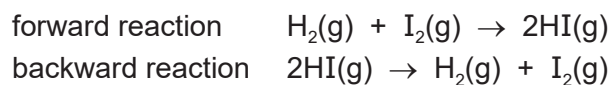
- (ii) Use information from (a)(ii) and your answer to (b)(i) to write the rate equation for the forward reaction.

rate = ... [1]

- (iii) Use your rate equation and data from experiment 1 to calculate the value of the rate constant, k , for the forward reaction at 400 K. Include units for k .

$k = \dots\dots\dots$ units = ... [2]

- (c) At 400 K the rate constant for the forward reaction is approximately 1000 times greater than the rate constant for the backward reaction. The overall orders of the forward and backward reactions are the same.



- (i) Use this information to explain what will happen if equal concentrations of $\text{HI}(\text{g})$, $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ are mixed at 400 K.

You should comment on:

- the relative initial rates of the forward and backward reactions
- the position of the equilibrium reached.

.....

 [1]

- (ii) At 700 K the rate constant for the forward reaction is approximately 50 times greater than the rate constant for the backward reaction.

Use this information and the information in (c)(i) to deduce the signs of the ΔH values of the forward and backward reactions. Explain your answer.

.....

 [2]

[Total: 12]

- 2 (a) Write an expression for the K_a of the weak acid HA in terms of the concentrations of the species involved.

$$K_a =$$

[1]

- (b) The hydroxylammonium ion, HONH_3^+ , is a weak acid. A $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ solution of hydroxylammonium ions has a pH of 4.41.

- (i) Calculate the K_a of HONH_3^+ .

$$K_a = \dots\dots\dots [2]$$

- (ii) Calculate the $\text{p}K_a$ of HONH_3^+ .

$$\text{p}K_a = \dots\dots\dots [1]$$

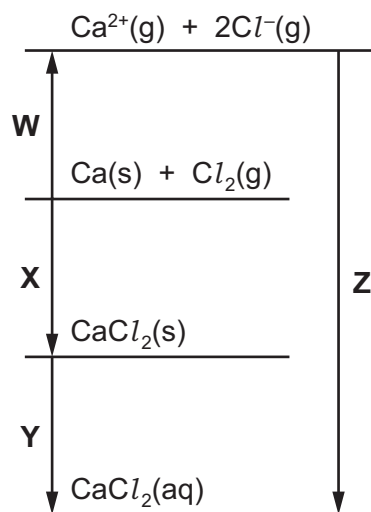
- (c) The solubility product of manganese(II) hydroxide, Mn(OH)_2 , in water is $1.1 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$ at 298 K.

Calculate the solubility of Mn(OH)_2 in water at 298 K.

$$\text{solubility} = \dots\dots\dots \text{mol dm}^{-3} [2]$$

[Total: 6]

- 3 (a) The energy cycle shown can be used, along with suitable data, to calculate the enthalpy change of hydration of $\text{Ca}^{2+}(\text{g})$. Each arrow indicates a transformation, **W**, **X**, **Y** and **Z**. Each transformation consists of one or more steps.



The following data and data from the *Data Booklet* should be used.

electron affinity of $\text{Cl}(\text{g})$	$= -349 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of $\text{Ca}(\text{s})$	$= +193 \text{ kJ mol}^{-1}$
enthalpy change of formation of $\text{CaCl}_2(\text{s})$	$= -795 \text{ kJ mol}^{-1}$
enthalpy change of solution of $\text{CaCl}_2(\text{s})$	$= -83 \text{ kJ mol}^{-1}$
enthalpy change of hydration of $\text{Cl}^{-}(\text{g})$	$= -364 \text{ kJ mol}^{-1}$

- (i) Calculate the value of the enthalpy change corresponding to transformation **W**. Show your working.

enthalpy change **W** = ... kJ mol^{-1} [2]

- (ii) Use your answer to (a)(i) and other data to calculate the value of the enthalpy change corresponding to transformation **Z**.

enthalpy change **Z** = ... kJ mol^{-1} [2]

- (iii) Use your answer to (a)(ii) to calculate the enthalpy change of hydration of $\text{Ca}^{2+}(\text{g})$.

enthalpy change of hydration of $\text{Ca}^{2+}(\text{g}) = \dots\dots\dots \text{kJ mol}^{-1}$ [2]

- (iv) Write an expression, in terms of **W**, **X**, **Y** and/or **Z**, to show how the enthalpy changes of **two** of the transformations can be used to calculate the lattice energy of $\text{CaCl}_2(\text{s})$.

lattice energy of $\text{CaCl}_2(\text{s}) = \dots\dots\dots$ [1]

- (v) State whether the lattice energy of $\text{CaCl}_2(\text{s})$ is more or less exothermic than the lattice energy of $\text{MgF}_2(\text{s})$.

Explain your answer.

.....

 [1]

- (b) The sulfates of the Group 2 elements vary in solubility down Group 2.

- (i) Give the names of **two** solutions that could be mixed to form barium sulfate.

..... [1]

- (ii) State and explain how the solubilities of the sulfates of the Group 2 elements vary down Group 2.

.....

 [4]

[Total: 13]

- 4 (a) Identify the substances liberated at the anode and at the cathode during the electrolysis of saturated KCl(aq) .

at the anode

at the cathode

[1]

- (b) When dilute sulfuric acid is electrolysed, oxygen is liberated at the anode.

Dilute sulfuric acid is electrolysed for 15.0 minutes using a current of 0.750 A.

Calculate the volume of oxygen that is liberated under room conditions.

volume of oxygen = ... cm^3 [3]

- (c) The halogens chlorine, bromine and iodine differ in their strengths as oxidising agents. These strengths are indicated by the E° values for these halogens.

