

CANDIDATE
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CHEMISTRY

9701/41

Paper 4 A Level Structured Questions

October/November 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **20** printed pages.

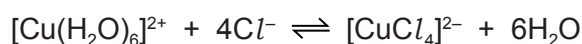
Answer **all** the questions in the spaces provided.

1 Copper is a transition element and has atomic number 29.

(a) Complete the electronic configuration for the copper atom and the copper ion in the +2 oxidation state.

- copper atom [Ar]
- copper ion in the +2 oxidation state [Ar] [2]

(b) The following equilibrium exists between two complex ions of copper in the +2 oxidation state.



(i) Name the *type of reaction* occurring here.

..... [1]

(ii) State the colours of these two complex ions.

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ $[\text{CuCl}_4]^{2-}$ [1]

(iii) State the shape of the $[\text{CuCl}_4]^{2-}$ ion.

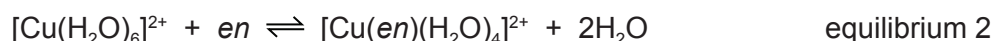
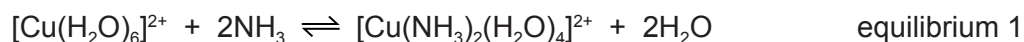
..... [1]

(iv) Write the expression for the stability constant, K_{stab} , for this equilibrium.

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

[1]

(c) Copper also forms the complex ions $[\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Cu}(\text{en})(\text{H}_2\text{O})_4]^{2+}$ where *en* is the bidentate ligand ethane-1,2-diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.



(i) What is meant by the term *bidentate ligand*?

.....
 [2]

- (ii) The table lists the values of stability constants for these two complexes.

	stability constant, K_{stab}
$[\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{2+}$	7.94×10^7
$[\text{Cu}(\text{en})(\text{H}_2\text{O})_4]^{2+}$	3.98×10^{10}

What do these K_{stab} values tell us about the relative positions of equilibria 1 and 2?

.....
 [1]

- (d) Nickel forms the complex ion $[\text{Ni}(\text{en})_3]^{2+}$ in which it is surrounded octahedrally by six nitrogen atoms.

- (i) Name the type of stereoisomerism displayed by $[\text{Ni}(\text{en})_3]^{2+}$.

..... [1]

- (ii) Draw three-dimensional diagrams to show the **two** stereoisomers of $[\text{Ni}(\text{en})_3]^{2+}$.

[3]

- (e) Ethane-1,2-diamine is a useful reagent in organic chemistry.

- (i) Explain how the amino groups in ethane-1,2-diamine allow the molecule to act as a Brønsted-Lowry base.

.....
 [2]

- (ii) Write an equation for the reaction of ethane-1,2-diamine with an excess of hydrochloric acid.

..... [1]

- (f) (i) Under certain conditions, ethane-1,2-diamine reacts with ethanedioic acid, $\text{HO}_2\text{CCO}_2\text{H}$, to form the polymer **Z**.

Draw the structure of this polymer, **Z**, showing **two** repeat units.

[2]

- (ii) Name the *type of reaction* occurring during this polymerisation.

..... [1]

- (iii) Polymer **Z** is an example of a biodegradable polymer.

Name a polymer that is non-biodegradable.

..... [1]

[Total: 20]

- 2 (a) When copper(II) carbonate is heated strongly, it decomposes in a similar way to Group 2 carbonates.

Predict what would be observed when anhydrous copper(II) carbonate is heated.

.....
 [1]

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

.....

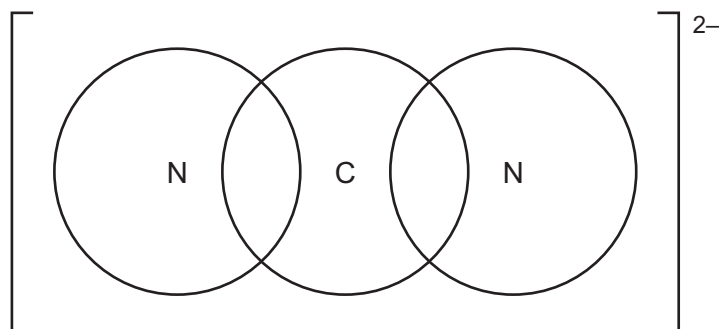
 [3]

- (c) Calcium cyanamide, CaCN_2 , can be used as a fertiliser.

- (i) Complete the 'dot-and-cross' diagram for the cyanamide ion, CN_2^{2-} .

Use the following key for the electrons.

- electrons from carbon
- × electrons from nitrogen
- added electron(s) responsible for the overall negative charge



[2]

- (ii) CaCN_2 decomposes readily on contact with water forming an insoluble white solid and ammonia only.

Suggest an equation for this reaction.

..... [2]

[Total: 8]

- 3 The spontaneity (feasibility) of a chemical reaction depends on the standard Gibbs free energy change, ΔG° . This is related to the standard enthalpy and entropy changes by the equation shown.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

- (a) State and explain whether the following processes will lead to an increase or decrease in entropy.

- (i) the reaction of magnesium with hydrochloric acid

entropy change

explanation

[1]

- (ii) solid potassium chloride dissolving in water

entropy change

explanation

[1]

- (iii) steam condensing to water

entropy change

explanation

[1]

- (b) Magnesium carbonate can be decomposed.



Standard entropies are shown in the table.

substance	MgCO ₃ (s)	MgO(s)	CO ₂ (g)
S° / J mol ⁻¹ K ⁻¹	+65.7	+26.9	+214

- (i) Calculate ΔG° for this reaction at 298 K.
Include a relevant sign and give your answer to **three** significant figures.

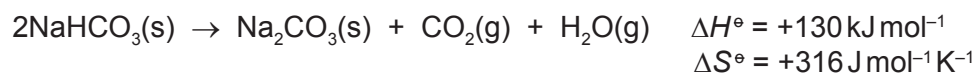
$\Delta G^\circ = \dots\dots\dots \text{ kJ mol}^{-1}$ [3]

- (ii) Explain, with reference to ΔG° , why this reaction becomes more feasible at higher temperatures.

.....

..... [1]

(c) On heating, sodium hydrogencarbonate decomposes into sodium carbonate as shown.



Calculate the **minimum** temperature at which this reaction becomes spontaneous (feasible).
Show your working.

temperature = ... K [2]

(d) The solubility of Group 2 sulfates decreases down the Group.

Explain this trend.

.....

 [2]

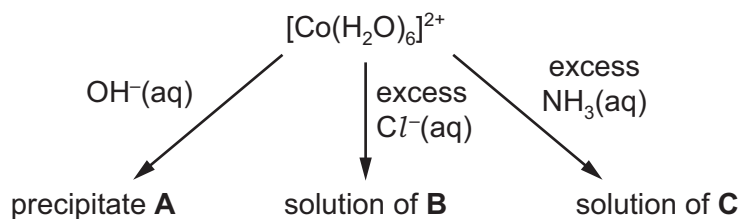
[Total: 11]

- 4 (a) Cobalt is a transition element that forms complex ions with oxidation states +2 and +3.

Explain what is meant by the term *transition element*.

.....
 [1]

- (b) The following scheme shows some reactions of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.



- (i) State the formula of each of the following.

A

B

C

[2]

- (ii) State the colour of the following solutions.

$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

solution of **B**

solution of **C**

[2]

- (c) Define the term *standard electrode potential*.

.....

 [2]

- (d) An electrochemical cell was set up to measure the standard electrode potential, $E_{\text{cell}}^{\ominus}$, of a cell made of a Co^{2+}/Co half-cell and a $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell.

- (i) Complete the table with the substance used to make the electrode in each of these half-cells.

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

[1]

- (ii) Write the equation for the overall cell reaction.

..... [1]

- (iii) Use the *Data Booklet* to calculate the $E_{\text{cell}}^{\ominus}$.

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

- (e) The electrochemical cell in (d) was set up again but this time the concentration of $\text{Co}^{2+}(\text{aq})$ was $0.050 \text{ mol dm}^{-3}$.

The Nernst equation can be used to calculate the value of an electrode potential at different concentrations.

$$E = E^{\ominus} + (0.059/z)\log[\text{Co}^{2+}(\text{aq})] \quad \text{Nernst equation}$$

- (i) Use the *Data Booklet* and the Nernst equation to calculate the value of E for the Co^{2+}/Co half-cell in this experiment.

$$E \text{ for } \text{Co}^{2+}/\text{Co} = \dots\dots\dots \text{V} \quad [1]$$

- (ii) Suggest how this change will affect the overall cell potential, E_{cell} , compared to $E_{\text{cell}}^{\ominus}$ in (d)(iii).

Circle your answer.

less positive no change more positive

[1]

- (f) Iron(III) ions can oxidise vanadium metal.

Construct an equation for the reaction of an excess of iron(III) ions with vanadium metal. Use of the *Data Booklet* will be helpful.

..... [2]

[Total: 14]

- 5 Compound **F** contains the elements carbon, hydrogen and oxygen only. All carbon-carbon bonds in **F** are single bonds. The structure of **F** was analysed by mass spectrometry and infra-red and NMR spectroscopy.

(a) The mass spectrum shows that the m/e value for the M peak is 90.

The ratio of the heights of the M and M+1 peaks is 22.1 : 0.7.

- (i) Use the ratio of the heights of the M and M+1 peaks to calculate the number of carbon atoms in a molecule of **F**.

number of carbon atoms = ... [2]

- (ii) Suggest the molecular formula of **F**.

molecular formula = C H O [1]

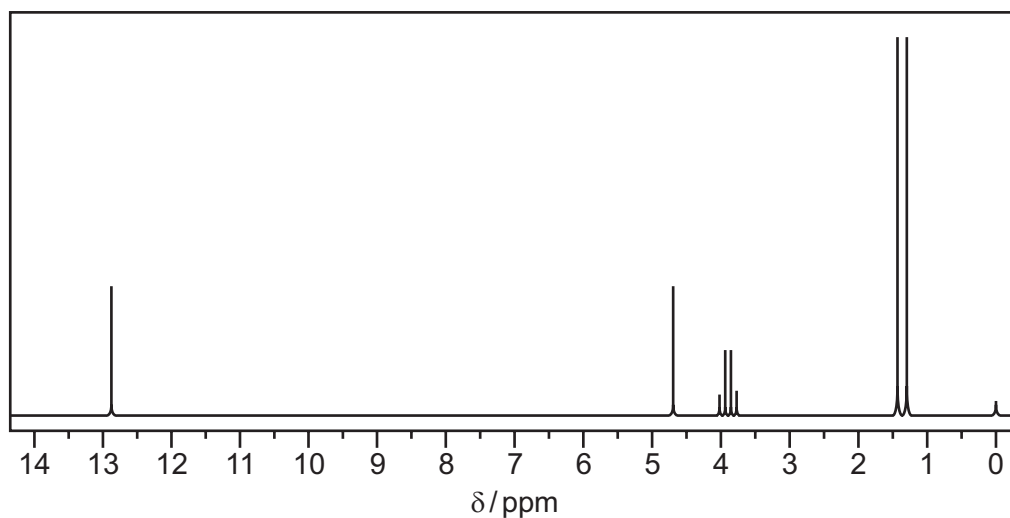
- (b) The infra-red spectrum of **F** was obtained.

