Cambridge International A2 Level Chemistry

Question Papers

Paper #4

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CONTENTS

Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME			
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2165639790

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2021**

2 hours

You must answer on the question paper.

You will need: Data booklet

INSTRUCTIONS

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

INFORMATION

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

This document has **24** pages. Any blank pages are indicated.

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

1 **(a)** An aqueous solution of chromium(III) contains the green $[Cr(H_2O)_6]^{3+}$ complex ion.

(i) Complete the electronic configuration of an isolated, gaseous Cr^{3+} ion.

$1s^2$ .... [1]

(ii) Define the term *complex ion*.

....

.... [1]

(b) $[Cr(H_2O)_6]^{3+}(aq)$ shows some similar chemical properties to $[Co(H_2O)_6]^{2+}(aq)$.

Samples of $[Cr(H_2O)_6]^{3+}$ are reacted separately with either NaOH(aq), $H_2O_2(aq)$, or excess $NH_3(aq)$.

Use this information and the *Data Booklet* to suggest the formula of the chromium species formed. State the type of reaction taking place in each case.

reagent added to $[Cr(H_2O)_6]^{3+}(aq)$	formula of chromium species formed	type of reaction
NaOH(aq)		
$H_2O_2(aq)$		
an excess of $NH_3(aq)$		

[5]

(c) $[Cr(H_2O)_6]^{2+}$ and $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ are both complexes of chromium(II) and have different colours.

Explain why the colours of these complexes are different.

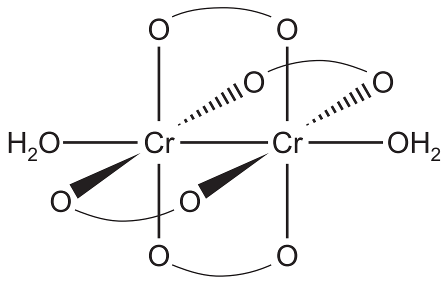
....

....

....

.... [2]

(d) The structure of $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ is shown. Ethanoate ions act as ligands in this complex. The ethanoate ligand, $CH_3CO_2^-$, is shown as $O \frown O$.



(i) Water and ethanoate ions behave as different types of ligand in this complex.

Suggest an explanation for this statement.

....

.... [1]

(ii) Deduce the coordination number of Cr and the geometry around each Cr atom in this structure.

coordination number ....

geometry around Cr atom ....
[1]

(iii) State the type of bond between the two atoms in the Cr–Cr bond.

.... [1]

(e) The $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ complex reacts with aqueous acid to form $Cr^{2+}(aq)$ ions.

$Cr^{2+}(aq)$ ions react with $O_2(aq)$ under acidic conditions. $Cr^{3+}(aq)$ ions are formed.

Use the *Data Booklet* to answer the following questions.

(i) Construct an ionic equation for the reaction of $Cr^{2+}(aq)$ with $O_2(aq)$ under acidic conditions.

.... [2]

(ii) Calculate $E^{\ominus}_{cell}$ for the reaction in **(e)(i)**.

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

[Total: 15]

2 **(a)** State and explain the trend observed in the thermal stability of the Group 2 nitrates.

....

....

....

....

.... [3]

(b) **(i)** Lead(II) nitrate, $Pb(NO_3)_2$, decomposes on heating in a similar manner to the Group 2 nitrates.

Write an equation for the decomposition of lead(II) nitrate.

.... [1]

(ii) Suggest how the ease of decomposition of $Pb(NO_3)_2$ would compare to that of $Ba(NO_3)_2$. Explain your answer. You may find it useful to refer to the *Data Booklet*.

....

.... [1]

(c) **(i)** Barium ethanedioate, BaC_2O_4, decomposes on heating to produce barium oxide and a mixture of two different gases.

Construct an equation for the decomposition of barium ethanedioate.

.... [1]

(ii) An impure sample of BaC_2O_4, of mass 0.500 g, is added to 50.0 cm^3 of 0.0200 mol dm^{-3} acidified MnO_4^-(aq), an excess. A redox reaction takes place and all the BaC_2O_4 reacts.

The resulting solution, containing unreacted acidified MnO_4^-, is titrated with 0.0500 mol dm^{-3} Fe^{2+}(aq).

The end-point is reached when 30.40 cm^3 of 0.0500 mol dm^{-3} Fe^{2+}(aq) has been added.

$$C_2O_4^{2-} \rightleftharpoons 2CO_2 + 2e^-$$

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

Calculate the percentage by mass of BaC_2O_4 in the 0.500 g impure sample. Show your working.
[M_r: BaC_2O_4, 225.3]

percentage by mass of BaC_2O_4 = ... [4]

(d) Barium hydroxide, $Ba(OH)_2$, is completely dissociated in aqueous solution.

Calculate the pH of 0.120 mol dm^{-3} $Ba(OH)_2$(aq) at 298 K.

pH = ... [2]

[Total: 12]

3 **(a)** **(i)** Define the term *standard electrode potential*.

....

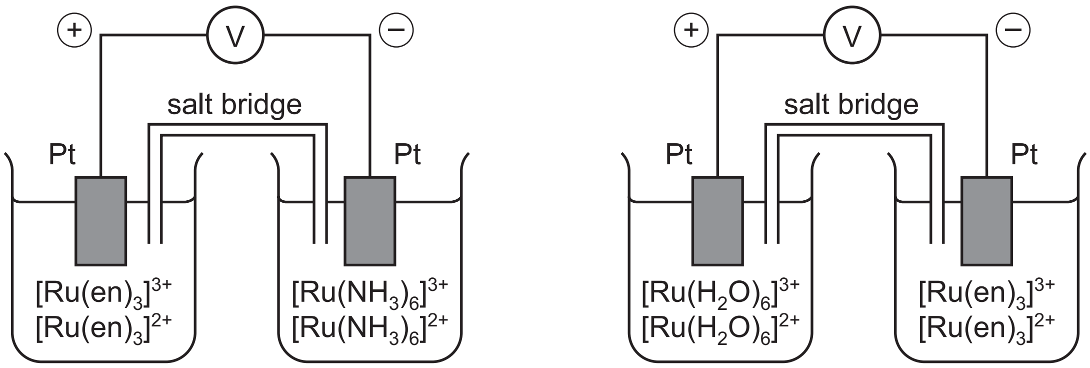
....

.... [2]

Three redox systems, **A**, **B** and **C**, are shown. The ligand 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, is represented by en.

A	$[Ru(H_2O)_6]^{3+} + e^- \rightleftharpoons [Ru(H_2O)_6]^{2+}$
B	$[Ru(NH_3)_6]^{3+} + e^- \rightleftharpoons [Ru(NH_3)_6]^{2+}$
C	$[Ru(en)_3]^{3+} + e^- \rightleftharpoons [Ru(en)_3]^{2+}$

Two electrochemical cells are set up to compare the standard electrode potentials, $E^\ominus$, of three half-cells. The diagrams show the relative potential of each electrode.

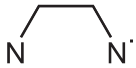


(ii) Use this information to complete the table by adding the labels **A**, **B** and **C** to deduce the order of $E^\ominus$ for the three half-cells.

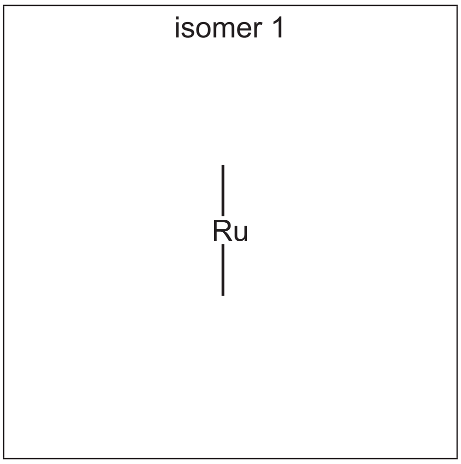
$E^\ominus$	redox system
most negative	
↑	
least negative	

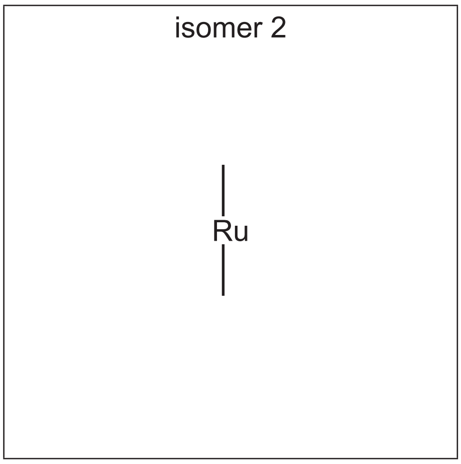
[1]

(iii) The complex $[Ru(en)_3]^{3+}$ shows stereoisomerism. The ligand en is bidentate.

Draw three-dimensional diagrams to show the two isomers of $[Ru(en)_3]^{3+}$. Represent the ligand en by using .

Name the type of stereoisomerism.





type of stereoisomerism ....

[3]

(b) (i) An electrochemical cell consists of a Br_2/Br^- half-cell and a Ag^+/Ag half-cell, under standard conditions.

Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$. Deduce the direction of electron flow in the wire through the voltmeter between these two half-cells.

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

direction of electron flow from .... to .... [1]

(ii) Water is added to the Ag^+/Ag half-cell in **(b)(i)**.

Suggest the effect of this addition on the E_{cell}. Place a tick (✓) in the appropriate box.

less positive	no change	more positive

Explain your answer.

....

....

.... [2]

(c) Silver bromide, AgBr, dissolves in an aqueous solution of $S_2O_3^{2-}$ ions to form the complex ion $[Ag(S_2O_3)_2]^{3-}$. The $S_2O_3^{2-}$ ions act as monodentate ligands.

equilibrium 1 $AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)$

(i) Define the term *ligand*.

....

.... [1]

(ii) Write an expression for the equilibrium constant, K_c, for equilibrium 1.

K_c =

[1]

(iii) Some additional data are given about the dissolution of AgBr in $S_2O_3^{2-}$(aq).

equilibrium constant	numerical value
solubility product, K_{sp}, of AgBr	5.4×10^{-13}
stability constant, K_{stab}, of $[Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}

Use your answer to **(c)(ii)** and these data to calculate K_c for equilibrium 1. Include the units for K_c.

K_c = ... units .... [2]

(d) The numerical values for the stability constants, K_{stab}, of two other silver(I) complexes are given.

silver(I) complex	numerical value of K_{stab}
$[Ag(CN)_2]^-$	5.3×10^{18}
$[Ag(NH_3)_2]^+$	1.6×10^{7}

An aqueous solution containing Ag^+ is added to a solution containing equal concentrations of CN^-(aq), NH_3(aq) and $S_2O_3^{2-}$(aq). The mixture is left to reach equilibrium.

Deduce the relative concentrations of $[Ag(CN)_2]^-$, $[Ag(NH_3)_2]^+$ and $[Ag(S_2O_3)_2]^{3-}$ present in the resulting mixture. Explain your answer.

.... > .... > ....

highest concentration lowest concentration

....

.... [2]

[Total: 15]

4 **(a)** **(i)** Define the term *lattice energy*.

....

....

.... [2]

(ii) Use the following data to calculate a value for the enthalpy change of solution of copper(II) chloride, $CuCl_2$(s). You might find it helpful to construct an energy cycle.

enthalpy change of hydration of Cl^- = –378 kJ mol^{-1}
enthalpy change of hydration of Cu^{2+} = –2099 kJ mol^{-1}
lattice energy of $CuCl_2$(s) = –2824 kJ mol^{-1}

enthalpy change of solution of $CuCl_2$(s) = ... kJ mol^{-1} [2]

(iii) The enthalpy change of hydration of Ca^{2+} is –1579 kJ mol^{-1}.

Use the *Data Booklet* to suggest why there is a big difference in the values of ΔH_{hyd} for Ca^{2+} and Cu^{2+}.

....

....

.... [2]

(b) **(i)** Identify the substances formed at the anode and at the cathode during the electrolysis of saturated $CaCl_2$(aq).

at the anode ....

at the cathode ....
[1]

(ii) Calcium can be produced by the electrolysis of molten calcium chloride, $CaCl_2$(l).

Calculate the mass, in g, of Ca formed when a current of 0.75A passes through $CaCl_2$(l) for 60 minutes.
[A_r: Ca, 40.1]

mass of Ca = ... g [2]

(c) **(i)** Explain what is meant by the term *entropy of a system*.

....

.... [1]

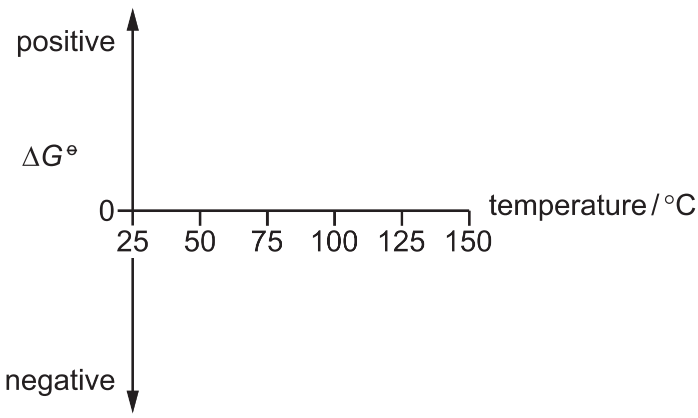
(ii) Place one tick (✓) in each row of the table to show the sign of each entropy change, ΔS.

process	ΔS is negative	ΔS is zero	ΔS is positive
NaCl dissolving in water			
water solidifying to ice			

[1]

(iii) The evaporation of one mole of water has a standard Gibbs free energy change, $\Delta G^{\ominus}$, of +8.6 kJ at 25 °C.

Sketch a graph on the axes to show how $\Delta G^{\ominus}$ changes for this process between 25 °C and 150 °C at 101 kPa.



[2]

(d) The reaction between A and B is feasible at low temperatures but is **not** feasible at high temperatures.

$$A + B \rightleftharpoons C + D$$

Deduce the signs of ΔH and ΔS for this reaction and explain why the feasibility changes with temperature.

sign of ΔH = ... sign of ΔS = ...

....

....

....

.... [2]

[Total: 15]

5 **(a)** Describe and explain the relative basicities of phenylamine, ethylamine and 4-nitrophenylamine.

.... > .... > ....

most basic   least basic

....

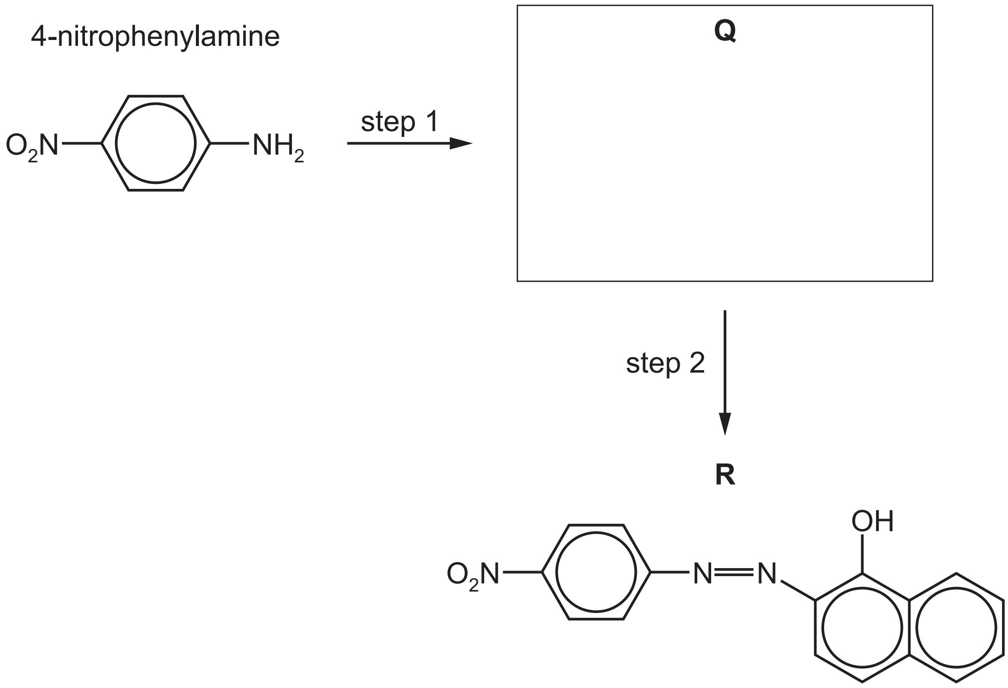
....

....

....

.... [4]

(b) The dye **R** can be synthesised from 4-nitrophenylamine in two steps.



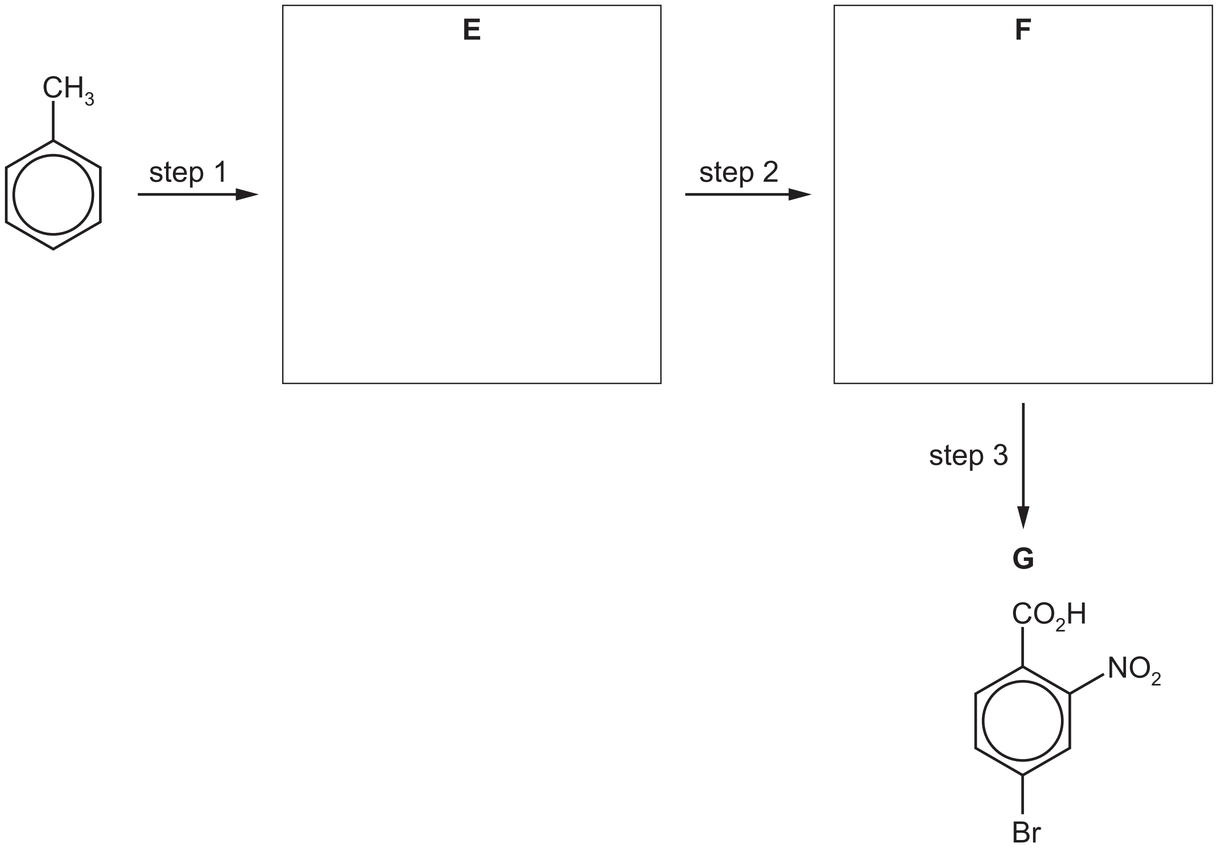
(i) Deduce and draw the structure of the organic salt **Q** in the box. [1]

(ii) Suggest reagents and conditions for step 1 and 2 in **(b)**.

step 1 ....

step 2 ....
[2]

(c) Compound **G** can be synthesised from methylbenzene in three steps.



(i) Give the systematic name of compound **G**.

.... [1]

(ii) Deduce the identities of **E** and **F** and draw their structures in the boxes. [2]

(iii) Suggest reagents and conditions for each of steps 1 to 3 in **(c)**.

step 1 ....

step 2 ....

step 3 ....
[3]

[Total: 13]

6 **(a)** There are four possible structural isomers of C_8H_{10} that contain a benzene ring.

Draw the **skeletal** formulae of the four structural isomers in the appropriate boxes. The number of peaks observed in the carbon-13 (^{13}C) NMR spectrum of each compound is given.

isomer 1

three peaks in ^{13}C NMR

isomer 2

four peaks in ^{13}C NMR

isomer 3

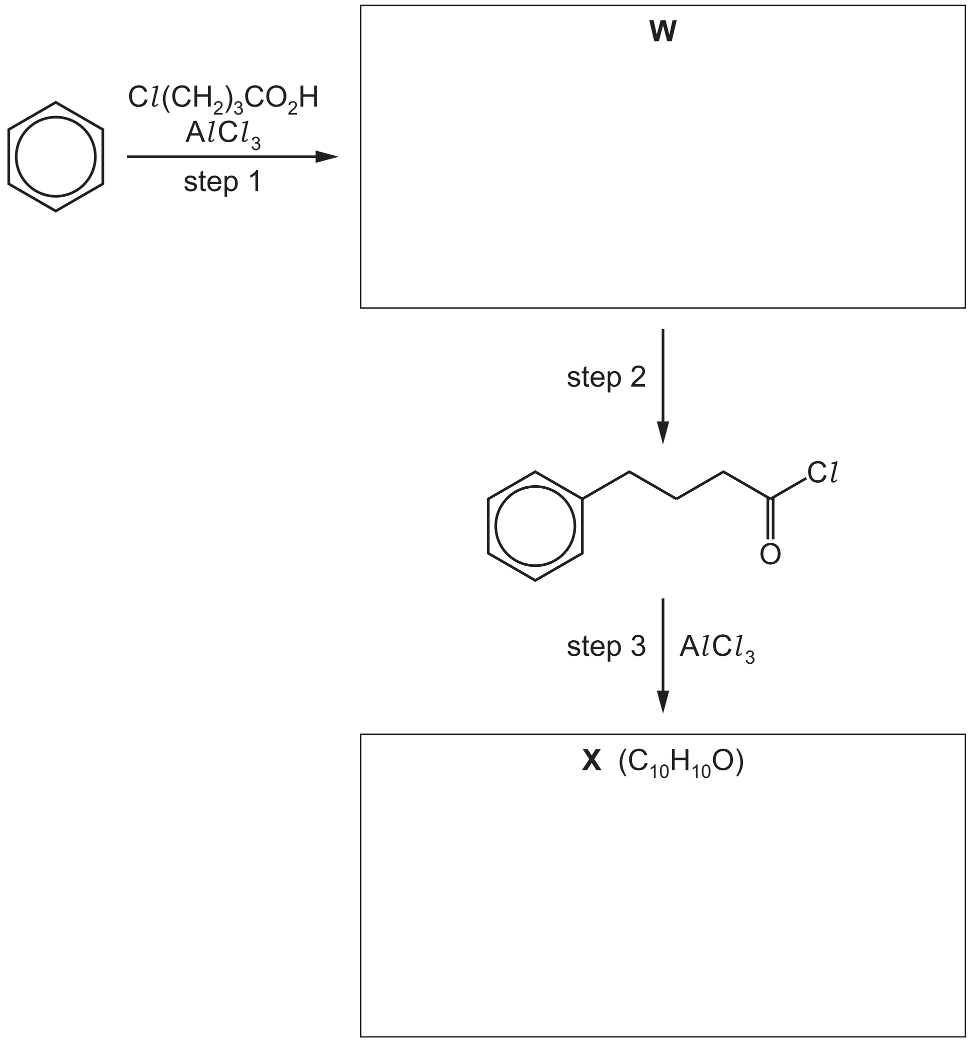
five peaks in ^{13}C NMR

isomer 4

six peaks in ^{13}C NMR

[4]

(b) A three-step synthesis of **X** ($C_{10}H_{10}O$) from benzene is suggested as shown.



(i) Step 1 is the alkylation of benzene by electrophilic substitution.
Use R–Cl to represent $Cl(CH_2)_3CO_2H$.

Write an equation for the formation of an electrophile from R–Cl and $AlCl_3$.

.... [1]

(ii) Deduce and draw the structures of **W** and **X** in the boxes. [2]

(iii) Suggest the reagents and conditions for step 2.

.... [1]

(iv) Complete the mechanism for the reaction of benzene with the electrophile formed in **(b)(i)**.

Include all relevant charges and curly arrows showing the movement of electron pairs.

Draw the structure of the intermediate.

[3]

[Total: 11]

7 **(a)** In aqueous solution, chlorine dioxide, ClO_2, reacts with hydroxide ions as shown.

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

A series of experiments is carried out using different concentrations of ClO_2 and OH^-. The table shows the results obtained.

experiment	$[ClO_2]$ / $mol\,dm^{-3}$	$[OH^-]$ / $mol\,dm^{-3}$	initial rate / $mol\,dm^{-3}\,min^{-1}$
1	0.020	0.030	7.20×10^{-4}
2	0.020	0.120	2.88×10^{-3}
3	0.050	0.030	4.50×10^{-3}

(i) Explain the term *order of reaction*.

....

.... [1]

(ii) Use the data in the table to determine the order of reaction with respect to each reactant, ClO_2 and OH^-.

Explain your reasoning.

....

....

....

....

....

.... [2]

(iii) Use your answer to **(a)(ii)** to construct the rate equation for this reaction.

rate = ... [1]

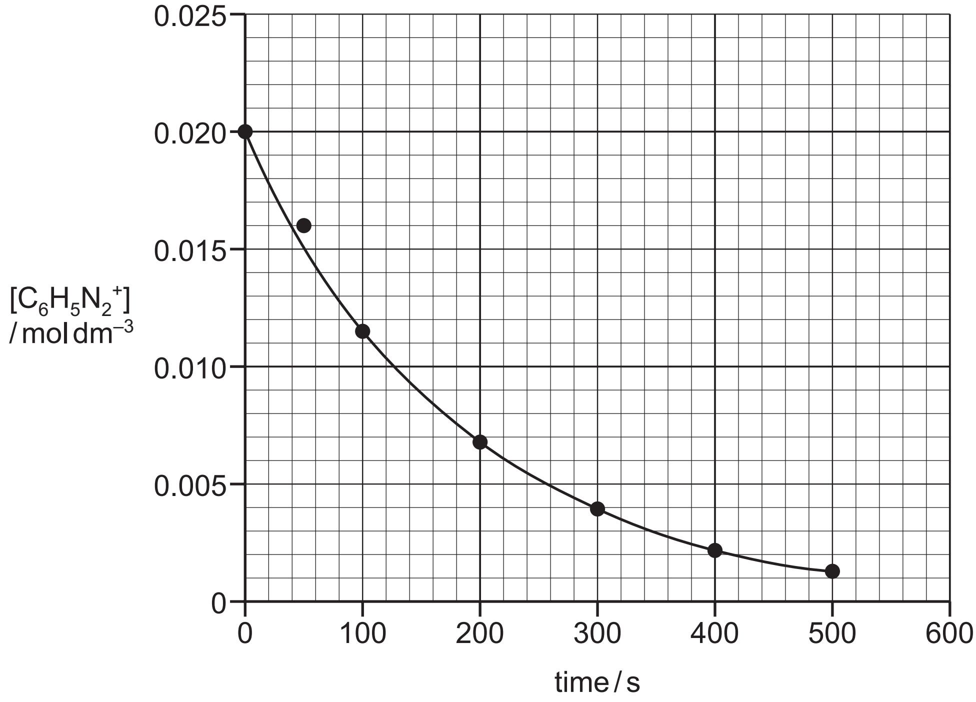
(iv) Use your rate equation and the data from experiment 1 to calculate the rate constant, *k*, for this reaction.
Include the units of *k*.

k = ... units .... [2]

Question 7 continues on the next page.

(b) The decomposition of benzenediazonium ions, $C_6H_5N_2^+$, using a large excess of water, is a first-order reaction.

The graph shows the results obtained.



(i) Draw the structure of the organic product formed in this reaction.

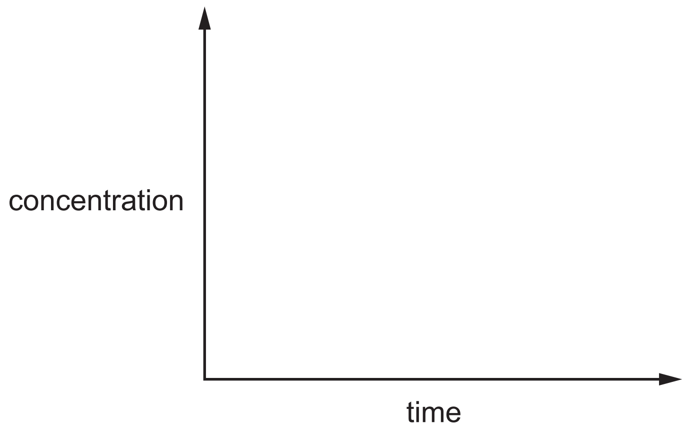
[1]

(ii) Use the graph to determine the rate of reaction at 100 s. Show your working.

rate = ... mol dm^{-3} s^{-1} [1]

(c) Sketch a concentration–time graph for a **zero-order** reaction.

Use your graph to suggest how successive half-lives for a zero-order reaction vary as the concentration of a reactant decreases. Indicate this by placing a tick (✓) in the appropriate box in the table.



successive half-lives decrease	no change in successive half-lives	successive half-lives increase

[1]

[Total: 9]

8 **(a)** State and explain the relative rate of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides.

.... > .... > ....
fastest slowest

....

....

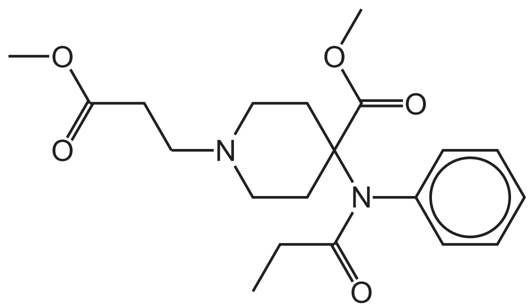
....

....

.... [3]

(b) The drug remifentanil is shown.

remifentanil

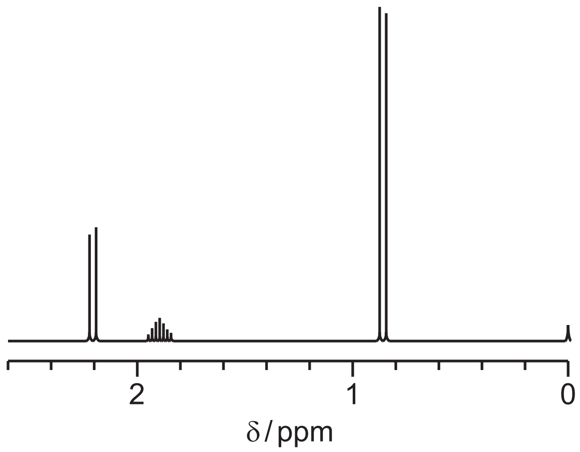


Remifentanil is **completely** hydrolysed under acidic conditions. Three different organic compounds are formed.

Draw the structures for these organic compounds in the boxes.

[3]

(c) Compound **Y**, $C_5H_{10}O_2$, reacts with Na_2CO_3(aq) to evolve bubbles of gas. The proton (^1H) NMR spectrum of compound **Y** in D_2O is shown.



(i) Use this information to suggest a structure for **Y**.

[1]

(ii) Use the *Data Booklet*, the proton (^1H) NMR spectrum and your answer to **(c)(i)** to complete the table.

chemical shift (δ)	environment of proton	splitting pattern	number of ^1H atoms responsible for the peak
0.95			
1.90			
2.20			

[3]

[Total: 10]

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Cambridge International AS & A Level

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* 3 9 5 2 4 5 7 6 7 2 *

CHEMISTRY **9701/42**

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

2 hours

You must answer on the question paper.

You will need: Data booklet

INSTRUCTIONS

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

INFORMATION

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

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

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

1 Radium is a Group 2 element.

The predicted lattice energy, $\Delta H^{\ominus}_{latt}$, of radium sulfide, RaS, is $-2612\,kJ\,mol^{-1}$.

(a) Define $\Delta H^{\ominus}_{latt}$.

....

.... [2]

Some data relating to radium and sulfur are listed. Select relevant data from this list for use in your answers to parts **(b)** to **(e)**.

process	value / $kJ\,mol^{-1}$
enthalpy change for $Ra(s) \rightarrow Ra^{2+}(g) + 2e^-$	+1619
first ionisation energy of sulfur	+1000
second ionisation energy of sulfur	+2260
first electron affinity of sulfur	–200
second electron affinity of sulfur	+532
enthalpy change for $\frac{1}{8}S_8(s) + 2e^- \rightarrow S^{2-}(g)$	+555
lattice energy of RaS(s)	–2612

(b) Write an equation for the process corresponding to the **second** electron affinity of sulfur. Include state symbols.

.... [1]

(c) Sulfur exists as S_8 molecules in the solid state.

Use the data in this question to calculate the enthalpy change for the reaction $S_8(s) \rightarrow 8S(g)$.

enthalpy change = ... $kJ\,mol^{-1}$ [3]

(d) Calculate the standard enthalpy change of formation, ΔH_f°, of radium sulfide.

standard enthalpy change, ΔH_f° = ... $kJ\,mol^{-1}$ [2]

(e) **(i)** State the **two** major factors that affect the numerical magnitude of a lattice energy.

....

.... [2]

(ii) For **each** factor you have identified in **(e)(i)**, state whether it tends to make the lattice energy of radium sulfide more or less exothermic than that of sodium chloride.

Explain your answer.

....

....

....

.... [2]

(iii) The lattice energies of sodium chloride, $NaCl$, and radium sulfide, RaS, are $-771\,kJ\,mol^{-1}$ and $-2612\,kJ\,mol^{-1}$, respectively.

Identify the **dominant** factor in determining the relative numerical magnitudes of the lattice energies of radium sulfide and sodium chloride.

Explain your answer.

....

.... [1]

[Total: 13]

2 Ethoxyethane, $C_2H_5OC_2H_5$, can dissolve both in water and in octan-1-ol. The expression and numerical value for the partition coefficient of ethoxyethane between water and octan-1-ol are given. Water and octan-1-ol are immiscible.

$$K_{pc} = \frac{\text{concentration of } C_2H_5OC_2H_5 \text{ in octan-1-ol}}{\text{concentration of } C_2H_5OC_2H_5 \text{ in water}} = 6.760 \text{ at } 20\,°C$$

(a) In an experiment, octan-1-ol at 20 °C is added to a solution of ethoxyethane in water at 20 °C. The mixture is analysed immediately and a value of K_{pc} is calculated.

The calculation is performed correctly; the value calculated is 5.625.

Explain why the value calculated is **less** than 6.760.

....

.... [2]

(b) A second experiment is performed and the value of K_{pc} is found to be 6.760. The concentration of ethoxyethane in the octan-1-ol layer is 7.62 g dm^{-3}.

(i) Calculate the concentration, in g dm^{-3}, of ethoxyethane in the aqueous layer.

.... g dm^{-3} [1]

(ii) 100 cm^3 of the octan-1-ol layer is taken and shaken with 100 cm^3 of water.

Calculate the maximum amount, in mol, of ethoxyethane that can be extracted into the water.

.... mol [3]

(c) An aqueous solution of lead(II) nitrate is mixed with an aqueous solution of sodium iodide. A yellow precipitate of lead(II) iodide is formed and is filtered out, leaving solution **X**.

The concentration of Pb^{2+} in solution **X** is $5.68 \times 10^{-3}\,mol\,dm^{-3}$.

The concentration of I^{-} in solution **X** is $4.20 \times 10^{-4}\,mol\,dm^{-3}$.

(i) Use these data to calculate a value for the solubility product, K_{sp}, of lead(II) iodide.

State the units of K_{sp}.

K_{sp} = ...

units = ...
[2]

(ii) Potassium iodide is very soluble in water.

Describe and explain what is seen if a few drops of saturated potassium iodide solution are added to a portion of solution **X**.

....

....

.... [2]

[Total: 10]

3 Pure water is a very poor conductor of electricity. However, when hydrogen chloride gas is dissolved in water, ions are formed and a current flows during electrolysis.

$$HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq)$$

The overall change after electrolysis is that hydrogen chloride gas is converted into hydrogen and chlorine.

$$2HCl(g) \rightarrow H_2(g) + Cl_2(g)$$

When a current of 3.10 A is passed through the solution for *Y* minutes, 351 cm^3 of chlorine are produced at the anode, measured under room conditions.

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

number of chlorine molecules = ... [2]

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

total number of electrons = ... [1]

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

quantity of charge = ... C [1]

(d) Calculate the time, *Y*, in minutes, for which the current flows.

Y = ... minutes [1]

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

species	$S^\ominus$ / J K^{-1} mol^{-1}
$HCl(g)$	+187
$H_2(g)$	+131
$Cl_2(g)$	+223

(i) Calculate $\Delta S^\ominus$ for the reaction $2HCl(g) \rightarrow H_2(g) + Cl_2(g)$.

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

(ii) $\Delta H^\ominus$ for the reaction $2HCl(g) \rightarrow H_2(g) + Cl_2(g)$ is +185 kJ mol^{-1}.

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

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

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

....

.... [1]

[Total: 9]

4 Separate samples of 0.01 mol of magnesium nitrate and 0.01 mol of strontium nitrate are heated until completely decomposed to the metal oxide, nitrogen dioxide and oxygen.