- (i) Give the E° values for chlorine, bromine and iodine acting as oxidising agents.

..... [1]

- (ii) Deduce which of chlorine, bromine and iodine will react with a solution of $\text{Sn}^{2+}(\text{aq})$ under standard conditions.

Explain your answer. Include a relevant equation in your explanation.

.....

.....

..... [3]

- (iii) An excess of chlorine is added to a solution of acidified $\text{Mn}^{2+}(\text{aq})$ under standard conditions.

Give the formula of the product of this reaction that contains manganese.

..... [1]

(d) An electrochemical cell can be made by connecting an $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell to an $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$ half-cell under standard conditions.

(i) Calculate the standard cell potential of this electrochemical cell.

$$E_{\text{cell}}^{\ominus} = \dots\dots\dots \text{V} \quad [1]$$

(ii) State the material that should be used as the electrode in each half-cell.

in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell

in the $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$ half-cell [1]

(iii) Describe **one** change to each half-cell that would **increase** the value of the cell potential. The temperature should remain at 298 K.

$\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell

.....

$\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$ half-cell

.....

[1]

[Total: 12]

- 5 (a) Define the term *transition element*.

.....
 [1]

- (b) (i) Complete the electronic configuration of an isolated gaseous Fe^{3+} ion.

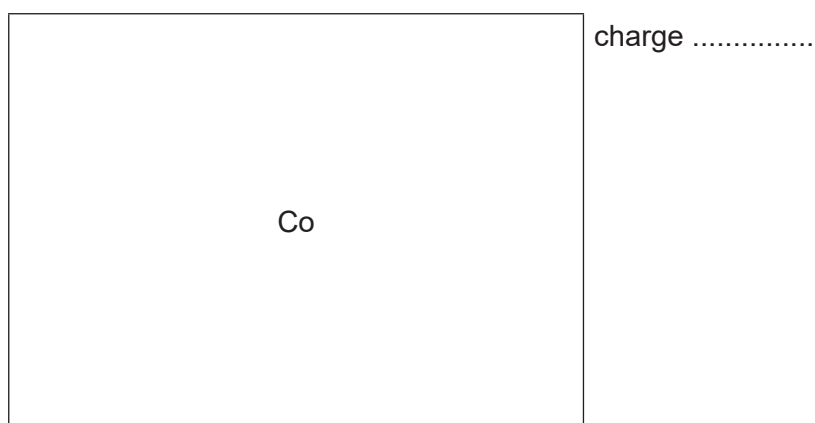
$1s^2$ [1]

- (ii) Name **two** transition elements whose isolated gaseous **atoms** have the same number of electrons in the 3d subshell as an isolated gaseous Fe^{3+} ion.

..... [1]

- (c) Cobalt(II) sulfate is added to water to form a pink solution containing complex ion **P**. An excess of concentrated hydrochloric acid is added to this solution to form a blue solution containing complex ion **Q**.

- (i) Complete the diagram to show the three-dimensional structure of **Q**.
 State the charge on this complex ion.



[2]

- (ii) Name the type of reaction in which **P** forms **Q**.

..... [1]

- (iii) Explain why solutions that contain transition element ions are often coloured.

.....

 [4]

- (iv) Explain why the colours of **P** and **Q** are different.

.....

 [2]

- (d) A solution of the bidentate ligand 1,2-diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, is added to an aqueous solution of cobalt(II) sulfate. Oxygen is then bubbled into the mixture forming a complex ion with the formula $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$.

This complex ion exists as a mixture of two isomers. The geometry of both of these isomeric complexes is octahedral.

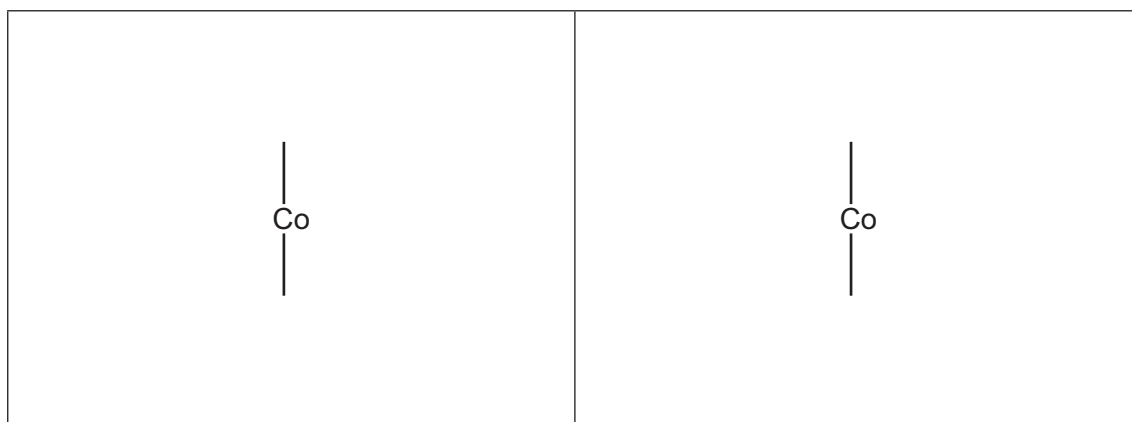
- (i) In this reaction, cobalt undergoes **two** types of reaction. One type of reaction is the same as that described in (c)(ii).

Name the **other** type of reaction that cobalt undergoes.

..... [1]

- (ii) Draw the three-dimensional structures of the two isomeric complexes in the boxes.

You may use $\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \end{array} \text{N}$ to represent a molecule of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.



[2]

- (iii) Name the type of stereoisomerism shown by these two isomeric complexes.

..... [1]

- (iv) State the co-ordination number of cobalt in these two isomeric complexes.