Use the *Data Booklet* and your knowledge of infra-red spectroscopy to identify the type of bond and the functional group responsible for these **three** absorptions.

absorption/cm ⁻¹	appearance of the peak	type of bond	functional group
3350	broad and strong		
2680	very broad and strong		
1725	strong		

[2]

- (c) **F** was dissolved in deuterated trichloromethane, CDCl_3 , and the proton NMR spectrum of this solution obtained.



- (i) Use the *Data Booklet* and your answer to (a)(ii) to complete Table 1 for the proton NMR spectrum of **F**.
The actual chemical shifts for the four absorptions in **F** have been added for you.

Table 1

δ/ppm	type of proton	relative peak area
1.4		
3.9		
4.7		
12.9		

[4]

- (ii) Describe and explain the splitting pattern for the absorption at $\delta = 1.4$.

.....
 [1]

- (iii) **F** was dissolved in D_2O and the proton NMR spectrum of this new solution obtained. Two of the absorptions in Table 1 were not present in this spectrum.

Which absorptions were **not** present?

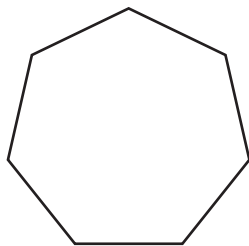
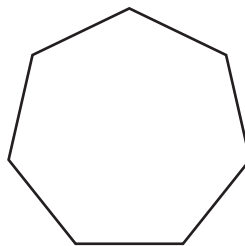
..... and [1]

- (iv) Suggest the structure of **F**.

[1]

(d) Molecules of cycloheptadiene, C_7H_{10} , consist of a seven-membered ring with two carbon-carbon double bonds.

(i) Complete the skeletal formulae of two isomers of cycloheptadiene.

**P****Q**

[1]

The isomers **P** and **Q** were analysed using carbon-13 NMR spectroscopy.

(ii) Predict the number of peaks that will be seen in the carbon-13 NMR spectra of **P** and **Q**.

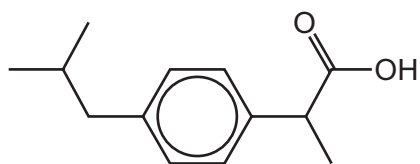
isomer	number of peaks
P	
Q	

[2]

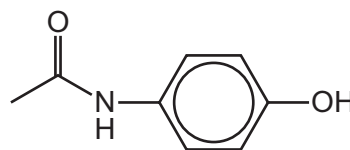
[Total: 15]

Question 6 starts on the next page.

6 Ibuprofen and paracetamol are pain-relief drugs.



ibuprofen



paracetamol

(a) Ibuprofen and paracetamol both contain the aryl (benzene) functional group.

Name the **other** functional groups present in each molecule.

ibuprofen

paracetamol

[2]

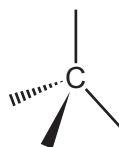
(b) Ibuprofen contains a chiral centre and shows stereoisomerism.

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

.....

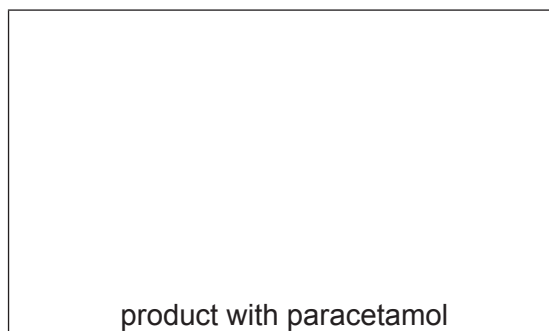
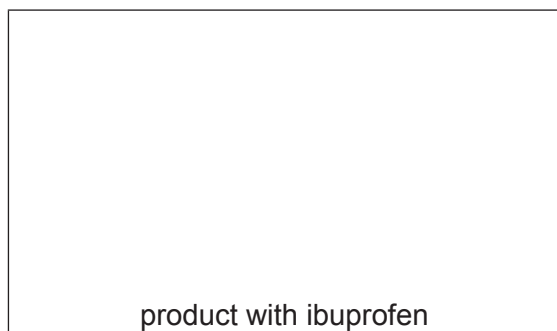
..... [1]

(ii) Draw the two stereoisomers of ibuprofen.



[2]

- (c) Draw the structures of the organic products when ibuprofen and paracetamol react separately with LiAlH_4 .



[2]

- (d) A student carried out some reactions with solutions of ibuprofen and paracetamol using reagents **D** and **E** and the following results were obtained.
(✓ means a reaction took place.)

reagent	ibuprofen	paracetamol
D	✓	✗
E	✗	✓

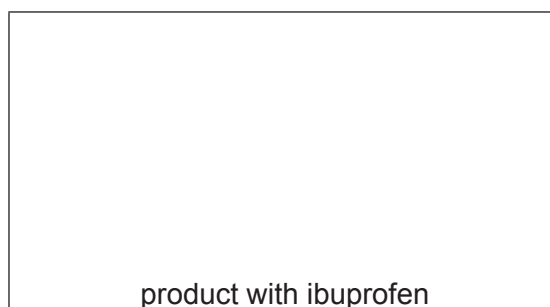
- (i) Suggest a possible identity for each reagent **D** and **E**.

D

E

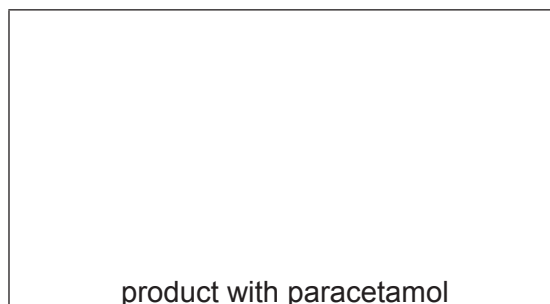
[2]

- (ii) Give the structure of the organic product formed when reagent **D** reacted with ibuprofen.



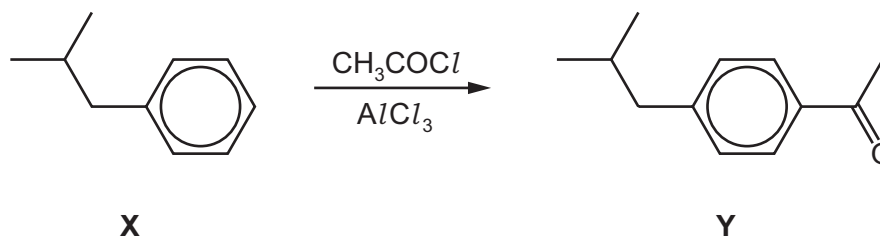
[1]

- (iii) Give the structure of the organic product formed when reagent **E** reacted with paracetamol.



[1]

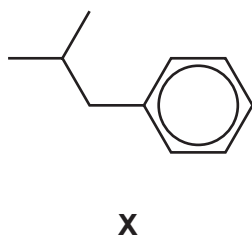
(e) One of the steps in the manufacture of ibuprofen is shown.



(i) Write an equation for the reaction between CH_3COCl and AlCl_3 .

..... [1]

(ii) Complete the mechanism for the conversion of **X** into **Y**. Include all necessary curly arrows, any relevant dipoles and charges.



[3]

(iii) Name the mechanism in (ii).

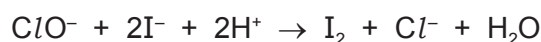
..... [1]

[Total: 16]

Question 7 starts on the next page.

- 7 (a) Sodium chlorate(I), NaClO , is the active ingredient in commercial bleach. The concentration of chlorate(I) ions was determined by titration.
- 10.0 cm^3 of a bleach solution was diluted to 250 cm^3 in a volumetric flask using distilled water.
 - Dilute sulfuric acid and an excess of potassium iodide solution were added to a 25.0 cm^3 portion of this solution to liberate iodine.
 - The resulting solution required 20.80 cm^3 of $0.100 \text{ mol dm}^{-3}$ aqueous sodium thiosulfate solution to react with the iodine produced.

The titration reactions are shown.



Calculate the concentration, in mol dm^{-3} , of ClO^- ions in the bleach solution.

concentration of ClO^- = ... mol dm^{-3} [3]

(b) An indicator was used in the thiosulfate-iodine titration.

(i) Name a suitable indicator for this titration.

..... [1]

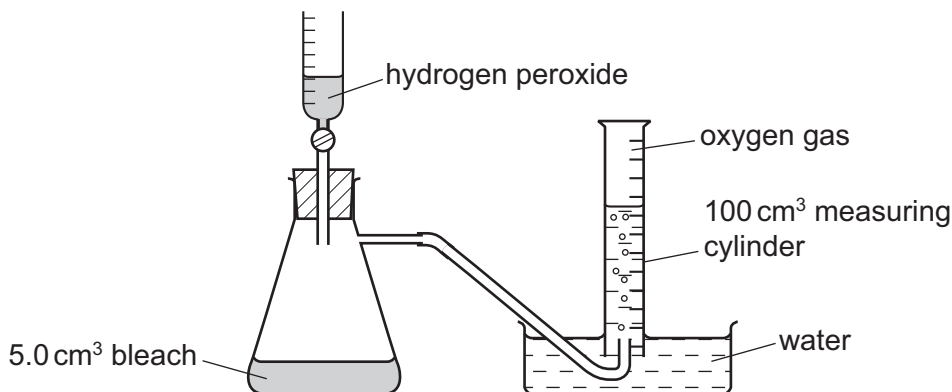
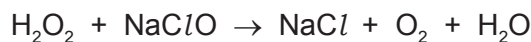
(ii) State the expected colour change you would observe at the end-point in this titration.

from to [1]

(iii) State when in the procedure you would add the indicator.