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

....

....

....

.... [2]

(b) After decomposition is complete the 0.01 mol sample of magnesium oxide is taken and increasing amounts of water are added to it, with stirring, until no solid remains.

This procedure is repeated with the 0.01 mol sample of strontium oxide.

Identify the sample to which most water must be added to cause all the solid to dissolve. Explain your answer by reference to the solubilities of the products formed when water is added to the oxides. You should refer to relevant energy terms in your answer.

....

....

....

....

.... [3]

(c) The nitrogen dioxide given off by the decomposition of 0.0100 mol of strontium nitrate is dissolved in water. The oxidising agent H_2O_2(aq) is then added to give 150.0 cm^3 of a solution in which nitric acid, HNO_3, is the only nitrogen-containing product.

(i) Calculate the concentration, in mol dm^{-3}, of HNO_3 in the 150.0 cm^3 of solution.

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

(ii) The HNO_3 present in 25.0 cm^3 of this solution is neutralised using 0.125 mol dm^{-3} NaOH(aq).

Calculate the minimum volume, in cm^3, of NaOH(aq) needed. Give your answer to three significant figures.

volume = ... cm^3 [1]

[Total: 7]

5 Transition elements form complexes.

(a) Molybdenum, Mo, forms an octahedral complex consisting of one Mo atom surrounded by carbon monoxide, CO, molecules. CO is a monodentate ligand. Iron forms an octahedral complex consisting of one Fe^{3+} and a number of cyanide, CN^{-}, ions. CN^{-} is a monodentate ligand.

(i) Define the term *monodentate ligand*.

....

.... [1]

(ii) Complete the table by stating the formulae and charges of the complexes described.

	formula	charge
molybdenum complex		
iron(III) complex		

[2]

(iii) Draw a three-dimensional diagram to show the shape of this iron(III) complex.

Label one 180° bond angle on your diagram.

Fe

[1]

(b) An excess of aqueous ammonia is added to dilute copper(II) sulfate solution. A dark blue complex, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, is formed.

(i) Write an ionic equation for this reaction.

.... [1]

(ii) Explain the origin of colour in copper(II) complexes.

....

....

....

....

....

.... [4]

(c) An excess of concentrated hydrochloric acid is added to the dark blue solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$. A new complex, **Z**, is formed. The colour of the solution changes.

(i) Write an equation for the formation of **Z** from the solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$. Include the formula and charge of **Z**.

.... [2]

(ii) Name the type of reaction when **Z** forms from $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

.... [1]

(iii) State the geometry of **Z**.

.... [1]

(iv) State the colour of a solution of **Z**.

.... [1]

(v) Explain why the colour of a solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is different from the colour of a solution of **Z**. You should refer to the energies of the orbitals involved in your answer.

....

.... [1]

[Total: 15]

6 An excess of aqueous ammonia is added to a solution containing the complex ion $[Co(H_2O)_6]^{2+}$.

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$$

(a) Complete the sentence to describe the colour change that will be seen during this reaction.

The colour changes from .... to .... [1]

(b) Write an expression for the stability constant, K_{stab}, of $[Co(NH_3)_6]^{2+}$.

K_{stab} =

[1]

(c) The numerical value of K_{stab} of $[Co(NH_3)_6]^{2+}$ is 7.7×10^4.

What deduction about the properties of $[Co(NH_3)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$ can be made from this K_{stab} value?

.... [1]

(d) Oxygen can oxidise $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ under standard conditions in alkaline solutions.

$$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+} \qquad E^\ominus = +0.10\,V$$

(i) Use this information and the *Data Booklet* to calculate the $E^\ominus_{cell}$ value for this oxidation of $[Co(NH_3)_6]^{2+}$.

....

....

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

(ii) Write an ionic equation for this oxidation of $[Co(NH_3)_6]^{2+}$.

.... [1]

(iii) Predict, by selecting suitable data from the *Data Booklet*, whether oxygen can oxidise Co^{2+}(aq) in **acidic** solution, in the absence of ammonia. Explain your answer.

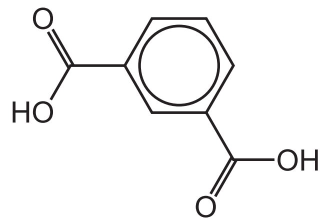
....

.... [2]

[Total: 7]

7 The structure of benzene-1,3-dicarboxylic acid is shown.

benzene-1,3-dicarboxylic acid



(a) State the empirical formula of benzene-1,3-dicarboxylic acid.

.... [1]

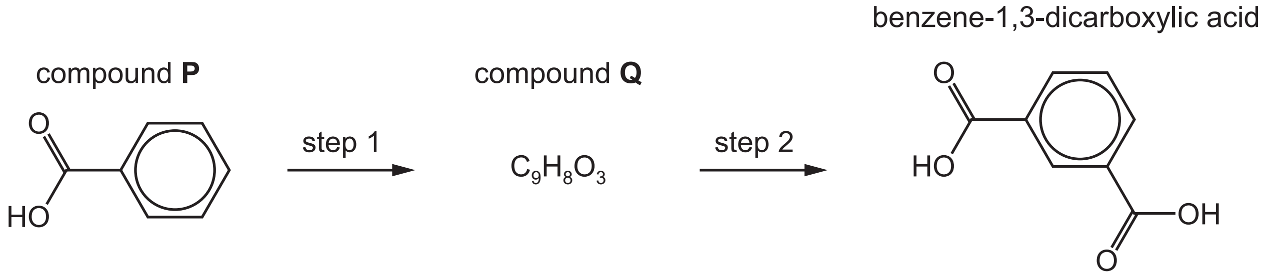
(b) Benzene-1,3-dicarboxylic acid is an isomer of benzene-1,4-dicarboxylic acid. These two isomers can be distinguished by carbon-13 (^{13}C) NMR spectroscopy.

State the number of peaks in the carbon-13 (^{13}C) NMR spectrum of each compound.

benzene-1,3-dicarboxylic acid	
benzene-1,4-dicarboxylic acid	

[2]

(c) Benzene-1,3-dicarboxylic acid can be made by the two-step synthesis shown below.



(i) Name compound **P**.

.... [1]

(ii) Explain why the major product of this two-step synthesis is benzene-1,3-dicarboxylic acid and **not** benzene-1,4-dicarboxylic acid.

....

.... [1]

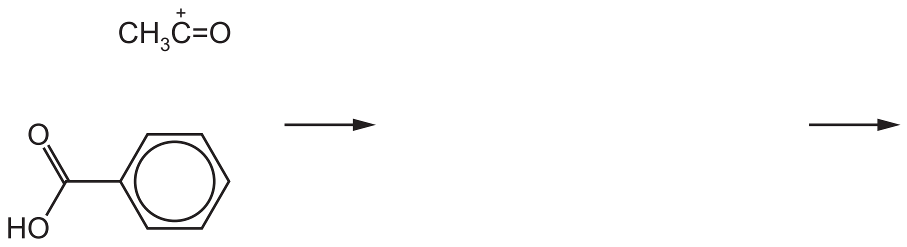
(iii) The reagents used for step 1 are CH_3COCl and $AlCl_3$. These reagents give rise to $CH_3\overset{+}{C}{=}O$ ions which react with compound **P**.

Name the mechanism of this reaction.

.... [1]

(iv) Draw the mechanism of the reaction of $CH_3\overset{+}{C}{=}O$ ions with compound **P**. Include all relevant curly arrows and charges, the structure of the intermediate and the structure of compound **Q**.

intermediate compound **Q**



[3]

(v) Suggest a reagent and conditions to convert compound **Q** into benzene-1,3-dicarboxylic acid, in step 2.

.... [1]

[Total: 10]

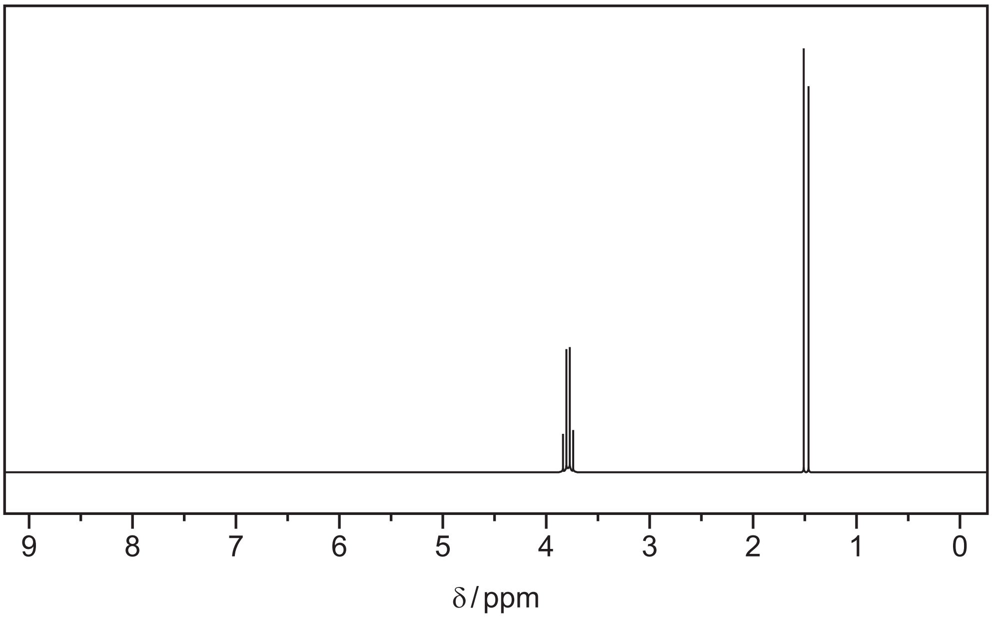
8 Alanine, $H_2NCH(CH_3)CO_2H$, and glutamic acid, $H_2NCH(CH_2CH_2CO_2H)CO_2H$, are two naturally occurring amino acids.

(a) $H_2NCH(CH_3)CO_2H$ exists as two optical isomers.

Draw three-dimensional structures of these two optical isomers.

[2]

(b) The proton (^1H) NMR spectrum of **either** alanine in D_2O or glutamic acid in D_2O is shown.



State whether this is the spectrum of alanine in D_2O or the spectrum of glutamic acid in D_2O. Explain your answer by reference to the number of peaks and splitting patterns.

....

....

....

.... [3]

(c) The mass spectrum of glutamic acid, $H_2NCH(CH_2CH_2CO_2H)CO_2H$, is obtained.

(i) State the *m*/*e* value of the molecular ion peak in this spectrum.

.... [1]

(ii) The spectrum has peaks with *m*/*e* values of 88 and 131.

Draw the structures of the ions responsible for these peaks.

m/*e*	structure of ion
88	
131	

[2]

(d) At pH 11 alanine exists as $H_2NCH(CH_3)CO_2^-$ ions and glutamic acid exists as $H_2NCH(CH_2CH_2CO_2^-)CO_2^-$ ions. A mixture of alanine and glutamic acid at pH 11 is subjected to electrophoresis.

(i) State how the mixture can be maintained at pH 11 during electrophoresis.

.... [1]

(ii) Draw a fully labelled diagram for the apparatus that would be used to carry out this electrophoresis. Your diagram should include the position of the mixture of alanine and glutamic acid at the start of the electrophoresis experiment.

[2]

(iii) Identify the electrode that each amino acid travels towards during electrophoresis at pH 11.

alanine ....

glutamic acid ....
[1]

(iv) In a particular electrophoresis experiment at pH 11, the glutamic acid travels 3.4 cm. Alanine travels a shorter distance.

Explain the factors that account for the difference in the distances travelled.

....

....

....

.... [2]

[Total: 14]

9 Butylamine, $CH_3CH_2CH_2CH_2NH_2$, can be synthesised from different organic compounds by using suitable reagents. Each reaction involves one step.

(a) Complete the table to describe three different syntheses.

- One of the three syntheses should involve a nucleophilic substitution reaction.
- The starting organic compound for each synthesis should contain a different functional group.
- A different reagent should be used for each synthesis.

starting organic compound	reagent and conditions

[6]

(b) Compare and explain the relative basicities of ammonia, butylamine and phenylamine.

.... > .... > ....
most basic least basic

....

....

....

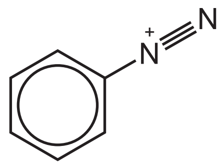
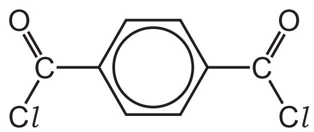
....

....

.... [4]

[Total: 10]

10 (a) Complete the table to show the structure of the organic product from each reaction of phenol, C_6H_5OH.

reaction	reaction mixture	structure of organic product
1	phenol + NaOH(aq)	
2	phenol + Na(s)	
3	phenol +  (aq) + NaOH, at 4 °C	
4	an excess of phenol + 	

[4]

(b) Identify **two** reactions from the table in which ethanol would behave in a similar way to phenol.

.... [1]

[Total: 5]

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CHEMISTRY **9701/42**

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

IB20 06_9701_42/3RP

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

1 $EDTA^{4-}$, is a polydentate ligand.

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

....

....

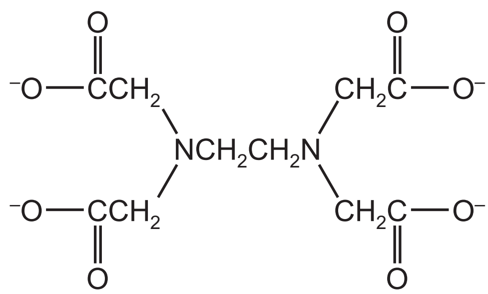
.... [2]

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

equilibrium **1** $[Cd(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [CdEDTA]^{2-} + 6H_2O$

Circle, on the structure of $EDTA^{4-}$, the **six** atoms that form bonds with the metal ion.

$EDTA^{4-}$



[1]

(iii) Write an expression for the stability constant, K_{stab1}, for equilibrium **1**, and state its units.

K_{stab1} =

units = ...

[2]

(b) Cadmium ions form complexes with methylamine, CH_3NH_2, and with 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, as shown in equilibriums **2** and **3**. 1,2-diaminoethane is shown as en.

equilibrium **2** $[Cd(H_2O)_6]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 4H_2O$ $K_{stab2} = 3.60 \times 10^6$

equilibrium **3** $[Cd(H_2O)_6]^{2+} + 2en \rightleftharpoons [Cd(en)_2(H_2O)_2]^{2+} + 4H_2O$ $K_{stab3} = 4.20 \times 10^{10}$

An equilibrium is set up between these two complexes as shown in equilibrium **4**.

equilibrium **4** $[Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 2en \rightleftharpoons [Cd(en)_2(H_2O)_2]^{2+} + 4CH_3NH_2$ $\Delta H^\ominus = +0.840\,kJ\,mol^{-1}$
$\Delta S^\ominus = +80.9\,J\,K^{-1}\,mol^{-1}$

(i) K_{eq4} is the equilibrium constant for equilibrium **4**.

Write an expression for K_{eq4} in terms of K_{stab2} and K_{stab3}.

K_{eq4} =

[1]

(ii) Calculate the value of the standard Gibbs free energy change, $\Delta G^\ominus$, for equilibrium **4** at 298 K.

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

(iii) State how the value of $\Delta G^\ominus$ changes as the temperature increases. Explain your answer.

....

....

.... [1]

[Total: 9]

2 **(a)** Describe and explain how the solubility of the Group 2 sulfates varies down the group.

....

....

....

....

....

.... [4]

(b) The trend in the decomposition temperatures of Group 2 peroxides, MO_2, is similar to that of Group 2 carbonates.

Suggest which of barium peroxide, BaO_2, and calcium peroxide, CaO_2, will decompose at the **lower** temperature. Explain your answer.

....

....

.... [2]

(c) Magnesium iodate(V), $Mg(IO_3)_2$, decomposes when heated to form magnesium oxide, oxygen and iodine.

Construct an equation for this reaction.

.... [1]

(d) Calcium iodate(V), $Ca(IO_3)_2$, is sparingly soluble in water.
The concentration of its saturated solution is 5.6×10^{-3} mol dm^{-3} at 298 K.

(i) Write an expression for the solubility product, K_{sp}, of $Ca(IO_3)_2$, and state its units.

K_{sp} =

units = ... [2]

(ii) Calculate the numerical value for K_{sp} $Ca(IO_3)_2$ at 298 K.

K_{sp} = ... [1]

(iii) When a few cm^3 of concentrated $Ca(NO_3)_2(aq)$ is added to a saturated solution of $Ca(IO_3)_2$ a white precipitate forms.

Identify the white precipitate and give an explanation for this observation.

....

....

.... [2]

(e) Iodised salt is sodium chloride mixed with a small amount of sodium iodate(V), $NaIO_3$.

- 50.00 g of iodised salt is dissolved in distilled water and the solution made up to 250 cm^3 in a volumetric flask with distilled water.
- 50.0 cm^3 of this solution is pipetted into an excess of aqueous acidified potassium iodide.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

- The iodine produced requires 12.40 cm^3 of 0.00200 $mol\,dm^{-3}$ aqueous sodium thiosulfate solution for complete reaction.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Calculate the mass of sodium iodate(V) present in 50.00 g of iodised salt.

mass of $NaIO_3$ = ... g [3]

(f) The half-equation for the reduction of iodate(V) ions is shown.

$$IO_3^- + 6H^+ + 5e^- \rightarrow \tfrac{1}{2}I_2 + 3H_2O \qquad E^\ominus = +1.19\,V$$

Use data from the *Data Booklet* to predict whether a reaction is feasible when aqueous solutions of acidified iodate(V) ions and bromide ions are mixed. Explain your answer.

....

.... [1]

(g) Iodate(V) ions react with sulfite ions in acidic solution at pH 5.00 as shown.

$$IO_3^- + 3SO_3^{2-} \rightarrow I^- + 3SO_4^{2-}$$

The initial rate of reaction was found to be first order with respect to IO_3^-, first order with respect to SO_3^{2-} and first order with respect to H^+.

(i) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = ... $mol\,dm^{-3}\,s^{-1}$

units of *k* = ...

[2]

(ii) The rate of reaction depends on the pH of the solution. Assume all other concentrations remain the same.

Use the expression $x = \dfrac{\text{rate at pH 5.00}}{\text{rate at pH 4.00}}$ to calculate the value of x.

x = ... [1]

[Total: 19]

3 **(a)** Complete the electronic configuration of an isolated gaseous nickel(II) ion, Ni^{2+}.

	3d						4s
[Ar]	$\uparrow\downarrow$						

[1]

(b) Explain the origin of colour in transition element complexes.

....

....

....

....

....

.... [4]

(c) Hexaaquanickel(II) ions are green. They form a green precipitate with hydroxide ions, OH^-, in equilibrium **1** and a blue complex with ammonia, NH_3, in equilibrium **2**.

equilibrium **1** $[Ni(H_2O)_6]^{2+} + 2OH^- \rightleftharpoons \underset{\text{green ppt.}}{Ni(OH)_2} + 6H_2O$

equilibrium **2** $[Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons \underset{\text{blue}}{[Ni(NH_3)_6]^{2+}} + 6H_2O$

Use Le Chatelier's principle to suggest explanations for the following observations.

(i) Explain why when aqueous NH_3 is added dropwise to $[Ni(H_2O)_6]^{2+}$ a green precipitate is formed.

....

....

.... [1]

(ii) Explain why when a large excess of aqueous NH_3 is added to $[Ni(H_2O)_6]^{2+}$, the green precipitate dissolves and a blue solution is formed.

....

....

.... [1]

(d) The complex ion $[NiBr_2(CN)_2]^{2-}$ shows stereoisomerism.

Draw diagrams to show the two isomers of $[NiBr_2(CN)_2]^{2-}$. Name the type of stereoisomerism.

isomer 1	isomer 2

type of stereoisomerism ....

[2]

[Total: 9]

4 (a) (i) When benzene undergoes nitration a nitro group substitutes at a carbon atom.

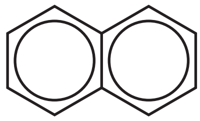
State the shape (geometry) around the substituted carbon atom

- in the benzene molecule, ...
- in the intermediate complex, ...
- in the nitrobenzene product. ....

[2]

(ii) Naphthalene, $C_{10}H_8$, is an arene hydrocarbon.

naphthalene



When naphthalene undergoes nitration, a mixture of two organic compounds is formed. Each compound contains **one** nitro group.

Suggest the structures of these compounds.

structure 1	structure 2

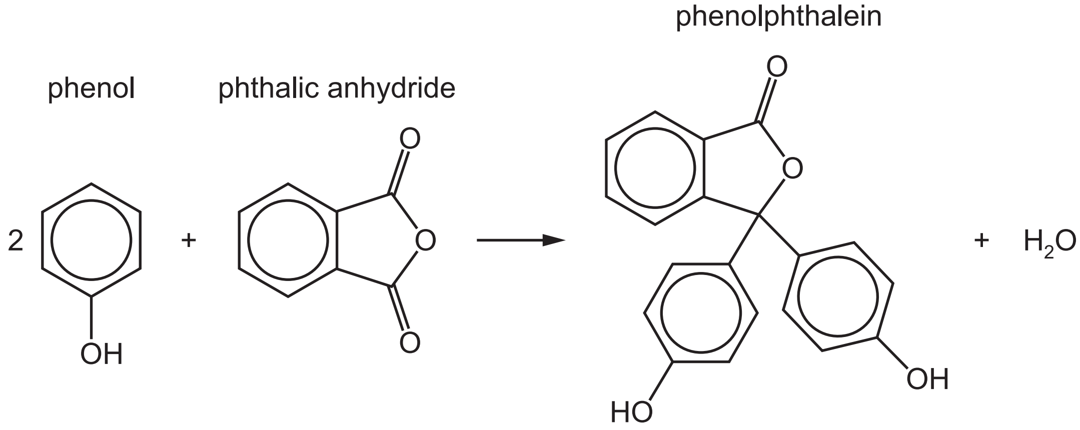
[1]

(b) Naphthalene can be oxidised under certain conditions to phthalic anhydride, $C_8H_4O_3$, carbon dioxide and water.

Construct an equation for this reaction. Use [O] to represent an atom of oxygen from the oxidising agent.

.... [1]

(c) The indicator, phenolphthalein, can be synthesised from phthalic anhydride and phenol under certain conditions.



Deduce the *type of reaction* shown by this equation.

.... [1]

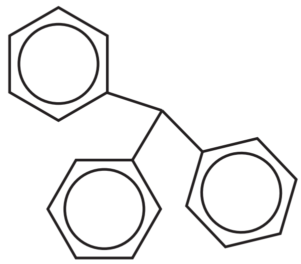
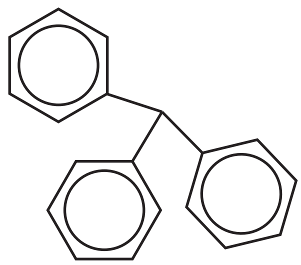
(d) (i) Name the functional groups, in addition to the benzene ring, present in a phenolphthalein molecule.

.... [1]

(ii) Phenolphthalein reacts separately with the two reagents shown in the table.

Complete the table by:

- drawing the structures of the organic products formed (part of the structure has been given for you)
- stating the types of reaction.

reagent	organic product structure	type of reaction
an **excess** of hot NaOH(aq)		
an **excess** of Br_2(aq)		

[4]

(e) Phenolphthalein is an indicator and is represented by the formula HIn. Phenolphthalein, HIn, is a weak acid.

$$HIn \rightleftharpoons H^+ + In^-$$

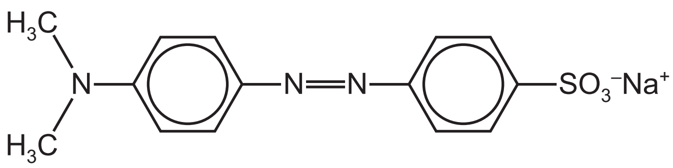
The K_a value for phenolphthalein is $5.0 \times 10^{-10}\,mol\,dm^{-3}$ at 298 K. This indicator changes colour at a pH of approximately 8.8.

Calculate the ratio $\frac{[In^-]}{[HIn]}$ at pH 8.8.

ratio $\frac{[In^-]}{[HIn]}$ = ... [2]

(f) Methyl orange is another acid-base indicator. Its structure in aqueous solution at pH 4.4 is shown.

methyl orange



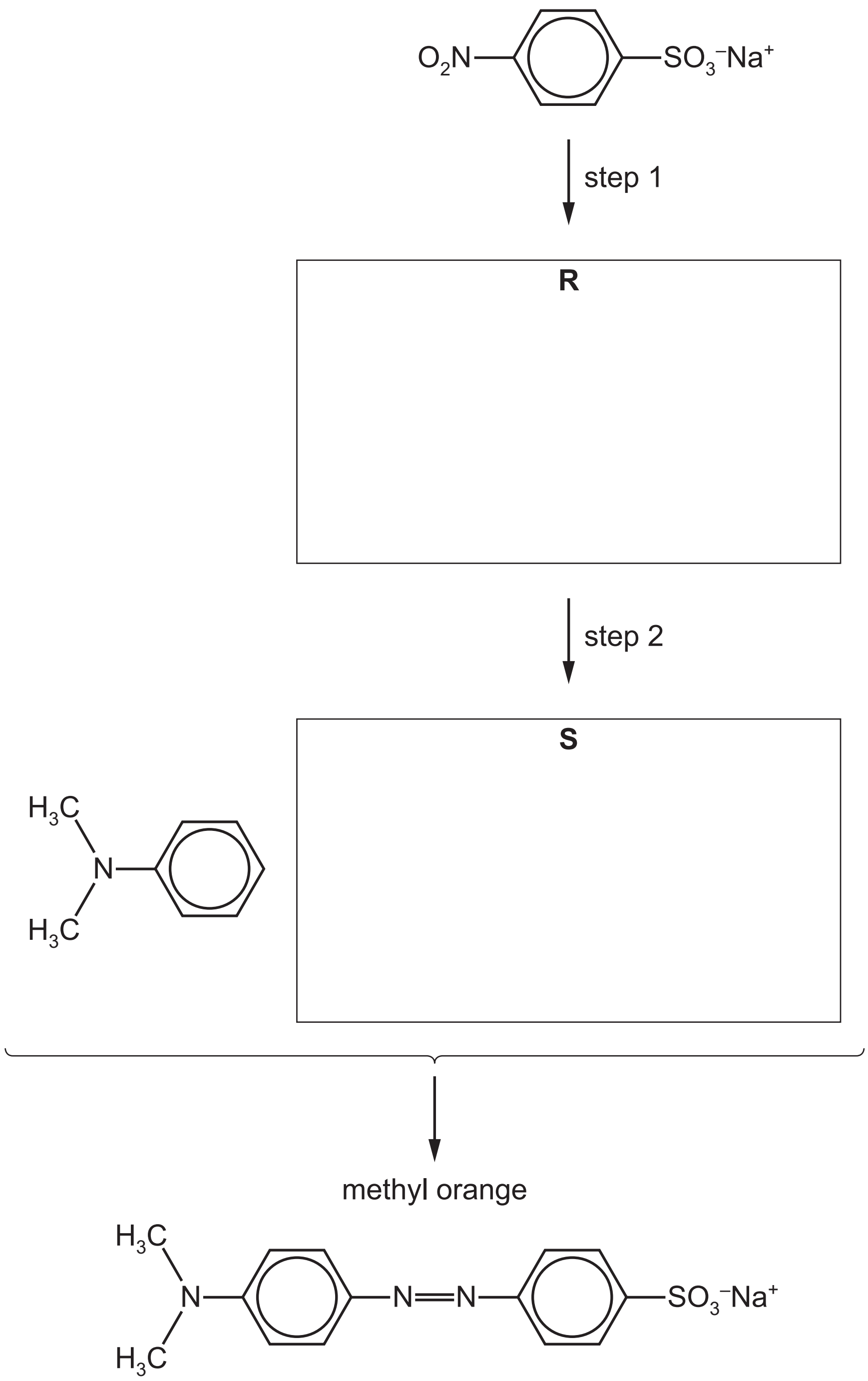
(i) On the structure of methyl orange, **circle** the bond or bonds that make this compound a dye. [1]

The colour of this indicator changes between pH 3.2 and pH 4.4.

(ii) Suggest the structure of methyl orange at pH 3.0. Assume the $-SO_3^-Na^+$ group is unreactive.

[1]

(g) Methyl orange can be synthesised as shown.



(i) Deduce the identities of compounds **R** and **S** and draw their structures in the boxes. [2]

(ii) Suggest reagents and conditions for step 1 and step 2.

step 1 ....

step 2 ....

[3]

[Total: 19]

5 **(a)** Define the term *partition coefficient,* K_{pc}.

....

....

.... [2]

(b) K_{pc} of benzoic acid between octan-1-ol and water is 79.4.

(i) A solution of 0.400 g of benzoic acid in 25.0 cm^3 octan-1-ol is shaken with 125 cm^3 of water.

Calculate the mass of benzoic acid extracted into the water layer.

mass of benzoic acid extracted = ... g [2]

(ii) K_{pc} of benzophenone, $C_6H_5COC_6H_5$, between octan-1-ol and water is different from the value of K_{pc} of benzoic acid given in **(b)(i)**.

Explain why.

....

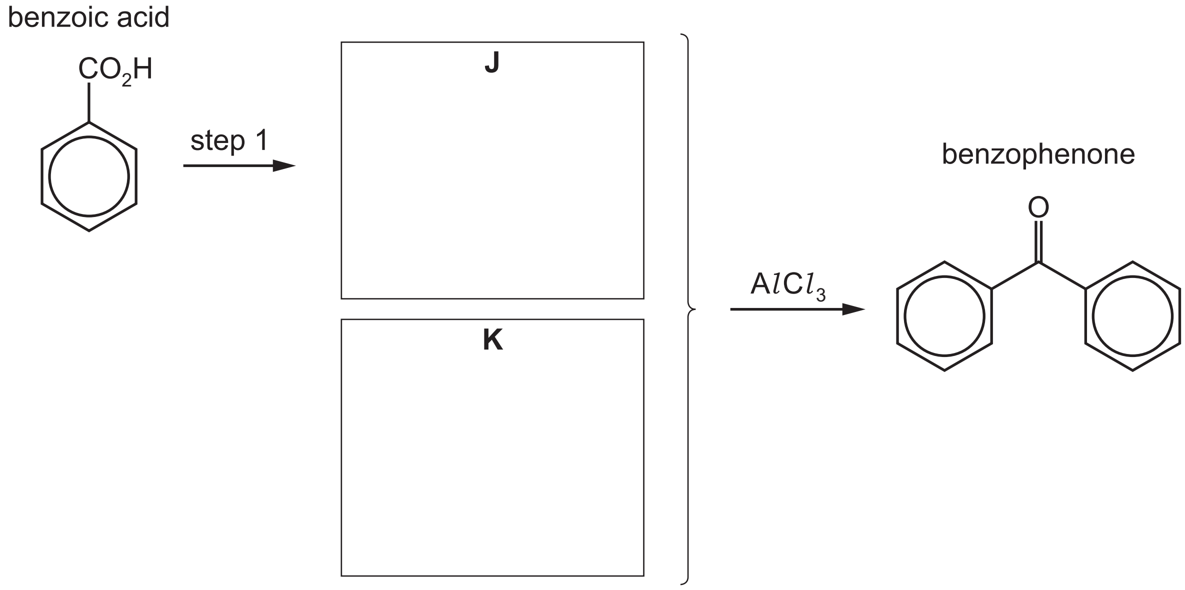
....

.... [1]

(c) Benzophenone can be synthesised from benzoic acid in two steps as shown.

In step 1 compound **J**, a reactive reaction intermediate, is formed.

Compound **J** then reacts with an organic compound, **K**, to form benzophenone.

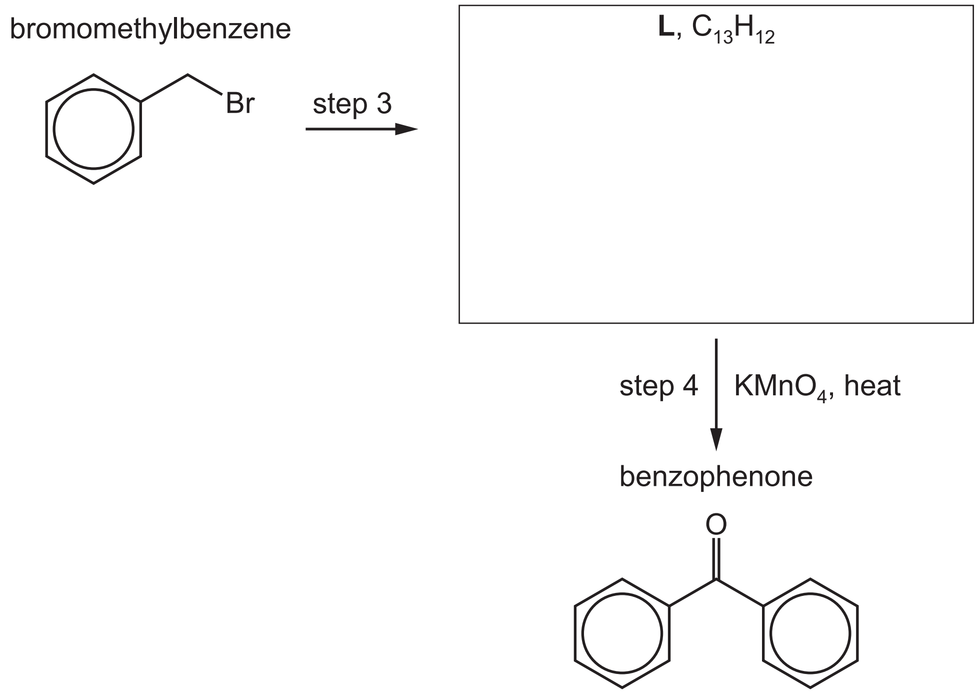


(i) Deduce the identities of organic compounds **J** and **K** and draw their structures in the boxes. [2]

(ii) Suggest reagents and conditions for step 1.

.... [1]

(d) Benzophenone can also be synthesised in two steps from bromomethylbenzene.



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

(ii) Name the mechanism of step 3 and suggest reagents and conditions for step 3.

mechanism of step 3 ....

reagents and conditions ....

[2]

(iii) Deduce the *type of reaction* in step 4.

.... [1]

(e) (i) Deduce the number of peaks that would be present in the carbon-13 NMR spectrum of benzophenone.

number of peaks .... [1]

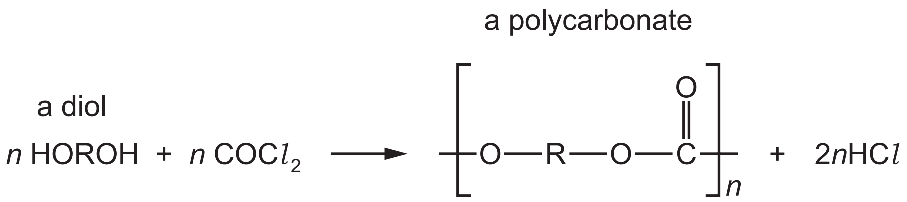
(ii) Identify **two** different environments of carbon atom that would result in different chemical shift ranges in this carbon-13 NMR spectrum of benzophenone.

environment of carbon atom	chemical shift range (δ)

[2]

[Total: 15]

6 The class of polymers called polycarbonates are made by the reaction of carbonyl dichloride, $COCl_2$, with a diol.

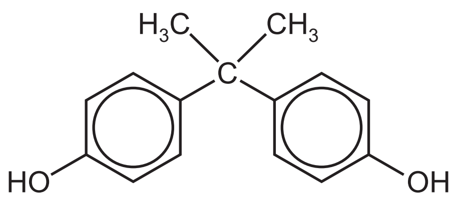


(a) **(i)** Deduce the *type of polymerisation* shown here.

.... [1]

Nalgene® is a polycarbonate formed from the diol **P** and $COCl_2$.

P



(ii) Draw **one** repeat unit of Nalgene®.

[1]

(iii) Nalgene® is a strong and tough polymer.

Identify **two** types of intermolecular force that are responsible for these properties of Nalgene®.

1 ....

2 ....
[1]

(b) Proteins are polymers of amino acids.

Complete the table to show how the secondary and tertiary structures of proteins are stabilised.

	one intermolecular force responsible	groups involved
secondary structure		
tertiary structure		

[2]

(c) Explain the significance of hydrogen bonding in DNA in relation to the accurate replication of genetic information.

....

....

.... [2]

(d) Many polymers are degradable.

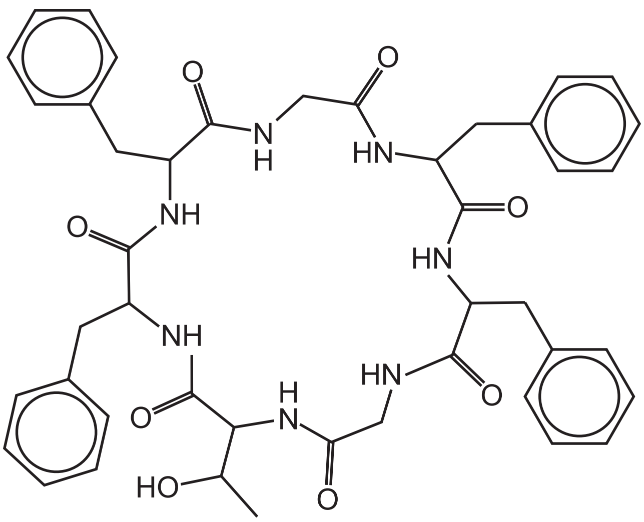
State **two** different processes by which some polymers can be degraded.

....

.... [1]

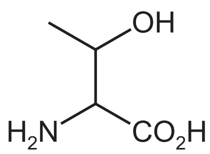
(e) The cyclic peptide **B** is shown.