..... [1]

- (e) The stability constants, K_{stab} , of three complexes of mercury(II) are given in the table.

complex	K_{stab}
$[\text{Hg}(\text{CN})_4]^{2-}$	2.5×10^{41}
$[\text{HgCl}_4]^{2-}$	1.7×10^{16}
$[\text{HgI}_4]^{2-}$	2.0×10^{30}

- (i) Write an expression for the K_{stab} of $[\text{Hg}(\text{CN})_4]^{2-}$.

$$K_{\text{stab}} =$$

[1]

- (ii) An aqueous solution containing Hg^{2+} is added to a solution containing equal concentrations of $\text{CN}^-(\text{aq})$, $\text{Cl}^-(\text{aq})$ and $\text{I}^-(\text{aq})$. The mixture is left to reach equilibrium.

Predict which of the complexes $[\text{Hg}(\text{CN})_4]^{2-}$, $[\text{HgCl}_4]^{2-}$ and $[\text{HgI}_4]^{2-}$ is present in the resulting mixture in the highest concentration and which is present in the lowest concentration. Explain your answer.

.....

.....

.....

..... [2]

[Total: 20]

- 6 (a)** Ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$ and trichloroethanoic acid, $\text{CCl}_3\text{CO}_2\text{H}$, are both carboxylic acids. Ethanoic acid can be used to make ethanamide, CH_3CONH_2 .

Place these three compounds in order of acidity, starting with the **least** acidic. Explain your answer.

..... < <

least acidic

most acidic

.....

.....

.....

.....

.....

[3]

- (b)** Methanoic acid, HCO_2H , and ethanedioic acid, $\text{HO}_2\text{CCO}_2\text{H}$, are two other carboxylic acids.

- (i) State which, if any, of ethanoic acid, methanoic acid and ethanedioic acid will react with Fehling's reagent.

..... [1]

- (ii) State which, if any, of ethanoic acid, methanoic acid and ethanedioic acid will react with warm acidified manganate(VII) ions.

..... [1]

- (c)** Ethanamide can be made from ethanoic acid in a two-step synthesis.



- (i) Compound **A** contains chlorine.

Give the structural formula and name of **A**.

structural formula

name

[2]

- (ii) Suggest suitable reagents for steps 1 and 2.

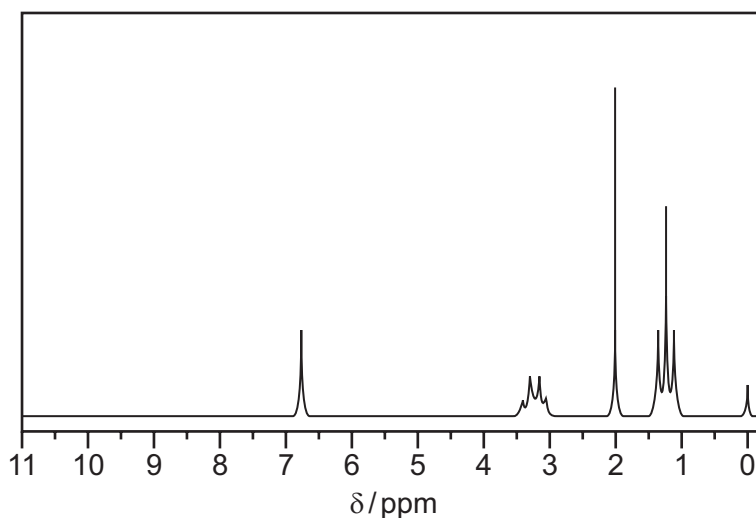
step 1

step 2

[2]

(d) Compound **A** can also be used to make the amide $\text{CH}_3\text{CONHC}_2\text{H}_5$.

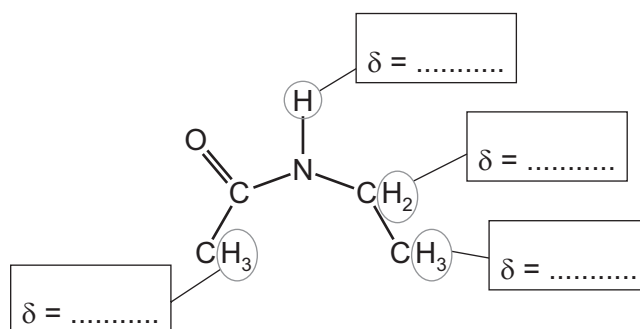
The proton NMR spectrum of the amide $\text{CH}_3\text{CONHC}_2\text{H}_5$ in the solvent CDCl_3 is shown.



(i) Explain why CDCl_3 is used as a solvent instead of CHCl_3 .

..... [1]

(ii) Complete the diagram with the chemical shifts, δ , of the protons labelled in the $\text{CH}_3\text{CONHC}_2\text{H}_5$ molecule.



[2]

(iii) State and explain how the proton NMR spectrum of the amide $\text{CH}_3\text{CONHC}_2\text{H}_5$ differs when dissolved in D_2O rather than CDCl_3 .

.....

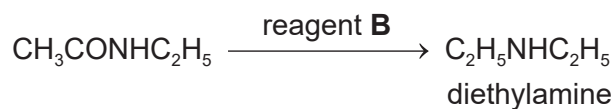
 [2]

- (e) The mass spectrum of the amide $\text{CH}_3\text{CONHC}_2\text{H}_5$ includes a fragment ion with m/e value of 58.

Give the molecular formula of this fragment ion.

fragment ion with m/e value of 58 is [1]

- (f) The amide undergoes the following reaction to produce diethylamine.



- (i) Identify reagent B.

..... [1]

- (ii) State the number of different absorptions in the carbon-13 NMR spectrum of diethylamine.