.....
 [1]

- (c) The concentration of chlorate(I) ions can also be determined by adding an excess of hydrogen peroxide to the sample of bleach and measuring the volume of oxygen gas produced.

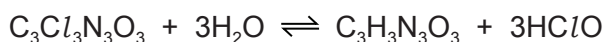


When an excess of aqueous hydrogen peroxide was added to 5.0 cm³ of a different bleach solution, 82 cm³ of oxygen was produced at room temperature and pressure.

Calculate the concentration of ClO⁻ ions in this bleach solution.

concentration of ClO⁻ = ... mol dm⁻³ [2]

- (d) Trichlorocyanuric acid, C₃Cl₃N₃O₃, acts as a chlorine buffer and disinfectant for swimming pools. It reacts with water to give chloric(I) acid, HClO.



- (i) Write the expression for K_c for this equilibrium.

$K_c =$

[1]

- (ii) In outdoor swimming pools, the HClO is decomposed by sunlight. The decomposition of HClO is a redox reaction which forms a gas that relights a glowing splint.

Describe and explain the effect of the decomposition of HClO on the equilibrium in (d). State the effect on K_c .

.....

effect on K_c

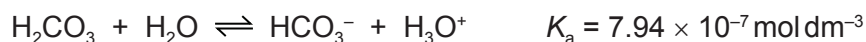
[2]

- (iii) The decomposition of HClO is a redox reaction.

Suggest an equation for this reaction.

..... [1]

- (e) The buffer solution in blood is a mixture of carbonic acid, H_2CO_3 , and hydrogencarbonate ions, HCO_3^- . Healthy blood has a pH of 7.40.



- (i) Explain how this buffer system acts to control the blood pH. Include equations in your answer.

.....

 [2]

- (ii) A patient's blood has a $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio of 9.5 : 1.

Calculate the pH of the patient's blood.

pH = ... [2]

[Total: 16]

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CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

October/November 2016

2 hours

Candidates answer on the Question Paper.

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The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **18** printed pages and **2** blank pages.

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

1 Transition elements are important metals because of their characteristic properties.

(a) Define what is meant by a *transition element*.

.....
 [1]

(b) (i) For each of the following complexes, state the co-ordination number and the oxidation number of the transition element present.

	co-ordination number	oxidation number
$[\text{Ni}(\text{CN})_2(\text{NH}_3)_2]$		
$[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$		

[2]

(ii) State the type of bonding that exists between the ligand and the metal ion in these complexes.

..... [1]

(iii) Suggest the structure of $[\text{Ni}(\text{CN})_2(\text{NH}_3)_2]$ and name its shape.

name of shape [2]

(c) The complex ion $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ can be converted into $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$.

(i) Suggest a suitable reagent for this conversion.

..... [1]

(ii) State the *type of reaction* in **(i)**.

..... [1]

(d) The $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ complex ion shows stereoisomerism.

(i) Name this type of stereoisomerism.

..... [1]

(ii) Draw three-dimensional diagrams to show the **two** stereoisomers of $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$.

[3]

[Total: 12]

- 2 Most car air bags contain a capsule of sodium azide, NaN_3 . In a crash, the NaN_3 decomposes into its elements.

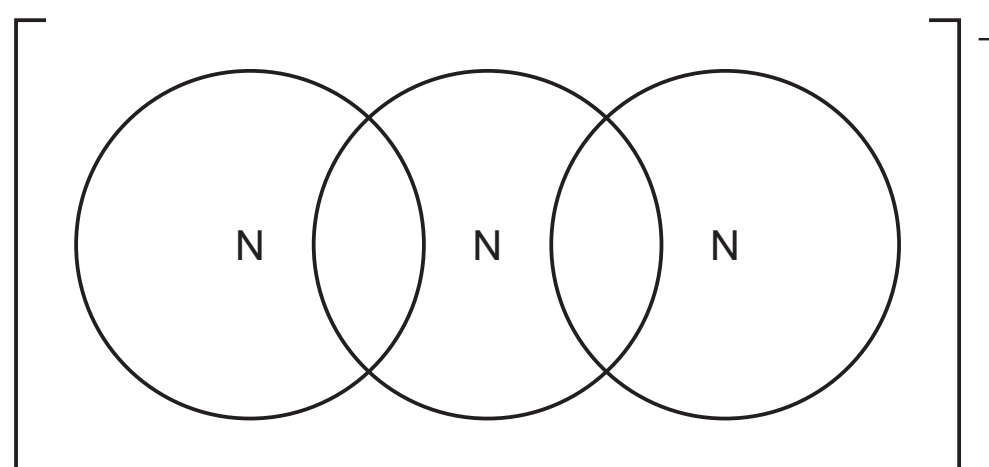
(a) Write an equation for the decomposition of NaN_3 .

..... [1]

(b) Complete the 'dot-and-cross' diagram for the azide ion, N_3^- .

Use the following key for the electrons.

- electrons from central nitrogen atom
- × electrons from the other two nitrogen atoms
- added electron(s) responsible for the overall negative charge



[3]

(c) Lattice energies are always negative showing that they represent exothermic changes.

(i) Explain what is meant by the term *lattice energy*.

.....

 [2]

(ii) Explain why lattice energy represents an exothermic change.

.....
 [1]

- (iii) Use the following data and any relevant data from the *Data Booklet* to calculate the standard enthalpy change of formation, $\Delta H_f^\ominus$, of $\text{NaN}_3(\text{s})$.
Include a sign in your answer. Show all your working.

lattice energy, $\Delta H_{\text{latt}}^\ominus$, of $\text{NaN}_3(\text{s})$	-732 kJ mol^{-1}
standard enthalpy change of atomisation, $\Delta H_{\text{at}}^\ominus$, of $\text{Na}(\text{g})$	$+107 \text{ kJ mol}^{-1}$
standard enthalpy change, $\Delta H^\ominus$, for $1\frac{1}{2}\text{N}_2(\text{g}) + \text{e}^- \rightarrow \text{N}_3^-(\text{g})$	$+142 \text{ kJ mol}^{-1}$

$\Delta H_f^\ominus$ of $\text{NaN}_3(\text{s}) = \dots\dots\dots \text{ kJ mol}^{-1}$ [3]

- (iv) The lattice energy, $\Delta H_{\text{latt}}^\ominus$, of $\text{RbN}_3(\text{s})$ is -636 kJ mol^{-1} .

Suggest why the lattice energy of $\text{NaN}_3(\text{s})$, -732 kJ mol^{-1} , is more exothermic than that of $\text{RbN}_3(\text{s})$.

.....
..... [1]

[Total: 11]

3 Iron has atomic number 26.

(a) Complete the electronic configuration for the iron atom and the iron ion in the +3 oxidation state.

- iron atom [Ar]
- iron ion in the +3 oxidation state [Ar]

[2]

(b) Fe^{3+} can act as a homogeneous catalyst in the reaction between peroxodisulfate ions ($\text{S}_2\text{O}_8^{2-}$) and iodide ions.

(i) What is meant by a *homogeneous* catalyst?

.....
 [1]

(ii) Write an equation for the overall reaction between $\text{S}_2\text{O}_8^{2-}(\text{aq})$ and $\text{I}^-(\text{aq})$.

..... [1]

(iii) Suggest why, in the absence of a catalyst, the activation energy for this reaction is high.

.....
 [1]

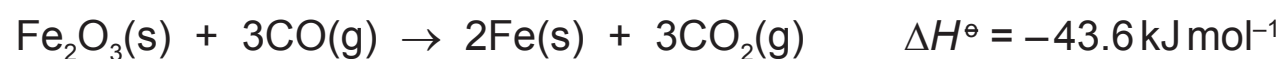
(iv) Write two equations to show how $\text{Fe}^{3+}(\text{aq})$ ions can catalyse the reaction between $\text{S}_2\text{O}_8^{2-}(\text{aq})$ ions and $\text{I}^-(\text{aq})$ ions.

equation 1

equation 2

[2]

(c) Iron(III) oxide can be reduced to iron metal using carbon monoxide at a temperature of 1000 °C.



Some relevant standard entropies are given in the table.

substance	$\text{Fe}_2\text{O}_3(\text{s})$	$\text{CO}(\text{g})$	$\text{Fe}(\text{s})$	$\text{CO}_2(\text{g})$
$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$	+90	+198	+27	+214

(i) What is meant by the term *entropy*?

.....
 [1]

(ii) Calculate the standard entropy change, ΔS° , for this reaction.

$\Delta S^\circ = \dots\dots\dots \text{J K}^{-1} \text{ mol}^{-1}$ [2]

(iii) Calculate the standard Gibbs free energy change, ΔG° , for this reaction at 25 °C.

$\Delta G^\circ = \dots\dots\dots \text{kJ mol}^{-1}$ [2]

(iv) Suggest why a temperature of 1000 °C is usually used for this reaction, even though the reaction is spontaneous (feasible) at 25 °C. Explain your answer.

.....

 [1]

[Total: 13]

- 4 (a) Explain why compounds of transition elements are usually coloured.

.....

 [3]

- (b) Copper is used to make alloys such as brass. The percentage of copper in a sample of brass can be determined by dissolving the sample in concentrated nitric acid and reacting the mixture with potassium iodide. The resulting solution is then titrated.

A 1.75 g sample of the brass was dissolved in excess concentrated nitric acid.

The reaction of the copper metal in the brass with the concentrated nitric acid released a brown gas and formed a green-blue solution.

- (i) Write an equation for this reaction.

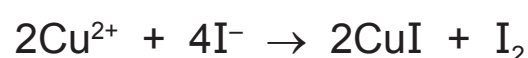
..... [2]

The resulting solution was neutralised and made up to 250 cm³ in a volumetric flask with distilled water.

An excess of aqueous potassium iodide was added to a 25.0 cm³ portion of this solution to liberate iodine.

The resulting solution required 22.40 cm³ of 0.100 mol dm⁻³ aqueous sodium thiosulfate solution to react with the iodine produced.

The reactions taking place in this titration are shown.

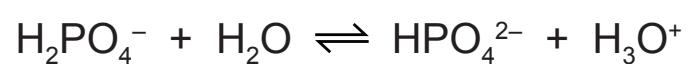


- (ii) Calculate the percentage of copper, by mass, in the sample of brass to **three** significant figures.

% of copper = ... [4]

[Total: 9]

- 5 The phosphate buffer system operates in biological cells. The buffer contains dihydrogen phosphate, H_2PO_4^- , which acts as a weak acid.



- (a) Write an expression for the K_a of H_2PO_4^- .

$$K_a =$$

[1]

- (b) (i) Explain what is meant by the term *buffer solution*.