B



Cyclic peptide **B** is broken into its monomers by heating under reflux with dilute hydrochloric acid. The amino acid threonine, Thr, and two other organic products are formed.

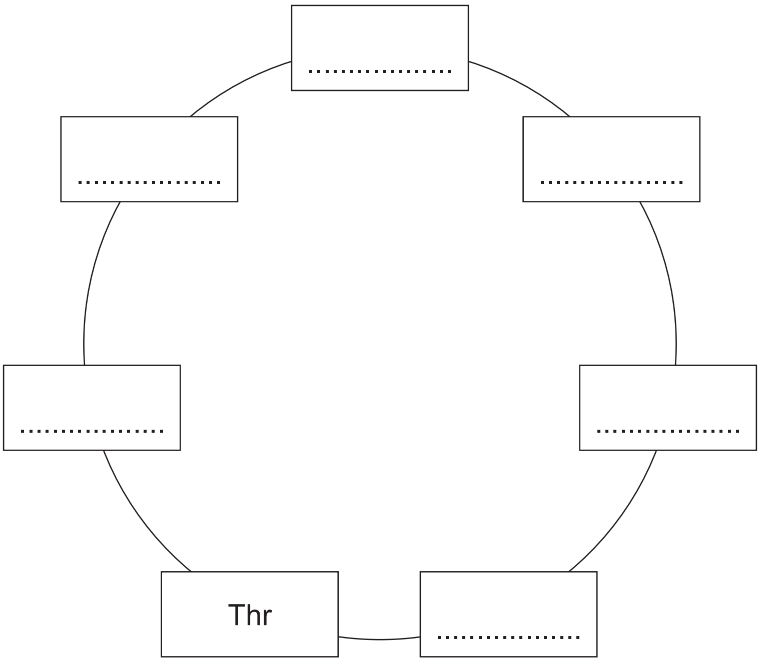
threonine



(i) Draw the structures of the two other organic products formed.

[2]

(ii) Using the 3-letter abbreviations for the amino acids as given in the *Data Booklet*, complete the sequence for the cyclic peptide, **B**.



[1]

(iii) Name **two** analytical techniques that could be used to separate these amino acids.

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

[Total: 12]

7 **(a)** **(i)** Define the term *electron affinity*.

....

....

.... [2]

(ii) Define the term *lattice energy*.

....

....

.... [2]

(b) Use the following data and relevant data from the *Data Booklet* to calculate a value for the enthalpy change of formation of zinc bromide, $ZnBr_2(s)$.

You might find it helpful to construct an energy cycle.

electron affinity of Br(g)	= $-325\,kJ\,mol^{-1}$
enthalpy change of atomisation of Zn(s)	= $+131\,kJ\,mol^{-1}$
enthalpy change of vaporisation of $Br_2(l)$	= $+31\,kJ\,mol^{-1}$
lattice energy of $ZnBr_2(s)$	= $-2678\,kJ\,mol^{-1}$

enthalpy change of formation of $ZnBr_2(s)$ = ... $kJ\,mol^{-1}$ [4]

(c) The lattice energies of $ZnBr_2$, $ZnCl_2$ and ZnO are shown.

compound	lattice energy / $kJ\,mol^{-1}$
$ZnBr_2$	–2678
$ZnCl_2$	–2734
ZnO	–3971

(i) Explain why there is a difference between the lattice energies of $ZnBr_2$ and $ZnCl_2$.

....

.... [1]

(ii) Explain why there is a difference between the lattice energies of $ZnCl_2$ and ZnO.

....

.... [1]

[Total: 10]

8 **(a)** **(i)** Define the term *standard cell potential*.

....

....

.... [2]

An electrochemical cell is set up to measure the standard electrode potential of a cell, $E^{\ominus}_{cell}$, made of a Co^{3+}/Co^{2+} half-cell and a Cl_2/Cl^- half-cell.

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

half-cell	electrode
Co^{3+}/Co^{2+}	
Cl_2/Cl^-	

[1]

(iii) Use data from the *Data Booklet* to calculate the $E^{\ominus}_{cell}$.

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

(iv) Write the equation for the overall cell reaction.

.... [1]

(b) A fuel cell is an electrochemical cell that can be used to generate electrical energy.
A methanol-oxygen fuel cell can be used as an alternative to a hydrogen-oxygen fuel cell. When the cell operates, the carbon atoms in the methanol molecules are converted into carbon dioxide.

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

Calculate the volume of CO_2, in cm^3, formed when a current of 2.5A is delivered by the cell for 30 minutes. Assume the cell is operated at room conditions.

volume of CO_2 = ... cm^3 [2]

[Total: 7]

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Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME			
CENTRE NUMBER		CANDIDATE NUMBER	

* 2 4 8 8 2 8 5 3 7 4 *

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.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working, use appropriate units and use an appropriate number of significant figures.

INFORMATION

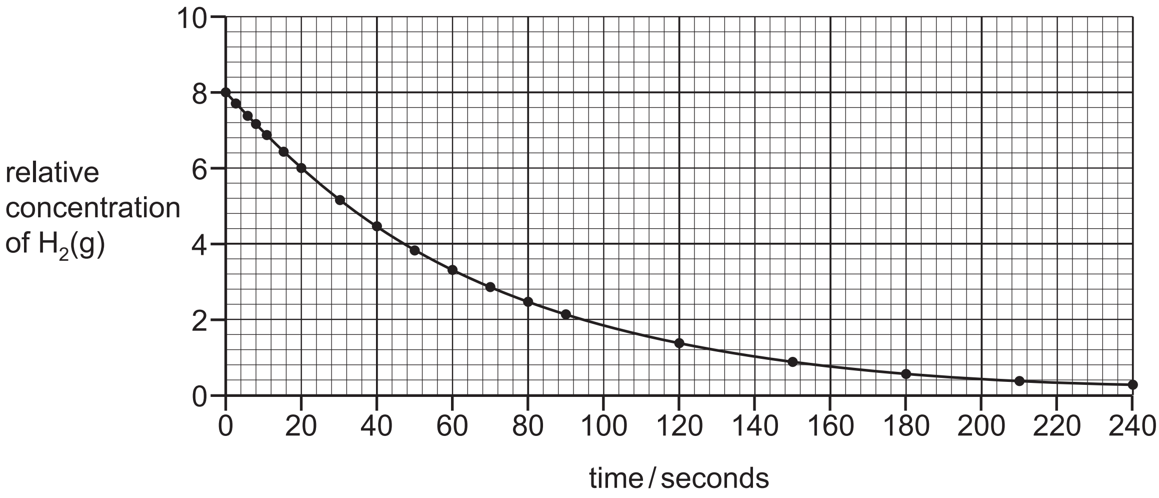
- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].

This document has **20** pages. Blank pages are indicated.

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

1 The rate of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is studied.

(a) A small amount of $H_2(g)$ is mixed with a large excess of $I_2(g)$ at a temperature of 400 K and the reaction is monitored. The graph obtained is shown.



(i) Suggest why a large excess of $I_2(g)$ is used in this experiment.

.... [1]

(ii) The reaction is first order with respect to $H_2(g)$.

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 H_2(g) and I_2(g). The results are shown in the table.

experiment	$[H_2(g)]$ / mol dm^{-3}	$[I_2(g)]$ / mol dm^{-3}	rate of reaction / mol dm^{-3} 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 H_2(g) given in **(a)(ii)**, to deduce the order of reaction with respect to I_2(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 = ... 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.

forward reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$
backward reaction $2HI(g) \rightarrow H_2(g) + I_2(g)$

(i) Use this information to explain what will happen if equal concentrations of $HI(g)$, $H_2(g)$ and $I_2(g)$ 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 $1.00 \times 10^{-3}\,mol\,dm^{-3}$ solution of hydroxylammonium ions has a pH of 4.41.

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

K_a = ... [2]

(ii) Calculate the pK_a of $HONH_3^+$.

pK_a = ... [1]

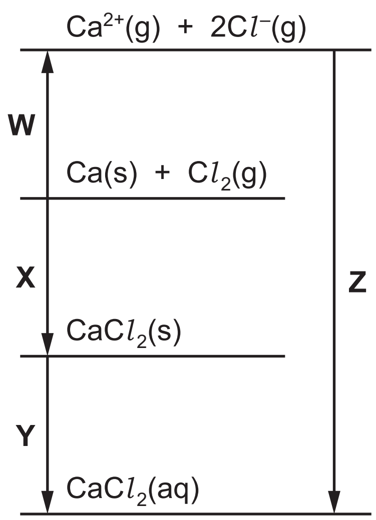
(c) The solubility product of manganese(II) hydroxide, $Mn(OH)_2$, in water is $1.1 \times 10^{-11}\,mol^3\,dm^{-9}$ at 298 K.

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

solubility = ... $mol\,dm^{-3}$ [2]

[Total: 6]

3 **(a)** The energy cycle shown can be used, along with suitable data, to calculate the enthalpy change of hydration of $Ca^{2+}(g)$.
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 $Cl(g)$	$= -349\,kJ\,mol^{-1}$
enthalpy change of atomisation of Ca(s)	$= +193\,kJ\,mol^{-1}$
enthalpy change of formation of $CaCl_2(s)$	$= -795\,kJ\,mol^{-1}$
enthalpy change of solution of $CaCl_2(s)$	$= -83\,kJ\,mol^{-1}$
enthalpy change of hydration of $Cl^-(g)$	$= -364\,kJ\,mol^{-1}$

(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 $Ca^{2+}(g)$.

enthalpy change of hydration of $Ca^{2+}(g)$ = ... $kJ\,mol^{-1}$ [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 $CaCl_2(s)$.

lattice energy of $CaCl_2(s)$ = ... [1]

(v) State whether the lattice energy of $CaCl_2(s)$ is more or less exothermic than the lattice energy of $MgF_2(s)$.

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 $E^\ominus$ values for these halogens.

(i) Give the $E^\ominus$ 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 $Sn^{2+}(aq)$ 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 $Mn^{2+}(aq)$ 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 Fe^{3+} / Fe^{2+} half-cell to an $S_2O_8^{2-}$ / SO_4^{2-} half-cell under standard conditions.

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

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

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

in the Fe^{3+} / Fe^{2+} half-cell ....

in the $S_2O_8^{2-}$ / 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.

Fe^{3+} / Fe^{2+} half-cell ....

....

$S_2O_8^{2-}$ / 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.

charge ....

Co

[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, $H_2NCH_2CH_2NH_2$, is added to an aqueous solution of cobalt(II) sulfate. Oxygen is then bubbled into the mixture forming a complex ion with the formula $[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$.

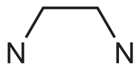
This complex ion exists as a mixture of two isomers. The geometry of both of these isomeric complexes is octahedral.

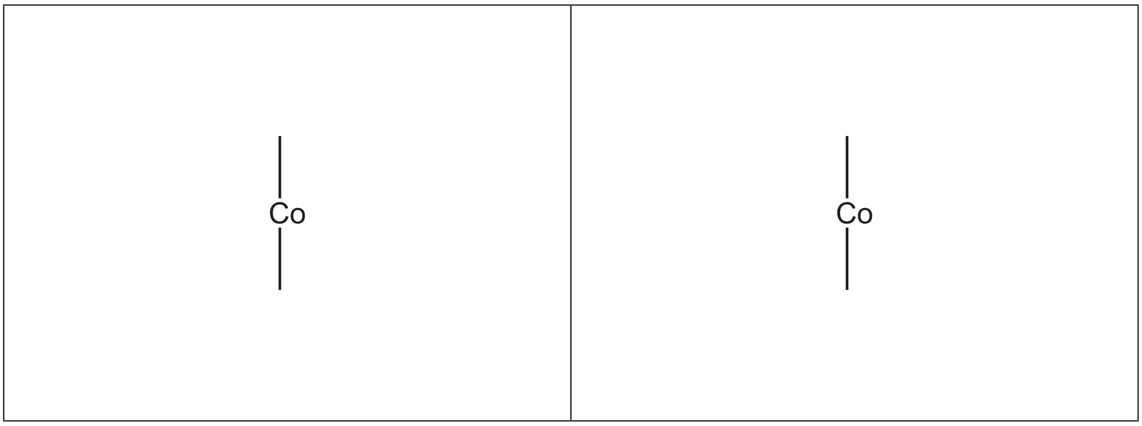
(i) In this reaction, cobalt undergoes **two** types of reaction. One type of reaction is the same as that described in **(c)(ii)**.

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  to represent a molecule of $H_2NCH_2CH_2NH_2$.



[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}
$[Hg(CN)_4]^{2-}$	2.5×10^{41}
$[HgCl_4]^{2-}$	1.7×10^{16}
$[HgI_4]^{2-}$	2.0×10^{30}

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

K_{stab} =

[1]

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

Predict which of the complexes $[Hg(CN)_4]^{2-}$, $[HgCl_4]^{2-}$ and $[HgI_4]^{2-}$ 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, CH_3CO_2H and trichloroethanoic acid, CCl_3CO_2H, 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, HO_2CCO_2H, 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.

$$\text{ethanoic acid} \xrightarrow{\text{step 1}} \mathbf{A} \xrightarrow{\text{step 2}} \text{ethanamide}$$

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

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

structural formula ....

name .... [2]

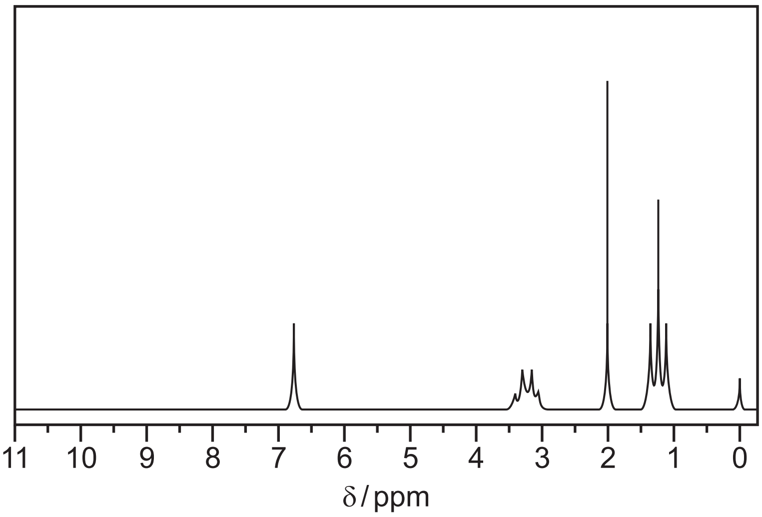
(ii) Suggest suitable reagents for steps 1 and 2.

step 1 ....

step 2 .... [2]

(d) Compound **A** can also be used to make the amide $CH_3CONHC_2H_5$.

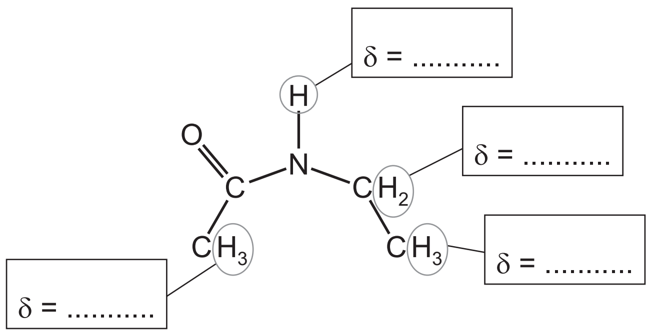
The proton NMR spectrum of the amide $CH_3CONHC_2H_5$ in the solvent $CDCl_3$ is shown.



(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 $CH_3CONHC_2H_5$ molecule.



[2]

(iii) State and explain how the proton NMR spectrum of the amide $CH_3CONHC_2H_5$ differs when dissolved in D_2O rather than $CDCl_3$.

....

....

.... [2]

(e) The mass spectrum of the amide $CH_3CONHC_2H_5$ 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.

$$CH_3CONHC_2H_5 \xrightarrow{\text{reagent } \mathbf{B}} \underset{\text{diethylamine}}{C_2H_5NHC_2H_5}$$

(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.

....

....

....

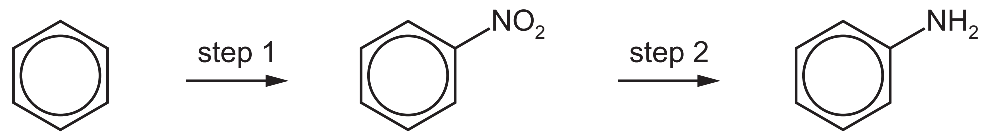
....

....

....

.... [4]

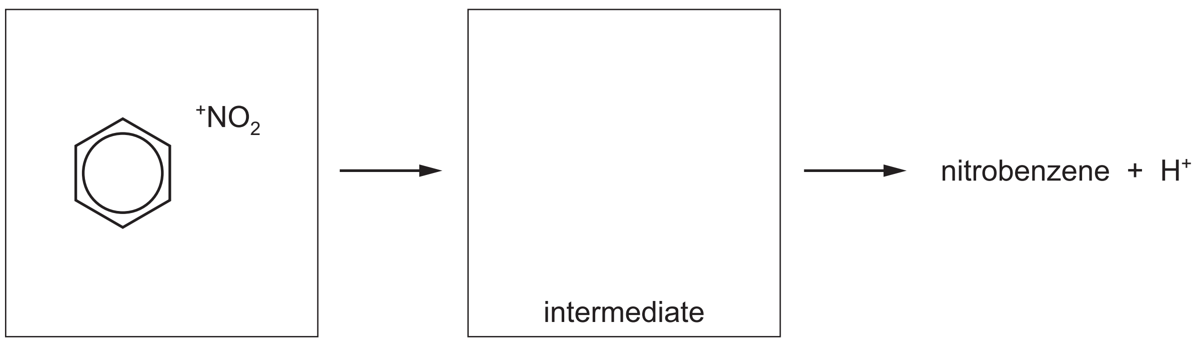
(b) Benzene can be used as a starting material to produce phenylamine by a two-step synthesis.



benzene   nitrobenzene   phenylamine

(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 Br_2(aq).

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

.... [1]

(ii) Name the organic product of this reaction.

.... [1]

(iii) Describe **two** observations that can be **seen** when phenylamine reacts with Br_2(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, $H_2NCH_2CH_2CH_2NH_2$, 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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Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

7021618830

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **October/November 2019**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.
You may lose marks if you do not show your working or if you do not use appropriate units.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **19** printed pages and **1** blank page.

IB19 11_9701_42/3RP

Cambridge Assessment International Education

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

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

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

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

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

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

(b) The cell is operated at 298 K.

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

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

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

E = ... V [2]

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

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

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

.... [2]

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

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

The relative atomic mass of copper is 63.5.

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

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

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

....

....

....

.... [2]

[Total: 13]

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

half-life of a reaction ....

....

rate-determining step ....

....
[2]

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

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

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

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

....

....

....

....

....

....

....

....

....

....

....

.... [4]

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

In a particular experiment,

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

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

rate = ...

k = ... units = ...

[3]

[Total: 9]

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

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

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

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

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

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

pK_a = ... [2]

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

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

....

.... [1]

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

....

.... [1]

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

Show your working.

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

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

Calculate the numerical value of K_w at 50 °C.

K_w = ... [2]

[Total: 8]

4 The table shows some standard entropy data.

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

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

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

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

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

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

T = ... K [3]

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

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

....

.... [1]

[Total: 6]

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

magnesium ....

strontium ....
[2]

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

calcium is burned in air

....

calcium carbonate is heated strongly

....
[2]

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

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

....

.... [1]

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

....

....

....

.... [3]

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

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

....

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

....
[2]

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

....

....

....

....

.... [3]

[Total: 13]

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

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

....

.... [1]

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

Complete the table below.

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

[4]

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

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

....

....

....

....

....

....

....

....

.... [3]

  [Turn over

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

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

Reference to electron movement between orbitals is not needed.

....

....

.... [2]

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

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

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

K_{stab} =

[1]

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

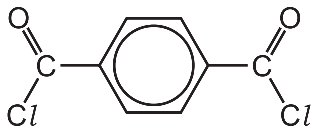
Calculate the concentration of $[Fe(H_2O)_6]^{3+}$ in a solution in which the concentration of Cl^- is 2.0 mol dm^{-3} and the concentration of $[FeCl_4]^-$ is 0.10 mol dm^{-3}.

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

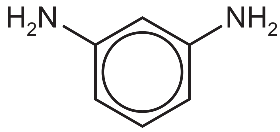
[Total: 12]

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

benzene-1,4-dioyl chloride



benzene-1,3-diamine



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

P

[2]

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

type of polymer	type of polymerisation	
	addition	condensation
polyalkene		
polyamide		
polyester		

[1]

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

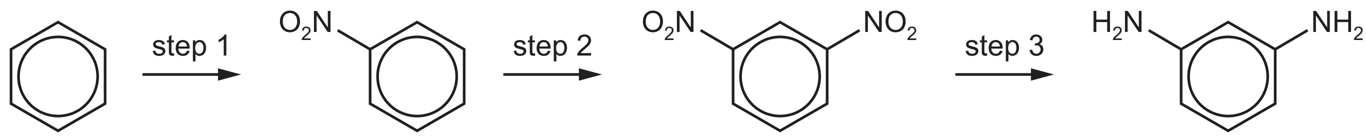
....

.... [1]

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

.... [1]

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



State the reagents used for steps 1 and 3.

step 1 ....

step 3 ....
[2]

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

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

primary structure ....

....

secondary structure ....

....

tertiary structure ....

....
[3]

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

.... [1]

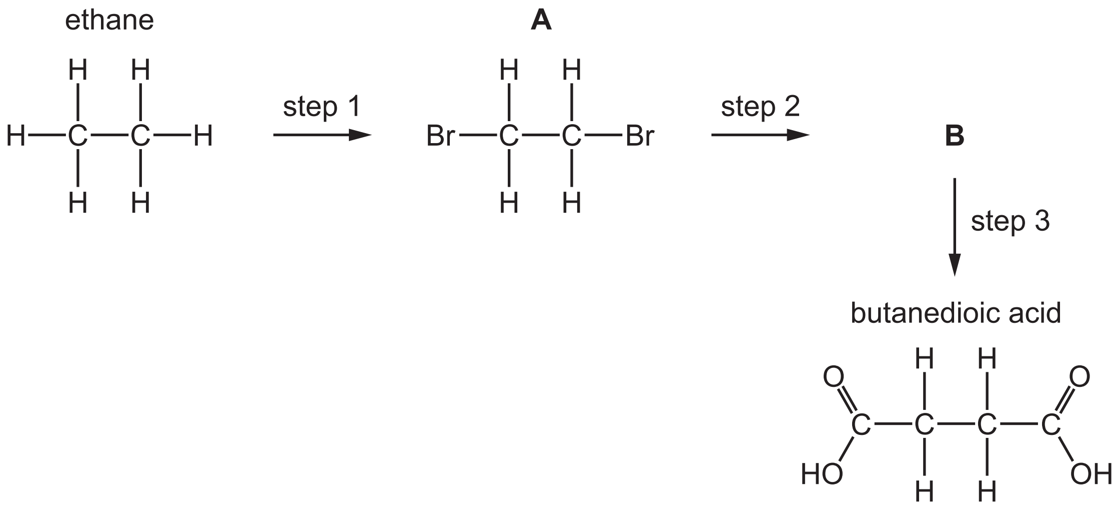
(iii) Name the forces or bonds responsible for the stabilisation of the secondary structure of a protein molecule, and identify the groups of atoms within the protein molecule that are held together by these forces or bonds.

....

.... [2]

[Total: 13]

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



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

.... [1]

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

.... [1]

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

[1]

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

.... [2]

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

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

.... [1]

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

.... [1]

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

....

....

....

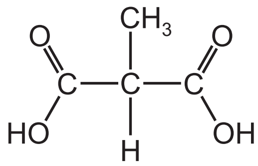
....

....

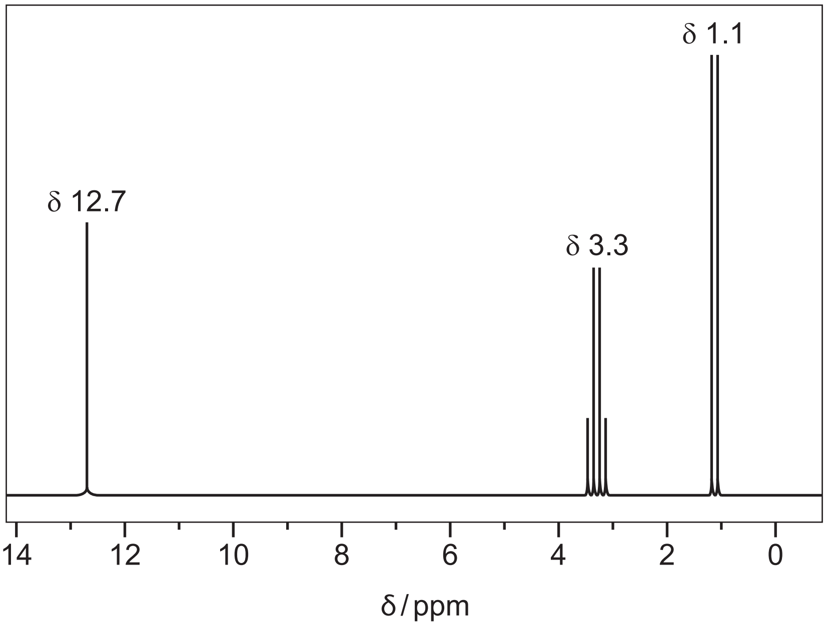
.... [3]

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

methylpropanedioic acid



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



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

δ 12.7 ....

δ 3.3 ....

δ 1.1 .... [2]

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

....

.... [1]

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

(iii) State the number of peaks

- in the carbon-13 NMR spectrum of butanedioic acid

....

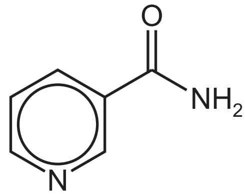
- in the carbon-13 NMR spectrum of methylpropanedioic acid.

....
[1]

[Total: 14]

9 The structure of nicotinamide is shown.

nicotinamide



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

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

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

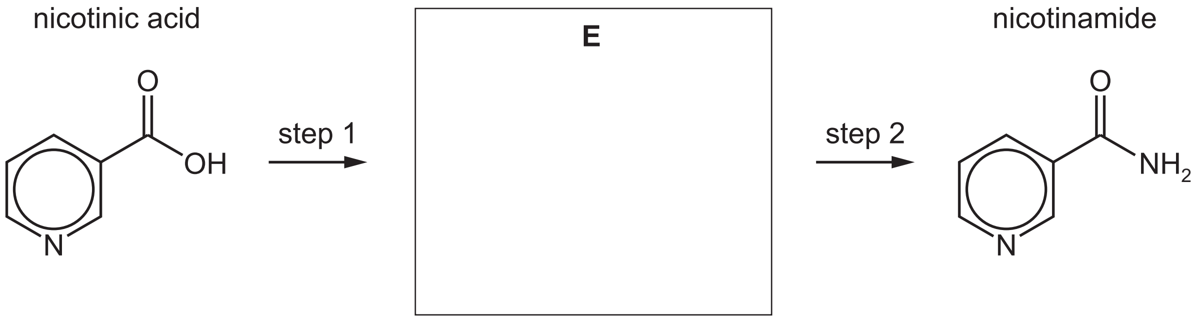
.... [1]

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

.... [1]

(b) Nicotinamide can be synthesised from nicotinic acid.

The synthesis involves two steps.



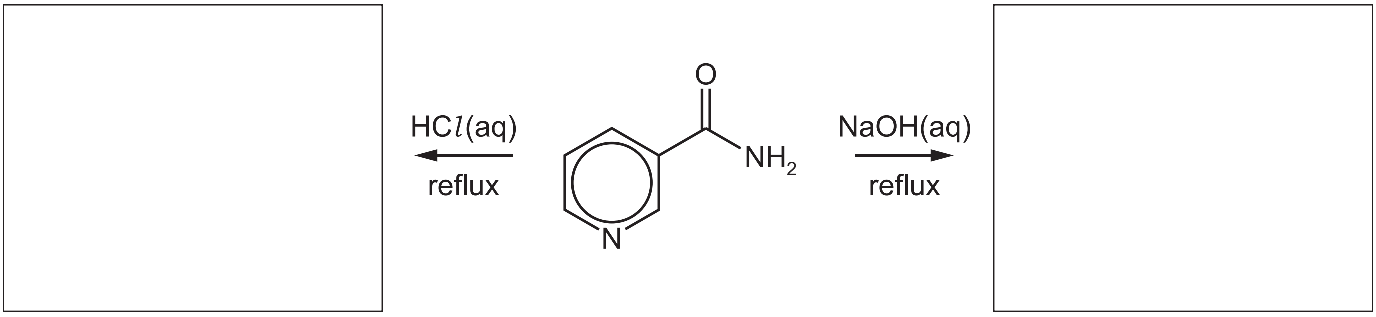
(i) Draw the structural formula of **E** in the box. [1]

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

.... [1]

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

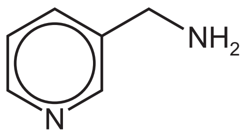
Complete the reaction scheme below to give the structural formula of the organic product of each reaction.



[2]

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

X



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

.... [1]

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

....

....

....

.... [3]

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

Calculate the expected height of the M+1 peak.

[2]

[Total: 12]

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CANDIDATE NAME	

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CHEMISTRY **9701/42**

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

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.
You may lose marks if you do not show your working or if you do not use appropriate units.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **23** printed pages and **1** blank page.

IB19 06_9701_42/3RP

Cambridge Assessment International Education

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

1 **(a)** **(i)** Complete the electronic configuration of the copper(II) ion.

$1s^2 2s^2 2p^6$ .... [1]

(ii) State the colour of the solutions containing the following ions.

- $[Cu(H_2O)_6]^{2+}(aq)$ ....
- $[CuCl_4]^{2-}(aq)$ ....

[1]

(iii) Octahedral complexes of Cu^{2+} with different ligands can have different colours.

Explain why.

....

....

....

....

.... [2]

(b) Copper(I) and silver(I) salts are colourless.

Suggest why.

....

....

....

.... [2]

(c) Consider the following two equilibria and associated data values at 298 K.

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \qquad \text{equilibrium } \mathbf{1} \qquad K_{sp} = 5.0 \times 10^{-13}\,mol^2\,dm^{-6}$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) \qquad \text{equilibrium } \mathbf{2} \qquad K_{stab} = 1.7 \times 10^{7}\,mol^{-2}\,dm^{6}$$

The equilibrium constant for equilibrium **1** is the solubility product, K_{sp}, of AgBr(s). The equilibrium constant for equilibrium **2** is the stability constant, K_{stab}, for the formation of $[Ag(NH_3)_2]^+$(aq).

(i) Calculate the solubility of AgBr at 298 K in mol dm^{-3}.

solubility of AgBr = ... mol dm^{-3} [1]

(ii) Use Le Chatelier's principle as applied to equilibria **1** and **2** to suggest why AgBr(s) dissolves in concentrated NH_3(aq).

....

....

....

.... [2]

(iii) Use equilibria **1** and **2** to construct an equation for the reaction of AgBr(s) with concentrated NH_3(aq). This is equilibrium **3**.

.... equilibrium **3** [1]

(iv) Write an expression for the equilibrium constant of equilibrium **3**, K_{eq3}, in terms of K_{sp} for equilibrium **1** and K_{stab} for equilibrium **2**.

K_{eq3} =

[1]

[Turn over

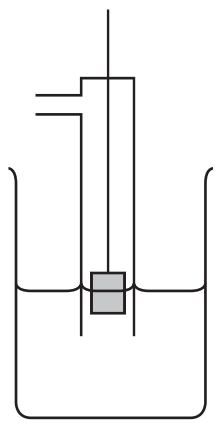
(d) Define the term *standard electrode potential, $E^\ominus$*.

....

....

.... [1]

(e) **(i)** Complete and **label** the diagram to show how the standard electrode potential, $E^\ominus$, of $Ag^+(aq)/Ag(s)$ could be measured under **standard conditions**.



[4]

(ii) Use the *Data Booklet* to label the diagram in **(e)(i)** to show

- which is the positive electrode,
- the direction of electron flow in the external circuit when a current flows.

[1]

[Total: 17]

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

Write an equation for the decomposition of the carbonate ion.

.... [1]

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

....

....

....

....

.... [3]

(c) Lead(II) carbonate, $PbCO_3$, and zinc carbonate, $ZnCO_3$, decompose on heating in a similar way to calcium carbonate, $CaCO_3$.

State relevant data from the *Data Booklet* and use it to predict the order of thermal stability of these three carbonates.

data ....

....

(most stable) .... > .... > .... (least stable)
[2]

(d) Dolomite contains the double carbonate of calcium and magnesium, $CaMg(CO_3)_2$, and some impurities. When 0.642 g of a sample of dolomite reacts with an excess of hydrochloric acid, 125.0 cm^3 of CO_2 is formed under room conditions.

Calculate the percentage of $CaMg(CO_3)_2$ in the sample of dolomite. Show all your working.

Assume that none of the impurities react with HC*l*.

% of $CaMg(CO_3)_2$ in dolomite = ... %
[3]

[Total: 9]

3 **(a)** Sketch the shape of a d orbital.

[1]

(b) **(i)** Explain what is meant by the term *transition element*.

....

.... [1]

Transition elements can form complex ions which contain ligands.

(ii) Name the *type of bonding* that occurs between a ligand and a transition element.

.... [1]

(c) Give the formulae of two oxides of iron. State the oxidation number of iron in each compound.

....

.... [1]

(d) CO and CN^- are monodentate ligands.

Complete the table for the following two complexes.

metal ion	ligand	co-ordination number	formula of complex ion	charge of complex ion
Ni^{2+}	CO	4		
Fe^{3+}	CN^-			3-

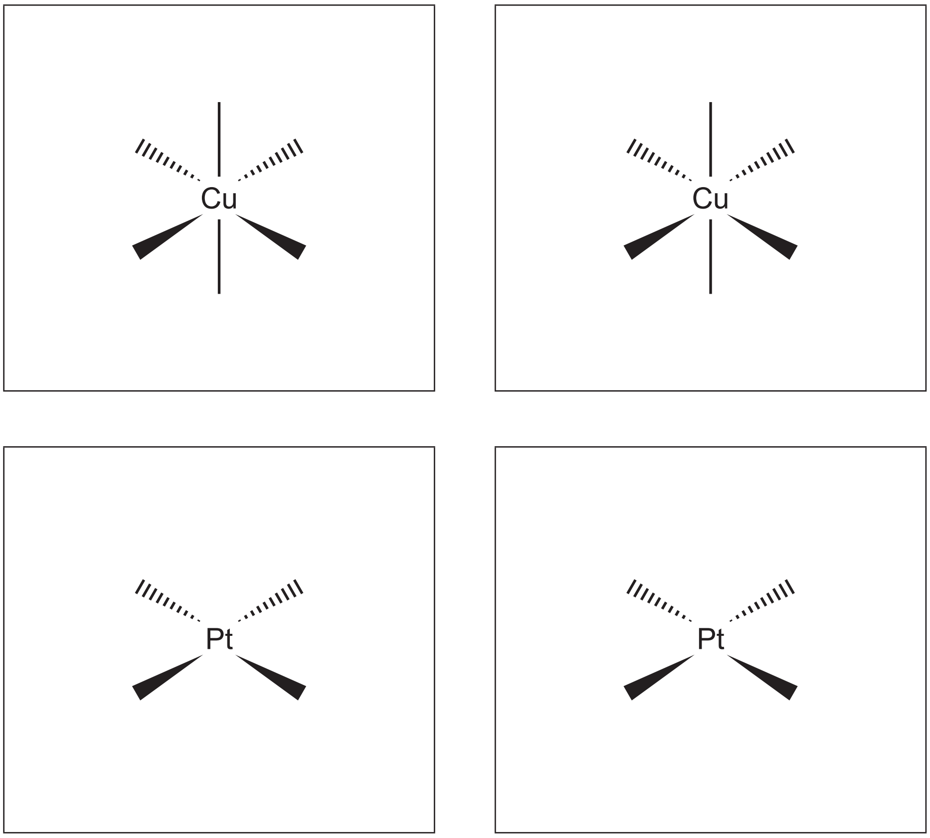
[2]

(e) Transition element complexes can exhibit stereoisomerism. $[Cu(H_2O)_4(NH_3)_2]^{2+}$ and $Pt(NH_3)_2Cl_2$ show the **same** type of isomerism.

(i) Name this type of isomerism.

.... [1]

(ii) Complete the three-dimensional diagrams of the two isomers for $[Cu(H_2O)_4(NH_3)_2]^{2+}$ and $Pt(NH_3)_2Cl_2$.



[2]

(f) Copper can form complexes with the ligands ammonia and *en*, $H_2NCH_2CH_2NH_2$, as shown.

$[Cu(H_2O)_6]^{2+}(aq) + en(aq) \rightleftharpoons [Cu(H_2O)_4(en)]^{2+}(aq) + 2H_2O(l)$ $K_{stab} = 3.98 \times 10^{10}$ equilibrium **4**

$[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightleftharpoons [Cu(H_2O)_4(NH_3)_2]^{2+}(aq) + 2H_2O(l)$ $K_{stab} = 5.01 \times 10^{7}$ equilibrium **5**

(i) Write an expression for the stability constant, K_{stab}, for equilibrium **5**. State its units.

K_{stab} =

units = ...

[2]

(ii) The standard entropy change, $\Delta S^\ominus$, for equilibrium **4** is $+23\,J\,K^{-1}\,mol^{-1}$ and for equilibrium **5** is $-8.4\,J\,K^{-1}\,mol^{-1}$.

Suggest an explanation for this difference by reference to both equilibria.