..... [1]

[Total: 17]

7 (a) Describe the structure of a benzene molecule, C_6H_6 .

Your answer should include:

- the shape of the molecule
- the relative lengths of the C–C bonds
- bond angles
- the hybridisation of the carbon atoms
- the overlap between orbitals that produces each type of bond present.

.....

.....

.....

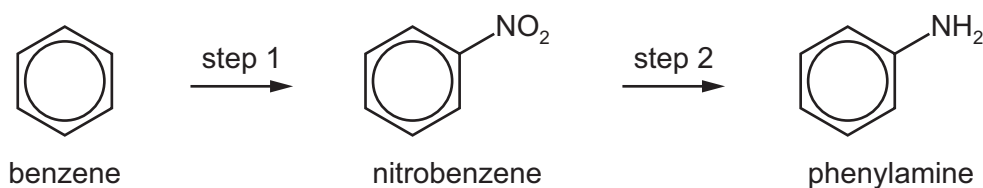
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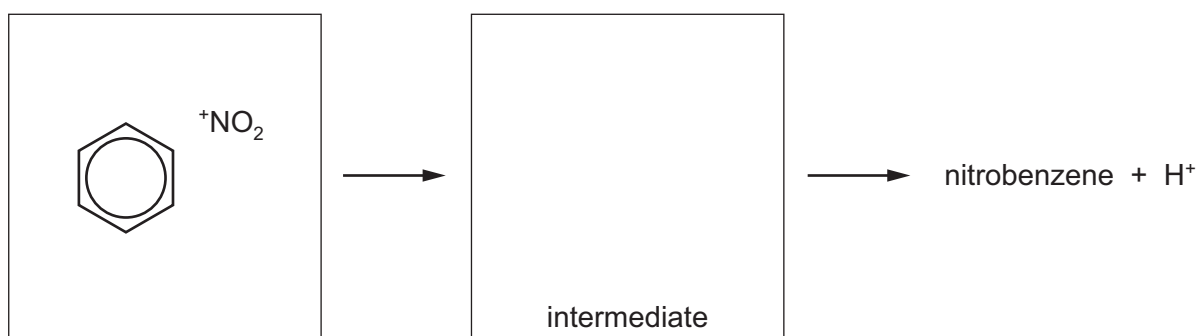
..... [4]

(b) Benzene can be used as a starting material to produce phenylamine by a two-step synthesis.



(i) Step 1 is the reaction of benzene with NO_2^+ ions.

Complete the mechanism and draw the intermediate of step 1.
Include all relevant charges and curly arrows to show the movement of electron pairs.



[2]

(ii) State the name of the mechanism in (b)(i).

..... [1]

- (iii)** Identify the reagents needed to produce NO_2^+ ions.

Write an equation to explain how these reagents produce NO_2^+ ions.

..... [2]

- (iv) Give reagents and conditions for the production of phenylamine from nitrobenzene in step 2.

..... [2]

- (c) Phenylamine reacts with $\text{Br}_2(\text{aq})$.

- (i) Write an equation for this reaction. You may use structural or displayed formulae.

..... [1]

- (ii) Name the organic product of this reaction.

- (iii) Describe **two** observations that can be **seen** when phenylamine reacts with $\text{Br}_2(\text{aq})$.

observation 1

observation 2 [1]

- (d) Describe the relative basicities of ammonia, ethylamine and phenylamine, starting with the **least** basic.

Explain your answer in terms of their structures.

..... < <
least basic most basic

[3]

(e) 1,3-diaminopropane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, can be used to make polyamides.

(i) Identify **one** compound that would react with 1,3-diaminopropane to form a polyamide.

..... [1]

(ii) Draw a section of the polymer chain formed from 1,3-diaminopropane and the compound you chose in (e)(i).

Your answer should:

- include four monomer residues (two of each type of monomer)
- show the amide link fully displayed
- clearly identify **one** repeat unit of this polymer.

[2]

[Total: 20]

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CHEMISTRY

9701/43

Paper 4 A Level Structured Questions

October/November 2020

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

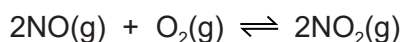
- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [].

This document has **24** pages. Blank pages are indicated.



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

- 1 Nitrogen monoxide, NO, reacts with oxygen to form nitrogen dioxide, NO₂.



The rate equation for the forward reaction is shown.

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

- (a) Complete the following table.

the order of reaction with respect to [NO]	
the order of reaction with respect to [O ₂]	
the overall order of reaction	

[1]

- (b) Two separate experiments are carried out at 30 °C to determine the rate of the forward reaction.

experiment	[NO]/mol dm ⁻³	[O ₂]/mol dm ⁻³	rate/mol dm ⁻³ s ⁻¹
1	0.00300	0.00200	1.51×10^{-4}
2		0.00500	6.05×10^{-5}

- (i) Use the data for experiment 1 to calculate the value of the rate constant, *k*. State the units of *k*.

$k = \dots\dots\dots$ units = $\dots\dots\dots$
[2]

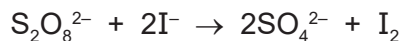
- (ii) Calculate the value of [NO] in experiment 2.

[NO] = $\dots\dots\dots$ mol dm⁻³ [1]

- (c) Define the term *rate-determining step*.

$\dots\dots\dots$ [1]

- (d) Peroxodisulfate ions, $\text{S}_2\text{O}_8^{2-}$, react with iodide ions, I^- .



The rate equation for the reaction in the absence of any catalyst is shown.

$$\text{rate} = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$$

- (i) Suggest equations for a two-step mechanism for this reaction, stating which of the two steps is the rate-determining step.

step 1

step 2

rate-determining step = ...