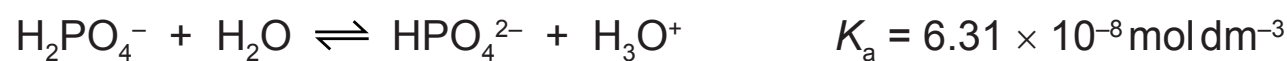
.....

 [2]

- (ii) Write **two** equations to show how a solution containing a mixture of H_2PO_4^- and HPO_4^{2-} acts as a buffer.

.....
 [2]

- (c) The pH in many living cells is 7.40.



Calculate the value of $[\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-]$ needed to give a pH of 7.40 in the cells.

$$[\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] = \dots\dots\dots [3]$$

- (d) (i) The H_2PO_4^- ion can also act as a base.

Write an equation to show H_2PO_4^- acting as a base.

..... [1]

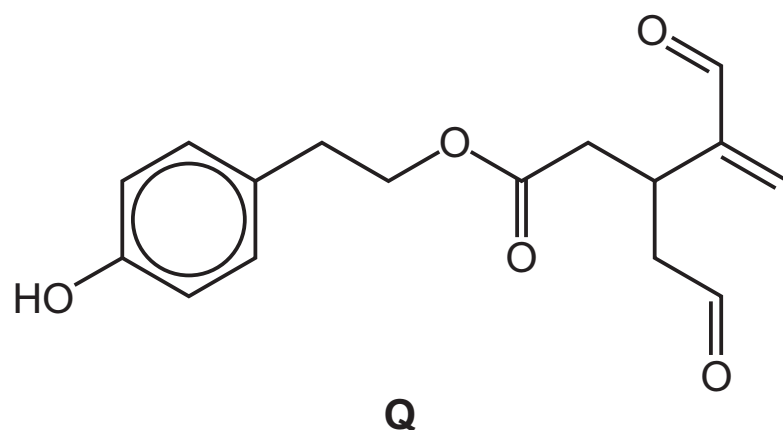
- (ii) The HPO_4^{2-} ion can also act as an acid.

Write an equation to show HPO_4^{2-} acting as an acid.

..... [1]

[Total: 10]

- 6 Oleocanthal, **Q**, is a natural compound found in olive oil. It has antioxidant and anti-inflammatory properties and is thought to have a protective effect against Alzheimer's disease.



- (a) **Q** shows optical and cis-trans isomerism.

On the structure of **Q** above, **circle** the functional group that shows cis-trans isomerism and indicate with an **asterisk** (*) the chiral carbon atom. [1]

- (b) **Q** can be isolated from olive oil by partitioning between two solvents.

- (i) Explain what is meant by the term *partition coefficient*.

.....

 [2]

- (ii) When 40.0 cm³ of hexane was shaken with 10.0 cm³ of a solution containing 0.25 g of **Q** in 10.0 cm³ of methanol, it was found that 0.060 g of **Q** was extracted into the hexane.

Calculate the partition coefficient, $K_{\text{partition}}$, of **Q** between hexane and methanol.

$$K_{\text{partition}} = \dots\dots\dots [2]$$

(c) Complete the following table to show the structures of the products formed when **Q** reacts with the three reagents.

reagent	structure of product(s)		type of reaction
excess $\text{Br}_2(\text{aq})$			
NaBH_4			
excess hot $\text{NaOH}(\text{aq})$			

[6]

(d) When a sample of **Q** synthesised in a laboratory was compared to a natural sample from olive oil, it was found that the therapeutic activity of the synthetic sample was lower.

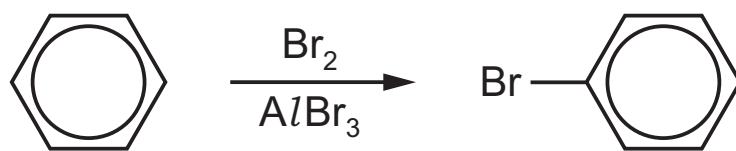
Suggest a reason for this.

.....
 [1]

[Total: 12]

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- 7 (a) Bromobenzene can be prepared from benzene as shown.



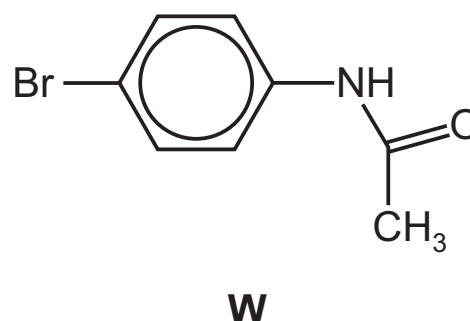
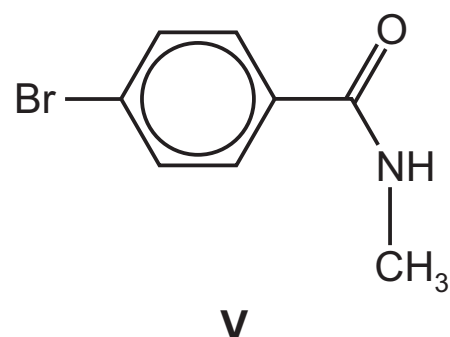
- (i) Name the mechanism of this reaction.

..... [1]

- (ii) Draw the mechanism of this reaction. Include all relevant curly arrows, any dipoles and charges.

[4]

- (b) Two isomeric aromatic compounds, **V** and **W**, each contain three functional groups, two of which are shown in the table.

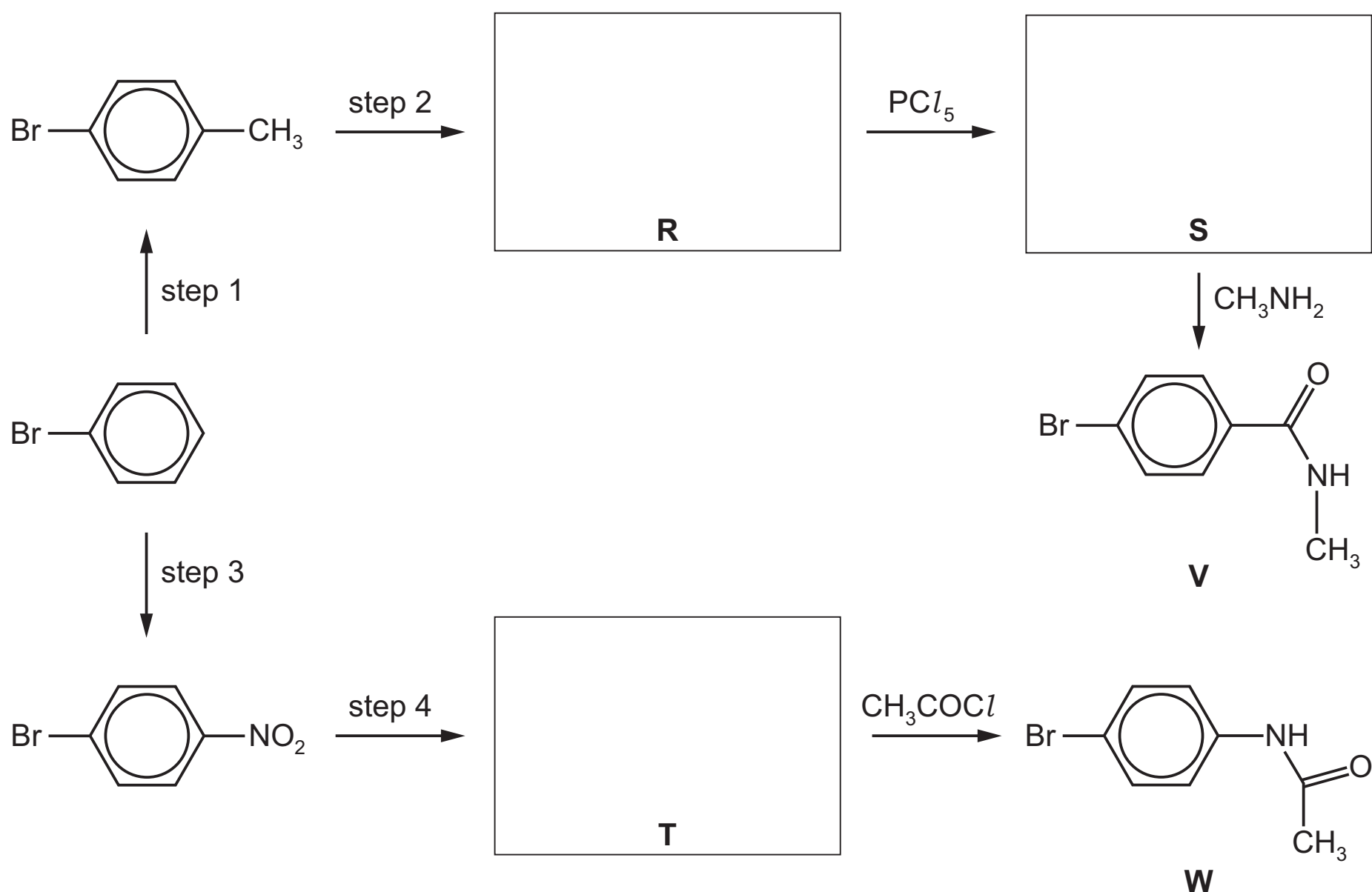


Complete the table with the **other** functional groups present in **V** and **W**.

substance	functional groups present		
V	bromo group	aryl (benzene) group	
W	bromo group	aryl (benzene) group	

[1]

(c) Compounds **V** and **W** can be synthesised from bromobenzene by the following routes.