....

....

.... [1]

(iii) Of the three copper complexes in equilibria **4** and **5**, state the formula of the copper complex that is the most stable and explain your choice.

copper complex ....

explanation ....

....

[1]

[Total: 13]

Question 4 starts on the next page.

4 The initial rate of reaction for propanone and iodine in acid solution is measured in a series of experiments at a constant temperature.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+ \text{ catalyst}} CH_3COCH_2I + HI$$

The rate equation was determined experimentally to be as shown.

$$\text{rate} = k[CH_3COCH_3][H^+]$$

(a) State the order of reaction with respect to

- CH_3COCH_3 ....
- I_2 ....
- H^+ ....

and state the overall order of this reaction. ....

[2]

(b) The rate of this reaction is $5.40 \times 10^{-3}\,mol\,dm^{-3}\,s^{-1}$ when

- the concentration of CH_3COCH_3 is $1.50 \times 10^{-2}\,mol\,dm^{-3}$
- the concentration of I_2 is $1.25 \times 10^{-2}\,mol\,dm^{-3}$
- the concentration of H^+ is $7.75 \times 10^{-1}\,mol\,dm^{-3}$.

(i) Calculate the rate constant, k, for this reaction. State the units of k.

k = ...

units = ...

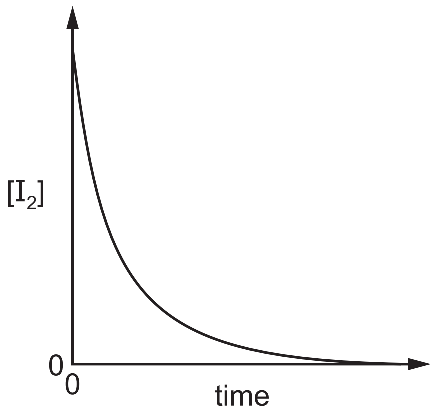
[2]

(ii) Complete the table by placing **one** tick (✓) in each row to describe the effect of **decreasing** the temperature on the rate constant and on the rate of reaction.

	decreases	no change	increases
rate constant			
rate of reaction			

[1]

(c) From the results, a graph is produced which shows how the concentration of I_2 changes during the reaction.



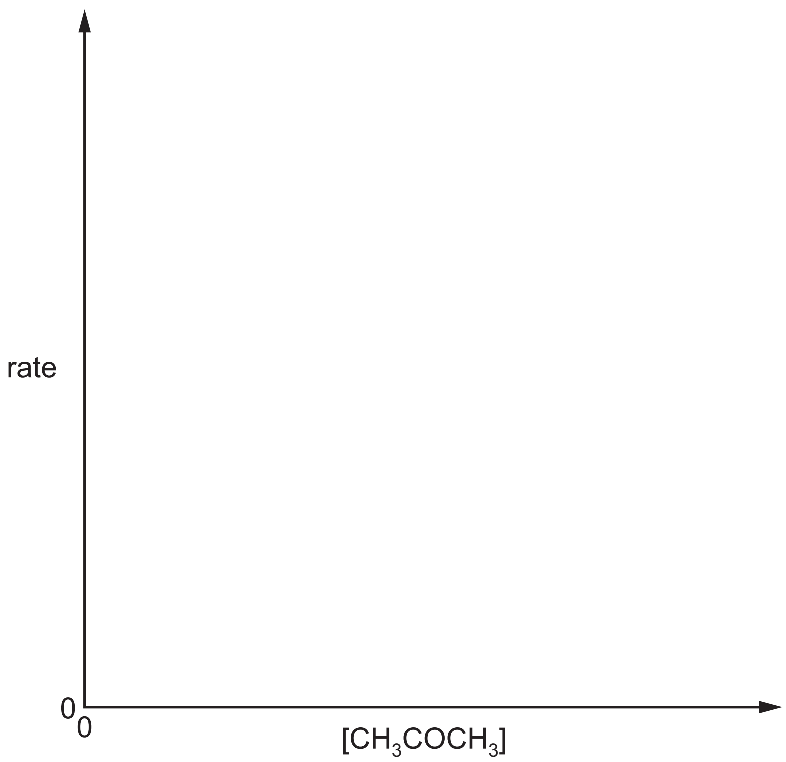
Describe how this graph could be used to determine the initial rate of the reaction.

....

....

.... [2]

(d) On the axes below, sketch a graph to show how the initial rate changes with different initial concentrations of CH_3COCH_3 in this reaction.



[1]

(e) The rate of a reaction between metal ions was studied. The following three-step mechanism has been suggested for this reaction. Step 1 is the rate-determining step.

step 1 $Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}$

step 2 $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$

step 3 $Mn^{4+} + Tl^{+} \rightarrow Tl^{3+} + Mn^{2+}$

(i) Explain the meaning of the term *rate-determining step*.

....

.... [1]

(ii) Use this mechanism to

- determine the overall equation for this reaction

....

- suggest the role of Mn^{2+} ions in this mechanism. Explain your answer.

....

....

....

[2]

[Total: 11]

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

energy change	always positive	always negative	either negative or positive
lattice energy			
enthalpy change of neutralisation			

[1]

(b) Define, in words, the term *enthalpy change of solution*.

....

.... [1]

(c) The following enthalpy changes are given.

enthalpy change	value / $kJ\,mol^{-1}$
standard enthalpy change of formation, $\Delta H^{\ominus}_{f}$, for $K_3PO_4(s)$	–2035
standard enthalpy change, $\Delta H^{\ominus}$, for $P(s) + 2O_2(g) + 3e^- \rightarrow PO_4^{3-}(aq)$	–1284
standard enthalpy change, $\Delta H^{\ominus}$, for $K(s) \rightarrow K^+(aq) + e^-$	–251

Determine the standard enthalpy change of solution of potassium phosphate, $K_3PO_4(s)$. It may be helpful to draw a labelled energy cycle.

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

(d) Some lattice energy values are shown in the table.

compound	lattice energy value / $kJ\,mol^{-1}$
$CaBr_2(s)$	–2176
KBr(s)	–679

Suggest an explanation for why $\Delta H^{\ominus}_{latt}$ $CaBr_2$ is **more** exothermic than $\Delta H^{\ominus}_{latt}$ KBr.

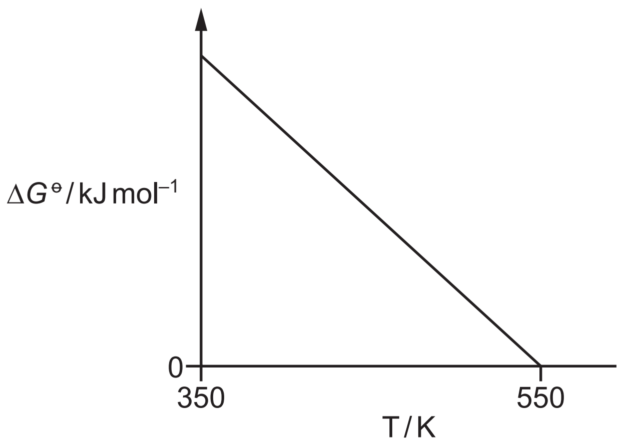
....

....

.... [2]

(e) For a particular gas phase reaction the variation in standard Gibbs free energy change, $\Delta G^{\ominus}$, with temperature is shown.

Assume standard enthalpy change, $\Delta H^{\ominus}$, and standard entropy change, $\Delta S^{\ominus}$, remain constant with temperature.



(i) Write the equation that relates $\Delta G^{\ominus}$ to $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$.

.... [1]

(ii) Use this equation to explain why $\Delta G^{\ominus}$ becomes **less** positive as temperature increases in this reaction.

....

.... [1]

[Total: 9]

Question 6 starts on the next page.

6 **(a)** By reference to the formation of σ and π bonds, describe and explain the shape of a benzene molecule, C_6H_6.

....

....

....

....

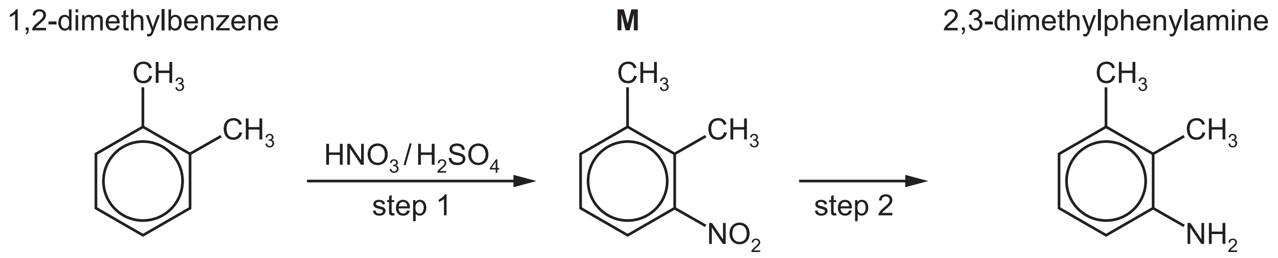
....

....

....

.... [3]

(b) 2,3-dimethylphenylamine can be prepared from 1,2-dimethylbenzene in two steps as shown.

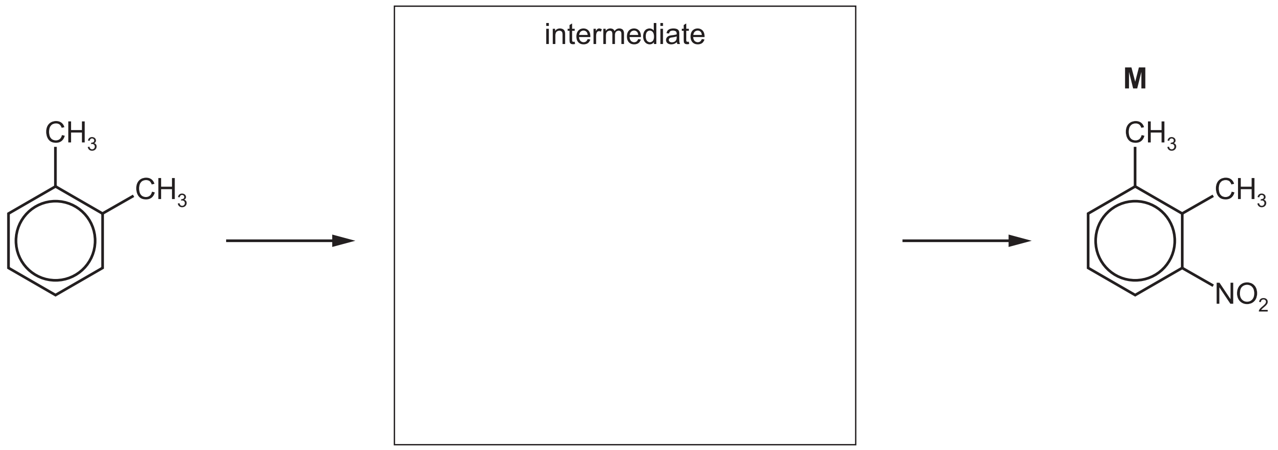


Step 1 is catalysed by H_2SO_4.

(i) Write an equation to show how H_2SO_4 generates the electrophile during step 1.

.... [1]

(ii) Draw the mechanism of the reaction between this electrophile and 1,2-dimethylbenzene to form **M**. Include all relevant curly arrows and charges.



[3]

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

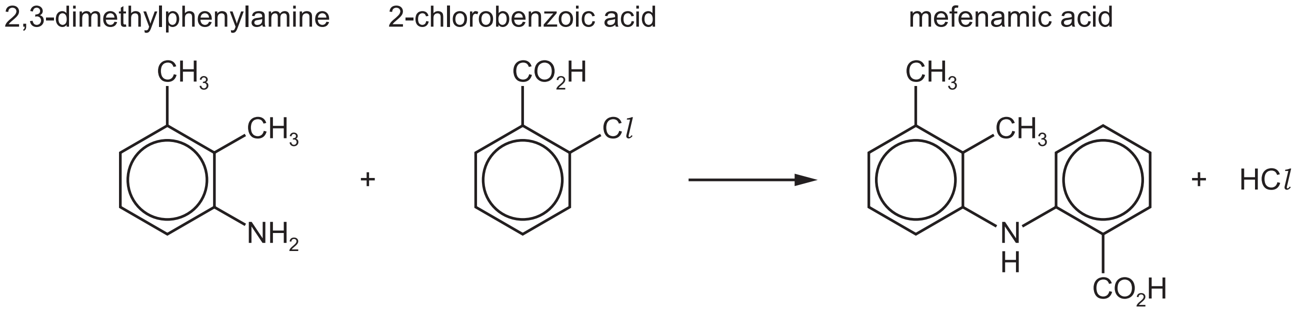
.... [1]

(iv) For step 2, suggest the reagents and conditions and name the *type of reaction*.

- reagents and conditions ....
- type of reaction ....

[2]

(c) The drug mefenamic acid can be made using 2,3-dimethylphenylamine in an excess of 2-chlorobenzoic acid.



(i) Deduce the molecular formula of mefenamic acid.

.... [1]

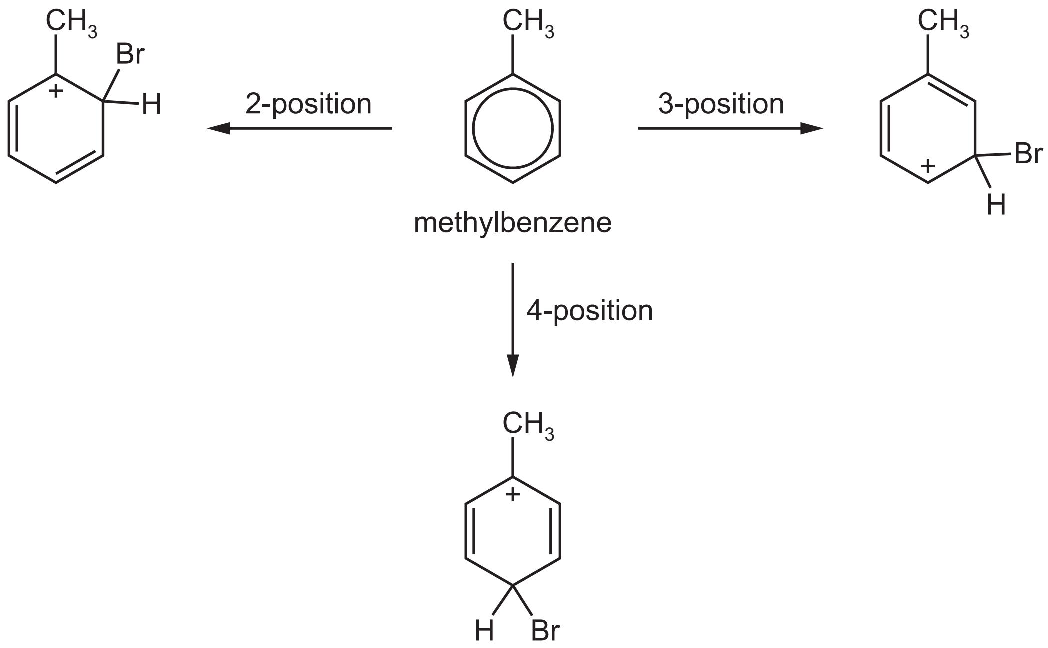
(ii) Name the functional groups, apart from the benzene ring, in mefenamic acid.

.... [1]

(iii) Calculate the maximum mass of mefenamic acid that could be formed from 5.00 g of 2,3-dimethylphenylamine in this reaction. Give your answer to **three** significant figures.

mass of mefenamic acid = ... g [2]

(d) The position of substitution in the electrophilic substitution of arenes can be explained based on the stability of the intermediate cations formed in the first step. The example given involves the bromination of methylbenzene.



Use this information and your knowledge about the stability of cations to suggest why the CH_3 group directs incoming electrophiles to the 2- and 4-positions in preference to the 3-position.

....

....

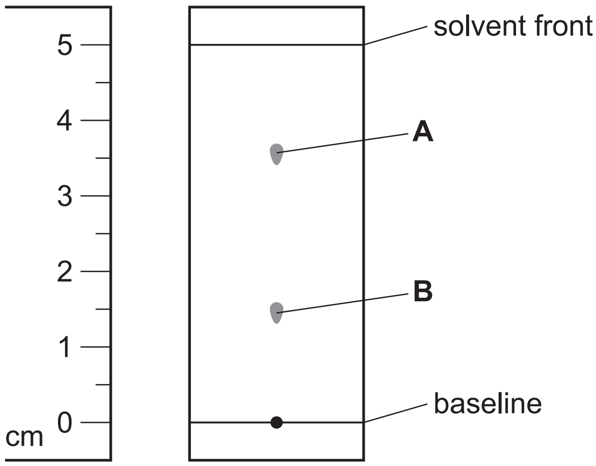
....

.... [2]

[Total: 16]

7 **(a)** Amino acids can be separated by thin-layer chromatography. A mixture of amino acids is analysed using this technique.

The chromatogram obtained is shown, drawn to scale. The table shows some R_f values for different amino acids in the solvent used.



amino acid	R_f value
alanine	0.40
glutamic acid	0.29
leucine	0.71
valine	0.61

(i) Use the chromatogram and the R_f values to deduce the amino acid responsible for spot **A** and spot **B**.

amino acid responsible for spot **A** ....

amino acid responsible for spot **B** ....
[1]

(ii) A second chromatogram of the same mixture is taken using a **more polar** solvent.

Predict the effect on the R_f values of the amino acids. Explain your reasoning.

....

....

....

.... [1]

(b) Glycine, $H_2NCH_2CO_2H$, is the simplest amino acid.

(i) Complete the equations to show the acid-base properties of glycine.

$H_2NCH_2CO_2H(aq) + HCl(aq) \rightarrow$ ....

$H_2NCH_2CO_2H(aq) + NaOH(aq) \rightarrow$ ....
[2]

(ii) In aqueous solution, amino acids exist as zwitterions.

Draw the zwitterionic structure of glycine. Explain how the zwitterion for glycine is formed.

....

....

....
[2]

(c) Apart from glycine, all naturally occurring amino acids have a chiral centre and exhibit stereoisomerism.

Draw the two stereoisomers of alanine, $CH_3CH(NH_2)CO_2H$.

[1]

(d) The amino acid alanine can be synthesised from 2-chloropropanoic acid, $CH_3CHClCO_2H$.

(i) State the reagents and conditions and name the mechanism for this reaction.

reagents and conditions ....

name of mechanism ....
[2]

(ii) State and explain the relative acidities of trichloroethanoic acid, chloroethanoic acid and ethanoic acid.

....

....

....

....

.... [3]

(e) Serine, $HOCH_2CH(NH_2)CO_2H$, can react with alanine, $CH_3CH(NH_2)CO_2H$, to form three different **structural** isomers, each with the molecular formula $C_6H_{12}N_2O_4$.

Draw the structures of these three structural isomers.

isomer 1 ($C_6H_{12}N_2O_4$)

isomer 2 ($C_6H_{12}N_2O_4$)

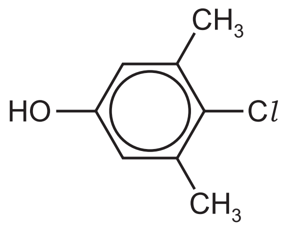
isomer 3 ($C_6H_{12}N_2O_4$)

[3]

[Total: 15]

8 Compound **R** is shown.

R



(a) State the systematic name of compound **R**.

.... [1]

(b) **(i)** **R** is dissolved in $CDCl_3$ and analysed using carbon-13 and proton NMR spectroscopy.

- Predict the number of peaks that are seen in the carbon-13 NMR spectrum of **R**.

....

- Predict the number of peaks that are seen in the proton NMR spectrum of **R**.

....
[2]

(ii) A separate sample of **R** is dissolved in D_2O. The proton NMR spectrum of this solution shows **one less** peak than is obtained in $CDCl_3$.

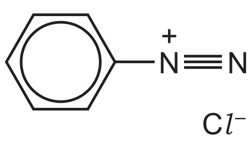
Explain why.

....

.... [1]

(c) Compound **R** reacts separately with the four reagents shown in the table.

Complete the table by
- drawing the structures of the organic products formed,
- stating the type of reaction.

reagent	organic product structure	type of reaction
Na		
CH_3COCl		
$Br_2(aq)$		
		

[6]

[Total: 10]

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Cambridge International AS & A Level

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Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME

CENTRE NUMBER

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5325823875

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2018**

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 **15** printed pages and **1** blank page.

IB18 06_9701_42/4RP

CAMBRIDGE
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[Turn over

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

1 Silicon tetrachloride, $SiCl_4$, is formed when silicon reacts with chlorine under suitable conditions. It is a colourless liquid with a low boiling point.

(a) Explain why $SiCl_4$ has a low boiling point.

....

....

.... [2]

(b) $SiCl_4$ reacts with water to produce an acidic solution.

(i) Write an equation for this reaction.

.... [1]

(ii) Describe **two** visual observations when silicon tetrachloride is added drop by drop to a small amount of water.

1 ....

2 ....
[2]

(iii) A sample of 0.8505 g of $SiCl_4$ is added to 800 cm^3 of water. All of the soluble acidic product is dissolved in the water.

Calculate the pH of the solution obtained.

pH = ... [3]

(c) **(i)** Silicon tetrachloride can be prepared according to reaction 1.

reaction 1 $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$ $\Delta S^{\ominus} = -225.7\,J\,K^{-1}\,mol^{-1}$

standard entropy of silicon, $S^{\ominus}$ Si(s)	18.7 $J\,K^{-1}\,mol^{-1}$
standard entropy of silicon tetrachloride, $S^{\ominus}$ $SiCl_4$(l)	239.0 $J\,K^{-1}\,mol^{-1}$

Calculate the standard entropy of chlorine, $S^{\ominus}$ Cl_2(g). Show all your working.

$S^{\ominus}$ Cl_2(g) = ... $J\,K^{-1}\,mol^{-1}$ [2]

(ii) Explain why the entropy change for reaction 1 is negative.

....

.... [1]

(d) The standard enthalpy change of formation of silicon tetrachloride, $\Delta H_f^{\ominus}$ $SiCl_4$(l), is $-640\,kJ\,mol^{-1}$.

Reaction 1 is spontaneous at lower temperatures, but it is not spontaneous at very high temperatures.

Calculate the temperature above which reaction 1 is **not** spontaneous.

temperature = ... K [2]

[Total: 13]

2 Iodine monochloride, ICl, is a yellow-brown gas. It reacts with hydrogen gas under certain conditions as shown.

$$2ICl(g) + H_2(g) \rightarrow 2HCl(g) + I_2(g)$$

Experiments are performed using different starting concentrations of ICl and H_2. The initial rate of each reaction is measured. The following results are obtained.

experiment	$[ICl]$ / mol dm^{-3}	$[H_2]$ / mol dm^{-3}	relative rate of reaction
1	4.00×10^{-3}	4.00×10^{-3}	1.00
2	4.00×10^{-3}	7.00×10^{-3}	1.75
3	4.00×10^{-3}	1.00×10^{-2}	2.50
4	5.00×10^{-3}	8.00×10^{-3}	2.50
5	7.00×10^{-3}	8.00×10^{-3}	3.50

(a) Identify a change, taking place in the reaction mixture, that would enable measurements of the rate of this reaction to be made.

.... [1]

(b) Use the data in the table to show that the reaction is first order with respect to $H_2(g)$.

....

....

....

.... [1]

(c) Use the data in the table to show that the reaction is first order with respect to $ICl(g)$.

....

....

....

.... [1]

(d) Complete the rate equation for the reaction between $ICl(g)$ and $H_2(g)$.

rate = ... [1]

(e) Use experiment 3 to calculate a numerical value for the rate constant, *k*.

k = ... [1]

(f) The reaction $2ICl(g) + H_2(g) \rightarrow 2HCl(g) + I_2(g)$ is first order with respect to $ICl(g)$ and first order with respect to $H_2(g)$.

Suggest a mechanism for this reaction. You should assume

- the mechanism has two steps,
- the first step is much slower than the second step.

first step .... $\rightarrow$ ....

second step .... $\rightarrow$ ....

[2]

(g) An alternative method is used to show that the reaction is first order with respect to $H_2(g)$. This method uses a large excess of $ICl(g)$ and measures how the concentration of $H_2(g)$ varies with time.

(i) Describe two ways of using these results to show the reaction is first order with respect to $H_2(g)$ concentration.

....

....

....

....

....

.... [3]

(ii) Explain the reason for using a large excess of $ICl(g)$.

....

.... [1]

(h) A chemical reaction may be speeded up by the presence of a catalyst.

Explain why a catalyst increases the rate of a chemical reaction.

....

.... [1]

[Total: 12]

3 **(a)** Complete the table by predicting the identity of the substance liberated at each electrode during electrolysis with inert electrodes.

electrolyte	substance liberated at the anode	substance liberated at the cathode
NaOH(aq)		
dilute $CuCl_2$(aq)		
concentrated $MgCl_2$(aq)		

[3]

(b) **(i)** The electrolysis of molten $ZnBr_2$ is a redox process.

Identify the ion that is oxidised and the ion that is reduced.

Use ionic half-equations to explain your answer.

....

....

....

....

.... [3]

(ii) Describe **one** visual observation that would be made during this electrolysis.

.... [1]

(c) Dilute sulfuric acid is electrolysed for 50.0 minutes using inert electrodes and a current of 1.20 A. A different gas is collected above each electrode. The volumes of the two gases are measured under room conditions.

Calculate the maximum volume of gas that could be collected at the **cathode**.

volume = ... cm^3 [3]

[Total: 10]

4 **(a)** **(i)** Write an equation, including state symbols, for the reaction that takes place when a sample of anhydrous calcium nitrate, $Ca(NO_3)_2$, is heated strongly in a test-tube.

.... [2]

(ii) Describe what will be seen during this reaction.

....

....

.... [2]

(b) Describe and explain how the solubility of the Group 2 sulfates varies down the group.

....

....

....

....

....

....

....

.... [4]

[Total: 8]

5 Cobalt is a transition element with atomic number 27. Cobalt forms ions with charges of +2 and +3. Both these ions form complexes.

(a) Complete the electronic configurations of a Co atom and a Co^{2+} ion.

Co atom $1s^2 2s^2 2p^6$ ....

Co^{2+} ion $1s^2 2s^2 2p^6$ ....

[2]

(b) One Co^{2+} ion can form a tetrahedral complex ion with four Cl^- ions. This complex is blue.

(i) What is meant by the term *complex ion*?

....

.... [1]

(ii) Draw the tetrahedral complex ion formed by one Co^{2+} ion with four Cl^- ions. Your drawing should clearly show three-dimensional shape, and should include the overall charge on the ion.

Co

[2]

(iii) Explain why many transition metal complexes are coloured.

....

....

....

....

.... [3]

(iv) Using ideas from your answer to **(iii)** suggest why the colour of the complex formed by one Co^{2+} ion with four Cl^- ions is **blue**.

....

.... [1]

(c) Describe the colour change that occurs when water is added to blue crystals of the cobalt(II)-chloride complex. Name the type of reaction responsible for this colour change.

colour change ....

type of reaction ....
[2]

(d) Co^{2+}(aq) can be oxidised to Co^{3+}(aq).

(i) Use the *Data Booklet* to suggest a suitable oxidising agent for this reaction.

.... [1]

(ii) Calculate the $E^{\ominus}_{cell}$ of this reaction.

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

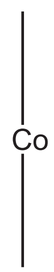
(iii) Write an equation for the reaction between Co^{2+} and the oxidising agent you chose in **(d)(i)**.

.... [1]

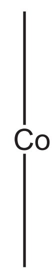
(e) Cobalt(III) forms two isomeric octahedral complexes with the formula $[Co(NH_3)_3(NO_2)_3]$. The NO_2^- ion is monodentate.

Complete the diagrams to show the three-dimensional structures of the two isomers and suggest the type of isomerism shown here.

isomer 1



isomer 2



type of isomerism ....
[3]

[Total: 17]

6 Phenol is an important industrial chemical used in the manufacture of dyestuff and other substances.

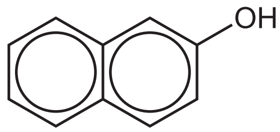
(a) Suggest **two** different substances that react with phenol to produce potassium phenoxide, $C_6H_5O^-K^+$. Identify the second product formed in each case.

substance .... second product ....

substance .... second product ....

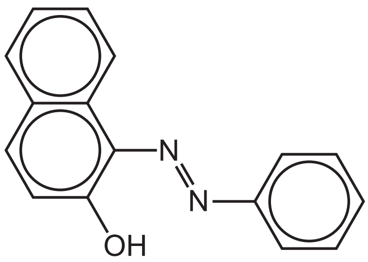
[3]

(b)



2-naphthol

2-naphthol can show similar properties to phenol. It can be used to produce Sudan I, an orange coloured dyestuff.



Sudan I

(i) On the diagram of Sudan I above **circle** the bond or bonds that make this substance a dyestuff. [1]

(ii) Describe how Sudan I can be made using phenylamine and 2-naphthol as the organic starting materials.

....

....

....

....

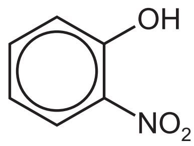
....

....

....

.... [3]

(c) Phenol can be used to make 2-nitrophenol.



2-nitrophenol

The nitration reaction of phenol to form 2-nitrophenol shows that phenol is more reactive than benzene.

(i) Describe the conditions used for the nitration of phenol.

Explain how these conditions show phenol to be more reactive than benzene.

conditions ....

explanation ....

....

.... [2]

(ii) Suggest why phenol is more reactive than benzene.

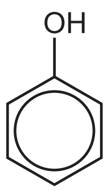
....

....

.... [1]

(iii) Complete the mechanism for the nitration of phenol to form 2-nitrophenol. You should assume that the mechanism is the same as that for the nitration of benzene.

- Include all relevant charges and curly arrows to show the movement of electron pairs.
- Draw the structure of the intermediate.
- You do not need to draw the products.



phenol

$^{+}NO_2$ $\longrightarrow$ [intermediate] $\longrightarrow$ products

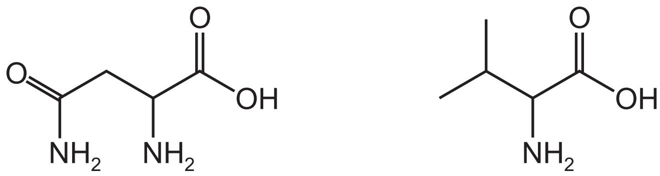
[3]

(iv) Name the isomer of 2-nitrophenol which is also a major product of this reaction.

.... [1]

[Total: 14]

7 Asparagine and valine are two naturally occurring amino acids.



asparagine valine

(a) Give the molecular formula of asparagine.

.... [1]

(b) Name **all** of the functional groups in an asparagine molecule.

.... [2]

(c) Draw the structure of the dipeptide formed by valine and asparagine.

The peptide bond should be shown displayed and should be clearly labelled.

[2]

(d) A solution of valine in water acts as a buffer solution.

(i) Explain what is meant by a *buffer solution*.

....

....

.... [2]

(ii) Write **two** equations to explain how valine can act as a buffer. Use the formula $H_2NCHRCO_2H$ for valine in your equations.

....

....

[2]

(e) Each valine molecule has one chiral carbon atom.

Draw three-dimensional diagrams to show the two optical isomers of valine.
The $(CH_3)_2CH$ group can be represented as R.

[2]

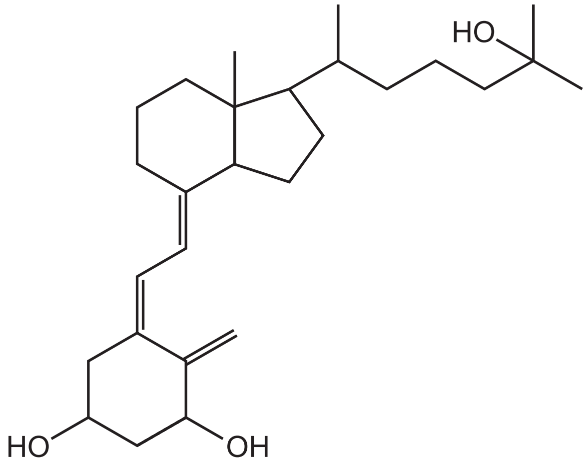
(f) Asparagine is hydrolysed when heated with aqueous sulfuric acid.

Write an equation for this reaction.

.... [2]

[Total: 13]

8 Calcitriol is a steroid hormone found in human blood.



calcitriol

(a) Give the number of primary, secondary and tertiary alcohol groups in one molecule of calcitriol.

primary .... secondary .... tertiary ....
[1]

(b) Give the number of chiral carbon atoms in one molecule of calcitriol.

.... [1]

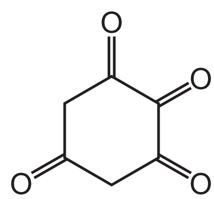
(c) Calcitriol shows geometrical isomerism.

Give the number of geometrical isomers of calcitriol, including calcitriol.

.... [1]

(d) A sample of calcitriol is treated with an excess of hot, concentrated, acidified potassium manganate(VII). There are three different carbon-containing products of this reaction.

One of these three products, **X**, is shown.



X

(i) Predict the number of peaks in the carbon-13 NMR spectrum of **X**.

.... [1]

(ii) For the carbon-13 NMR spectrum of **X**, state the expected chemical shift ranges (δ) of the peaks predicted in **(i)** and the number of peaks in each range.

....

....

....

.... [3]

(iii) Predict the number of peaks this compound would show in its proton NMR spectrum.

.... [1]

(iv) For each of the peaks in the proton NMR spectrum you have identified in **(iii)** give the expected splitting pattern. Explain your reasoning.

....

....

.... [2]

(e) In addition to the product shown in **(d)**, two other carbon-containing products are formed when a sample of calcitriol is treated with an excess of hot, concentrated, acidified potassium manganate(VII).

(i) Of these two other carbon-containing products, identify the product with the **smaller** molecular mass. Explain how this product is formed.

....

....

....

.... [2]

(ii) Of these two other carbon-containing products, identify the product with the **larger** molecular mass by drawing its skeletal formula in the space below.

[1]

[Total: 13]

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CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **October/November 2018**

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 **23** printed pages and **1** blank page.

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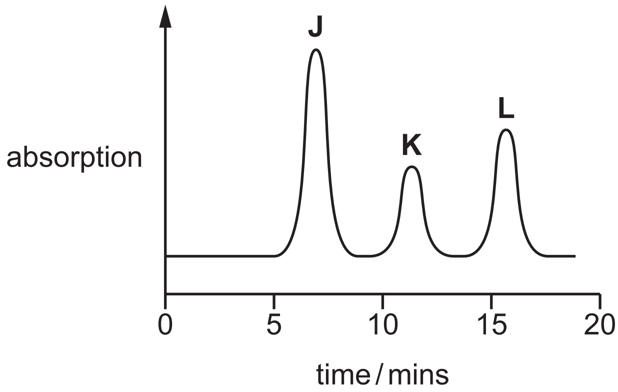
Answer **all** the questions in the spaces provided.

1 **(a)** An alkene, a carboxylic acid and a ketone, all of similar volatility, are mixed together. The mixture is then analysed by gas chromatography.

The gas chromatogram produced is shown.



The separation of the three compounds depends on their relative solubilities in the liquid stationary phase. The liquid stationary phase is an alkane.

(i) Complete the table to suggest which compound in the mixture is responsible for each peak **J**, **K** and **L**. Explain your answer by reference to the intermolecular forces of each compound.

peak	organic compound	explanation
J		
K		
L		

[2]

A student calculates the areas underneath the three peaks in the chromatogram.

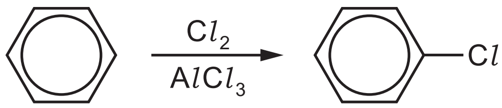
peak	**J**	**K**	**L**
area / mm^2	46	18	28

(ii) The area underneath each peak is proportional to the mass of the respective compound.

Calculate the percentage **by mass** in the original mixture of the compound responsible for peak **K**.

% of mixture responsible for peak **K** = ... [1]

(b) Chlorobenzene can be prepared from benzene as shown.



Aluminium chloride, $AlCl_3$, catalyses this reaction.

(i) Write an equation to show how $AlCl_3$ generates the electrophile needed in this reaction.

.... [1]

(ii) Draw the mechanism of the reaction between this electrophile and benzene to form chlorobenzene. Include all relevant curly arrows and charges.

[4]

(iii) Write an equation to show how the catalyst is regenerated.

.... [1]

(c) **(i)** Catalysts can be heterogeneous or homogeneous.

Explain what is meant by a *homogeneous catalyst*.

....

.... [1]

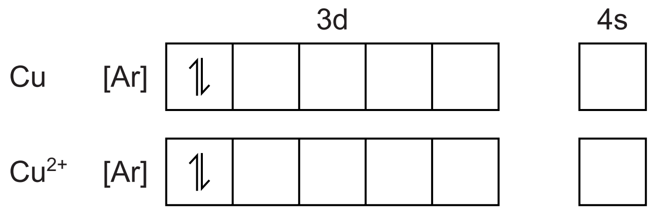
(ii) Complete the table by placing **one** tick (✓) in **each row** to indicate the mode of action of the catalyst in each reaction.

	heterogeneous	homogeneous
Rh in the removal of NO_2 from exhaust gases of cars		
Fe^{3+} in the $I^-/S_2O_8^{2-}$ reaction		

[1]

[Total: 11]

2 **(a)** Complete the electronic configuration for Cu and Cu^{2+}.