[2]

- (ii) A large excess of peroxodisulfate ions is mixed with iodide ions. Immediately after mixing, $[\text{I}^-] = 0.00780 \text{ mol dm}^{-3}$. Under the conditions used, the half-life of $[\text{I}^-]$ is 48 seconds.

Calculate the iodide ion concentration 192 seconds after the peroxodisulfate and iodide ions are mixed.

iodide ion concentration = ... mol dm^{-3} [1]

[Total: 8]

- 2 (a) The lattice energies of three ionic compounds are given.

compound	lattice energy / kJ mol^{-1}
LiF(s)	–1022
CaO(s)	–3513
SrO(s)	–3310

- (i) Define the term *lattice energy*.

.....

 [2]

- (ii) Explain why the lattice energy of CaO is more exothermic than the lattice energy of LiF.

.....

 [1]

- (iii) Use the data in the table to estimate approximate values for the lattice energies of magnesium oxide and barium oxide.

$$\Delta H_{\text{latt}} \text{MgO(s)} = \dots\dots\dots \text{kJ mol}^{-1}$$

$$\Delta H_{\text{latt}} \text{BaO(s)} = \dots\dots\dots \text{kJ mol}^{-1}$$

[1]

- (b) (i) Write an equation for the reaction between BaO and H_2O .
 Include state symbols.

..... [1]

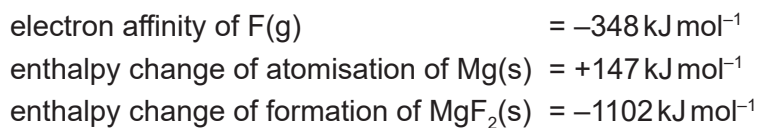
- (ii) State and explain how the solubilities of the hydroxides of the Group 2 elements vary down the group.

.....

 [4]

- (c) Use the following data and relevant data from the *Data Booklet* to calculate a value for the lattice energy of magnesium fluoride, $\text{MgF}_2(\text{s})$.

You might find it helpful to construct an energy cycle.
Show your working.



$$\Delta H_{\text{latt}} \text{MgF}_2(\text{s}) = \dots\dots\dots [3]$$

- (d) (i) Define the term *electron affinity*.

.....
 [2]

- (ii) The electron affinity of carbon, $\text{C}(\text{g})$, is -120 kJ mol^{-1} .

Suggest an explanation for the difference between the electron affinity of fluorine and the electron affinity of carbon.

.....

 [1]

[Total: 15]

- 3 (a) Identify the substances liberated at the anode and at the cathode during the electrolysis of aqueous sodium sulfate, $\text{Na}_2\text{SO}_4(\text{aq})$.

anode

cathode

[1]

- (b) When molten sodium chloride is electrolysed, chlorine is liberated at the anode and sodium is liberated at the cathode.

A sample of molten sodium chloride is electrolysed for 1.50 hours using a current of 4.50A.

Calculate the volume of chlorine and the mass of sodium that are liberated under room conditions.

volume of chlorine = ... dm^3

mass of sodium = ... g
[4]

- (c) The equation representing the standard electrode potential, E° , for the reduction of $\text{MnO}_4^-(\text{aq})$ to $\text{Mn}^{2+}(\text{aq})$ in acid solution is given.



- (i) Draw a diagram of the apparatus that would be used to measure the E° value of this half-cell. Your diagram should be fully labelled to identify all apparatus, substances and conditions.

[4]

- (ii) Use the *Data Booklet* to identify a substance that could be used to oxidise Mn^{2+} ions to MnO_4^- ions under standard conditions.

Write an equation for the reaction.

.....

 [2]

[Total: 11]

- 4 (a) (i) Give the mathematical expression for each of the terms pH and K_w .

pH = ...

K_w = ... [2]

- (ii) Calculate the pH of $0.027 \text{ mol dm}^{-3} \text{ NaOH(aq)}$.

pH = ... [1]

- (b) The K_a value of chloric(I) acid, HClO , is $3.72 \times 10^{-8} \text{ mol dm}^{-3}$.

Calculate the pH of $0.010 \text{ mol dm}^{-3} \text{ HClO(aq)}$.

pH = ... [1]

- (c) Water and octan-1-ol form two layers when mixed.

Ethanamide is more soluble in water than it is in octan-1-ol. When 1.00 g of ethanamide is added to 50.0 cm^3 of water and this is then shaken with 50.0 cm^3 of octan-1-ol, it is found that the water layer contains 0.935 g of ethanamide at equilibrium.

- (i) Calculate the partition coefficient, K_{pc} , for ethanamide in water and octan-1-ol.

K_{pc} = ... [1]

- (ii) The 50.0 cm^3 of water containing 0.935 g of ethanamide is then shaken with 100.0 cm^3 of pure octan-1-ol under the same conditions.

Calculate the mass of ethanamide that is dissolved in the 100.0 cm^3 of octan-1-ol at equilibrium.

mass of ethanamide = ... g
[2]

[Total: 7]

- 5 A solution is made by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in an excess of aqueous ammonia. This solution contains the copper complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

(a) (i) Write an expression for the K_{stab} of $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

$$K_{\text{stab}} =$$

[1]

(ii) State the colour of the solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

..... [1]

The solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is heated gently in a fume cupboard so that NH_3 is released. Some NH_3 remains in solution and some forms NH_3 gas. The colour of the solution changes; a precipitate of $\text{Cu}(\text{OH})_2$ forms and is collected.

A sample of $\text{Cu}(\text{OH})_2$ is added to concentrated hydrochloric acid. A reaction takes place forming a coloured copper complex, **Y**.

A sample of $\text{Cu}(\text{OH})_2$ is added to dilute sulfuric acid. A reaction takes place forming a coloured copper complex, **Z**.

$[\text{Cu}(\text{NH}_3)_4]^{2+}$, **Y** and **Z** are different colours.