(i) Suggest reagents for each of the steps 1–4.

step 1

step 2

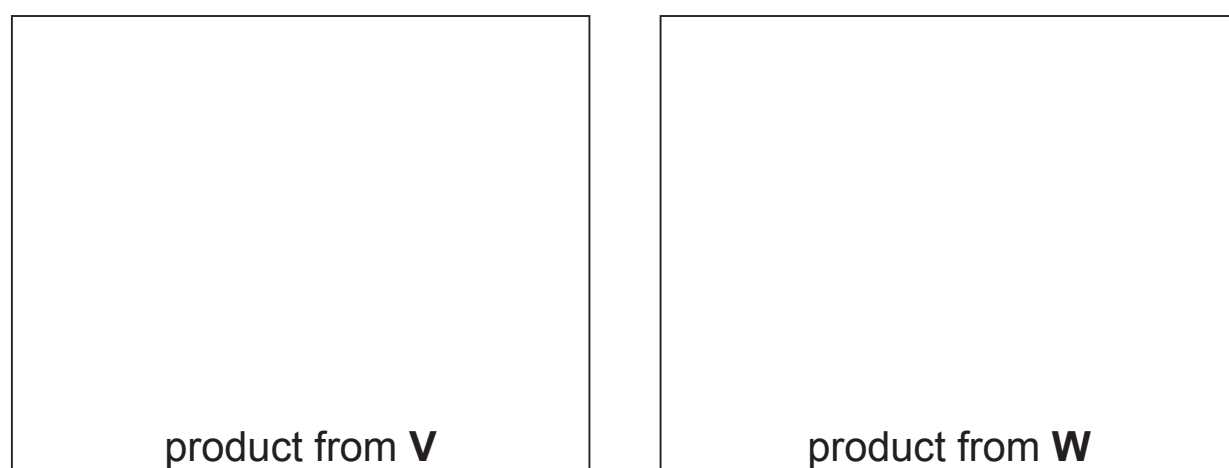
step 3

step 4

[4]

(ii) Deduce structures for **R**, **S** and **T** and draw their structural formulae in the boxes. [3]

(d) (i) Draw the structures of the two organic products from the reaction of **V** and **W** with LiAlH_4 .



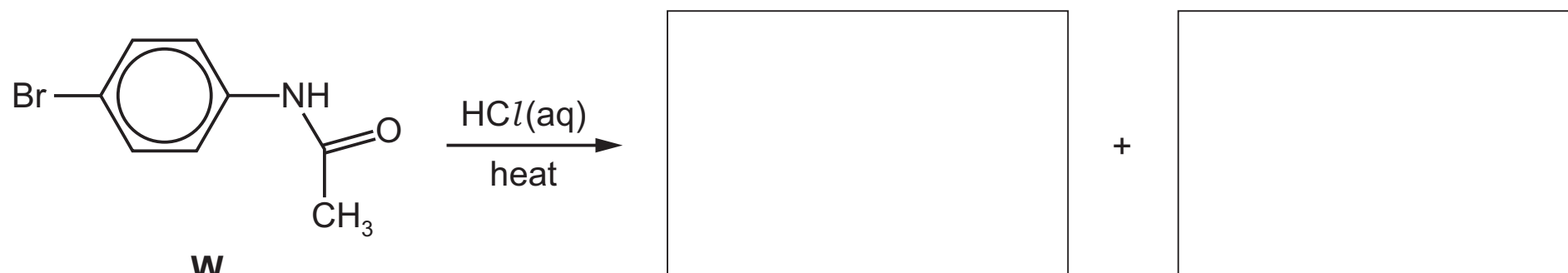
[2]

- (ii) Name the *type of reaction* occurring between LiAlH_4 and **V** or **W**.

..... [1]

- (e) **V** and **W** can be hydrolysed using hot HCl(aq) .

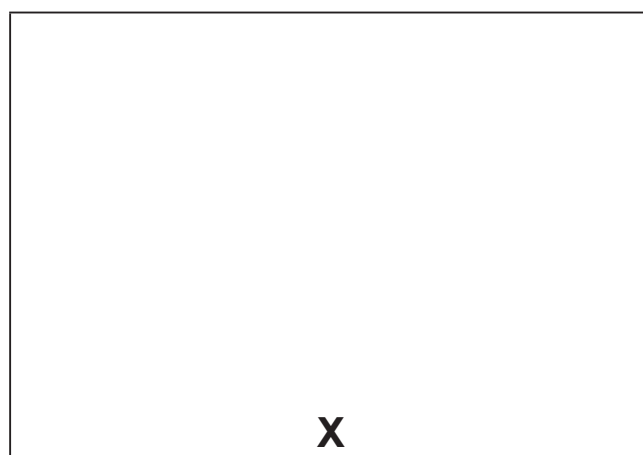
- (i) Draw the structures of the two organic products of the hydrolysis of **W**.



[2]

- (ii) The products formed from the hydrolysis of **W** are soluble in aqueous acid, whereas a precipitate, **X**, is formed on hydrolysing **V**.

Draw the structure of compound **X**.



[1]

- (iii) Suggest why **X** is insoluble in water.

.....
 [1]

[Total: 20]

8 Compound **F** is a carboxylic acid.

- (a) Compound **F** contains 31.4% oxygen by mass and its mass spectrum has a molecular ion peak at $m/e = 102$.

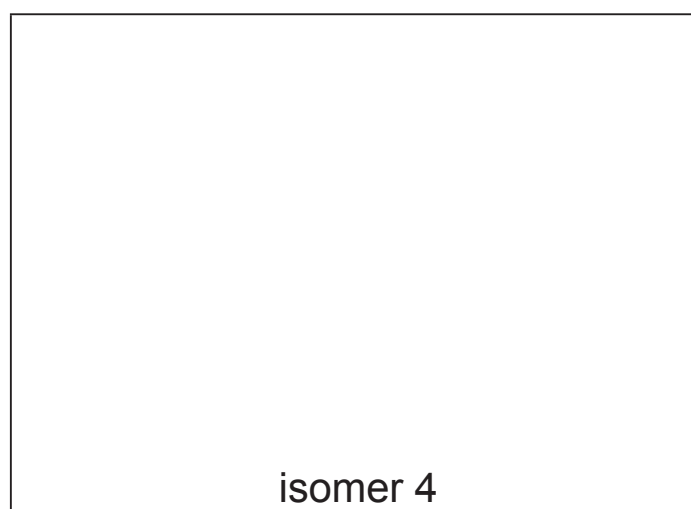
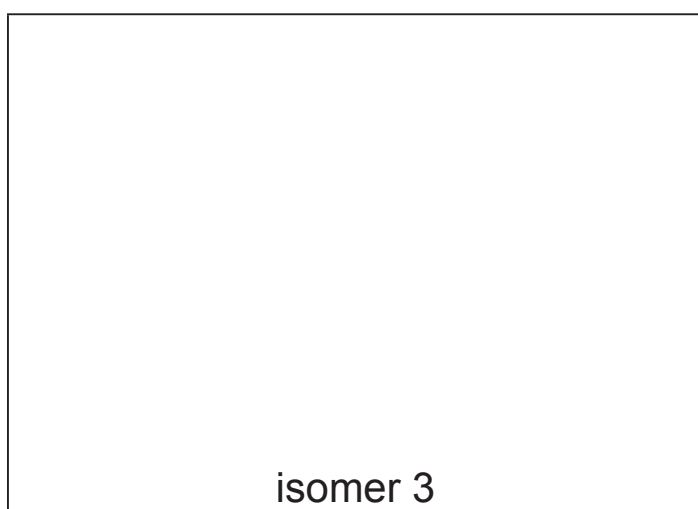
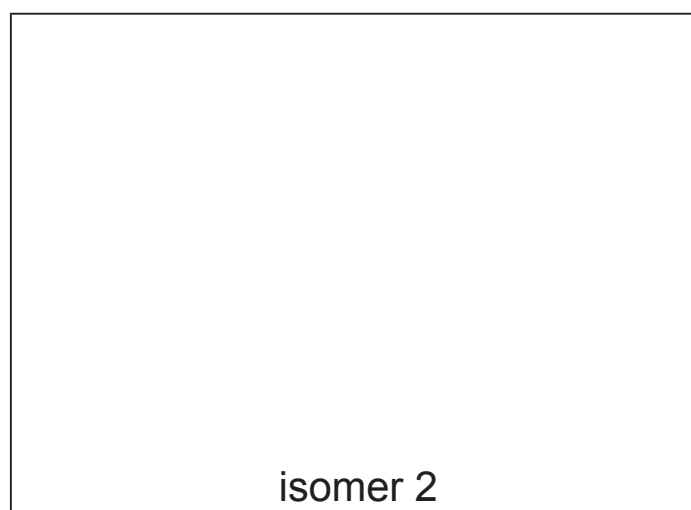
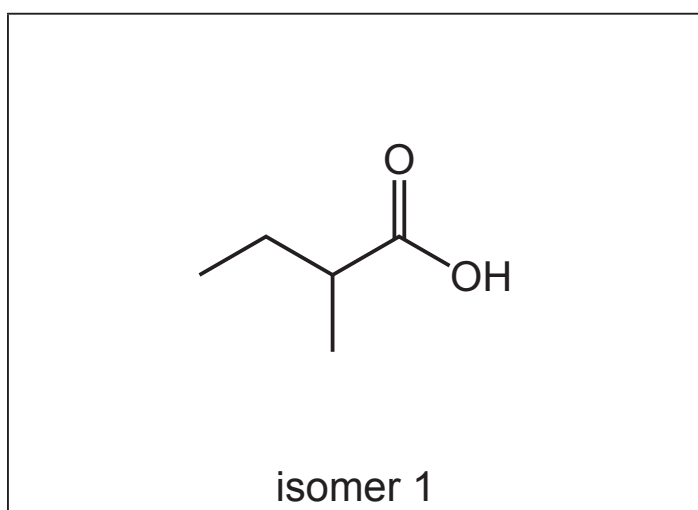
Use all of this information to show that the molecular formula of compound **F** is $C_5H_{10}O_2$.
Show all your working.

[1]

- (b) There are **four** possible structural isomers of $C_5H_{10}O_2$ that are carboxylic acids.

- (i) The first isomer has been drawn.

Draw the skeletal formulae of the three **other** structural isomers.