[2]

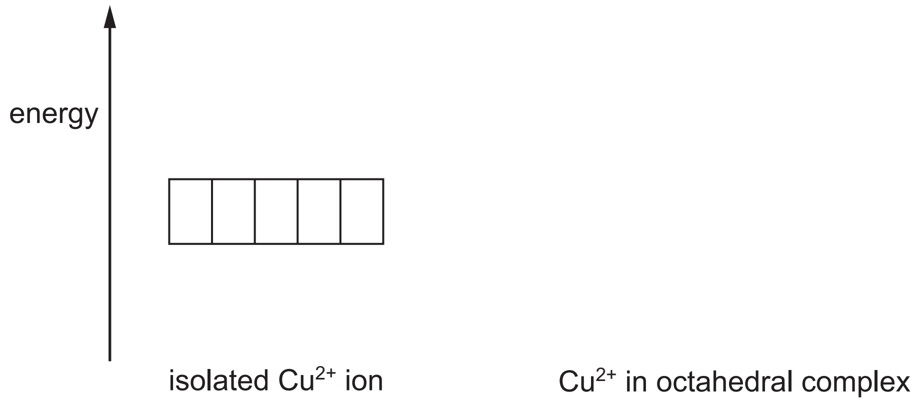
(b) **(i)** The 3d orbitals in an isolated Cu^{2+} ion are degenerate.

Explain what is meant by the term *degenerate* in this context.

....

.... [1]

(ii) Complete the diagram to describe the splitting of the 3d orbital energy levels in an octahedral complex.



[1]

(c) (i) 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, *en*, is a bidentate ligand.

Explain what is meant by the term *bidentate*.

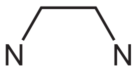
....

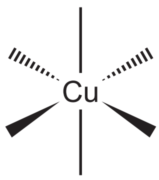
....

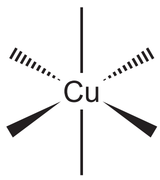
.... [1]

(ii) Cu^{2+} ions and *en* form the complex ion $[Cu(en)_3]^{2+}$.

Draw the two optical isomers of this complex ion.

You may use  to represent *en*.

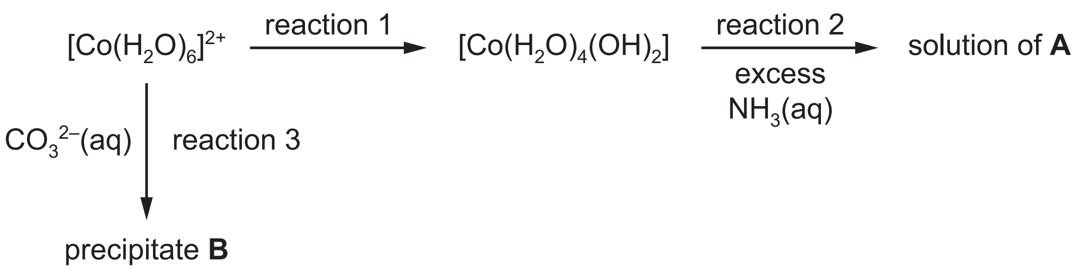




[2]

[Total: 7]

3 **(a)** The reaction scheme shows some reactions of $[Co(H_2O)_6]^{2+}$.



(i) Write the formulae of the following species.

A ....

B ....

[2]

(ii) State a suitable reagent for reaction 1.

.... [1]

(iii) Write an equation for reaction 2.

.... [1]

(iv) Write an ionic equation for reaction 3.

.... [1]

(b) Co^{2+} ions catalyse the oxidation of 2,3-dihydroxybutanedioate ions, $C_4H_4O_6^{2-}$, to methanoate ions, HCO_2^-, carbon dioxide and water.

(i) What property of transition elements allows Co^{2+} ions to act as a catalyst?

.... [1]

(ii) Draw the structure of the 2,3-dihydroxybutanedioate ion.

[1]

(iii) Complete the equation for the oxidation of 2,3-dihydroxybutanedioate. Use [O] for the oxidising agent in this reaction.

$C_4H_4O_6^{2-}$ + ... $\rightarrow$ .... [1]

(c) Platin, $Pt(NH_3)_2Cl_2$, displays *cis-trans* isomerism.

(i) Draw the structures of these isomers.

cis isomer

trans isomer

[2]

(ii) *Cis*-platin is an effective anti-cancer drug.

Describe the action of *cis*-platin in this role.

....

....

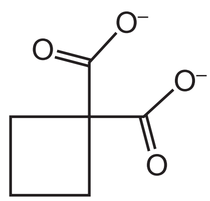
....

.... [2]

(d) The use of *cis*-platin can cause side effects so carboplatin has been developed.

Carboplatin can be synthesised from *cis*-platin, $Pt(NH_3)_2Cl_2$, by replacing the two chloride ion ligands with a **single** cyclobutane-1,1-dicarboxylate ion ligand as shown.

$Pt(NH_3)_2Cl_2$ +



$\longrightarrow$ carboplatin + $2Cl^-$

cis-platin

$[C_6H_6O_4]^{2-}$

cyclobutane-1,1-dicarboxylate ion

Suggest the structure for carboplatin and draw it in the box. [1]

[Total: 13]

4 **(a)** Calcium nitride, Ca_3N_2, reacts readily with water to form a white precipitate suspended in an alkaline solution. The oxidation number of nitrogen does not change during the reaction.

Construct an equation for the reaction of Ca_3N_2 with water.

.... [2]

(b) The enthalpy changes of solution, $\Delta H^{\ominus}_{sol}$, of the hydroxides of the Group 2 elements become less endothermic down the group.

State and explain the trend in the solubilities of the Group 2 hydroxides.

....

....

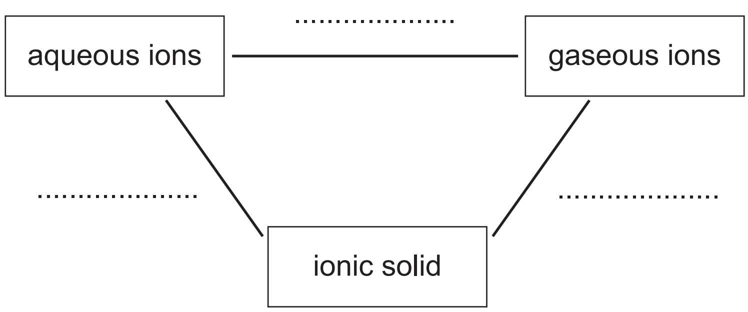
....

.... [3]

(c) Complete the energy cycle to show the enthalpy changes that occur in the transformations between aqueous ions, gaseous ions and an ionic solid.

On your diagram label each enthalpy change with its appropriate symbol; lattice energy, $\Delta H^{\ominus}_{latt}$, enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, or enthalpy change of solution, $\Delta H^{\ominus}_{sol}$.

Complete the three arrows showing the correct direction of each enthalpy change.



[3]

(d) The numerical value of the solubility product, K_{sp}, of CaF_2 is 3.45×10^{-11} at 298 K.

(i) Write an expression for the solubility product of CaF_2. Include its units.

K_{sp} =

units = ...
[2]

(ii) Calculate the solubility of CaF_2 at 298 K.

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

[Total: 11]

5 **(a)** Explain why the thermal stability of the Group 2 nitrates increases down the group.

....

....

.... [2]

(b) Sodium nitrite, $NaNO_2$, is a decomposition product from heating sodium nitrate, $NaNO_3$.

A student analysed a sample of sodium nitrite by titration with aqueous cerium(IV) ions, $Ce^{4+}(aq)$. The equation for the titration reaction is shown.

$$NO_2^-(aq) + 2Ce^{4+}(aq) + H_2O(l) \rightarrow 2Ce^{3+}(aq) + NO_3^-(aq) + 2H^+(aq)$$

- 0.138 g of impure sodium nitrite was dissolved in water and made up to 100 cm^3 in a volumetric flask.
- 25.0 cm^3 of this solution required 21.80 cm^3 of 0.0400 $mol\,dm^{-3}$ $Ce^{4+}(aq)$ to reach the end-point.

You should assume the impurity does not react with $Ce^{4+}(aq)$.

Calculate the percentage purity of the sample of sodium nitrite.

.... % [3]

(c) Acidified manganate(VII) ions, MnO_4^-, can also be used to analyse solutions containing nitrite ions, NO_2^-, by titration. In acidic solution, NO_2^- ions exist as HNO_2.

(i) Use the *Data Booklet* to construct an ionic equation for this reaction.

....

....

.... [2]

(ii) Use $E^{\ominus}$ values to calculate the $E^{\ominus}_{cell}$ for this reaction.

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

(d) Nitrous acid, HNO_2, is a weak acid with a K_a of 6.9×10^{-4} mol dm^{-3} at 298 K.

(i) Explain the difference between a strong acid and a weak acid.

....

.... [1]

(ii) Write the expression for the acid dissociation constant, K_a, for HNO_2.

K_a =

[1]

(iii) Calculate the pH of 0.15 mol dm^{-3} HNO_2.

pH = ... [2]

(iv) Calculate the percentage of HNO_2 molecules that are ionised in 0.15 mol dm^{-3} HNO_2.

% ionisation = ... [1]

(e) Solutions containing a mixture of HNO_2 and $NaNO_2$ are buffer solutions.

(i) Define what is meant by the term *buffer solution*.

....

....

.... [2]

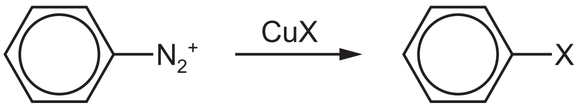
(ii) Write **two** equations to show how a solution containing a mixture of HNO_2 and $NaNO_2$ acts as a buffer.

....

.... [2]

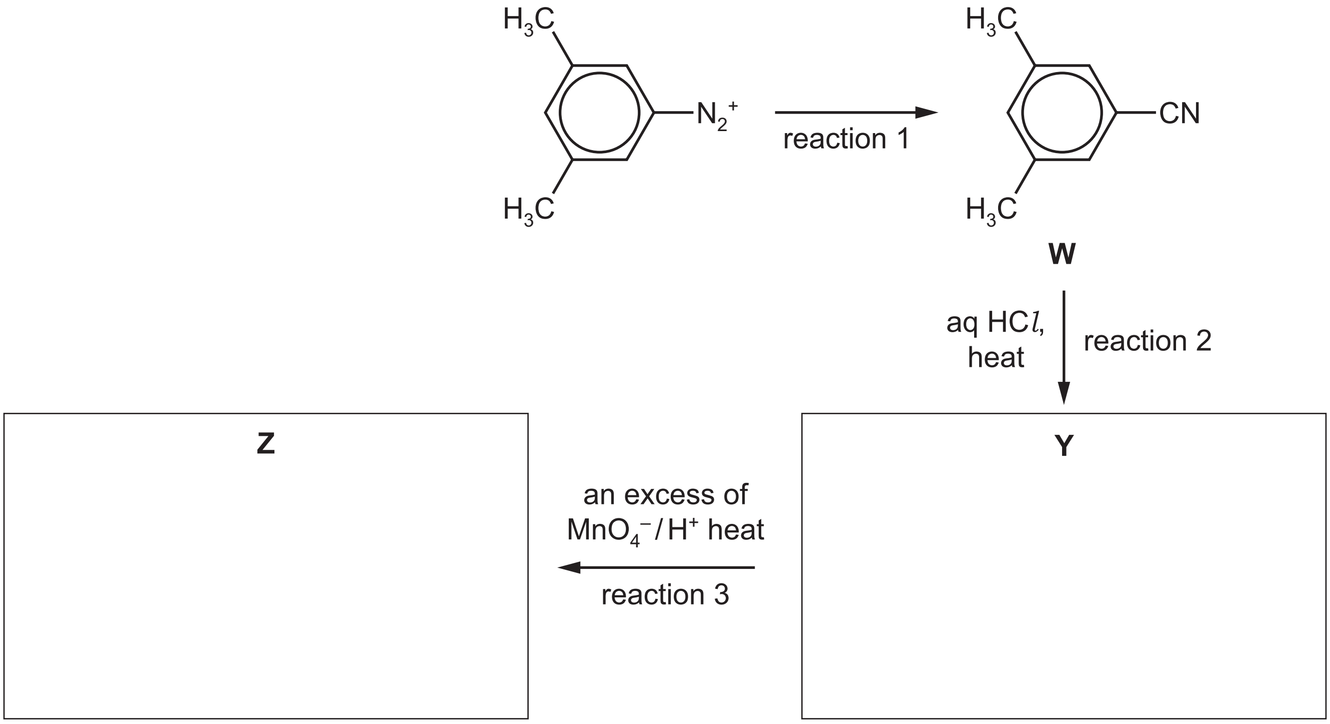
(f) Nitrous acid is used in the preparation of diazonium salts. The $–N_2^+$ group in the diazonium ion can be replaced with C*l*, Br or CN as shown.

The reagent used is a copper(I) salt, CuX.



diazonium ion   where X = C*l*, Br or CN

This reaction can be used in the synthesis of compound **Z** as shown.



(i) Suggest the reagent used in reaction 1.

.... [1]

(ii) Suggest structures of compounds **Y** and **Z** and draw them in the boxes above. [2]

Compounds **W** and **Z** were analysed using carbon-13 NMR spectroscopy.

(g) Predict the number of peaks in the carbon-13 NMR spectra of **W** and **Z**.

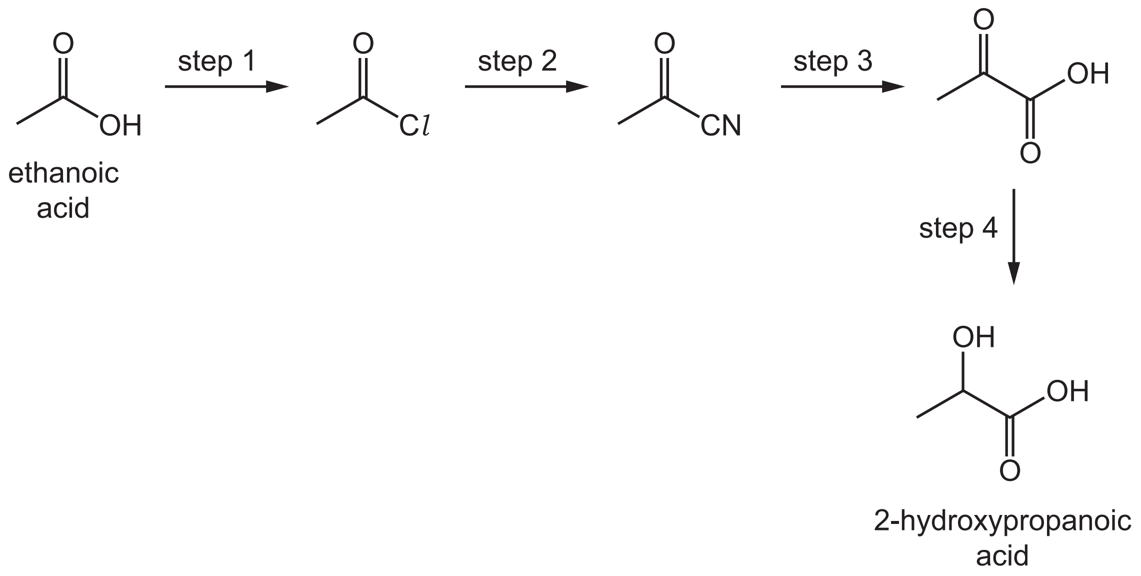
	number of peaks
W	
Z	

[2]

[Total: 22]

Question 6 starts on the next page.

6 2-hydroxypropanoic acid can be synthesised in four steps from ethanoic acid.



(a) **(i)** Suggest a reagent for step 2.

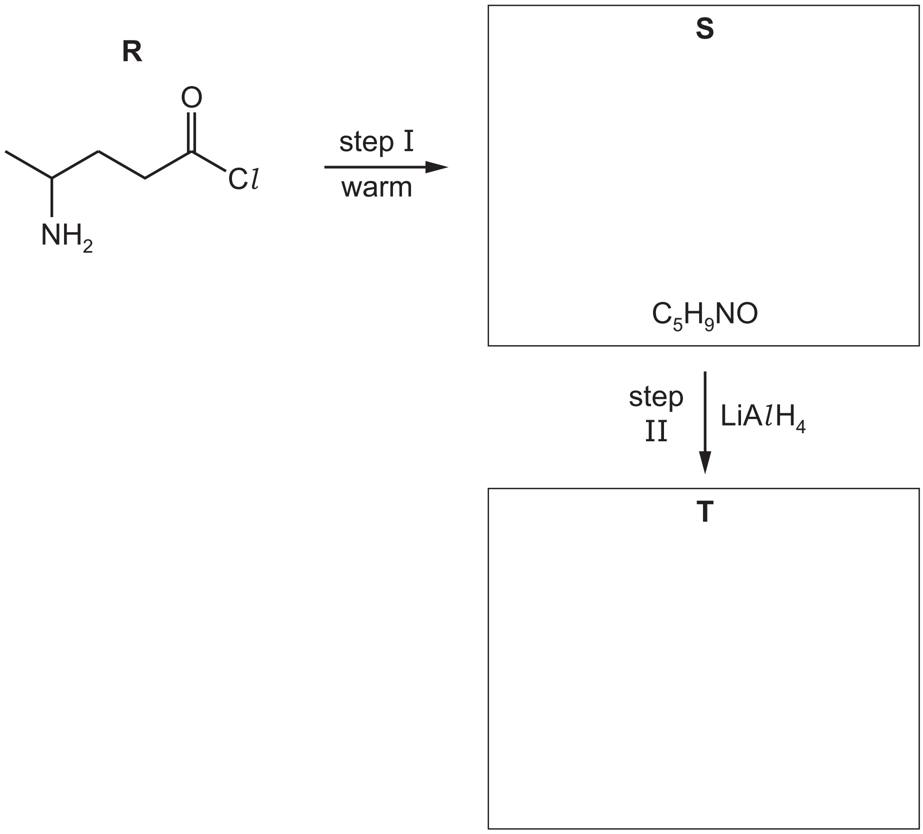
.... [1]

(ii) Suggest reagents and conditions for steps 1 and 4.

step 1 ....

step 4 ....
[2]

(b) Compound **R** can be used in the synthesis of compound **T** as shown.



(i) Suggest the structures of **S** and **T** and draw them in the boxes. [2]

(ii) Name the *type of reaction* for step I and step II.

step I ....

step II ....

[2]

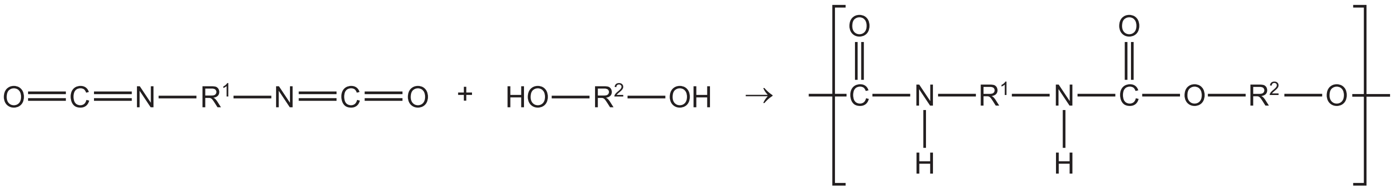
(c) Compound **R** can be polymerised.

Draw a section of this polymer showing **two** repeat units.

[2]

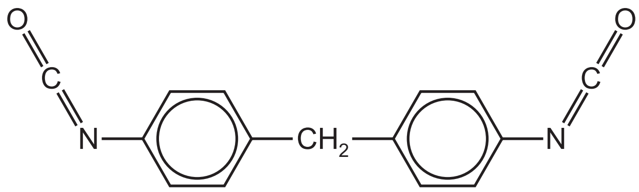
[Total: 9]

7 **(a)** Polyurethanes are polymers made by the reaction of a diisocyanate with a diol as shown. R^1 and R^2 are hydrocarbon groups.



a diisocyanate a diol a polyurethane

Lycra® is a polyurethane formed from the diisocyanate **P** and $HOCH_2CH_2OH$.



P

(i) Give the molecular formula for **P**.

.... [1]

(ii) Draw the repeat unit of Lycra®.

[2]

(iii) Fibres of Lycra® are strong due to the intermolecular forces between the polymer chains.

Complete the table to identify two intermolecular forces responsible for this property and the group(s) involved.

intermolecular force	group(s) involved

[2]

(b) Name **one** example of each of the following types of polymer.

type of polymer	example
synthetic polyamide	
synthetic polyester	
conducting polymer	
non-solvent based adhesive	

[3]

[Total: 8]

8 **(a)** Chloramine, NH_2Cl, can be used in the treatment of drinking water to kill bacteria. Excess chloramine in water is destroyed using UV light. The mechanism for this involves free radicals.

The initiation step in this process is shown.

$$NH_2Cl \xrightarrow{UV} \bullet NH_2 + \bullet Cl$$

(i) What is meant by the term *free radical*?

....

.... [1]

The equation for a possible propagation step in the process is shown.

$$NH_2Cl + \bullet Cl \rightarrow \bullet NHCl + HCl$$

(ii) Suggest an equation for a possible termination step in this process.

.... [1]

(b) **(i)** Draw the 'dot-and-cross' diagram of NH_2Cl. Show outer electrons only.

[1]

(ii) State the hybridisation of the nitrogen atom and suggest the H–N–Cl bond angle in the NH_2Cl molecule.

hybridisation of N ....

H–N–Cl bond angle ....
[1]

(c) Some values for standard enthalpy changes of formation, $\Delta H_f^\ominus$, and standard entropies, $S^\ominus$, are given in the table.

	$\Delta H_f^\ominus$ / kJ mol^{-1}	$S^\ominus$ / J K^{-1} mol^{-1}
$NH_2Cl(g)$	+80.1	+241
$NH_3(g)$	–45.9	+198
$N_2H_4(g)$	+95.4	+237
$HCl(g)$	–92.3	+187

(i) Define the meaning of the term *entropy*.

....

.... [1]

Hydrazine, N_2H_4, can be produced from chloramine and ammonia as shown.

$$NH_2Cl(g) + NH_3(g) \rightarrow N_2H_4(g) + HCl(g)$$

(ii) Calculate the standard entropy change, $\Delta S^\ominus$, for this reaction.

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

(iii) Calculate the standard enthalpy change, $\Delta H^\ominus$, for this reaction.

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

(iv) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for this reaction at 298 K.

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

(v) Explain, with reference to $\Delta G^\ominus$, why this reaction becomes **less** feasible at higher temperatures.

....

....

.... [1]

(d) Compare and explain the basicities of ammonia, ethylamine and phenylamine.

....

....

....

....

....

....

....

.... [4]

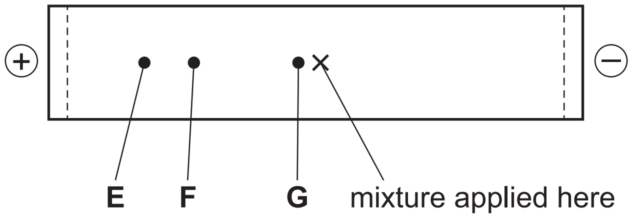
[Total: 14]

9 **(a)** Use information from the *Data Booklet* to draw the structure of the dipeptide glu-cys.

[2]

The isoelectric point is the pH at which an amino acid exists as a zwitterion. The isoelectric point of glutamic acid is 3.2 and of cysteine is 5.0.

A mixture of the dipeptide glu-cys and its two constituent amino acids, glutamic acid and cysteine, was analysed by electrophoresis using a buffer at pH 5.2. The results obtained are shown.



(b) Suggest identities for the species responsible for spots **E**, **F** and **G**. Explain your answers.

spot	identity
E	
F	
G	

explanation ....

....

....

[3]

[Total: 5]

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Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME

CENTRE NUMBER | CANDIDATE NUMBER

* 1 5 0 5 2 9 7 9 1 1 *

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2017**

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.

IB17 06_9701_42/6RP

CAMBRIDGE International Examinations

[Turn over

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

1 **(a)** **(i)** Describe and explain the variation in the thermal stabilities of the carbonates of the Group 2 elements.

....

....

....

....

.... [3]

(ii) Suggest and explain a reason why sodium carbonate is more stable to heat than magnesium carbonate.

....

....

.... [1]

(b) Sodium hydrogencarbonate, $NaHCO_3$, and potassium hydrogencarbonate, $KHCO_3$, decompose on heating to produce gases and the solid metal carbonate.

(i) Write an equation for the decomposition of $KHCO_3$.

.... [1]

(ii) Predict which of $NaHCO_3$ or $KHCO_3$ will decompose at the **lower** temperature. Explain your answer.

....

.... [1]

(c) **(i)** Use the data in the table below, and relevant data from the *Data Booklet*, to calculate the lattice energy, ΔH°_{latt}, of potassium oxide, $K_2O(s)$.

energy change	value / $kJ\,mol^{-1}$
enthalpy change of atomisation of potassium, ΔH°_{at} K(s)	+89
electron affinity of O(g)	–141
electron affinity of O^-(g)	+798
enthalpy change of formation of potassium oxide, ΔH°_{f} $K_2O(s)$	–361

ΔH°_{latt} = ... $kJ\,mol^{-1}$ [3]

(ii) State whether the lattice energy of Na_2O would be more negative, less negative or the same as that of K_2O. Give reasons for your answer.

....

.... [1]

[Total: 10]

2 **(a)** Complete the table to show how **both** $AgNO_3(aq)$ and $NH_3(aq)$ could be used to distinguish between solutions of $NaCl(aq)$ and $NaI(aq)$.

test performed	observation with $NaCl$	observation with NaI

[2]

Important information for this question

- In this question (pr) means 'a solution in propanone'.
- Sodium iodide is soluble in propanone giving $Na^+(pr)$ and $I^-(pr)$.
- Sodium chloride is insoluble in propanone.

The reaction between 2-chlorobutane and sodium iodide in propanone is shown.

$$CH_3CH_2CHClCH_3(pr) + Na^+(pr) + I^-(pr) \rightarrow CH_3CH_2CHICH_3(pr) + NaCl(s)$$

The rate of this reaction can be investigated by measuring the electrical conductivity of the reaction mixture. The electrical conductivity changes as the reaction progresses due to the precipitation of the $NaCl$ produced.

(b) **(i)** Suggest how the electrical conductivity will change as the reaction proceeds. Explain your answer.

....

.... [1]

(ii) Describe a suitable method for studying the rate of this reaction at a temperature of 40 °C, using the following.

- an electrical conductance meter which measures the electrical conductivity of solutions
- solutions of known concentrations of 2-chlorobutane in propanone and sodium iodide in propanone
- stopclock
- access to standard laboratory equipment

....

....

....

....

....

....

....

.... [3]

(c) The rate of this reaction was measured at different initial concentrations of the two reagents. The table shows the results obtained.

experiment	$[CH_3CH_2CHClCH_3]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	relative rate
1	0.06	0.03	3
2	0.10	0.03	5
3	0.06	0.05	5
4	0.08	0.04	to be calculated

(i) Deduce the order of reaction with respect to each of $[CH_3CH_2CHClCH_3]$ and $[I^-]$. Explain your reasoning.

order with respect to $[CH_3CH_2CHClCH_3]$ ....

....

order with respect to $[I^-]$ ....

.... [2]

(ii) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = ... mol dm^{-3} s^{-1}

units of *k* = ... [1]

(iii) Calculate the relative rate for experiment 4.

relative rate for experiment 4 = ... [1]

(d) **(i)** Suggest the mechanism for the reaction of 2-chlorobutane with iodide ions. Draw out the steps involved, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structure of any transition state or intermediate

[3]

(ii) This reaction was carried out using a single optical isomer of 2-chlorobutane.

Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

....

.... [1]

(e) **(i)** State the number of peaks that would be seen in the carbon-13 NMR spectrum of $CH_3CH_2CHClCH_3$.

.... [1]

(ii) There are two isomers of $CH_3CH_2CHClCH_3$ that have **fewer** peaks in their carbon-13 NMR spectra than $CH_3CH_2CHClCH_3$.

Draw the structures of the isomers and state the number of peaks for each isomer.

isomer 1

isomer 2

number of peaks = ...

number of peaks = ...

[3]

[Total: 18]

Question 3 starts on the next page.

3 **(a)** In a molecule of $SOCl_2$ the sulfur atom has four bonds.

Draw a 'dot-and-cross' diagram of $SOCl_2$. Show the outer shell electrons only.

[2]

(b) When $SOCl_2$ is reacted with a carboxylic acid to produce an acyl chloride, two acidic gases are formed.

$$SOCl_2(l) + RCO_2H(l) \rightarrow RCOCl(l) + SO_2(g) + HCl(g)$$

A 1.00 g sample of a carboxylic acid RCO_2H was treated in this way, and the gases were absorbed in 60.0 cm^3 of 0.500 mol dm^{-3} NaOH(aq), an excess.

(i) Write equations for the reactions between

NaOH and HCl, ...

NaOH and SO_2. ....
[2]

The excess NaOH was titrated with 0.500 mol dm^{-3} H^+(aq). It required 10.8 cm^3 of the H^+(aq) solution to reach the end-point.

(ii) Calculate the total number of moles of NaOH that reacted with the SO_2 and HCl.

moles of NaOH = ... [2]

(iii) Calculate the number of moles of RCO_2H that produced the SO_2 and HCl.

moles of RCO_2H = ... [1]

(iv) Hence calculate the M_r of the carboxylic acid, RCO_2H.

M_r RCO_2H = ... [1]

(v) The R group contains carbon and hydrogen only.

Suggest the molecular formula of RCO_2H.

.... [1]

(c) The following synthetic route shows how a carboxylic acid can be converted into an amine.

$$CH_3CO_2H \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{\text{step 3}} CH_3CH_2NH_2$$

(i) Suggest a reagent for step 3.

.... [1]

Angelic acid, $C_5H_8O_2$, is a natural product isolated from the roots of the angelica plant.

- Angelic acid reacts with H_2 + Ni to form **T**, $C_5H_{10}O_2$.
- **T** undergoes the above synthetic route to form the amine **U**, $C_5H_{13}N$.
- **U** can also be made by reacting 1-bromo-2-methylbutane with ammonia.

Both angelic acid and **T** exist as stereoisomers.

(ii) Suggest structures for angelic acid, **T** and **U**.

angelic acid	**T**	**U**

[3]

(iii) State the type of stereoisomerism shown by angelic acid and **T**.

angelic acid ....

compound **T** ....
[1]

[Total: 14]

[Turn over

4 **(a)** A number of isomers with the formula $Cr(H_2O)_6Cl_3$ exist. Their general formula is $[Cr(H_2O)_{6-n}Cl_n]Cl_{3-n}.nH_2O$.
Each isomer contains a six co-ordinated Cr(III) ion in an octahedral complex.
Water molecules not directly bonded with the Cr atom are held in the crystal lattice as water of crystallisation.
The Cr–Cl bond is not easily broken and so chloride bonded with the Cr(III) ion in the complex does not react.

1.00 g samples of three of the isomers, **A**, **B** and **C**, were dissolved in separate samples of water. An excess of $AgNO_3(aq)$ was added to each and the mass of AgCl(s) formed was measured.

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

The number of moles of AgCl(s) formed was calculated. The table shows the results.

isomer	moles of AgCl formed from 1.00 g of isomer
A	3.75×10^{-3}
B	7.50×10^{-3}
C	1.13×10^{-2}

(i) Calculate the M_r of $Cr(H_2O)_6Cl_3$.

M_r $Cr(H_2O)_6Cl_3$ = ... [1]

(ii) Use the data in the table above to calculate the value of n for each of the isomers, **A**, **B** and **C**. Complete the table below with the values of n and the molecular formula of each isomer, in the style of the general formula given above.

Show your working for at least one calculation of n.

isomer	n	molecular formula
A		
B		
C		

[2]

(b) Two isomers have the same shape and their formula is $Ni(R_3P)_2(CN)_2$, where R = CH_3.
Only one of these isomers has a dipole moment.

(i) Name the *type of isomerism* shown by $Ni(R_3P)_2(CN)_2$.

.... [1]

(ii) Draw structures of these two isomers.

isomer 1	isomer 2

[1]

(iii) State which isomer has a dipole moment. Explain your answer.

....

.... [1]

[Total: 6]

5 (a) 1,2-diaminoethane, *en*, $H_2NCH_2CH_2NH_2$, is a bidentate ligand.

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

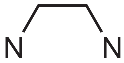
bidentate ....

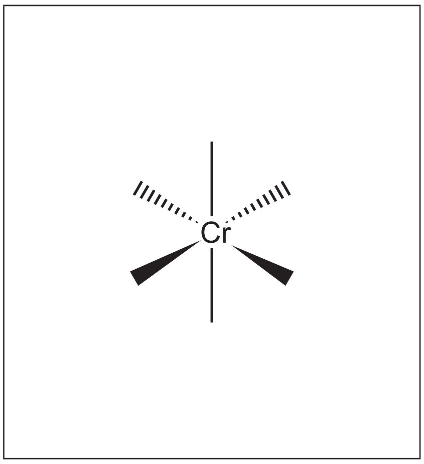
ligand ....

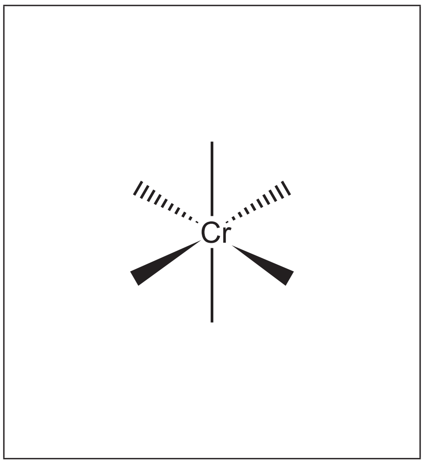
.... [2]

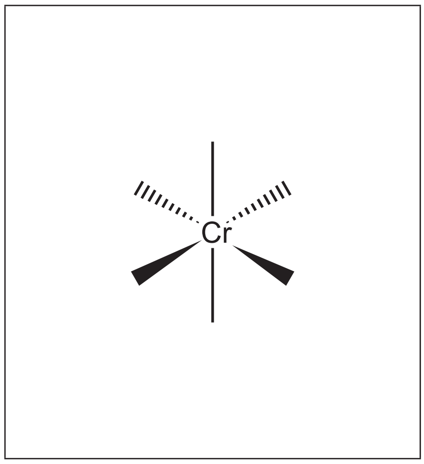
(ii) There are three isomeric complex ions with the formula $[Cr(en)_2Cl_2]^+$.

Complete the three-dimensional diagrams of the isomers in the boxes.

You may use  to represent *en*.







[3]

(b) Copper forms complexes with NH_3 and *en* according to equlibria 1 and 2.

equilibrium 1 $\quad Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$

equilibrium 2 $\quad Cu^{2+}(aq) + 2en(aq) \rightleftharpoons [Cu(en)_2]^{2+}(aq)$

(i) Write the expressions for the stability constants, K_{stab1} and K_{stab2}, for equilibria 1 and 2. Include units in your answers.

K_{stab1} =

units = ...

K_{stab2} =

units = ...
[3]

(ii) An equilibrium is set up when both *en* and NH_3 ligands are added to a solution containing Cu^{2+}(aq) as shown in equilibrium 3.

equilibrium 3 $[Cu(NH_3)_4]^{2+}(aq) + 2en(aq) \rightleftharpoons [Cu(en)_2]^{2+}(aq) + 4NH_3(aq)$

Write an expression for the equilibrium constant, K_{eq3}, in terms of K_{stab1} and K_{stab2}.

K_{eq3} = ... [1]

(iii) The numerical values for these stability constants are shown.

$K_{stab1} = 1.2 \times 10^{13}$ $K_{stab2} = 5.3 \times 10^{19}$

Calculate the value of K_{eq3} stating its units.

K_{eq3} = ... unit = ...
[2]

(c) $\Delta S^{\ominus}$ values for equilibria 1 and 2 differ greatly, as can be seen in the table. All values are at a temperature of 298 K.

equilibrium	$\Delta H^{\ominus}$ / kJ mol^{-1}	$\Delta S^{\ominus}$ / J K^{-1} mol^{-1}	$\Delta G^{\ominus}$ / kJ mol^{-1}
1	–92	–60	–74
2	–100	+40	

(i) Explain why $\Delta S^{\ominus}_{eq2}$ is so different from $\Delta S^{\ominus}_{eq1}$.

....

.... [1]

(ii) Calculate $\Delta G^{\ominus}_{eq2}$ at 298 K.

$\Delta G^{\ominus}_{eq2}$ = ... kJ mol^{-1}
[2]

(iii) What conclusion can be made about the relative feasibility of equilibria 1 and 2?

Explain your answer.

.... [1]

(iv) Using data from the table, suggest a value of $\Delta H^{\ominus}$ for equilibrium 3.

.... [1]

(v) State the *type of reaction* that is occurring in equilibrium 2.

.... [1]

[Total: 17]

6 The table lists some organic acids and their pK_a values.

acid	formula	pK_a
ethanoic acid	CH_3CO_2H	4.76
chloroethanoic acid	$ClCH_2CO_2H$	2.86
aminoethanoic acid (glycine)	$H_2NCH_2CO_2H$	9.87

(a) **(i)** State the relationship between pK_a and the strength of an acid.

.... [1]

(ii) State the mathematical relationship between pK_a and the acidity constant K_a.

.... [1]

(iii) Give reasons for why the pK_a value for chloroethanoic acid is **smaller** than that for ethanoic acid.

....

....

.... [2]

(b) **(i)** Use the zwitterionic structure for aminoethanoic acid (glycine) in aqueous solution to write an equation for its dissociation giving H^+(aq) ions.