(b) Suggest an equation for the reaction of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ to form $\text{Cu}(\text{OH})_2$ as the aqueous solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is heated.

..... [1]

(c) Suggest an equation for the reaction of $\text{Cu}(\text{OH})_2$ with concentrated hydrochloric acid, forming **Y**.

..... [2]

(d) Complete the table with the colour and geometry of complex **Y** and the colour, geometry and formula of complex **Z**.

	Y	Z
colour of complex		
geometry of complex		
formula of complex		

[2]

(e) Explain why complexes **Y** and **Z** are coloured and why their colours are different.

.....

.....

.....

.....

.....

.....

.....

..... [5]

[Total: 12]

- 6 (a) When $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3(\text{aq})$ is added to a solution containing $\text{Ag}^+(\text{aq})$ ions, a linear complex, **P**, is formed. $\text{S}_2\text{O}_3^{2-}$ ions are present in **P** as monodentate ligands.

(i) Define the term *monodentate ligand*.

.....
 [2]

(ii) Give the formula of **P**, including its charge.

..... [1]

- (b) When $1.0 \text{ mol dm}^{-3} \text{ NaCN}(\text{aq})$ is added to a solution of **P**, a mixture which includes a second linear complex, **Q**, is formed. In this mixture the concentration of **Q** is much greater than the concentration of **P**.

(i) Write an equation for the reaction that occurs when $\text{NaCN}(\text{aq})$ is added to a solution of **P**.

..... [1]

(ii) Suggest a reason why the concentration of **Q** is much greater than the concentration of **P** in the mixture.

.....

 [1]

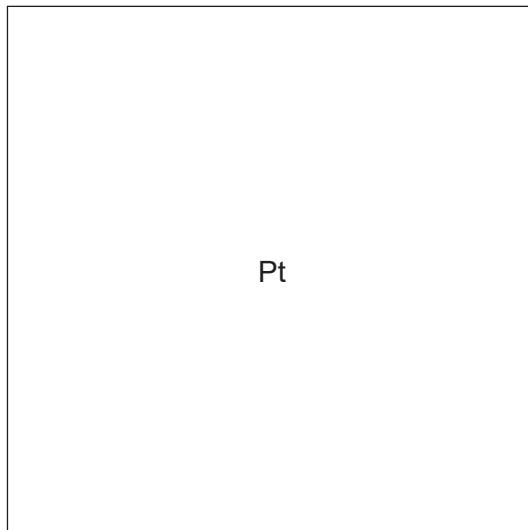
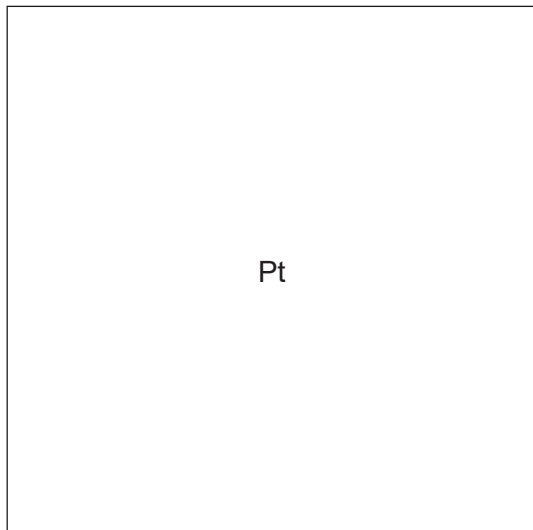
(iii) Name the type of reaction in which **P** forms **Q**.

..... [1]

(c) Platinum forms a complex ion with the formula $[\text{Pt}(\text{CN})_2\text{Cl}_2]^{2-}$. In this complex ion the carbon atom of each CN^- ligand bonds to the platinum ion. This complex shows stereoisomerism.

(i) There are only two isomers of this complex.

Draw structures of these two isomers in the boxes below.



[1]

(ii) Describe the geometry of $[\text{Pt}(\text{CN})_2\text{Cl}_2]^{2-}$.

..... [1]

(iii) Name the type of stereoisomerism shown by $[\text{Pt}(\text{CN})_2\text{Cl}_2]^{2-}$.

..... [1]

[Total: 9]

7 Phenol, $\text{C}_6\text{H}_5\text{OH}$, is a weak acid.

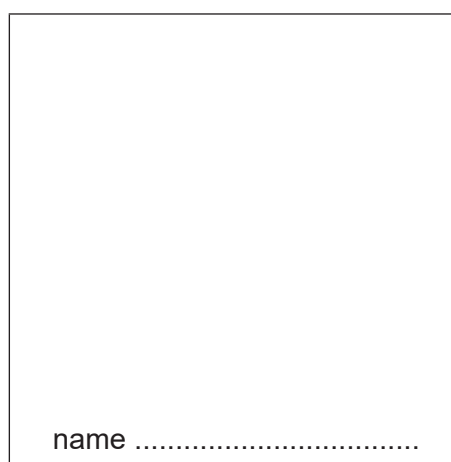
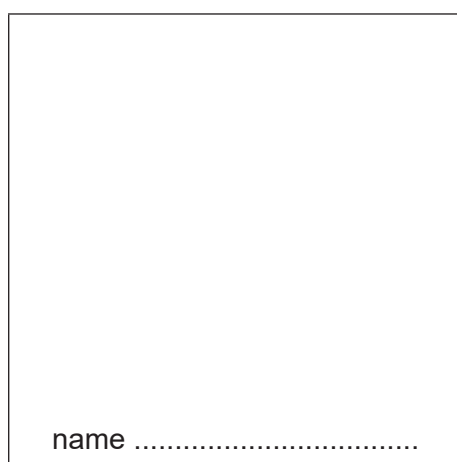
(a) Phenol can be made from phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$.