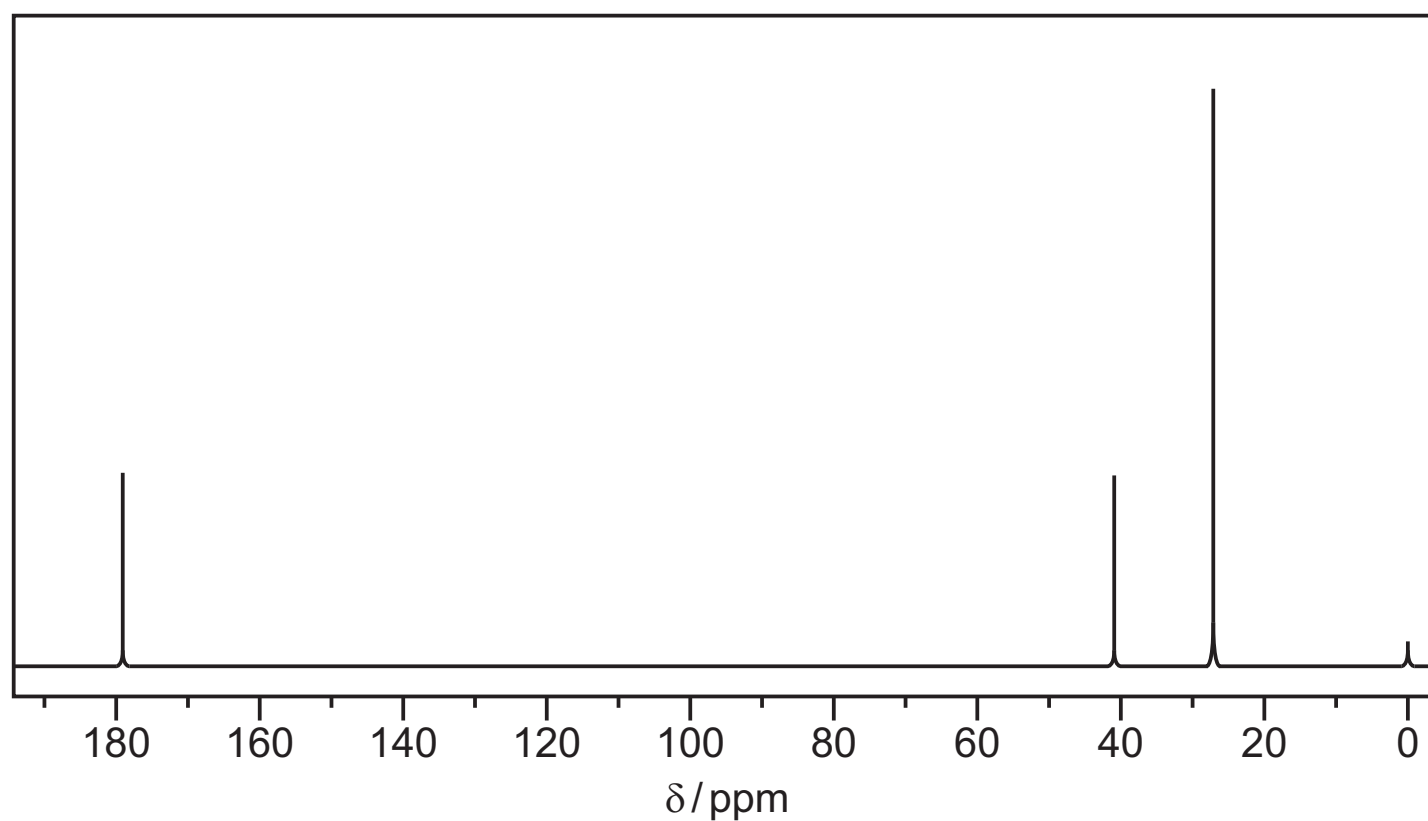


[2]

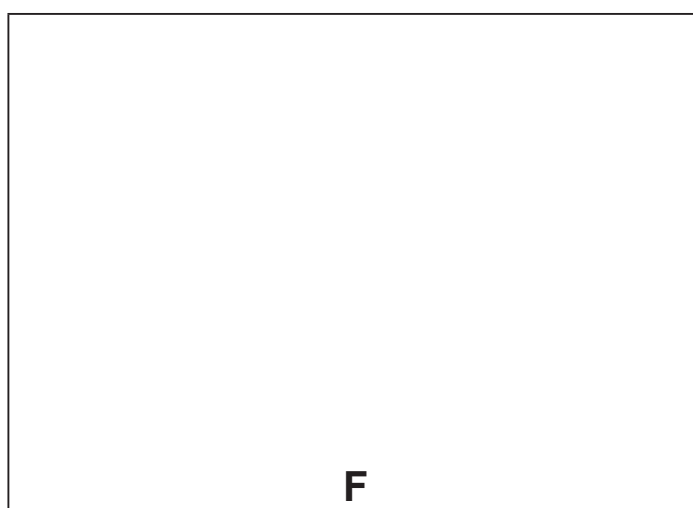
- (ii) State the systematic name of isomer 1.

..... [1]

(c) **F** is one of the four structural isomers in (b)(i). A carbon-13 NMR spectrum of **F** is shown.



(i) Use the spectrum to identify isomer **F**. Draw its structure in the box below.



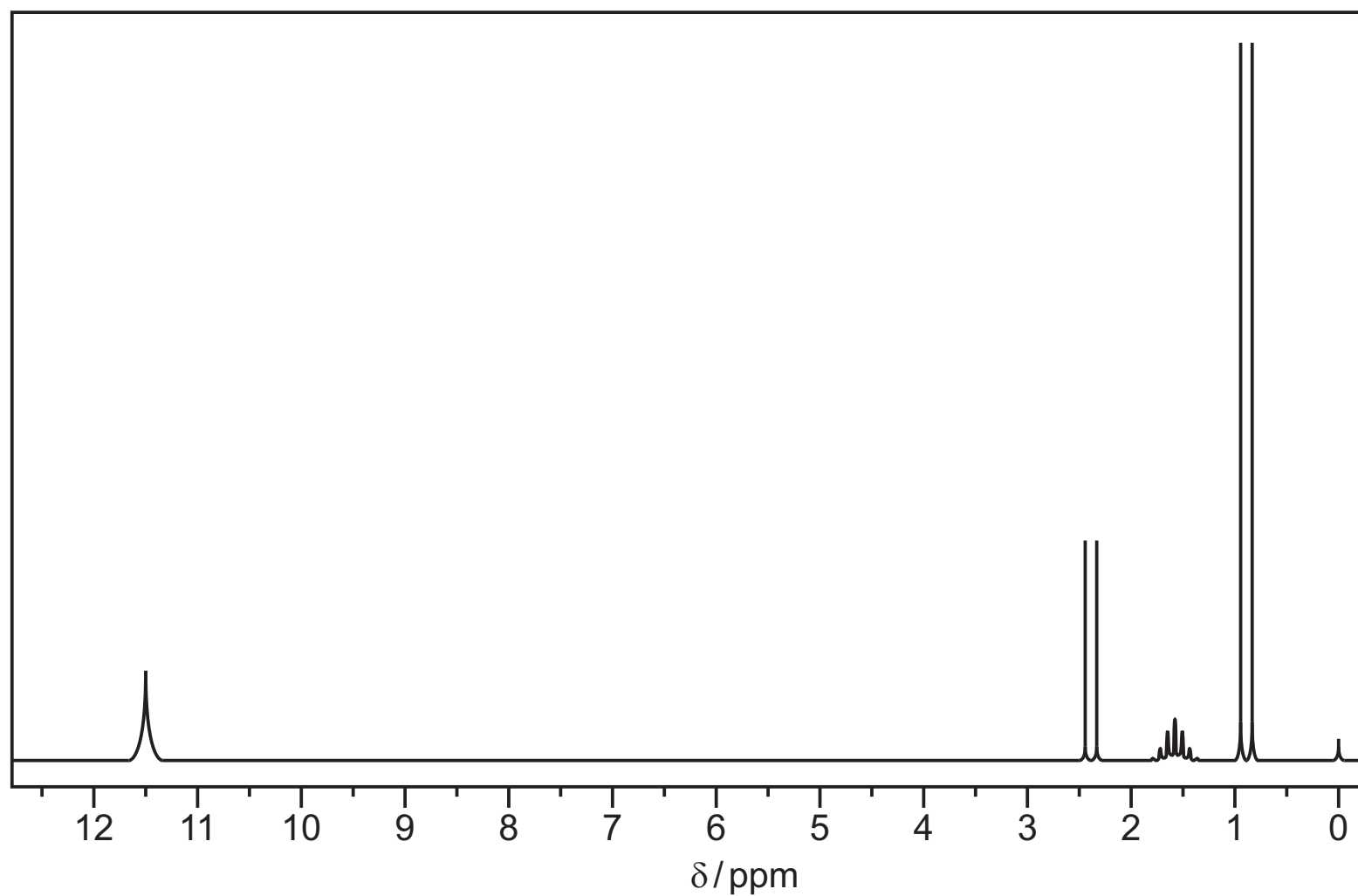
[1]

(ii) Use the *Data Booklet* and your knowledge of carbon-13 NMR spectroscopy to identify the environments and hybridisations of the carbon atoms responsible for each of the three absorptions.

δ/ppm	environment of the carbon atom	hybridisation of the carbon atom
27		
41		
179		

[2]

(d) **G** is another of the four structural isomers in (b)(i). The proton NMR spectrum of **G** is shown.



(i) Use the *Data Booklet* and the spectrum to complete the table below.

The actual chemical shifts for the four absorptions in **G** and the splitting pattern at $\delta = 1.6$ ppm have been added for you.

δ /ppm	type of proton	number of protons	splitting pattern
0.9			
1.6			multiplet
2.4			
11.5			

[4]

(ii) Deduce which isomer is **G** and draw its structure in the box.



[1]

(e) Name or give the formula of a suitable solvent for obtaining a proton NMR spectrum.

..... [1]

[Total: 13]

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CHEMISTRY

9701/43

Paper 4 A Level Structured Questions

October/November 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **20** printed pages.



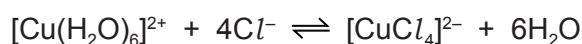
Answer **all** the questions in the spaces provided.

1 Copper is a transition element and has atomic number 29.

(a) Complete the electronic configuration for the copper atom and the copper ion in the +2 oxidation state.

- copper atom [Ar]
- copper ion in the +2 oxidation state [Ar] [2]

(b) The following equilibrium exists between two complex ions of copper in the +2 oxidation state.



(i) Name the *type of reaction* occurring here.

..... [1]

(ii) State the colours of these two complex ions.

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ $[\text{CuCl}_4]^{2-}$ [1]

(iii) State the shape of the $[\text{CuCl}_4]^{2-}$ ion.

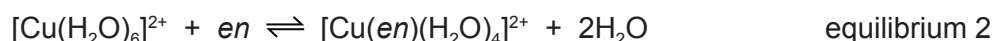
..... [1]

(iv) Write the expression for the stability constant, K_{stab} , for this equilibrium.

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

[1]

(c) Copper also forms the complex ions $[\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Cu}(\text{en})(\text{H}_2\text{O})_4]^{2+}$ where *en* is the bidentate ligand ethane-1,2-diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.



(i) What is meant by the term *bidentate ligand*?

.....
 [2]

- (ii) The table lists the values of stability constants for these two complexes.

	stability constant, K_{stab}
$[\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{2+}$	7.94×10^7
$[\text{Cu}(\text{en})(\text{H}_2\text{O})_4]^{2+}$	3.98×10^{10}

What do these K_{stab} values tell us about the relative positions of equilibria 1 and 2?