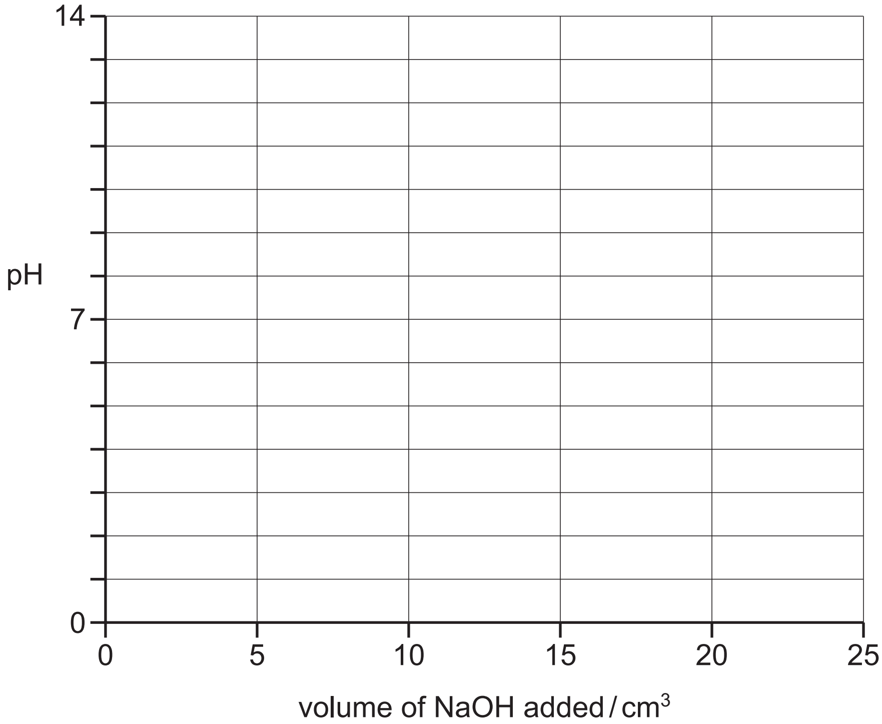
.... [1]

(ii) Calculate the pH of a 0.100 $mol\,dm^{-3}$ solution of aminoethanoic acid.

pH = ... [2]

A 10.0 cm^3 sample of 0.100 mol dm^{-3} aminoethanoic acid (glycine) was titrated with 0.100 mol dm^{-3} NaOH. After 20.0 cm^3 of NaOH, an excess, had been added, the pH was found to be 12.5.

(iii) Using the following axes, sketch a graph showing how the pH changes during this titration.



[3]

[Total: 10]

7 Compounds **W**, **X**, **Y** and **Z** are isomers of each other with the molecular formula C_8H_7ClO.
All four isomers contain a benzene ring.
Only **one** of the isomers contains a chiral centre.
The results of six tests carried out on **W**, **X**, **Y** and **Z** are shown in the table.

test		observations with each isomer			
		W	**X**	**Y**	**Z**
1	add cold $AgNO_3$(aq)	white ppt. forms immediately	none	white ppt. forms very slowly	none
2	heat with NaOH(aq), then add dilute HNO_3 + $AgNO_3$(aq)	white ppt.	none	white ppt.	none
3	add NaOH(aq) + I_2(aq)	none	pale yellow ppt.	none	none
4	warm with Fehling's solution	none	none	red ppt.	none
5	add cold, dilute, acidified $KMnO_4$(aq)	no change	no change	no change	decolourises
6	add Br_2(aq)	no change	no change	no change	decolourises and forms white ppt.

(a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in the four isomers **W**, **X**, **Y** and **Z**.

Complete the table below, identifying the group(s) present in each isomer.

group(s) in compound			
W	**X**	**Y**	**Z**
....	....	....	....
....	....	....	....
....	....	....	....

[5]

(b) Isomers **W**, **X**, **Y** and **Z** all have the molecular formula C_8H_7ClO.

(i) Use the information in **(a)** to suggest a structure for each of these isomers and draw these in the boxes.

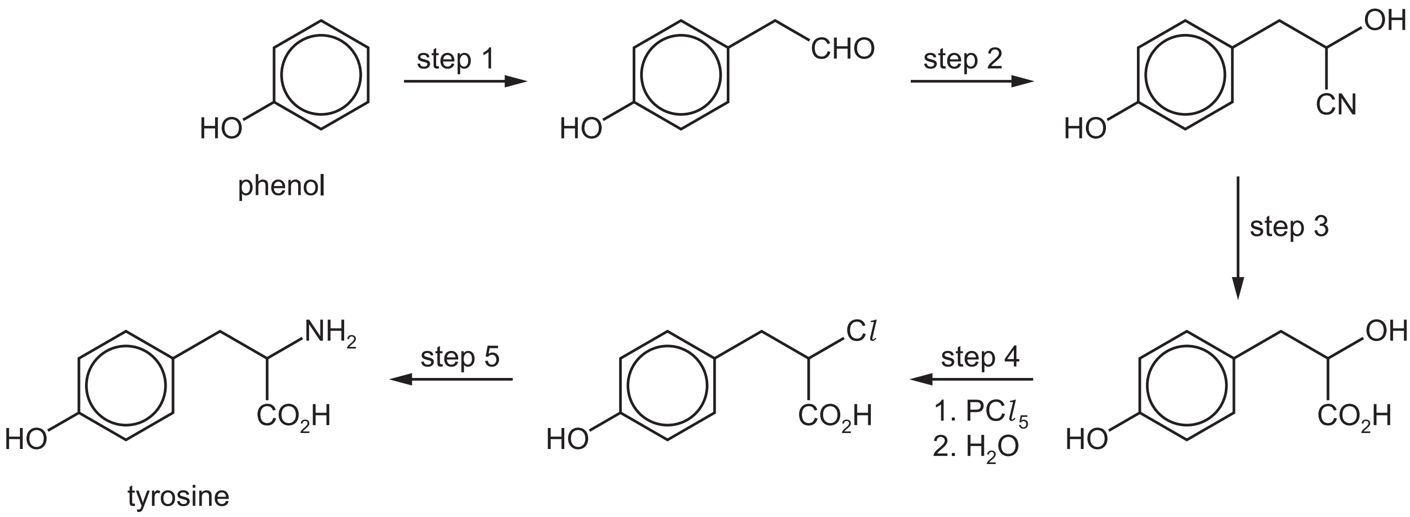
W	**X**
Y	**Z**

[4]

(ii) Draw a **circle** around the chiral centre in **one** of the above structures. [1]

[Total: 10]

8 **(a)** The amino acid tyrosine can be synthesised from phenol by the route shown.



(i) Name the mechanism occurring in the following steps.

step 1 ....

step 2 ....
[2]

(ii) What *type of reaction* is occurring in step 3?

.... [1]

(iii) Suggest reagents and conditions for each of the following steps.

step 1 ....

step 2 ....

step 3 ....

step 5 ....
[5]

(iv) Draw the structures of the products of the reactions of tyrosine with an **excess** of each of the following reagents.

with NaOH(aq)

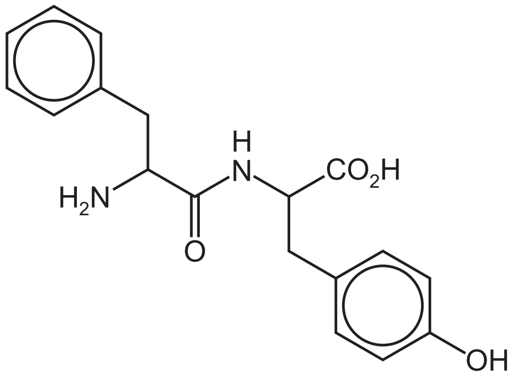
with HCl(aq)

with Br_2(aq)

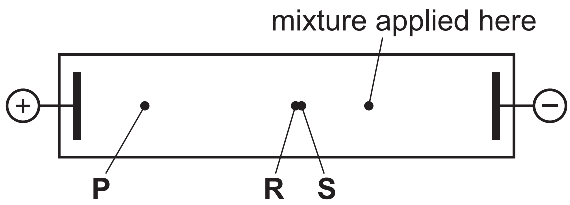
[4]

Question 8 continues on the next page.

(b) The dipeptide phe-tyr has the following structure.



A mixture of this dipeptide (phe-tyr) and its two constituent amino acids (phe and tyr) was subjected to electrophoresis in a buffer at pH 12. At the end of the experiment the following results were seen. Spots **R** and **S** remained very close together.



The three spots are due to the three species phe, tyr and phe-tyr.

(i) Which species is responsible for spot **P**? Explain your answer.

....

.... [2]

(ii) Suggest why the other two species give spots **R** and **S** that are so close together.

....

.... [1]

[Total: 15]

Cambridge International AS & A Level

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CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **October/November 2017**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.
You may lose marks if you do not show your working or if you do not use appropriate units.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **19** printed pages and **1** blank page.

IB17 11_9701_42/6RP

CAMBRIDGE
International Examinations

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

1 The compound chlorine dioxide, ClO_2, can be prepared by the reaction shown.

$$NaClO_2 + \tfrac{1}{2}Cl_2 \rightarrow ClO_2 + NaCl$$

(a) Using oxidation numbers, explain why this reaction is a redox reaction.

....

....

.... [2]

(b) The central atom in the molecule of ClO_2 is chlorine.

Draw the 'dot-and-cross' diagram for ClO_2. Show outer electrons only.

[2]

(c) The reaction between ClO_2 and F_2 is shown.

$$2ClO_2 + F_2 \rightarrow 2ClO_2F$$

The rate of the reaction was measured at various concentrations of the two reactants and the following results were obtained.

experiment	$[ClO_2]$ / mol dm^{-3}	$[F_2]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.010	0.060	2.20×10^{-3}
2	0.025	0.060	to be calculated
3	to be calculated	0.040	7.04×10^{-3}

The rate equation is rate = $k[ClO_2][F_2]$.

(i) What is meant by the term *order of reaction* with respect to a particular reagent?

....

.... [1]

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

rate constant, *k* = ... units .... [2]

(iii) Use the data in the table to calculate

- the initial rate in experiment 2,

initial rate = ... $mol\,dm^{-3}\,s^{-1}$

- $[ClO_2]$ in experiment 3.

$[ClO_2]$ = ... $mol\,dm^{-3}$

[2]

(d) **(i)** What is meant by the term *rate-determining step*?

....

.... [1]

(ii) The equation for the reaction between ClO_2 and F_2 is shown.

$$2ClO_2 + F_2 \rightarrow 2ClO_2F$$

$$\text{rate} = k[ClO_2][F_2]$$

The mechanism for this reaction has two steps.

Suggest equations for the **two** steps of this mechanism, stating which of the two steps is the rate-determining step.

step 1 ....

step 2 ....

rate-determining step = ...

[2]

(e) By considering the rate equation, explain why the rate increases with increasing temperature.

....

.... [1]

[Total: 13]

2 **(a)** When water is added to magnesium nitride, Mg_3N_2, the products are a white suspension of $Mg(OH)_2$ and an alkaline gas.

(i) Write an equation for this reaction.

.... [1]

(ii) A 2.52 g sample of Mg_3N_2 is added to an excess of water.

Calculate the mass of $Mg(OH)_2$ formed.

mass of $Mg(OH)_2$ = ... g [2]

(b) State and explain how the solubility of the Group 2 hydroxides varies down the group.

....

....

....

....

.... [4]

(c) Magnesium hydroxide is sparingly soluble in water. The concentration of its saturated solution at 298 K is 1.7×10^{-4} mol dm^{-3}.

(i) Write an expression for the solubility product, K_{sp}, of $Mg(OH)_2$.

K_{sp} =

[1]

(ii) Calculate the value of K_{sp} for $Mg(OH)_2$ at 298 K and state its units.

K_{sp} = ... units .... [2]

(d) The temperature at which the Group 2 hydroxides and carbonates start to decompose increases down the group.

Suggest an explanation for this trend in the decomposition temperature of the Group 2 hydroxides.

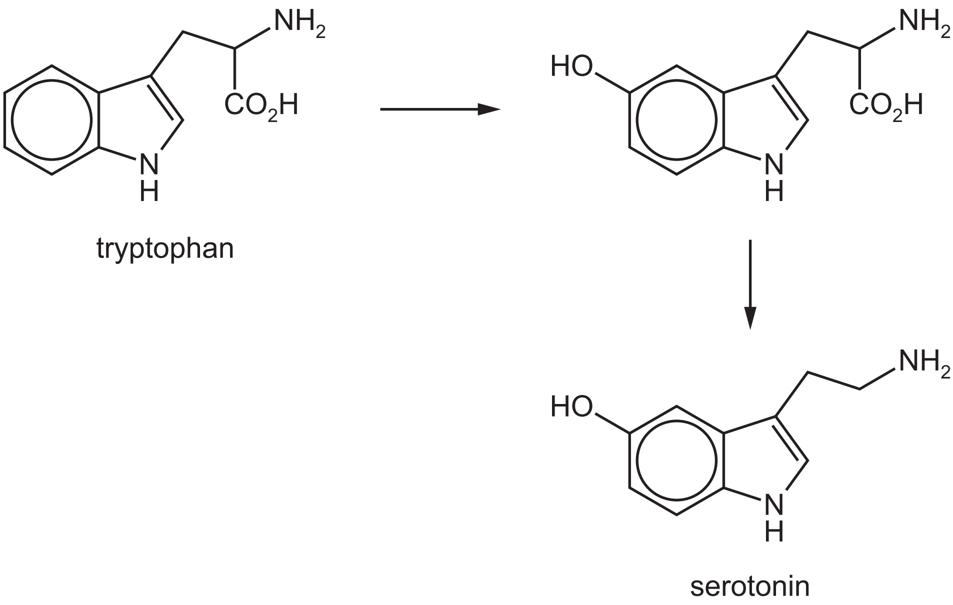
....

....

.... [2]

[Total: 12]

3 Serotonin can be synthesised from the amino acid tryptophan in two steps.



(a) (i) In a buffer solution at pH 5.9, a sample of tryptophan does **not** move during electrophoresis.

Draw the structures of the ions formed by tryptophan at pH 1.0 and pH 5.9.

pH 1.0	pH 5.9

[2]

(ii) Tryptophan can combine with valine to form a dipeptide.

Use the *Data Booklet* to draw the structure of this dipeptide.

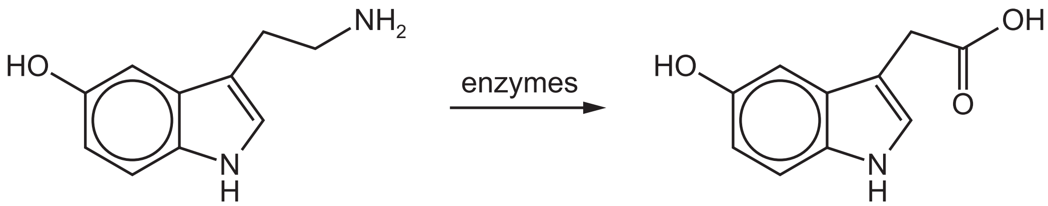
[2]

(b) Complete the following table to show the structures of the products formed and the *type of reaction* occurring when **serotonin** reacts with the four reagents in separate reactions.

reagent	structure of product	*type of reaction*
Na		
excess $Br_2(aq)$		
excess CH_3COCl		
excess H_2 / Pt catalyst		

[8]

(c) Serotonin is converted by enzymes in the liver to compound **M**.



serotonin **M**

(i) By reference to the *Data Booklet*, suggest how the infra-red spectrum of **M** would differ from that of serotonin.

....

.... [1]

(ii) The proton NMR spectrum of **M** dissolved in $CDCl_3$ shows eight peaks due to the eight different types of proton present in the molecule.

The proton NMR spectrum of **M** dissolved in D_2O was recorded.

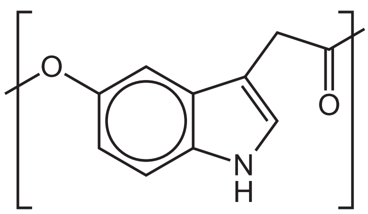
Predict the number of peaks that would be seen in the proton NMR spectrum of **M** in D_2O. Explain your answer.

number of peaks ....

explanation ....

....
[2]

(d) Compound **M** can be polymerised under certain conditions to form polymer **N**, shown.



N

Polymer **N** is biodegradable, unlike polyethene which is not.

Explain why **N** is biodegradable.

....

.... [1]

[Total: 16]

4 An electrochemical cell consists of a half-cell containing $V^{3+}(aq)$ and $V^{2+}(aq)$ ions and another half-cell containing $VO_2^{+}(aq)$ and $VO^{2+}(aq)$ ions.

(a) (i) Use data from the *Data Booklet* to calculate a value for the $E^{\ominus}_{cell}$.

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

(ii) Write the ionic equation for the cell reaction.

.... [1]

(iii) Draw a fully labelled diagram of the apparatus you could use to measure the potential of this cell. Include the necessary chemicals.

[4]

(b) Use data from the *Data Booklet* to predict whether a reaction might take place when the following pairs of aqueous solutions are mixed. If a reaction occurs, write an equation for it and calculate the $E^{\ominus}_{cell}$.

- V^{2+}(aq) and Sn^{4+}(aq)

Does a reaction occur? ....

equation ....

$E^{\ominus}_{cell}$ ....

- VO^{2+}(aq) and Fe^{3+}(aq)

Does a reaction occur? ....

equation ....

$E^{\ominus}_{cell}$ ....

[3]

[Total: 9]

5 **(a)** The arrangement of the anions around a cation is called the geometry of the cation; e.g. in $[CuCl_4]^{2-}$ the geometry of copper is tetrahedral and the co-ordination number of copper is 4.

The geometry of a cation in an ionic compound can be predicted from the ratio of the ionic radii of the cation and anion involved.

$\frac{\text{cation radius}}{\text{anion radius}}$	geometry of cation
0.155–0.225	trigonal planar
0.225–0.414	tetrahedral
0.414–0.732	octahedral

Use data from the *Data Booklet* to predict the geometry of, and hence the co-ordination number of, the cation for

- sodium chloride, $NaCl$,

geometry of Na^+ = ... co-ordination number of Na^+ = ...

- magnesium chloride, $MgCl_2$.

geometry of Mg^{2+} = ... co-ordination number of Mg^{2+} = ...
[2]

(b) Magnesium(I) chloride, $MgCl$, is an unstable compound and readily decomposes as shown.

$$2MgCl(s) \rightarrow Mg(s) + MgCl_2(s)$$

Use the following data to calculate the enthalpy change of this reaction.

$\Delta H_f^\ominus$ $MgCl(s)$ = –106 kJ mol^{-1}
$\Delta H_f^\ominus$ $MgCl_2(s)$ = –642 kJ mol^{-1}

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

(c) **(i)** The equation for which Δ*H* is the lattice energy for $MgCl$ is shown.

$$Mg^+(g) + Cl^-(g) \rightarrow MgCl(s)$$

Use the equation, the following data, and relevant data from the *Data Booklet* to calculate a value for the lattice energy of $MgCl$. You might find it helpful to construct an energy cycle.

electron affinity of $Cl(g)$ = $-349\,kJ\,mol^{-1}$
enthalpy change of atomisation of $Mg(s)$ = $+147\,kJ\,mol^{-1}$
enthalpy change of formation of $MgCl(s)$ = $-106\,kJ\,mol^{-1}$

lattice energy $MgCl$ = ... $kJ\,mol^{-1}$ [3]

(ii) Suggest how the lattice energies of $MgCl_2$ and $NaCl$ will compare to that of $MgCl$. Explain your answers.

$MgCl_2$ and $MgCl$ ....

....

$NaCl$ and $MgCl$..

....
[3]

(d) Define the term *electron affinity*.

....

.... [2]

[Total: 11]

6 **(a)** Define the term *transition metal complex*.

....

.... [1]

(b) Platinum can form the compound $[Pt(NH_3)_4Cl_2][PtCl_4]$.

State the co-ordination numbers and the oxidation numbers of the platinum in the two ions of this compound.

	co-ordination number	oxidation number
$[Pt(NH_3)_4Cl_2]^{2+}$		
$[PtCl_4]^{2-}$		

[2]

(c) Draw three-dimensional diagrams to show the structures of the two isomers of $[Pt(NH_3)_4Cl_2]^{2+}$.

[2]

(d) Solutions of the compounds $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$ can be distinguished from each other by a simple chemical test. Assume that any species bonded to the platinum ion does not react in this test.

Complete the table with a test that could be used to positively identify each compound. Give details of expected observations with each compound.

test	observation with $[Pt(NH_3)_4Cl_2]Br_2$	observation with $[Pt(NH_3)_4Br_2]Cl_2$

[2]

(e) In this question you should consider geometrical and optical isomerism.

What type of isomerism is shown by the following complexes?
You should answer **geometrical**, **optical**, **both** or **neither**.

octahedral $[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$ ....

square planar $[Ni(CN)_2Cl_2]^{2-}$ ....

tetrahedral $[CuBr_2Cl_2]^{2-}$ ....
[3]

(f) Many enzymes contain transition metal complexes.

Describe, with the aid of a suitably labelled diagram, how an enzyme catalyses the breakdown of a substrate molecule.

....

....

....

.... [3]

[Total: 13]

7 **(a)** Calcium carbide, CaC_2, reacts readily with water, forming ethyne, C_2H_2, and a sparingly soluble white ionic compound.

(i) Write an equation for the reaction of CaC_2 with water.

.... [1]

(ii) Draw a 'dot-and-cross' diagram for the carbide ion, C_2^{2-}. Show outer electrons only.

[1]

(b) Ethyne is the simplest member of the alkyne homologous series.

$$H-C\equiv C-H$$

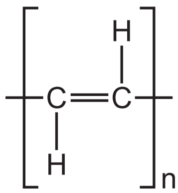
ethyne

Propyne, C_3H_4, and butyne, C_4H_6, are the next two members of the series.

Deduce the general formula for the alkynes.

.... [1]

(c) Ethyne can be polymerised into poly(acetylene), which is a conducting polymer.



poly(acetylene)

(i) Suggest why this polymer conducts electricity.

....

.... [1]

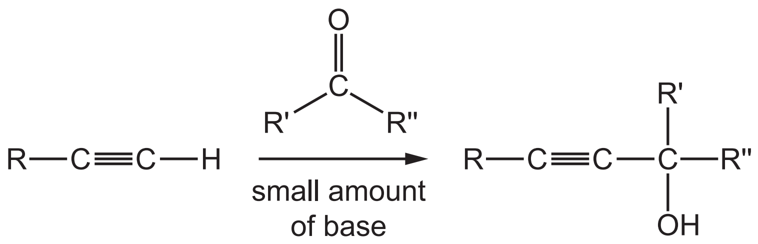
(ii) State the empirical formula of poly(acetylene).

.... [1]

(iii) By reference to a physical or chemical property, suggest **one** advantage of a conducting polymer when compared with metals.

.... [1]

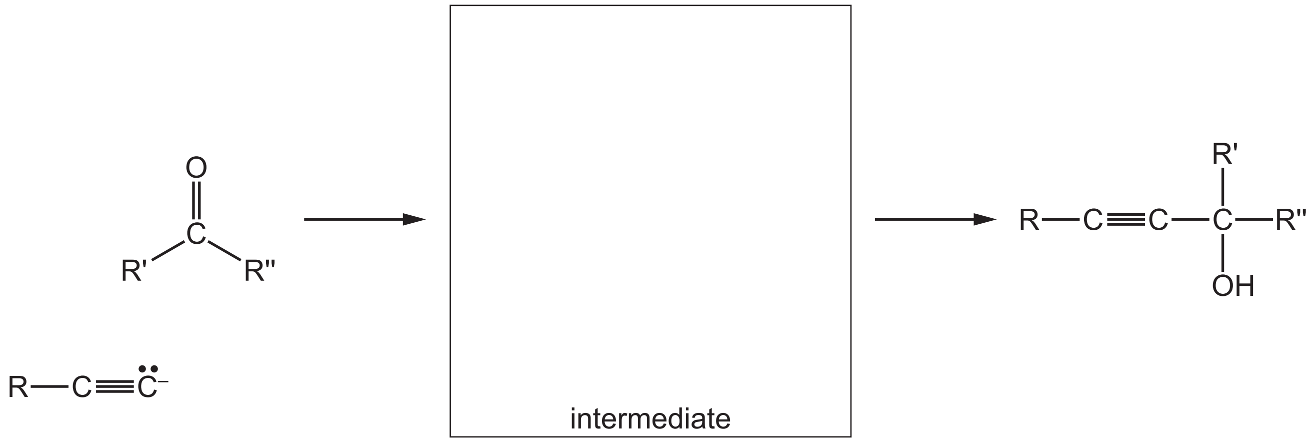
(d) Alkynes can react with carbonyl compounds under basic conditions as shown in reaction 1.



reaction 1

(i) The first step of the mechanism of reaction 1 involves the alkyne anion reacting with the carbonyl compound.

Complete the first step of the mechanism and draw the intermediate for this reaction. Include all relevant dipoles, charges and curly arrows.

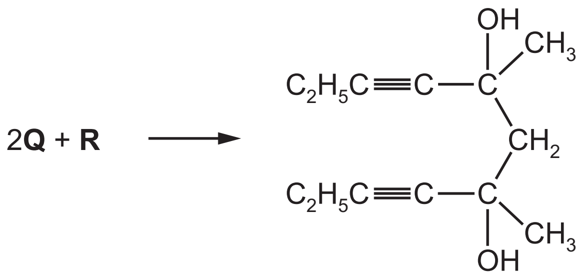


[3]

(ii) Suggest the name of the mechanism in reaction 1.

.... [1]

(iii) An alkyne, **Q**, and a carbonyl compound, **R**, react together to form compound **P** as shown.



P

Use reaction 1 to suggest the structures of **Q** and **R**.

Q	**R**

[2]

(e) A series of twelve separate experiments is carried out as shown in the table.

Complete the table by writing in **each** box a tick (✓) if a reaction occurs, or a cross (✗) if no reaction occurs.

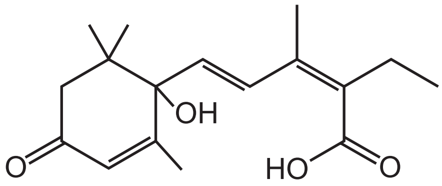
	CH_3CHO	HCO_2H	CH_3COCH_3	HO_2CCO_2H
hot, acidified MnO_4^-(aq)				
alkaline I_2(aq)				
warm Tollens' reagent				

[4]

[Total: 16]

8 **(a)** Compound **A** can be produced from a plant hormone.

A



(i) Compound **A** shows optical and geometrical isomerism.

On the structure of **A** above,

- draw a **line** through the bond(s) that give rise to geometrical isomerism,
- **circle** all chiral carbon atoms.

[2]

(ii) Give the **names** of four functional groups present in **A**.

....

.... [2]

(iii) A molecule of **A** has 17 carbon atoms.

State the number of carbon atoms that are sp, sp^2 and sp^3 hybridised in **A**.

sp carbons = ... sp^2 carbons = ... sp^3 carbons = ...

[1]

(iv) When **A** is reacted with an excess of hot, concentrated manganate(VII) ions, a mixture of three organic compounds is formed.

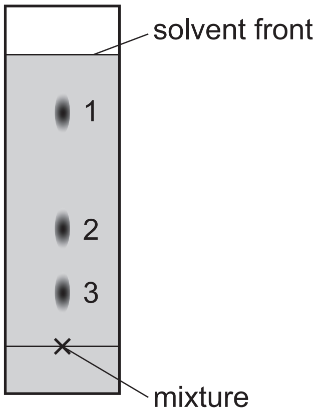
A → **X** ($C_{10}H_{14}O_7$) and **Y** ($C_3H_4O_3$) and **Z** ($C_4H_6O_3$)

Suggest the structures of **Y** and **Z**.

Y ($C_3H_4O_3$)	**Z** ($C_4H_6O_3$)

[2]

(b) A mixture of three different compounds, **J**, **K** and **L**, was analysed by thin layer chromatography using a polar stationary phase and a non-polar mobile phase. The three compounds all have similar molecular masses. The resulting chromatogram is shown.



(i) Identify which spot corresponds to each compound.

compound	spot
J CH_3COCO_2H	
K HO_2CCO_2H	
L $CH_3CH_2COCH_2CH_3$	

[1]

(ii) Explain your answers to **(b)(i)**.

....

.... [1]

(iii) What is meant by the term R_f *value*?

....

.... [1]

[Total: 10]

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Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME			
CENTRE NUMBER		CANDIDATE NUMBER	

1230666070

CHEMISTRY **9701/42**

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

IB16 06_9701_42/5RP

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

1 **(a)** Magnesium nitrate, $Mg(NO_3)_2$, is very soluble in water. When a hot saturated solution of magnesium nitrate is cooled, crystals of the hydrate, $Mg(NO_3)_2.6H_2O$, are formed.
In the crystals, six water molecules bond to each Mg^{2+} ion, and some of these water molecules are **also** bonded to the nitrate ions.

(i) Suggest the type of bonding that occurs between

H_2O and Mg^{2+}, ...

H_2O and NO_3^-. .... [2]

(ii) Describe the arrangement of the water molecules around the Mg^{2+} ion.

.... [1]

(iii) Describe in detail what you would observe when crystals of $Mg(NO_3)_2.6H_2O$ are heated in a boiling tube, gently at first and then more strongly.
Write equations for any reactions that occur.

....

....

....

....

....

....

....

.... [4]

(iv) Calculate the percentage **loss** in mass when $Mg(NO_3)_2.6H_2O$ is heated strongly to constant mass.

percentage loss = ... % [2]

(b) Explain why the Group 2 nitrates become more stable to heat down the group.

....

....

....

....

.... [2]

(c) Magnesium nitrate and silver nitrate, $AgNO_3$, decompose on heating to produce the same gases. Silver nitrate also produces silver metal during decomposition.

Write an equation for the decomposition of $AgNO_3$.

.... [1]

[Total: 12]

2 Ethanoic acid is a weak acid.

(a) Explain what is meant by the term *weak* acid.

....

.... [1]

(b) The pK_a values of four acids are listed below.

acid	structural formula	pK_a
1	CH_3CO_2H	4.8
2	$CH_3CH_2CO_2H$	4.9
3	$CH_3CHClCO_2H$	2.8
4	$CH_2ClCH_2CO_2H$	4.0

(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a.

.... [1]

(ii) With reference to acidity, explain the difference in pK_a values between

- acid 1 and acid 2,

....

....

- acid 2 and acid 3,

....

....

- acid 3 and acid 4.

....

....

[3]

(c) **(i)** Draw a fully labelled diagram of the equipment needed to measure the voltage of an electrochemical cell consisting of the standard hydrogen electrode and the standard Cu/Cu^{2+} electrode.

[4]

(ii) For the cell drawn in **(i)**, calculate the $E^{\ominus}_{cell}$ and state which electrode is positive.

$E^{\ominus}_{cell}$ = ... identity of the positive electrode ....
[1]

(d) A monobasic acid, **D**, has $K_a = 1.23 \times 10^{-5}\,mol\,dm^{-3}$.

(i) Calculate the pH of a $0.100\,mol\,dm^{-3}$ solution of **D**.

pH = ... [2]

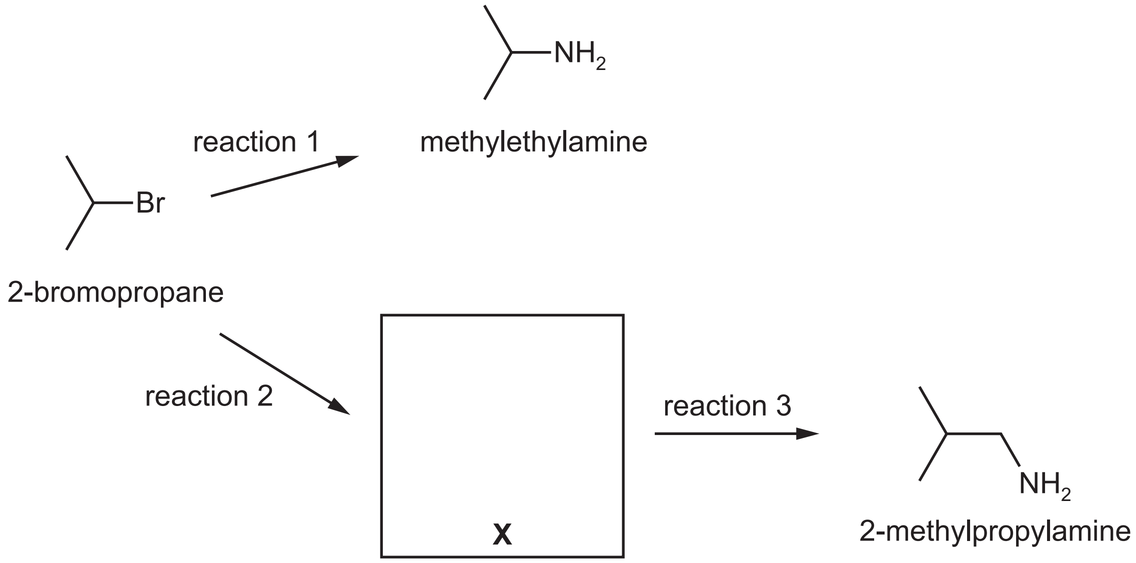
(ii) An electrochemical cell similar to the one you have drawn in **(c)(i)** was set up using a $0.100\,mol\,dm^{-3}$ solution of **D** in the hydrogen electrode instead of the standard solution.

Use the data and the Nernst equation, $E = E^{\ominus} + 0.059\log[H^+(aq)]$, to calculate the new E_{cell} in this experiment.

E_{cell} = ... V [2]

[Total: 14]

3 **(a)** 2-bromopropane can be used to synthesise methylethylamine and 2-methylpropylamine.



(i) Draw the structure of the intermediate **X** in the box above. [1]

(ii) Suggest reagents and conditions for

- reaction 1, ...
- reaction 2, ...
- reaction 3. ....

[3]

(b) **(i)** Write an equation showing why aqueous solutions of ethylamine are alkaline.

.... [1]

(ii) Compare the basicities of ethylamine and ammonia. Explain your answer.

....

....

....

.... [2]

(c) Solutions containing mixtures of amines and their salts are buffer solutions.

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

....

.... [1]

(ii) Write two equations to show how a solution containing a mixture of CH_3NH_2 and CH_3NH_3Cl acts as a buffer.

....

.... [2]

[Total: 10]

4 **(a)** There are two isomeric complexes with the formula $Pt(NH_3)_2Cl_2$, one of which is an anti-cancer drug.

(i) Draw diagrams to show the three-dimensional structures of the two isomers.

isomer 1

isomer 2

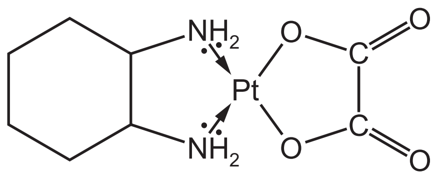
[2]

(ii) Comment on the polarity of the two isomers of $Pt(NH_3)_2Cl_2$. Explain your answer.

....

.... [1]

Oxaloplatin is another successful anti-cancer drug in which the stereochemistry around the platinum atom is the same as that in $Pt(NH_3)_2Cl_2$.



oxaloplatin

(iii) Explain why there are no isomers of oxaloplatin.

....

.... [1]

(b) Only one structure of the complex $[Ni(R_3P)_2Cl_2]$ is known. (R = CH_3, R_3P is a monodentate ligand)

(i) What does this indicate about the stereochemistry around the nickel atom?

.... [1]

(ii) Draw a three-dimensional diagram showing the structure of this complex.

[1]

[Total: 6]

5 Cadmium ions form complexes with primary amines and with 1,2-diaminoethane.

$Cd^{2+}(aq) + 4CH_3NH_2(aq) \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}(aq)$ $K_{stab} = 3.6 \times 10^6$ equilibrium **I**

$Cd^{2+}(aq) + 2H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Cd(H_2NCH_2CH_2NH_2)_2]^{2+}(aq)$ $K_{stab} = 4.2 \times 10^{10}$ equilibrium **II**

(a) (i) Write an expression for the stability constant, K_{stab}, for equilibrium **I**, and state its units.

K_{stab} =

units ....
[2]

Cadmium ions are poisonous and need to be removed from some water supplies. This is often done by adding a complexing agent.

(ii) In a sample of ground water the concentration of $Cd^{2+}(aq)$ is 1.00×10^{-4} mol dm^{-3}.

Calculate the concentration of $CH_3NH_2(aq)$ needed to reduce the concentration of $Cd^{2+}(aq)$ in this dilute solution by a factor of one thousand.

concentration of $CH_3NH_2(aq)$ = ... mol dm^{-3} [2]

(b) Values for $\Delta H^{\ominus}$ and $\Delta G^{\ominus}$ for equilibria **I** and **II**, and the value of $\Delta S^{\ominus}$ for equilibrium **I**, are given in the table below. All values are at a temperature of 298 K.

equilibrium	$\Delta H^{\ominus}$ / kJ mol^{-1}	$\Delta G^{\ominus}$ / kJ mol^{-1}	$\Delta S^{\ominus}$ / J K^{-1} mol^{-1}
I	–57.3	–37.4	–66.8
II	–56.5	–60.7	to be calculated

(i) Suggest a reason why the $\Delta H^{\ominus}$ values for the two equilibria are very similar.

....

.... [1]

(ii) Calculate $\Delta S^{\ominus}$ for equilibrium **II**.

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

(iii) Suggest a reason for the difference between the $\Delta S^{\ominus}$ you have calculated for equilibrium **II** and that for equilibrium **I** given in the table.

....

....

.... [1]

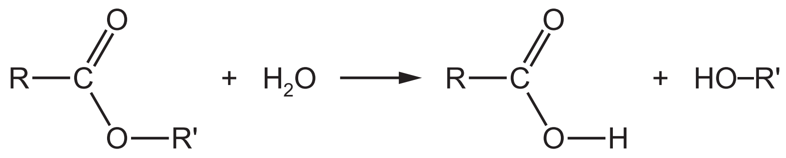
(iv) Which of the two complexes is the more stable? Give a reason for your answer.