Give the reagents and conditions for this reaction.

.....
..... [2]

(b) Phenol reacts with dilute aqueous nitric acid under room conditions to give a mixture of two isomeric products with molecular formula $\text{C}_6\text{H}_5\text{NO}_3$.

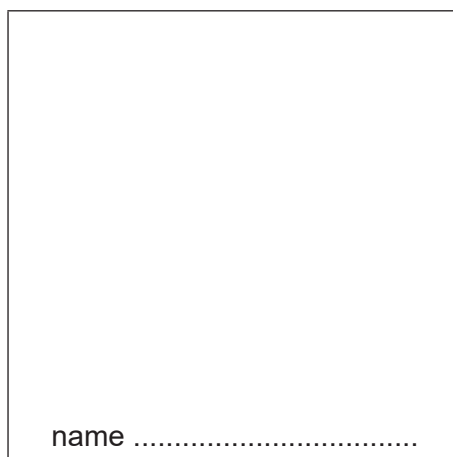
Use the *Data Booklet* to draw the structural formulae of these two products in the boxes and name each product.



[2]

(c) Phenol reacts with an excess of aqueous bromine.

(i) Draw and name the organic product of this reaction in the box.



[2]

- (ii) Describe **two** visual observations that can be made when phenol reacts with an excess of aqueous bromine.

observation 1

observation 2

[1]

- (d) Write an equation for a neutralisation reaction in which phenol behaves as an acid.

..... [1]

- (e) Water, phenol and ethanol can all behave as acids.

Place these three compounds in order of acidity, starting with the **most** acidic.
Explain your answer.

..... > >
most acidic least acidic

.....
.....
.....
.....
.....
.....

[3]

[Total: 11]

8 Benzene, C_6H_6 , can be obtained from crude oil.

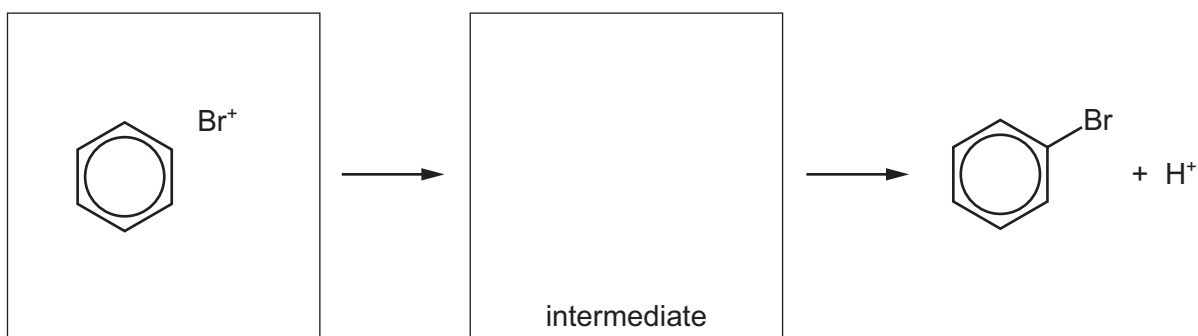
(a) Benzene reacts with bromine, in the presence of a suitable catalyst, forming bromobenzene as one product.

(i) Give the name or formula of the other product of this reaction.

..... [1]

(ii) In the presence of the catalyst, bromine can be considered to form the electrophile Br^+ .

Complete the mechanism by which benzene reacts with Br^+ , using curly arrows to show the movement of electron pairs.

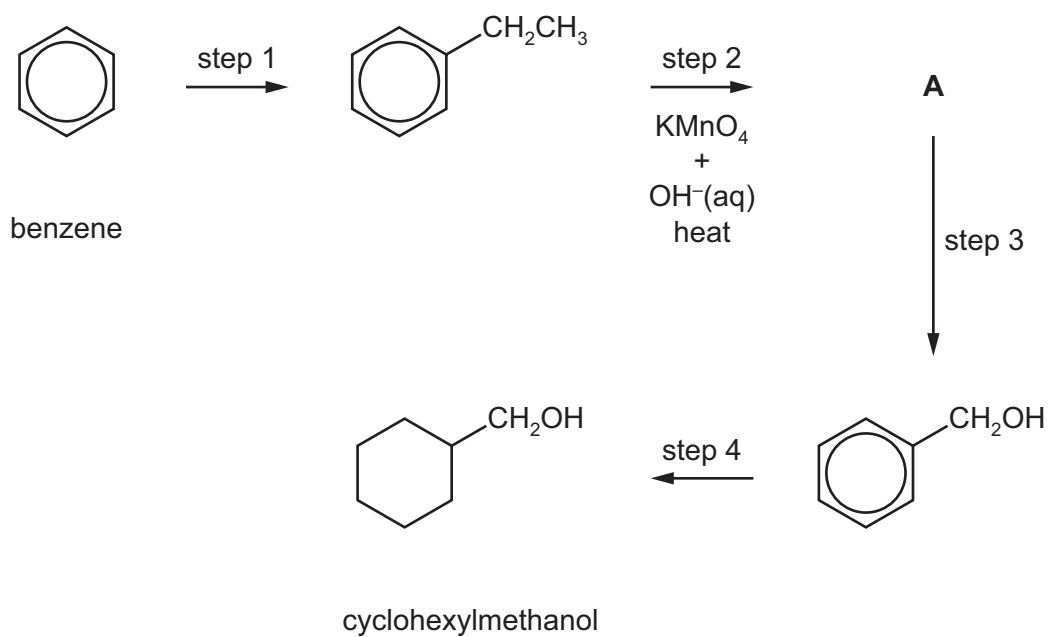


[2]

(iii) Name this mechanism.