.....
 [1]

- (d) Nickel forms the complex ion $[\text{Ni}(\text{en})_3]^{2+}$ in which it is surrounded octahedrally by six nitrogen atoms.

- (i) Name the type of stereoisomerism displayed by $[\text{Ni}(\text{en})_3]^{2+}$.

..... [1]

- (ii) Draw three-dimensional diagrams to show the **two** stereoisomers of $[\text{Ni}(\text{en})_3]^{2+}$.

[3]

- (e) Ethane-1,2-diamine is a useful reagent in organic chemistry.

- (i) Explain how the amino groups in ethane-1,2-diamine allow the molecule to act as a Brønsted-Lowry base.

.....
 [2]

- (ii) Write an equation for the reaction of ethane-1,2-diamine with an excess of hydrochloric acid.

..... [1]

- (f) (i) Under certain conditions, ethane-1,2-diamine reacts with ethanedioic acid, $\text{HO}_2\text{CCO}_2\text{H}$, to form the polymer **Z**.

Draw the structure of this polymer, **Z**, showing **two** repeat units.

[2]

- (ii) Name the *type of reaction* occurring during this polymerisation.

..... [1]

- (iii) Polymer **Z** is an example of a biodegradable polymer.

Name a polymer that is non-biodegradable.

..... [1]

[Total: 20]

- 2 (a) When copper(II) carbonate is heated strongly, it decomposes in a similar way to Group 2 carbonates.

Predict what would be observed when anhydrous copper(II) carbonate is heated.

.....
 [1]

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

.....

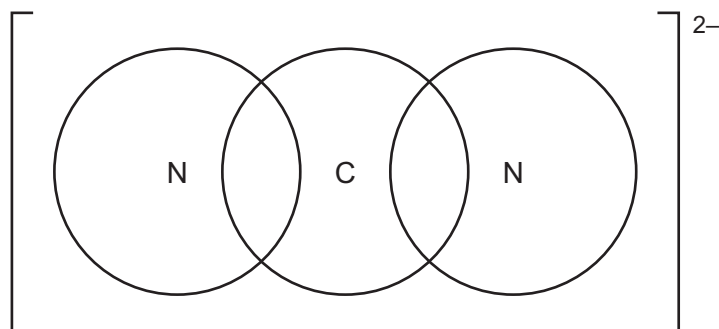
 [3]

- (c) Calcium cyanamide, CaCN_2 , can be used as a fertiliser.

- (i) Complete the 'dot-and-cross' diagram for the cyanamide ion, CN_2^{2-} .

Use the following key for the electrons.

- electrons from carbon
- × electrons from nitrogen
- added electron(s) responsible for the overall negative charge



[2]

- (ii) CaCN_2 decomposes readily on contact with water forming an insoluble white solid and ammonia only.

Suggest an equation for this reaction.

..... [2]

[Total: 8]

- 3 The spontaneity (feasibility) of a chemical reaction depends on the standard Gibbs free energy change, ΔG° . This is related to the standard enthalpy and entropy changes by the equation shown.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

- (a) State and explain whether the following processes will lead to an increase or decrease in entropy.

- (i) the reaction of magnesium with hydrochloric acid

entropy change

explanation

[1]

- (ii) solid potassium chloride dissolving in water

entropy change

explanation

[1]

- (iii) steam condensing to water

entropy change

explanation

[1]

- (b) Magnesium carbonate can be decomposed.



Standard entropies are shown in the table.

substance	MgCO ₃ (s)	MgO(s)	CO ₂ (g)
$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$	+65.7	+26.9	+214

- (i) Calculate ΔG° for this reaction at 298 K.
Include a relevant sign and give your answer to **three** significant figures.

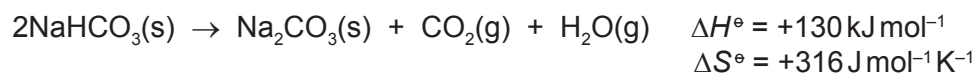
$\Delta G^\circ = \dots\dots\dots \text{kJ mol}^{-1}$ [3]

- (ii) Explain, with reference to ΔG° , why this reaction becomes more feasible at higher temperatures.

.....

..... [1]

(c) On heating, sodium hydrogencarbonate decomposes into sodium carbonate as shown.



Calculate the **minimum** temperature at which this reaction becomes spontaneous (feasible).
Show your working.

temperature = ... K [2]

(d) The solubility of Group 2 sulfates decreases down the Group.

Explain this trend.

.....

 [2]

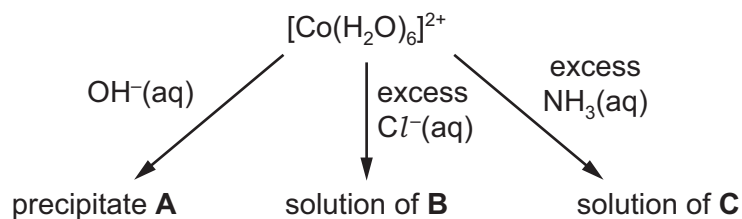
[Total: 11]

- 4 (a) Cobalt is a transition element that forms complex ions with oxidation states +2 and +3.

Explain what is meant by the term *transition element*.

.....
 [1]

- (b) The following scheme shows some reactions of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.



- (i) State the formula of each of the following.

A

B

C [2]

- (ii) State the colour of the following solutions.

$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

solution of **B**

solution of **C** [2]

- (c) Define the term *standard electrode potential*.

.....

 [2]

- (d) An electrochemical cell was set up to measure the standard electrode potential, $E_{\text{cell}}^{\ominus}$, of a cell made of a Co^{2+}/Co half-cell and a $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell.

- (i) Complete the table with the substance used to make the electrode in each of these half-cells.

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

[1]

- (ii) Write the equation for the overall cell reaction.

..... [1]

- (iii) Use the *Data Booklet* to calculate the $E_{\text{cell}}^{\ominus}$.

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

- (e) The electrochemical cell in (d) was set up again but this time the concentration of $\text{Co}^{2+}(\text{aq})$ was $0.050 \text{ mol dm}^{-3}$.

The Nernst equation can be used to calculate the value of an electrode potential at different concentrations.

$$E = E^{\ominus} + (0.059/z) \log [\text{Co}^{2+}(\text{aq})] \quad \text{Nernst equation}$$

- (i) Use the *Data Booklet* and the Nernst equation to calculate the value of E for the Co^{2+}/Co half-cell in this experiment.

$$E \text{ for } \text{Co}^{2+}/\text{Co} = \dots\dots\dots \text{V} \quad [1]$$

- (ii) Suggest how this change will affect the overall cell potential, E_{cell} , compared to $E_{\text{cell}}^{\ominus}$ in (d)(iii).

Circle your answer.

less positive no change more positive

[1]

- (f) Iron(III) ions can oxidise vanadium metal.

Construct an equation for the reaction of an excess of iron(III) ions with vanadium metal. Use of the *Data Booklet* will be helpful.

..... [2]

[Total: 14]

- 5 Compound **F** contains the elements carbon, hydrogen and oxygen only. All carbon-carbon bonds in **F** are single bonds. The structure of **F** was analysed by mass spectrometry and infra-red and NMR spectroscopy.

(a) The mass spectrum shows that the m/e value for the M peak is 90.

The ratio of the heights of the M and M+1 peaks is 22.1 : 0.7.

- (i) Use the ratio of the heights of the M and M+1 peaks to calculate the number of carbon atoms in a molecule of **F**.

number of carbon atoms = ... [2]

- (ii) Suggest the molecular formula of **F**.

molecular formula = C H O [1]

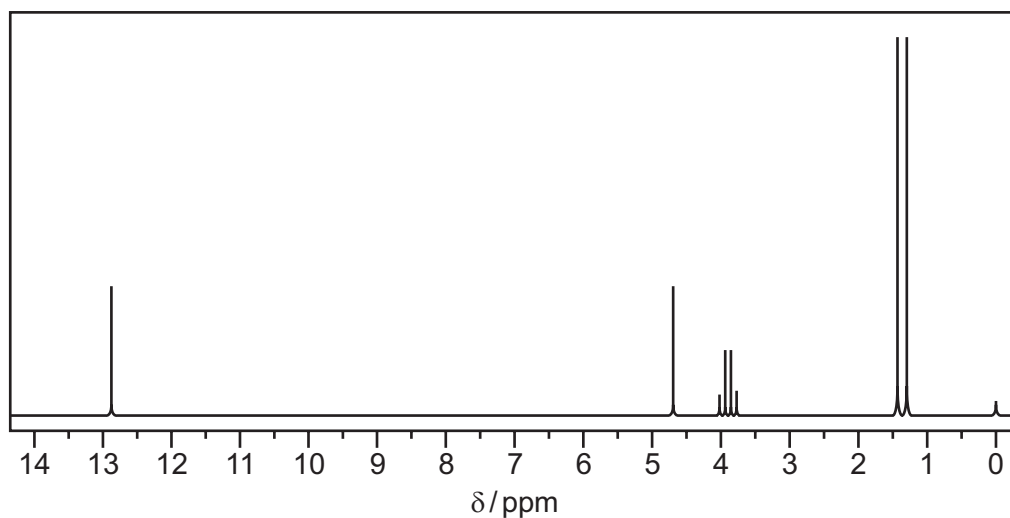
- (b) The infra-red spectrum of **F** was obtained.

Use the *Data Booklet* and your knowledge of infra-red spectroscopy to identify the type of bond and the functional group responsible for these **three** absorptions.

absorption/cm ⁻¹	appearance of the peak	type of bond	functional group
3350	broad and strong		
2680	very broad and strong		
1725	strong		

[2]

- (c) **F** was dissolved in deuterated trichloromethane, CDCl_3 , and the proton NMR spectrum of this solution obtained.



- (i) Use the *Data Booklet* and your answer to (a)(ii) to complete Table 1 for the proton NMR spectrum of **F**.
The actual chemical shifts for the four absorptions in **F** have been added for you.

Table 1

δ/ppm	type of proton	relative peak area
1.4		
3.9		
4.7		
12.9		

[4]

- (ii) Describe and explain the splitting pattern for the absorption at $\delta = 1.4$.

.....
 [1]

- (iii) **F** was dissolved in D_2O and the proton NMR spectrum of this new solution obtained. Two of the absorptions in Table 1 were not present in this spectrum.

Which absorptions were **not** present?