....

.... [1]

[Total: 8]

6 Esterases are enzymes that hydrolyse esters.



Enzymes can be quite specific in the structures of the substrates they act upon. For example, an esterase isolated from the mould *Aspergillus niger* will hydrolyse phenyl ethanoate, $CH_3CO_2C_6H_5$, but not its isomer methyl benzoate, $C_6H_5CO_2CH_3$.

(a) Outline how enzymes catalyse reactions, and explain their specificity.
Use diagrams in your answer where appropriate.

....

....

.... [3]

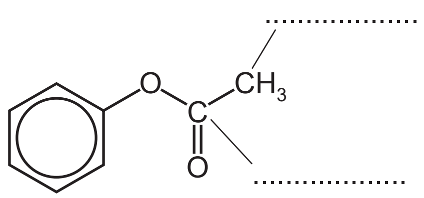
(b) Sample bottles of each of the isomers phenyl ethanoate and methyl benzoate have lost their labels and so have been named isomer **A** and isomer **B**.

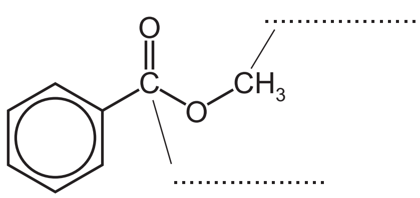
(i) The carbon-13 NMR spectra of isomers **A** and **B** contain the following peaks.

isomer **A**	isomer **B**
δ 52	δ 26
δ 128	δ 122
δ 129	δ 126
δ 130	δ 129
δ 133	δ 151
δ 167	δ 169

The identity of the compound responsible for each spectrum can be deduced by studying the chemical shifts (δ) of the peaks in the spectra.

Use the *Data Booklet* to assign the correct peaks to the labelled carbon atoms in the structures of the isomers below. Write each value next to the relevant carbon atom and hence deduce the identity of each isomer.





phenyl ethanoate is isomer ....   methyl benzoate is isomer ....

[2]

(ii) These two isomers are difficult to distinguish chemically.

Describe a method of converting them to suitable products in step 1 which can then be tested in step 2.
You should state the reagents and conditions for each step, and any observations you would make.

step 1 ....

....

....

step 2 ....

....

....

[3]

[Total: 8]

7 **(a)** Amino acids can be separated by electrophoresis.

(i) Draw a labelled diagram of the apparatus used to separate a mixture by electrophoresis.

[3]

(ii) Explain the principles of the separation of amino acids by electrophoresis.

....

....

.... [2]

(b) Electrophoresis is usually carried out in a buffer solution.

Given three buffers, with pH values of 2.0, 7.0 and 12.0, suggest, with a reason, which buffer would be the most suitable for the separation of the following amino acid mixtures.
Your reasons should refer to the structure of each molecule.
(The structures of these amino acids are given in the *Data Booklet*.)

(i) Asp and Val

buffer pH ....

reason ....

....

(ii) Lys and Ser

buffer pH ....

reason ....

....

(iii) Tyr and Phe

buffer pH ....

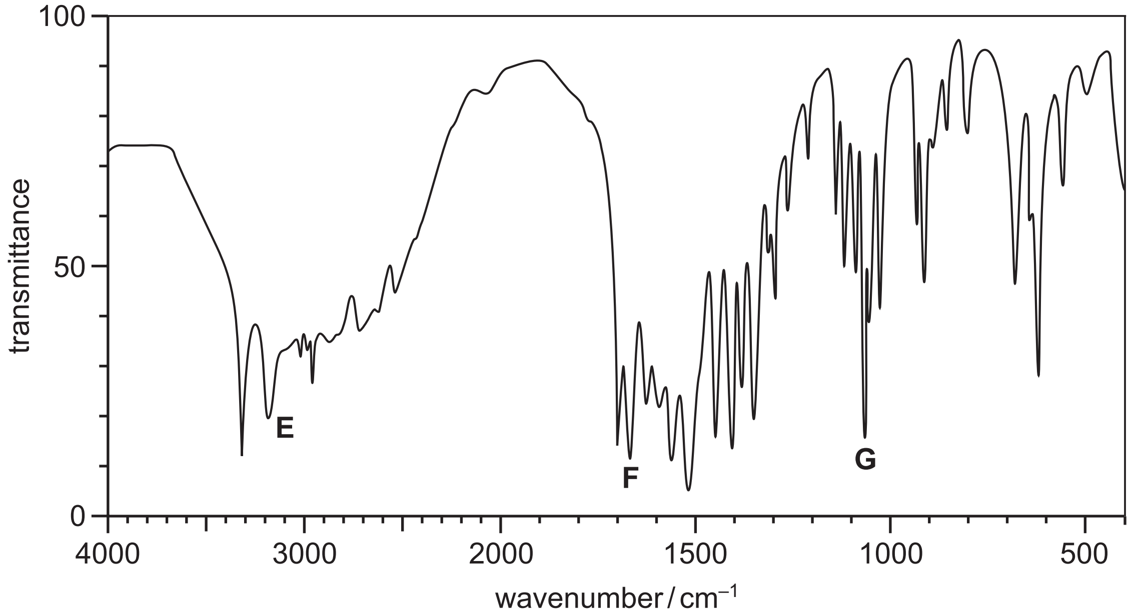
reason ....

....
[3]

(c) (i) Draw the structure of the dipeptide Gly-Ser, showing the peptide bond in full.

[2]

The infra-red spectrum of Gly-Ser is shown below.



(ii) Use the *Data Booklet* to identify the bond in the molecule of Gly-Ser that is responsible for each of the peaks indicated on the above infra-red spectrum.

E ....

F ....

G ....

[2]

[Total: 12]

8 **(a)** Describe and explain the trend in the solubility of the hydroxides down Group 2.

....

....

....

.... [3]

(b) Calcium reacts vigorously with $HCl(aq)$ producing $H_2(g)$.

$$Ca(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$$

(i) How would you expect the enthalpy change for this reaction to compare with the enthalpy change for the reaction where $HNO_3(aq)$ is used in place of HCl but all other conditions are the same?
Explain your answer.

....

.... [1]

(ii) The ionic equation for this reaction is shown.

$$Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g) \qquad \Delta H^{\ominus} = \mathbf{x}\ kJ\,mol^{-1}$$

Construct a **fully labelled** Hess' Law cycle to connect each side of this equation to the relevant gas phase ions.

Use your cycle, the following data, **and** data from the *Data Booklet*, to calculate a value for **x**.

standard enthalpy of atomisation of Ca(s), $\Delta H^{\ominus}_{at}(Ca)$	$+178\ kJ\,mol^{-1}$
standard enthalpy of hydration of $Ca^{2+}(g)$, $\Delta H^{\ominus}_{hyd}(Ca^{2+})$	$-1576\ kJ\,mol^{-1}$
standard enthalpy of hydration of $H^+(g)$, $\Delta H^{\ominus}_{hyd}(H^+)$	$-1090\ kJ\,mol^{-1}$

x = ... $kJ\,mol^{-1}$ [4]

(c) The standard enthalpy change for the reaction between Ca(s) and $CH_3CO_2H(aq)$ is **less negative** than **x** by $2\ kJ\,mol^{-1}$.

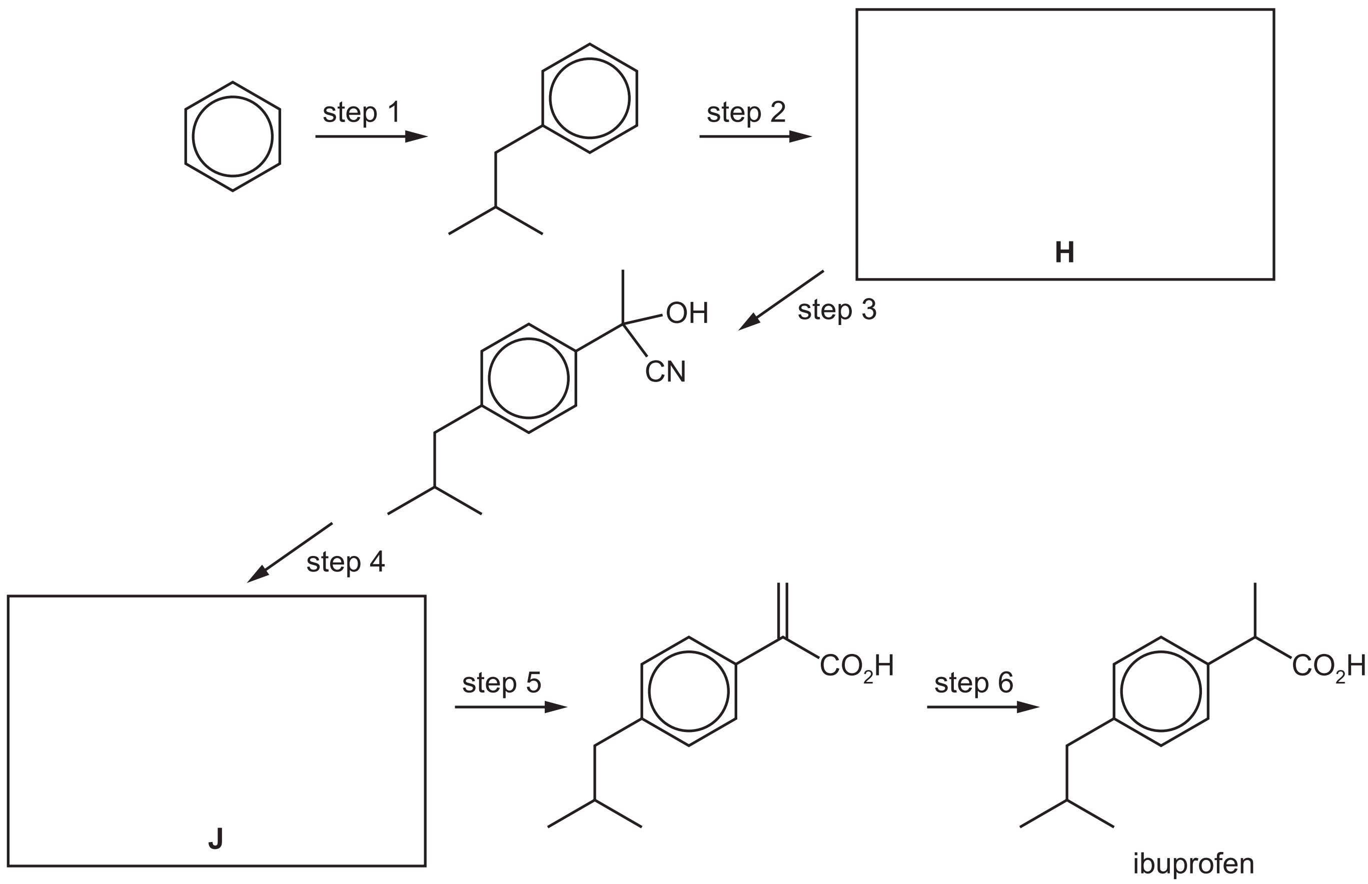
Suggest an explanation for this.

....

.... [2]

[Total: 10]

9 The anti-inflammatory drug ibuprofen can be synthesised from benzene via the following six steps.



(a) Draw circles around any chiral carbon atoms in the above five formulae. [1]

(b) Suggest the structures of compounds **H** and **J** and draw them in the boxes above. [2]

(c) Suggest reagents and conditions for steps 1-6.

step 1 ....

step 2 ....

step 3 ....

step 4 ....

step 5 ....

step 6 ....

[6]

(d) Name the mechanism of step 1 and state the *type of reaction* for step 6.

step 1 ....

step 6 ....

[2]

[Total: 11]

10 **(a)** **(i)** Complete the electronic configuration of the iron atom.

Fe $1s^2 2s^2 2p^6$.................................. [1]

(ii) In some of its complexes, the Fe^{3+} ion has **only one** unpaired electron in its d orbitals.

Using the symbols ↑ and ↓ to represent electrons of opposite spins, complete the following diagram to show the d orbital electronic configuration of **this** Fe^{3+} ion.

[1]

(b) A solution containing a mixture of Sn^{2+}(aq) and Sn^{4+}(aq) is added to a solution containing a mixture of Fe^{2+}(aq) and Fe^{3+}(aq).

Use $E^{\ominus}$ data from the *Data Booklet* to predict the reaction that might take place when the two solutions are mixed, and write an equation for the reaction.

....

....

.... [2]

(c) Hexaaquairon(III) ions are pale violet. They form a colourless complex with fluoride ions, F^-, equilibrium **1**, and a deep-red complex with thiocyanate ions, SCN^-, equilibrium **2**.

$[Fe(H_2O)_6]^{3+}$ + F^- $\rightleftharpoons$ $[Fe(H_2O)_5F]^{2+}$ + H_2O equilibrium **1** $K_{stab} = 2.0 \times 10^5\,mol^{-1}\,dm^3$
violet colourless

$[Fe(H_2O)_6]^{3+}$ + SCN^- $\rightleftharpoons$ $[Fe(H_2O)_5SCN]^{2+}$ + H_2O equilibrium **2** $K_{stab} = 1.0 \times 10^3\,mol^{-1}\,dm^3$
violet deep-red

(i) Predict and explain the **sequence** of colour changes you would observe in each of the following experiments.

- A few drops of KSCN(aq) are added to $5\,cm^3$ of Fe^{3+}(aq), followed by a few drops of KF(aq).

....

....

....

- A few drops of KF(aq) are added to $5\,cm^3$ of Fe^{3+}(aq), followed by a few drops of KSCN(aq).

....

....

.... [4]

(ii) What *type of reaction* is occurring during the experiments in **(i)**?

.... [1]

[Total: 9]

Cambridge International AS & A Level

Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

4457571208

CHEMISTRY **9701/42**

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.
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Answer **all** questions.

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

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CAMBRIDGE International Examinations

[Turn over

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
$[Ni(CN)_2(NH_3)_2]$		
$[CrCl_2(H_2O)_4]^+$		

[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 $[Ni(CN)_2(NH_3)_2]$ and name its shape.

name of shape ....

[2]

(c) The complex ion $[Cr(H_2O)_6]^{3+}$ can be converted into $[CrCl_2(H_2O)_4]^+$.

(i) Suggest a suitable reagent for this conversion.

.... [1]

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

.... [1]

(d) The $[CrCl_2(H_2O)_4]^+$ complex ion shows stereoisomerism.

(i) Name this type of stereoisomerism.

.... [1]

(ii) Draw three-dimensional diagrams to show the **two** stereoisomers of $[CrCl_2(H_2O)_4]^+$.

[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.

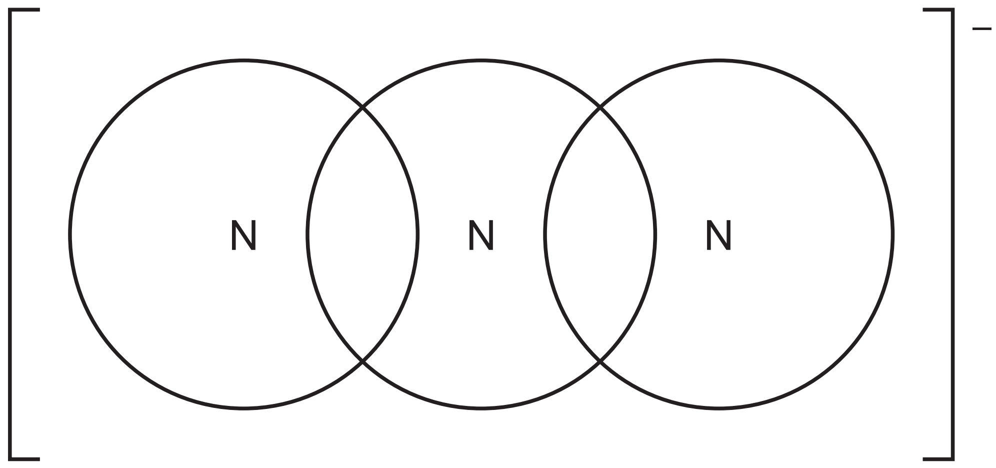
(a) Write an equation for the decomposition of NaN_3.

.... [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 NaN_3(s).
Include a sign in your answer. Show all your working.

lattice energy, $\Delta H_{latt}^\ominus$, of NaN_3(s)	–732 kJ mol^{-1}
standard enthalpy change of atomisation, $\Delta H_{at}^\ominus$, of Na(g)	+107 kJ mol^{-1}
standard enthalpy change, $\Delta H^\ominus$, for $1\frac{1}{2}N_2(g) + e^- \rightarrow N_3^-(g)$	+142 kJ mol^{-1}

$\Delta H_f^\ominus$ of NaN_3(s) = ... kJ mol^{-1} [3]

(iv) The lattice energy, $\Delta H_{latt}^\ominus$, of RbN_3(s) is –636 kJ mol^{-1}.

Suggest why the lattice energy of NaN_3(s), –732 kJ mol^{-1}, is more exothermic than that of RbN_3(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 ($S_2O_8^{2-}$) and iodide ions.

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

....

.... [1]

(ii) Write an equation for the overall reaction between $S_2O_8^{2-}$(aq) and I^-(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 Fe^{3+}(aq) ions can catalyse the reaction between $S_2O_8^{2-}$(aq) ions and I^-(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.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H^{\ominus} = -43.6\,kJ\,mol^{-1}$$

Some relevant standard entropies are given in the table.

substance	$Fe_2O_3(s)$	$CO(g)$	$Fe(s)$	$CO_2(g)$
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	+90	+198	+27	+214

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

....

.... [1]

(ii) Calculate the standard entropy change, $\Delta S^{\ominus}$, for this reaction.

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

(iii) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for this reaction at 25 °C.

$\Delta G^{\ominus}$ = ... $kJ\,mol^{-1}$ [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 cm^3 in a volumetric flask with distilled water.

An excess of aqueous potassium iodide was added to a 25.0 cm^3 portion of this solution to liberate iodine.

The resulting solution required 22.40 cm^3 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.

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

(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.

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$$

(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.

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \qquad K_a = 6.31 \times 10^{-8}\,\mathrm{mol\,dm^{-3}}$$

Calculate the value of $[HPO_4^{2-}]/[H_2PO_4^-]$ needed to give a pH of 7.40 in the cells.

$[HPO_4^{2-}]/[H_2PO_4^-]$ = ... [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]

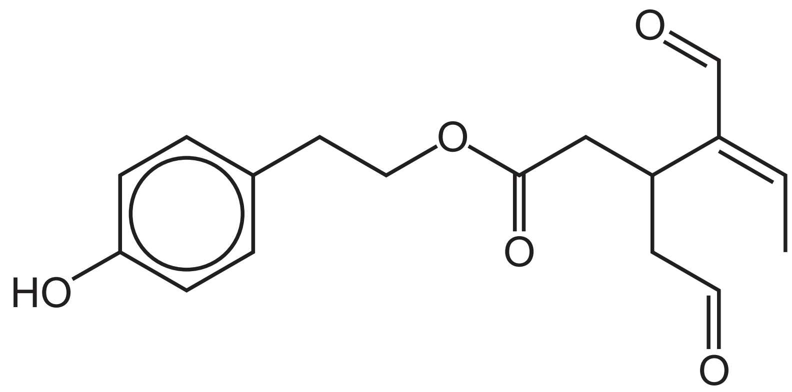
(ii) The HPO_4^{2-} ion can also act as an acid.

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.



Q

(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 cm^3 of hexane was shaken with 10.0 cm^3 of a solution containing 0.25 g of **Q** in 10.0 cm^3 of methanol, it was found that 0.060 g of **Q** was extracted into the hexane.

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

$K_{partition}$ = ... [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 Br_2(aq)			
$NaBH_4$			
excess hot NaOH(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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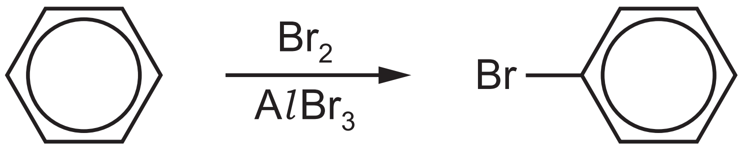
7 **(a)** Bromobenzene can be prepared from benzene as shown.



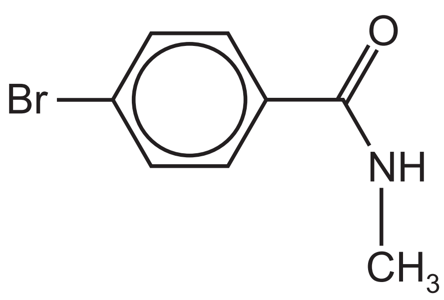
(i) Name the mechanism of this reaction.

.... [1]

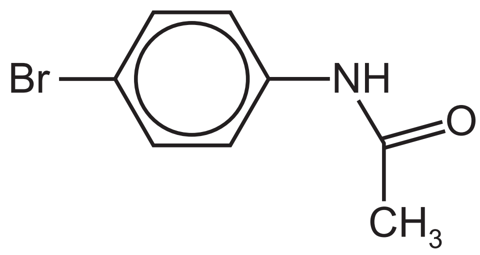
(ii) Draw the mechanism of this reaction. Include all relevant curly arrows, any dipoles and charges.

[4]

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



V



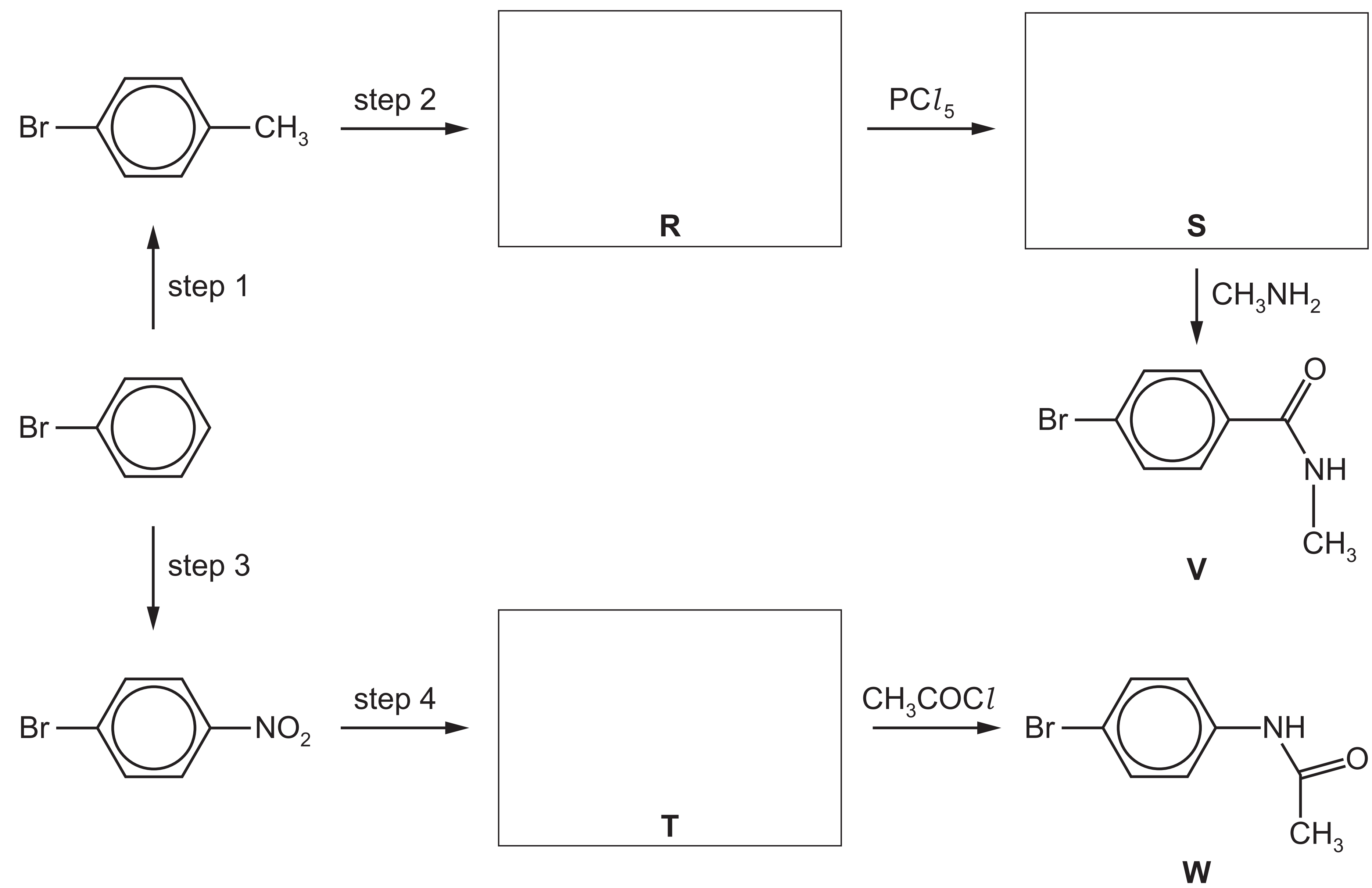
W

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 $LiAlH_4$.

product from **V**	product from **W**

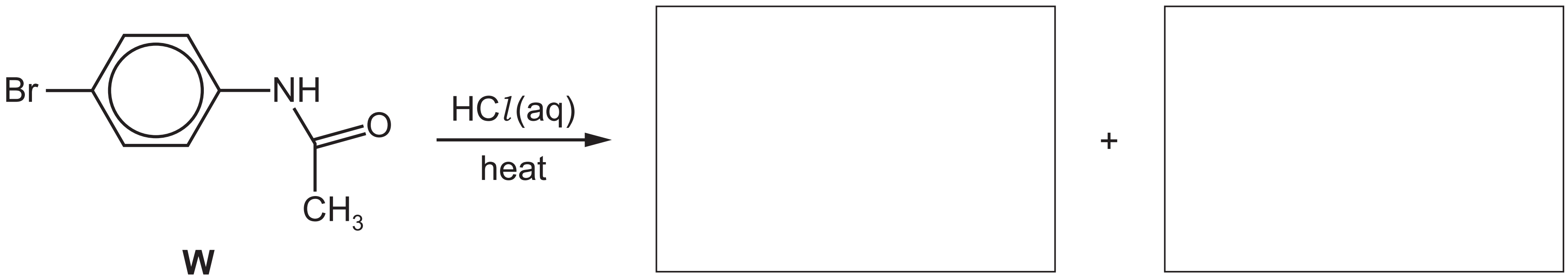
[2]

(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**.



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**.

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 $m/e = 102$.

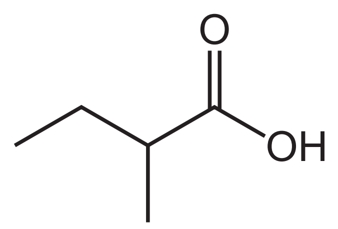
Use all of this information to show that the molecular formula of compound **F** is $C_5H_{10}O_2$.
Show all your working.

[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.



isomer 1

isomer 2

isomer 3

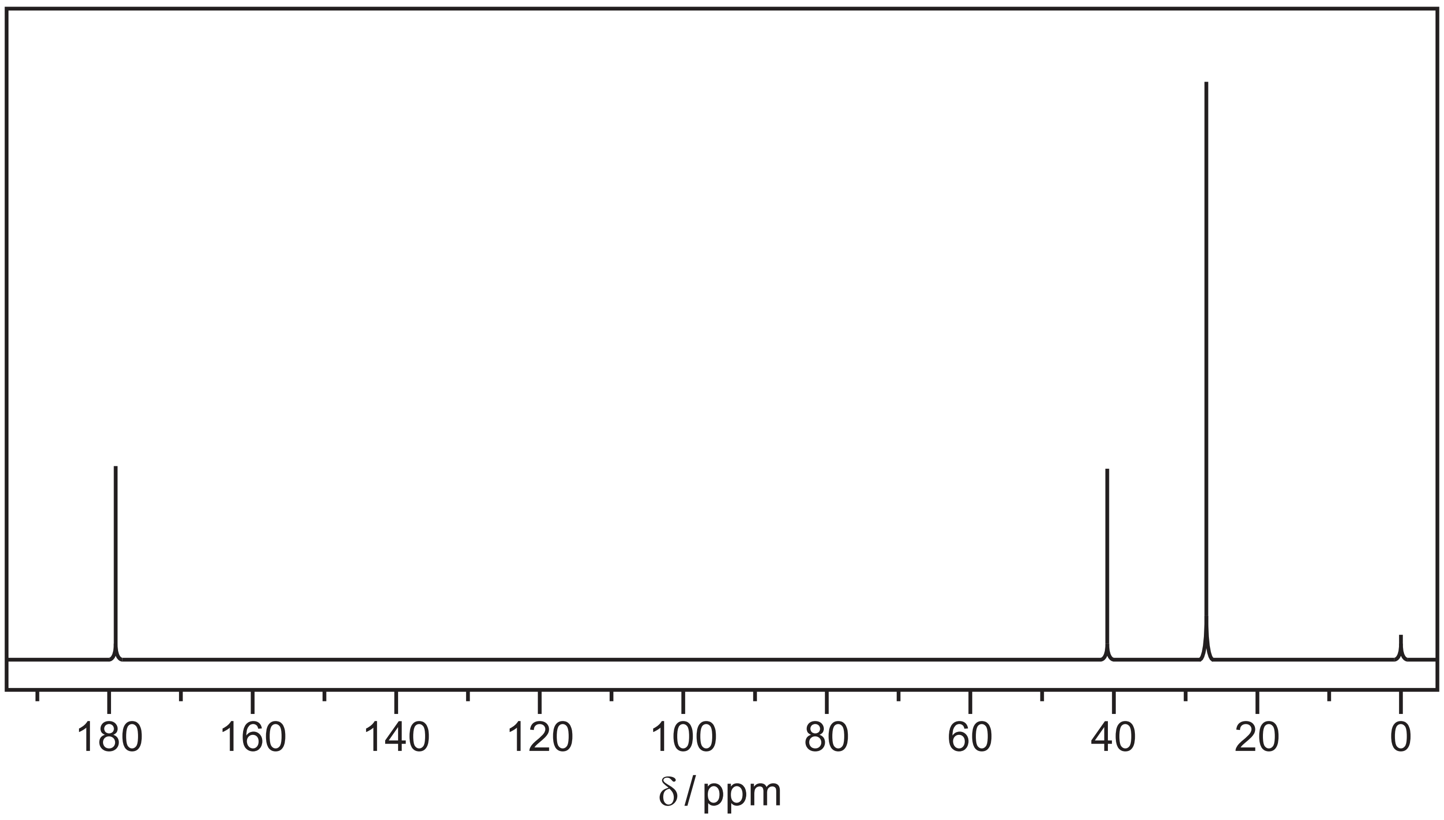
isomer 4

[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.

F

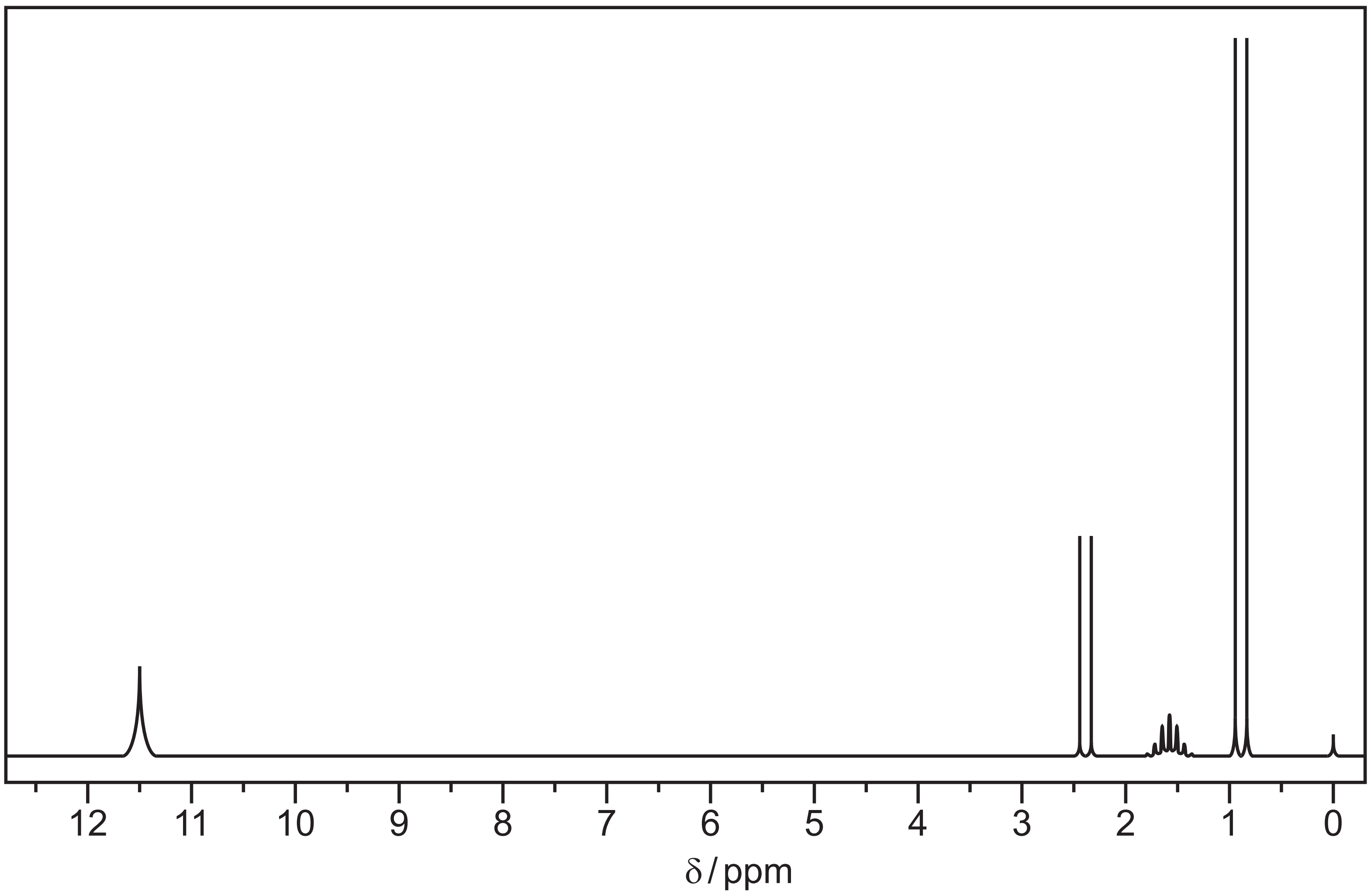
[1]

(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 δ = 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.

G

[1]

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

.... [1]

[Total: 13]

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Cambridge International Examinations
Cambridge International Advanced Level

CANDIDATE NAME

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9412850145

CHEMISTRY **9701/42**

Paper 4 Structured Questions **May/June 2015**

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.

Section A
Answer **all** questions.

Section B
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.

For Examiner's Use	
1	
2	
3	
4	
5	
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7	
8	
9	
Total	

This document consists of **17** printed pages and **3** blank pages.

IB15 06_9701_42/FP

CAMBRIDGE International Examinations

[Turn over

Section A

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

1 **(a)** Complete the electronic configurations of the following atoms.

fluorine: $1s^2$...

sulfur: $1s^2$...

[1]

(b) **(i)** Write an equation to show the thermal decomposition of HCl.

.... [1]

(ii) Using all relevant bond energy values from the *Data Booklet*, explain why the thermal stability of HF is **much** more than that of HCl.

....

....

.... [1]

(c) Explain what is meant by the term *electronegativity*, and how it relates to the concept of *bond polarity*.

....

....

....

.... [2]

(d) Sulfur and fluorine react together to give the covalent compound SF_4.

(i) Draw a 'dot-and-cross' diagram to show the bonding in SF_4. Include **all** outer shell electrons in your diagram.

[2]

(ii) State whether a molecule of SF_4 has a dipole moment. Explain your answer.

....

.... [1]

(e) Suggest a reason why sulfur can form both SF_4 and SF_6 whereas oxygen can only form OF_2.

....

.... [1]

(f) **(i)** State a major source of atmospheric sulfur dioxide.

.... [1]

(ii) State **one** environmental consequence of atmospheric sulfur dioxide.

.... [1]

[Total: 11]

2 **(a)** A sample of lead consists of the following isotopes in the percentage abundances stated.

isotope	% abundance
^{204}Pb	1.9
^{206}Pb	24.8
^{207}Pb	21.4
^{208}Pb	51.9

Use these data to calculate the relative atomic mass of the sample of lead to **two** decimal places.

A_r (Pb) = ... [2]

(b) Tin and lead both form oxides in oxidation states (II) and (IV).

(i) How does the acid-base nature of tin(II) oxide compare to that of tin(IV) oxide?

.... [1]

(ii) Illustrate your answer to **(i)** with equations, showing the reaction of each oxide with a suitable acid or base, as appropriate.

SnO ....

SnO_2 ....
[2]

(iii) Describe the reactions, if any, that occur when separate samples of tin(IV) oxide and lead(IV) oxide are heated in air.
Include any relevant observations and write equations for any reactions that occur.

....

....

....

....

....

.... [3]

[Total: 8]

3 **(a)** Complete the table with the symbol of the ion that contains the number of protons, electrons and neutrons stated in the following table. The first line has been completed as an example.

protons	electrons	neutrons	*symbol*
3	2	4	$^{7}Li^{+}$
15	16	18	

[2]

(b) Describe and explain the trend in the solubilities of the sulfates of the Group II elements down the group.

....

....

....

....

.... [4]

(c) Calcium sulfate is sparingly soluble in water.

Describe and explain what you would see when a few cm^3 of concentrated $Na_2SO_4(aq)$ were added to a saturated solution of $CaSO_4(aq)$.