..... [1]

- (b) Benzene can be used as a starting material in the synthesis of cyclohexylmethanol, $\text{C}_6\text{H}_{11}\text{CH}_2\text{OH}$, as outlined below.



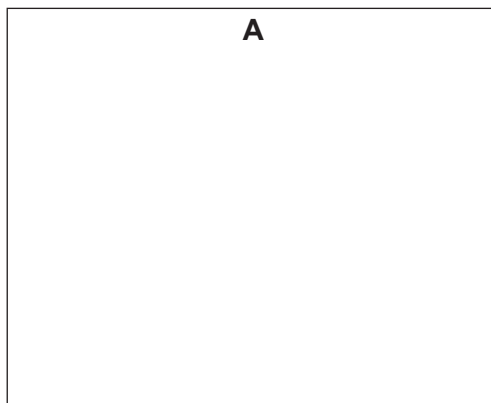
- (i) Identify a suitable reagent and a suitable catalyst for step 1.

reagent

catalyst

[2]

- (ii) Draw the structure of **A**.



[1]

(iii) Identify suitable reagents for steps 3 and 4.

step 3

step 4

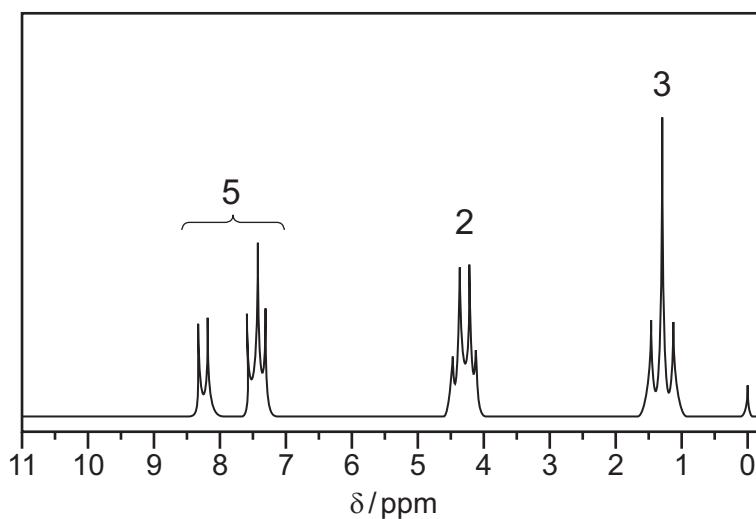
[2]

(iv) Deduce the number of peaks in the carbon-13 NMR spectrum of cyclohexylmethanol.

..... [1]

[Total: 10]

- 9 The proton NMR spectrum of compound **E** in the solvent CDCl_3 is shown. The molecular formula of compound **E** is $\text{C}_9\text{H}_{10}\text{O}_2$.



- (a) Explain why CDCl_3 is used as a solvent instead of CHCl_3 .

..... [1]

- (b) Explain why TMS is added to give the small peak at chemical shift $\delta = 0$.

..... [1]

- (c) Compound **E** is hydrolysed by hot NaOH(aq) , giving two organic products only. One of these products is ethanol.

Name the functional group in compound **E** that is hydrolysed by hot NaOH(aq) .

..... [1]

- (d) (i) Describe and explain the splitting patterns of the peaks at $\delta = 1.4$ and $\delta = 4.3$.

splitting pattern at $\delta = 1.4$

reason for splitting pattern at $\delta = 1.4$

splitting pattern at $\delta = 4.3$

reason for splitting pattern at $\delta = 4.3$

[2]

- (ii) Each molecule of compound **E** contains five protons which give rise to the peaks between $\delta = 7.0$ and $\delta = 8.5$.

Identify the functional group in compound **E** which contains these protons.

..... [1]

(iii) Give the structural formula of compound **E**.

[1]

(e) The mass spectrum of compound **E** includes fragment ions with m/e values of 29 and 77.

Give the formulae of these fragment ions.

fragment ion with $m/e = 29$

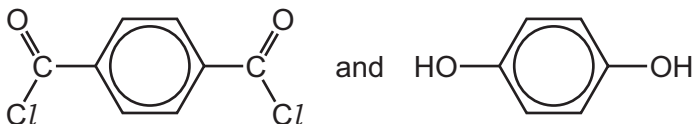
fragment ion with $m/e = 77$

[2]

[Total: 9]

- 10 (a) The table shows three pairs of monomers that are capable of polymerisation.

Complete the table by identifying each type of polymerisation.

pair of monomers	type of polymerisation
$\text{HOCH}_2\text{CH}_2\text{OH}$ and $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$	
	
CH_3CHCF_2 and CH_3CHCH_2	

[1]

- (b) 2-aminopropanoic acid, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, can polymerise under suitable conditions. No other monomer is involved in this reaction.

- (i) Draw a section of the polymer chain formed including **three** monomer residues. Clearly identify **one** repeat unit on your diagram.

[3]

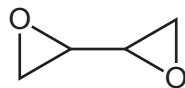
- (ii) 2-aminopropanoic acid, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, exists as two stereoisomers.

Draw three-dimensional diagrams to show the two stereoisomers of 2-aminopropanoic acid. State the type of stereoisomerism shown.

type of stereoisomerism

[2]

(c) The skeletal formula of compound **W** is shown.



When **W** is mixed with a second compound, called a hardener, a polymerisation reaction occurs, producing a non-solvent-based adhesive.

(i) Give the name of this type of non-solvent-based adhesive.

..... [1]

(ii) The hardener is a diamine. A diamine has an alkyl chain with two amine groups which are not bonded to the same carbon atom.

Draw the structural formula of a compound that would make a suitable hardener.

[1]

[Total: 8]

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