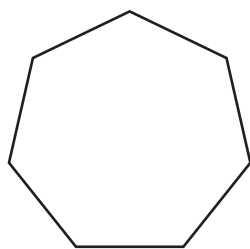
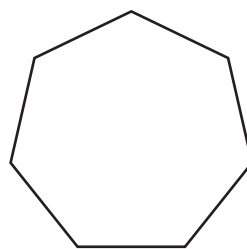
..... and [1]

- (iv) Suggest the structure of **F**.

[1]

(d) Molecules of cycloheptadiene, C_7H_{10} , consist of a seven-membered ring with two carbon-carbon double bonds.

(i) Complete the skeletal formulae of two isomers of cycloheptadiene.

**P****Q**

[1]

The isomers **P** and **Q** were analysed using carbon-13 NMR spectroscopy.

(ii) Predict the number of peaks that will be seen in the carbon-13 NMR spectra of **P** and **Q**.

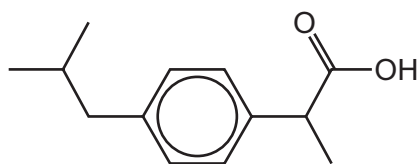
isomer	number of peaks
P	
Q	

[2]

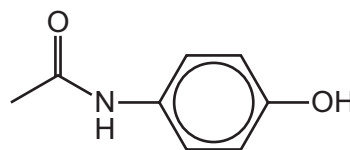
[Total: 15]

Question 6 starts on the next page.

- 6 Ibuprofen and paracetamol are pain-relief drugs.



ibuprofen



paracetamol

- (a) Ibuprofen and paracetamol both contain the aryl (benzene) functional group.

Name the **other** functional groups present in each molecule.

ibuprofen

paracetamol

[2]

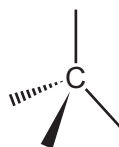
- (b) Ibuprofen contains a chiral centre and shows stereoisomerism.

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

.....

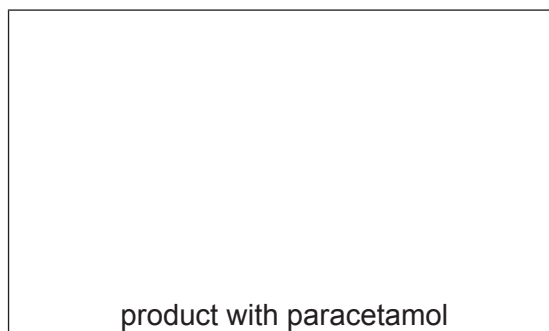
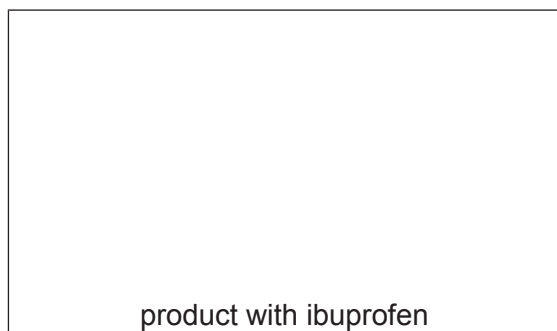
..... [1]

- (ii) Draw the two stereoisomers of ibuprofen.



[2]

- (c) Draw the structures of the organic products when ibuprofen and paracetamol react separately with LiAlH_4 .



[2]

- (d) A student carried out some reactions with solutions of ibuprofen and paracetamol using reagents **D** and **E** and the following results were obtained.
(✓ means a reaction took place.)

reagent	ibuprofen	paracetamol
D	✓	✗
E	✗	✓

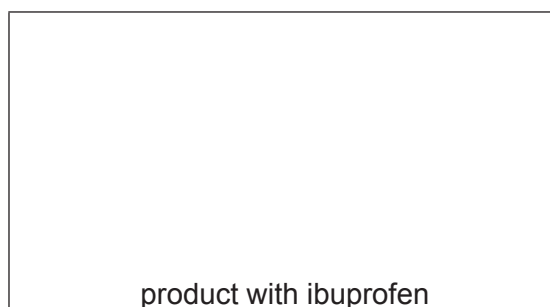
- (i) Suggest a possible identity for each reagent **D** and **E**.

D

E

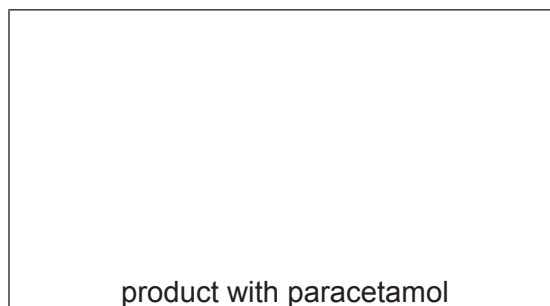
[2]

- (ii) Give the structure of the organic product formed when reagent **D** reacted with ibuprofen.



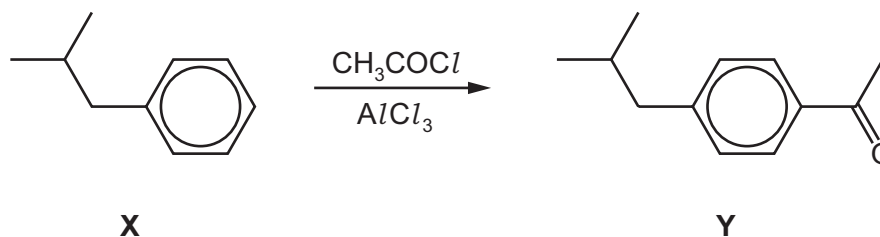
[1]

- (iii) Give the structure of the organic product formed when reagent **E** reacted with paracetamol.



[1]

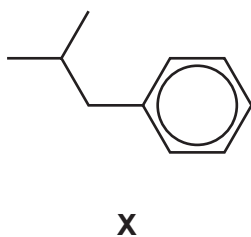
(e) One of the steps in the manufacture of ibuprofen is shown.



(i) Write an equation for the reaction between CH_3COCl and AlCl_3 .

..... [1]

(ii) Complete the mechanism for the conversion of **X** into **Y**. Include all necessary curly arrows, any relevant dipoles and charges.



[3]

(iii) Name the mechanism in (ii).

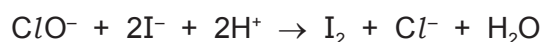
..... [1]

[Total: 16]

Question 7 starts on the next page.

- 7 (a) Sodium chlorate(I), NaClO , is the active ingredient in commercial bleach. The concentration of chlorate(I) ions was determined by titration.
- 10.0 cm^3 of a bleach solution was diluted to 250 cm^3 in a volumetric flask using distilled water.
 - Dilute sulfuric acid and an excess of potassium iodide solution were added to a 25.0 cm^3 portion of this solution to liberate iodine.
 - The resulting solution required 20.80 cm^3 of 0.100 mol dm^{-3} aqueous sodium thiosulfate solution to react with the iodine produced.

The titration reactions are shown.



Calculate the concentration, in mol dm^{-3} , of ClO^- ions in the bleach solution.

concentration of ClO^- = ... mol dm^{-3} [3]

(b) An indicator was used in the thiosulfate-iodine titration.

(i) Name a suitable indicator for this titration.

..... [1]

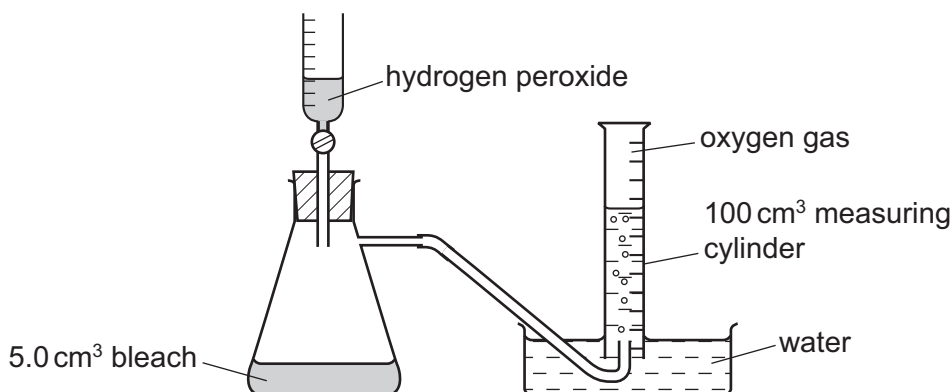
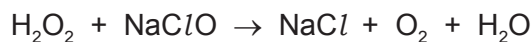
(ii) State the expected colour change you would observe at the end-point in this titration.

from to [1]

(iii) State when in the procedure you would add the indicator.

.....
 [1]

- (c) The concentration of chlorate(I) ions can also be determined by adding an excess of hydrogen peroxide to the sample of bleach and measuring the volume of oxygen gas produced.

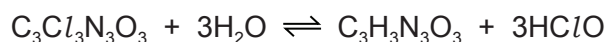


When an excess of aqueous hydrogen peroxide was added to 5.0 cm³ of a different bleach solution, 82 cm³ of oxygen was produced at room temperature and pressure.

Calculate the concentration of ClO⁻ ions in this bleach solution.

concentration of ClO⁻ = ... mol dm⁻³ [2]

- (d) Trichlorocyanuric acid, C₃Cl₃N₃O₃, acts as a chlorine buffer and disinfectant for swimming pools. It reacts with water to give chloric(I) acid, HClO.



- (i) Write the expression for K_c for this equilibrium.

$K_c =$

[1]

- (ii) In outdoor swimming pools, the HClO is decomposed by sunlight. The decomposition of HClO is a redox reaction which forms a gas that relights a glowing splint.

Describe and explain the effect of the decomposition of HClO on the equilibrium in (d). State the effect on K_c .

.....

effect on K_c

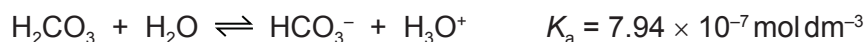
[2]

- (iii) The decomposition of HClO is a redox reaction.

Suggest an equation for this reaction.

..... [1]

- (e) The buffer solution in blood is a mixture of carbonic acid, H_2CO_3 , and hydrogencarbonate ions, HCO_3^- . Healthy blood has a pH of 7.40.



- (i) Explain how this buffer system acts to control the blood pH. Include equations in your answer.

.....

 [2]

- (ii) A patient's blood has a $[\text{HCO}_3^-] : [\text{H}_2\text{CO}_3]$ ratio of 9.5 : 1.

Calculate the pH of the patient's blood.

pH = ... [2]

[Total: 16]

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