....

....

....

.... [2]

(d) When a solution of a chromium salt **X** is electrolysed, chromium metal is deposited on the cathode, according to the following equation.

$$Cr^{n+}(aq) + ne^{-} \rightarrow Cr(s)$$

When a current of 1.8A was passed for 40 minutes through a solution of salt **X**, it was found that 0.776g of chromium had been deposited.

Calculate the value of *n* in the above equation. Show your working.

n = ... [4]

[Total: 12]

4 **(a)** **(i)** What is meant by the term *buffer solution*?

....

....

.... [2]

(ii) Write equations to show how the hydrogencarbonate ion, HCO_3^-, controls the pH of blood.

....

.... [2]

(iii) A solution containing both Na_2HPO_4 and NaH_2PO_4 is commonly used as a buffer solution. The following equilibrium is present in the solution.

$$H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq) \qquad K_a = 6.2 \times 10^{-8}\,mol\,dm^{-3}$$

Calculate the pH of a buffer solution made by mixing $100\,cm^3$ of $0.5\,mol\,dm^{-3}$ Na_2HPO_4 and $100\,cm^3$ of $0.3\,mol\,dm^{-3}$ NaH_2PO_4.

pH = ... [2]

(b) Silver phosphate, Ag_3PO_4, is sparingly soluble in water.

(i) Write an expression for the solubility product, K_{sp}, of Ag_3PO_4, and state its units.

K_{sp} = units: .... [1]

(ii) The numerical value of K_{sp} is 1.25×10^{-20} at 298 K. Use this value to calculate $[Ag^+(aq)]$ in a saturated solution of Ag_3PO_4.

$[Ag^+(aq)]$ = ... $mol\,dm^{-3}$ [3]

(c) The half-equation for the redox reaction between phosphoric(III) acid and phosphoric(V) acid is shown.

$$H_3PO_4(aq) + 2H^+(aq) + 2e^- \rightleftharpoons H_3PO_3(aq) + H_2O(l) \qquad E^\ominus = -0.28\,V$$

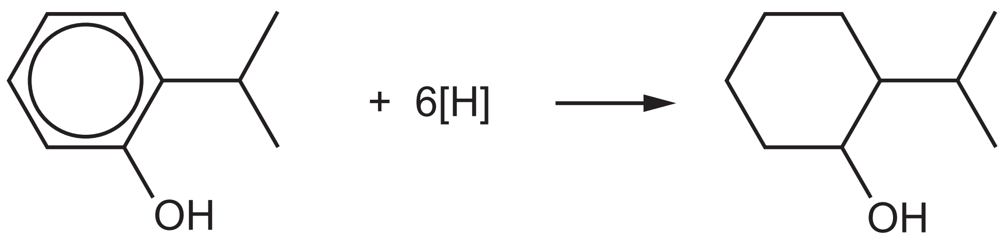
Find suitable data from the *Data Booklet* to write an equation for the reaction between H_3PO_3 and Fe^{3+}(aq) ions, and calculate the $E^\ominus_{cell}$ for the reaction.

equation: ....

$E^\ominus_{cell}$ = ... V [2]

[Total: 12]

5 **(a)** Compound **B** is a component of several perfumes and flavourings. It can be obtained by the hydrogenation of compound **A**.
During the reaction, the hydrogen atoms all add onto the same side of the benzene ring.



A **B**

(i) Suggest reagents and conditions for this reaction.

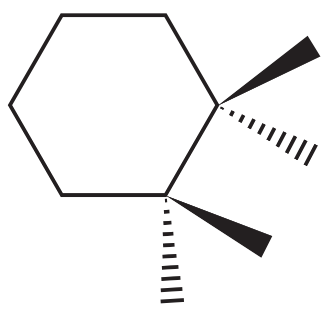
.... [1]

(ii) Circle all the chiral atoms on the structure of **B** above. [1]

(iii) How many possible optical isomers are there with the same structural formula as **B**?

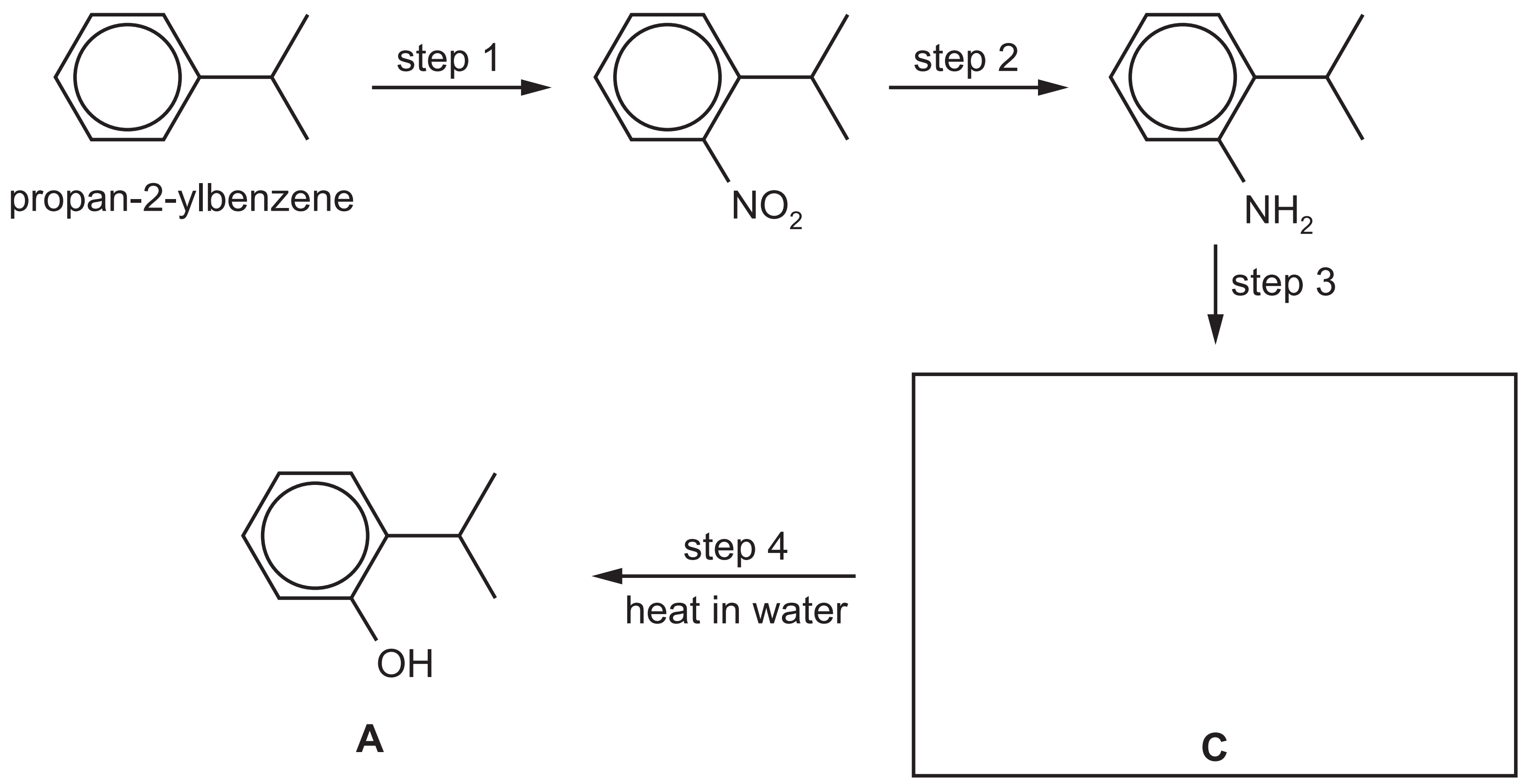
.... [1]

(iv) Complete the following part-structure to show the structure of one of the isomers of **B** that would be formed during the above reaction.



[1]

(b) Compound **A** can be obtained from propan-2-ylbenzene by the following route.



(i) Suggest the structure of the intermediate cation **C** and draw it in the box above. [1]

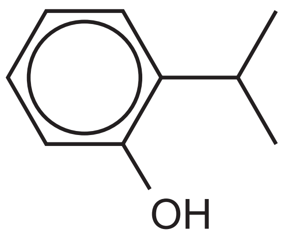
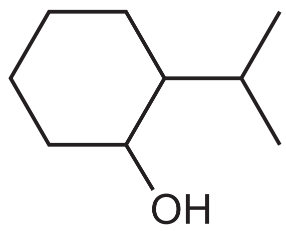
(ii) Suggest reagents and conditions for the following steps.

step 1 ....

step 2 ....

step 3 ....
[4]

(c) Suggest the structures of the organic products of the reactions between each of the compounds **A** and **B** and the following reagents. If no reaction occurs write 'no reaction' in the relevant box.

reagent	product with **A**, 	product with **B**, 
HBr		
Na		
NaOH(aq)		

[5]

[Total: 14]

6 **(a)** Carboxylic acids can be converted into primary amines by the following sequence of reactions.

$$RCO_2H \xrightarrow{\text{step 1}} \boxed{\mathbf{D}} \xrightarrow{\text{step 2}} RCONH_2 \xrightarrow{\text{step 3}} RCH_2NH_2$$

(i) Suggest the identity of intermediate **D** and write its structure in the box above. [1]

(ii) Suggest the reagents for

step 1 ....

step 2 ....

step 3 ....
[2]

(b) Four compounds, **E**, **F**, **G** and **H**, are isomers of each other.
Each compound contains an aromatic ring and **two** functional groups from the following list.

- alcohol
- amide
- amine
- carboxylic acid
- ester
- phenol

(i) Which of these functional groups react readily with cold $HCl(aq)$?

.... [1]

(ii) Which of these functional groups react readily with cold NaOH(aq)?

.... [1]

The molecular formula of the four isomers, **E**, **F**, **G** and **H**, is $C_8H_9NO_2$. All four compounds are insoluble in water. **Table 1** shows their solubilities in acid or alkali.

compound	solubility in $HCl(aq)$	solubility in NaOH(aq)
E	insoluble	insoluble
F	soluble	soluble
G	soluble	insoluble
H	insoluble	soluble

Table 1

(iii) Use this information to suggest the **two** functional groups, taken from the list on page 10, that each compound contains.

compound	first functional group	second functional group
E		
F		
G		
H		

[4]

(iv) Suggest a structure for each compound.

E	**F**
G	**H**

[4]

[Total: 13]

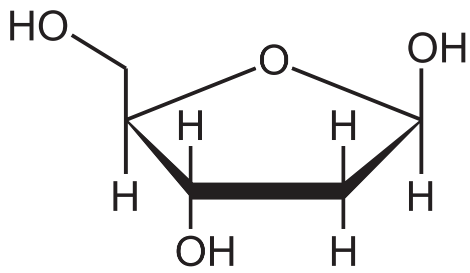
Section B

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

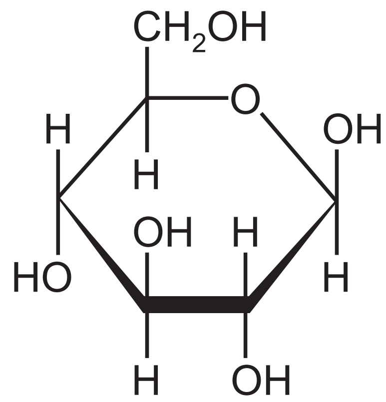
7 This question is about the structures and roles of DNA and RNA in protein synthesis.

(a) Study the structures of the three molecules below.
One of the molecules could be a building block for a protein while the other two could be building blocks for other biological polymers.

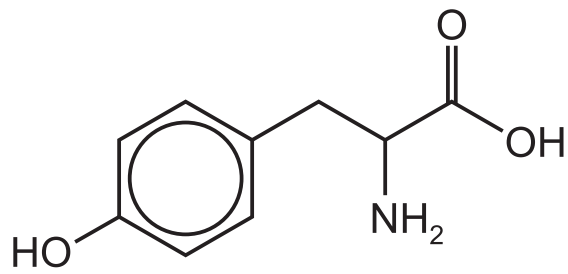
J



K



L



Which of the three could be a building block for a protein? Explain your answer.

....

.... [1]

(b) Outline the **different** roles played by mRNA and tRNA in producing a protein with a specific primary structure.

mRNA ....

....

....

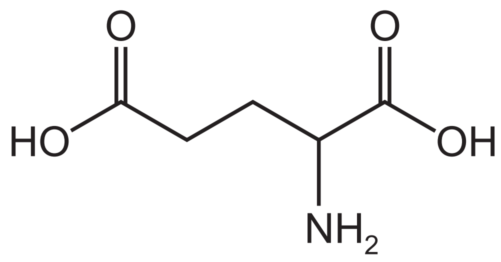
tRNA ....

....

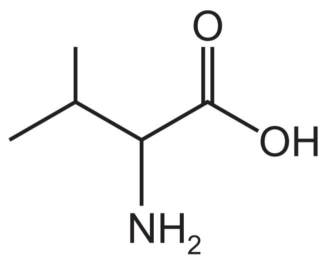
....

[4]

(c) Sickle cell anaemia is a genetic-based disease in which one of the glutamic acid residues is replaced by a valine residue.



glutamic acid



valine

Suggest and explain how this change in the primary structure of the protein would affect the overall structure and function of the protein.

....

....

....

....

.... [3]

[Total: 8]

8 **(a)** NMR spectroscopy and X-ray crystallography can both be used to examine the structure of organic compounds.

NMR is very useful at examining hydrogen atoms in compounds, but hydrogen atoms are invisible to X-rays.

(i) Explain why NMR spectroscopy can detect hydrogen atoms in molecules.

....

.... [1]

(ii) Explain why hydrogen atoms are invisible to X-rays.

....

.... [1]

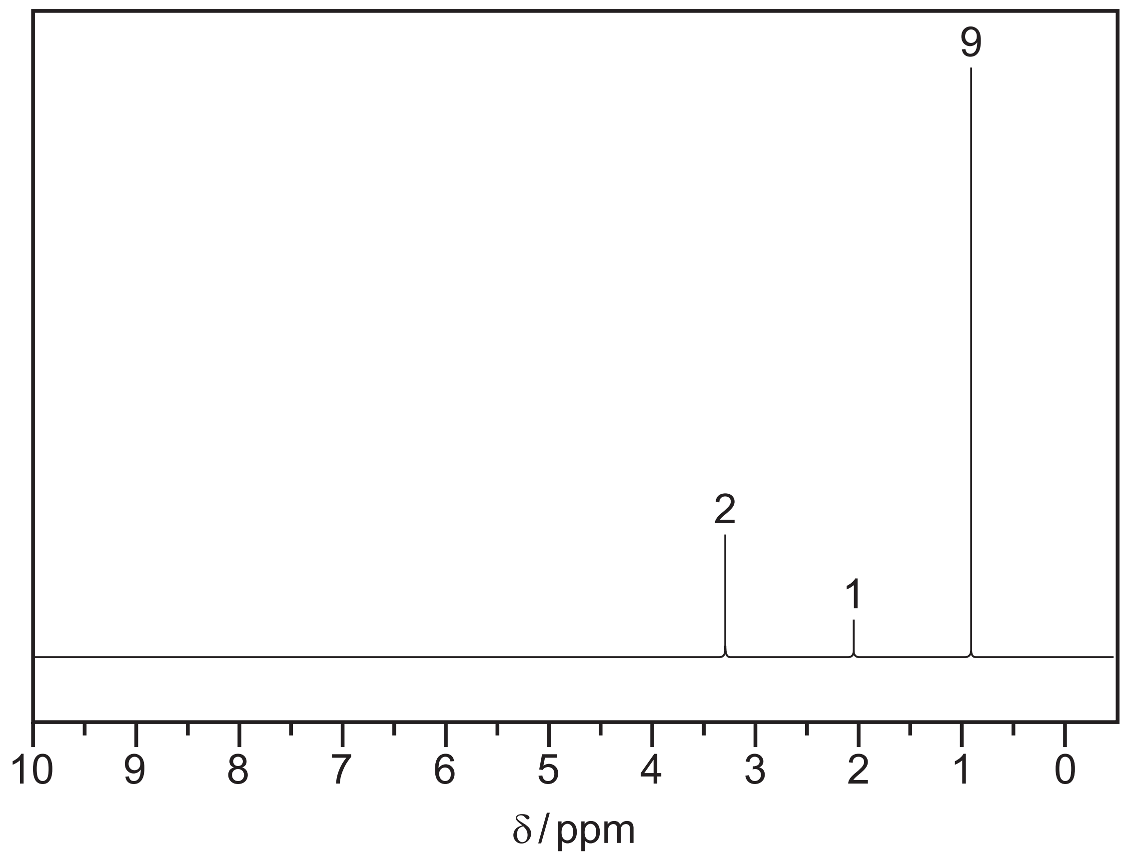
(iii) The molecular formula of the amino acid cysteine is $C_3H_7O_2NS$.

Explain which of the atoms present would show the greatest absorption on exposure to X-rays.

....

.... [1]

(b) The NMR spectrum below was obtained from an organic liquid, **P**, which contains five carbon atoms per molecule.



(i) How many protons are present in one molecule of **P**? Explain your answer.

number of protons ....

....

.... [1]

(ii) When a little D_2O is added to **P**, the absorption at $\delta\,2.0$ disappears.

Explain what this tells you about the group responsible for this absorption and why.

....

....

.... [2]

(iii) What does the absorption at $\delta\,0.9$ tell you about the adjacent carbon atom?

....

.... [1]

(iv) What group(s) is/are responsible for the absorption at $\delta\,0.9$?

.... [1]

(v) Suggest a structure for **P**.

[1]

(c) When an isomer of **P** is heated with concentrated H_2SO_4 it forms a new compound, **Q**. This new compound **Q** reacts with bromine to give a dibromide, **R**.

(i) A mass spectrum was obtained of **R**. The ratio of the heights of the M : M+1 peaks was 9.3 : 0.5.

Show that there are five carbon atoms present in one molecule of **R**.

[1]

(ii) Predict the ratio of the heights of the M : M+2 : M+4 peaks as a result of the two bromine atoms in the dibromide **R**. Show your working.

ratio .... [1]

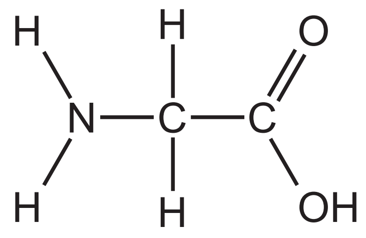
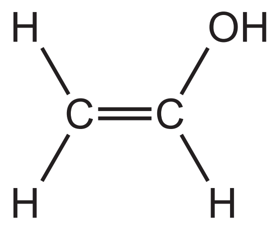
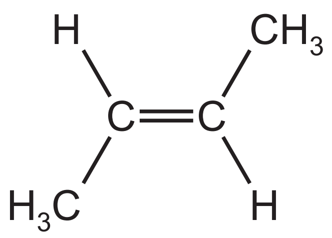
(iii) What is the molecular formula of **R**?

.... [1]

[Total: 12]

9 Polymers consist of monomers joined either by addition or condensation reactions.

(a) Complete the table by placing a tick (✓) in the correct column to indicate the type of reaction that would polymerise each of the monomers.

monomer	addition	condensation	both
			
			
			

[3]

(b) Poly(ethene) bags pollute the environment for a long time because they are non-biodegradable.

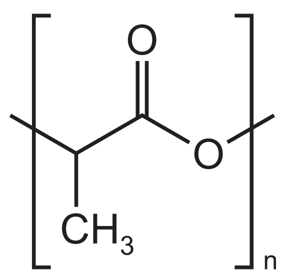
Suggest why.

....

....

.... [2]

(c) There has been considerable research into making biodegradable plastic bags. The repeat unit for one of the polymers used, polylactic acid (PLA), is shown.



(i) Draw the structure of the monomer for PLA.

[1]

(ii) Suggest why PLA breaks down **more** easily in the environment than poly(ethene).

....

....

.... [1]

(d) The table shows the melting points of three polymers.

polymer	melting point / °C
polyethene	137
polychloroethene (PVC)	212
nylon 6,6	265

Explain the differences in melting point of these three polymers in terms of the intermolecular forces between the chains.

....

....

....

....

....

....

....

.... [3]

[Total: 10]

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Cambridge International A Level

Cambridge International Examinations
Cambridge International Advanced Level

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* 2 4 9 2 6 7 2 4 9 7 *

CHEMISTRY **9701/42**

Paper 4 Structured Questions **October/November 2015**

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.

Section A
Answer **all** questions.

Section B
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.

For Examiner's Use	
1	
2	
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6	
7	
8	
9	
10	
Total	

This document consists of **19** printed pages and **1** blank page.

IB15 11_9701_42/FP

CAMBRIDGE
International Examinations

[Turn over

Section A

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

1 **(a)** Calcium has atomic number 20.

Complete the electronic structures for a

calcium atom, $1s^2 2s^2 2p^6$................................

calcium ion in the +2 oxidation state. $1s^2 2s^2 2p^6$................................

[1]

(b) Calcium nitrate, $Ca(NO_3)_2$, is used in fertilisers and can be prepared by an acid-base reaction.

Write an equation for the preparation of calcium nitrate by an acid-base reaction.

.... [1]

(c) **(i)** When anhydrous calcium nitrate is heated strongly, it decomposes to leave a white solid.

Identify this white solid and suggest **another** observation for this reaction.

....

.... [1]

(ii) The ease of thermal decomposition of the Group II nitrates **decreases** down the group.

Explain this trend.

....

....

.... [2]

(d) **(i)** What is meant by the term *standard enthalpy change of hydration*, $\Delta H^{\ominus}_{hyd}$?

....

....

.... [2]

(ii) Use the following data to calculate the lattice energy, $\Delta H^{\ominus}_{latt}$, of calcium nitrate, $Ca(NO_3)_2(s)$. You may find it helpful to construct an energy cycle.

enthalpy change	value
$\Delta H^{\ominus}_{hyd}$ (Ca^{2+}(g))	$-1650\,kJ\,mol^{-1}$
$\Delta H^{\ominus}_{hyd}$ (NO_3^-(g))	$-314\,kJ\,mol^{-1}$
enthalpy change of solution for $Ca(NO_3)_2$(s)	$-19\,kJ\,mol^{-1}$

$\Delta H^{\ominus}_{latt}$ $Ca(NO_3)_2$(s) = ... $kJ\,mol^{-1}$ [3]

(e) The standard enthalpy change of hydration for Ba^{2+}, $\Delta H^{\ominus}_{hyd}$ (Ba^{2+}(g)), is $-1305\,kJ\,mol^{-1}$.

Suggest an explanation for why the $\Delta H^{\ominus}_{hyd}$ of the Ba^{2+} ion is **less** exothermic than the $\Delta H^{\ominus}_{hyd}$ of the Ca^{2+} ion.

....

....

.... [2]

[Total: 12]

2 **(a)** Complete the table to show the number of **unpaired** electrons in the outer shell of each of the gaseous atoms, Na to Ar.

	Na	Mg	Al	Si	P	S	Cl	Ar
number of unpaired electrons								

[3]

(b) **(i)** Complete the table for the reactions of two Period 3 chlorides with water.

Period 3 chloride	observations	pH of solution formed
$SiCl_4$		
PCl_5		

[3]

(ii) Write an equation for the reaction between $SiCl_4$ and H_2O.

.... [1]

[Total: 7]

3 The transition element iron is the most abundant element in the Earth's core.

(a) What is meant by the term *transition element*?

....

.... [1]

(b) In aqueous solution, iron can form complex ions which contain ligands.

(i) Name the *type of bonding* that occurs between a ligand and a transition element.

.... [1]

(ii) Which of the following species can act as a ligand?
Complete the table by placing a tick (✓) in the appropriate column to indicate whether the species can act as a ligand or not.

species	can act as a ligand	cannot act as a ligand
NO_3^-		
BF_3		
$H_2NCH_2CH_2NH_2$		
NH_4^+		

[2]

(c) Manganese ions, Mn^{2+}(aq), show some similar chemical properties to those of copper(II) ions, Cu^{2+}(aq).

Use this information and the *Data Booklet* to suggest the formula of the manganese species formed in each of the following reactions. State the *type of reaction* taking place in each case.

	formula of manganese species formed	type of reaction
Mn^{2+}(aq) + NaOH(aq)		
Mn^{2+}(aq) + concentrated HCl		
Mn^{2+}(aq) + H_2O_2(aq)		

[5]

[Total: 9]

4 In aqueous solution, 2-chloro-2-methylpropane, $(CH_3)_3CCl$, reacts with sodium hydroxide, NaOH. This is a nucleophilic substitution reaction.

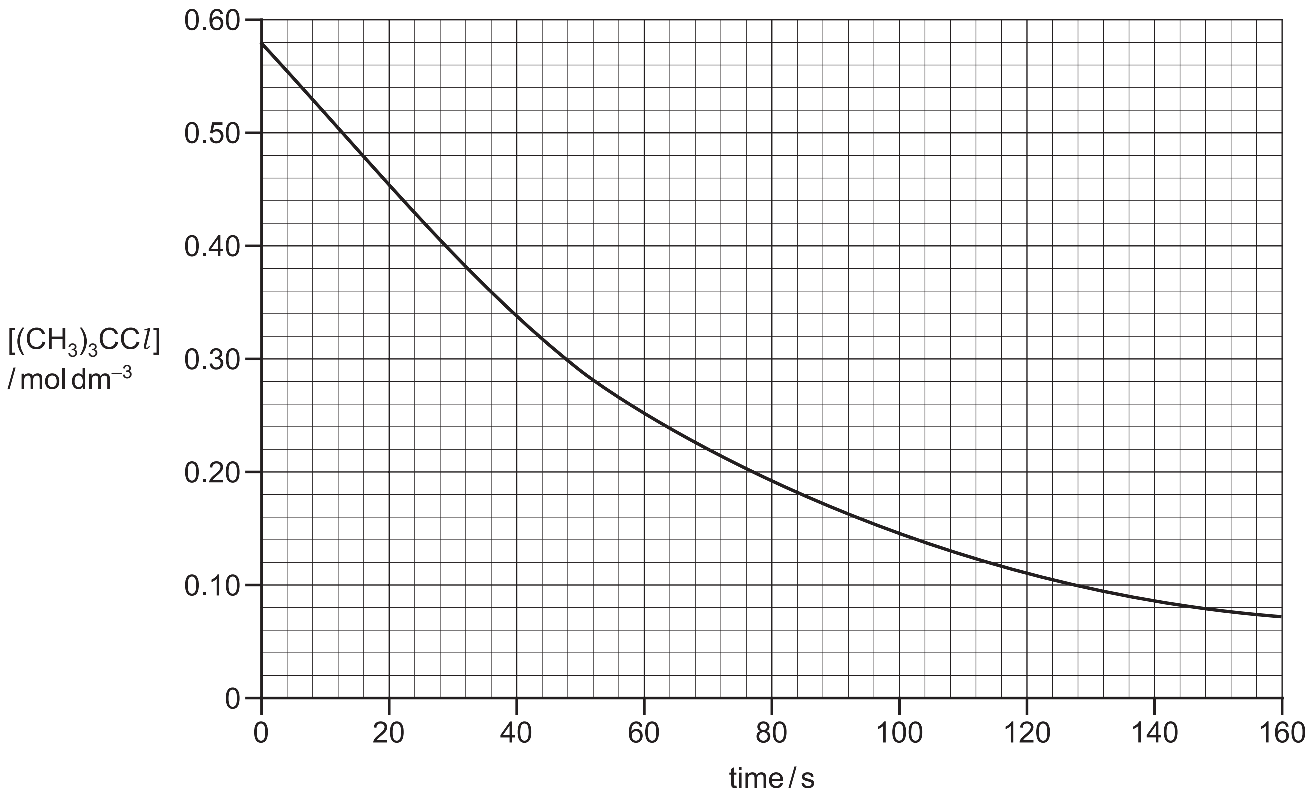
$$(CH_3)_3CCl(aq) + NaOH(aq) \rightarrow (CH_3)_3COH(aq) + NaCl(aq)$$

(a) Show the mechanism for this reaction. Include all necessary curly arrows, lone pairs and relevant dipoles.

[3]

The rate of this reaction was investigated using a **large excess** of sodium hydroxide.

(b) The graph below shows the results of the experiment.



The reaction is first order with respect to $[(CH_3)_3CCl]$. This can be confirmed from the graph using half-lives.

(i) What is meant by the *half-life* of a reaction?

....

.... [1]

(ii) Calculate the half-life for this reaction. Show all your working and show clearly any construction lines on the graph.

[1]

(iii) What would be the effect on the half-life of this reaction if the initial concentration of $[(CH_3)_3CCl]$ was **doubled**?

.... [1]

(c) **(i)** Use the graph in **(b)** to determine the rate of reaction at 80 s.
Show all your working.

rate = ... units .... [2]

The rate equation for this reaction is shown.

$$\text{rate} = k[(CH_3)_3CCl]$$

(ii) Calculate the value of the rate constant, k, for this reaction and give its units.

k = ... units .... [1]

[Total: 9]

5 **X** is a metallic element.

(a) **(i)** Draw a fully labelled diagram to show how the standard electrode potential, $E^{\ominus}$, of $\mathbf{X}^{2+}$(aq) / **X**(s) could be measured.

[4]

(ii) What are the conditions needed for the value measured to be a **standard** electrode potential?

.... [1]

(iii) State the charge carriers that transfer current through

the solutions, ... the wire. .... [1]

(b) An electrochemical cell was set up consisting of an $\mathbf{X}^{2+}(aq)/\mathbf{X}(s)$ half-cell ($E^\ominus = -0.40\,V$) and an $Ag^{+}(aq)/Ag(s)$ half-cell ($E^\ominus = +0.80\,V$).

(i) Write an equation for the reaction that would take place if the electrodes of this cell were connected by a wire.

.... [1]

When the current was allowed to pass for a period of time,

- the Ag electrode gained 1.30 g in mass,
- the electrode made of metal **X** lost 0.67 g in mass.

(ii) Calculate the A_r of metal **X**; hence suggest an identity for **X**.
Show all your working. Use of the *Data Booklet* is relevant to this question.

A_r = ...

X is ....
[4]

[Total: 11]

6 Boron forms many useful compounds.

(a) The compound diborane, B_2H_6, can be used as a rocket fuel.
It can be prepared by the reaction of boron trifluoride, BF_3, with sodium borohydride, $NaBH_4$.

Balance this equation.

$$.......BF_3 + ...NaBH_4 \rightarrow ....B_2H_6 + ...NaBF_4$$

[1]

(b) Primary and secondary alcohols can be formed by the reaction of carbonyl compounds with $NaBH_4$, which is a source of hydride ions, H^-.

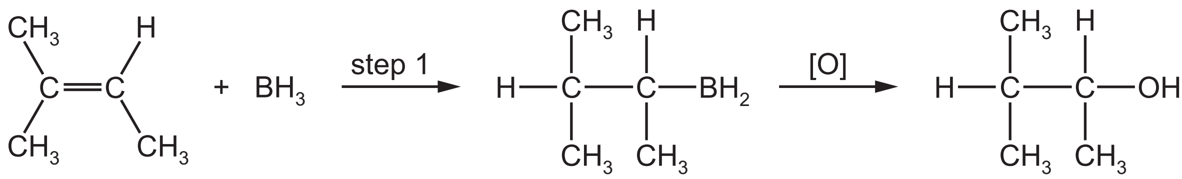
Complete the mechanism for the reaction of butanone with hydride ions, H^-, and draw the intermediate in the box. Include all necessary curly arrows and relevant dipoles.

intermediate

[3]

(c) Borane, BH_3, is used to synthesise alcohols from alkenes.
The reaction occurs in two steps.

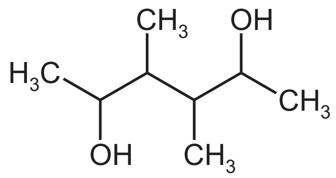
The BH_2 group from BH_3 bonds to the **least** substituted carbon atom of the double bond, and the remaining H from BH_3 bonds to the other carbon.



(i) Suggest the *type of reaction* in step 1.

.... [1]

(ii) The diol **Y** can be prepared by the same method.



Y

Draw the structure of the **diene** which could be used to prepare diol **Y**.

[1]

(d) Benzene, C_6H_6, and borazine, $B_3N_3H_6$, have planar, cyclic structures.

(i) Describe the structure of and bonding in benzene, C_6H_6.

....

....

....

....

....

....

.... [3]

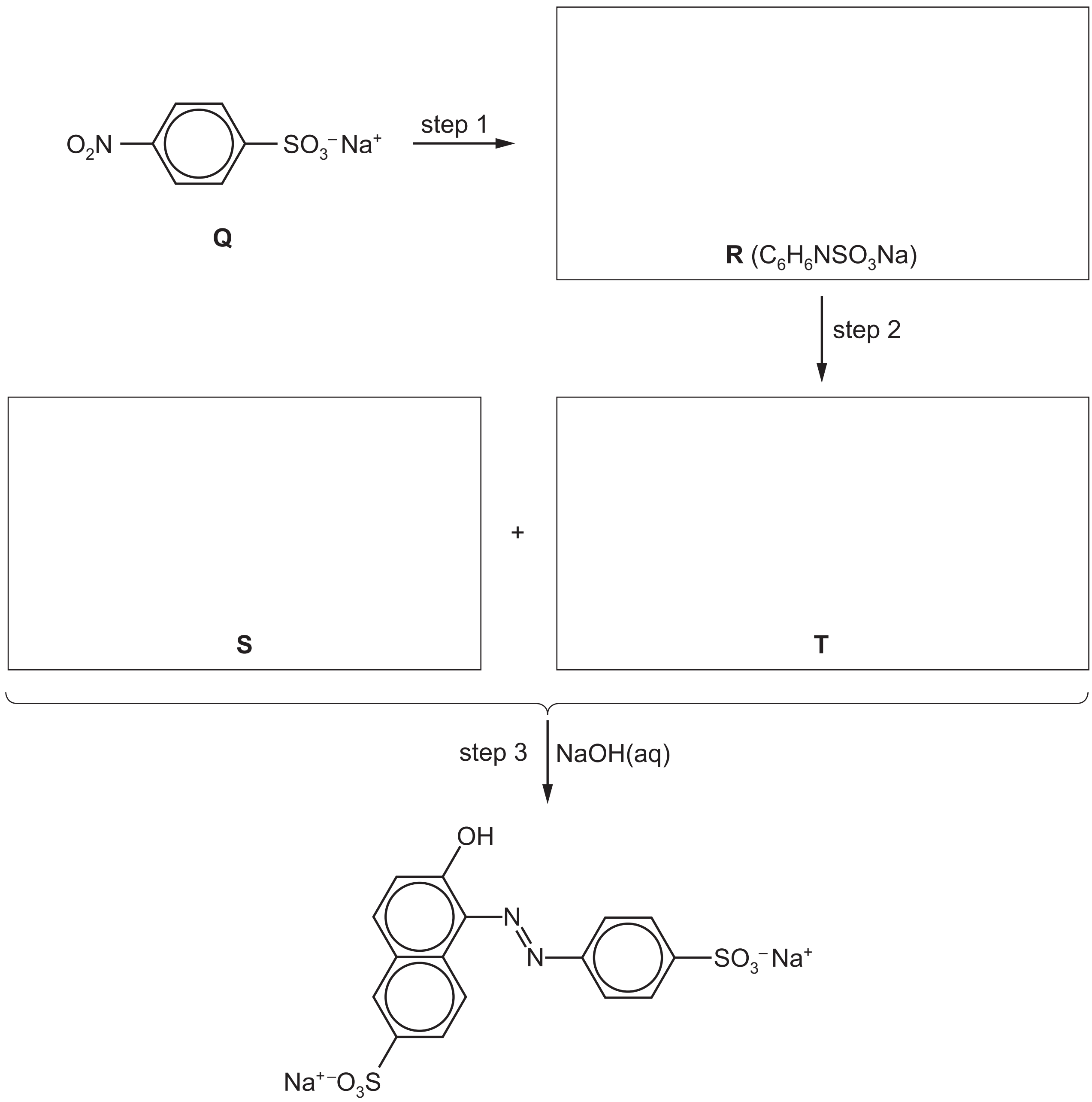
(ii) In borazine, $B_3N_3H_6$, the boron and nitrogen atoms alternate around the ring. Each ring atom has a single hydrogen atom bonded to it.
All boron-nitrogen bonds in borazine are 0.144 nm in length, whereas in simple compounds B–N and B=N bond lengths are 0.154 nm and 0.136 nm respectively.

Suggest and draw the structure of borazine.

[1]

[Total: 10]

7 (a) *Sunset Yellow* is a yellow colouring agent used in food and drinks, which can be made by the following route.
In step 3 of this synthesis, a phenol-like compound, **S**, reacts with intermediate **T** made from amine **R**.
Assume that the $–SO_3^-Na^+$ group does not react.



Sunset Yellow

(i) Suggest structures for compounds **R**, **S** and **T** and draw them in the boxes above. [3]

(ii) Suggest reagents and conditions for

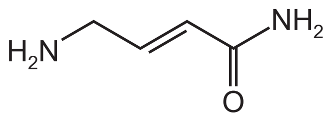
step 1, ...

step 2. ....
[3]

(iii) What type of organic salt is formed in step 2?

.... [1]

(b) Compound **W** has the following structure.



(i) How many σ and π bonds are present in a molecule of **W**?

σ bonds .... π bonds .... [2]

(ii) The products of the reactions of **W** with cold HCl and with CH_3CH_2Br are soluble in water but **not** in organic solvents.

Complete the table for these reactions of **W**.

reagent	structure of product (molecular formula given)	type of reaction
HCl	($C_4H_9N_2OCl$)	
CH_3CH_2Br	($C_6H_{13}N_2BrO$)	

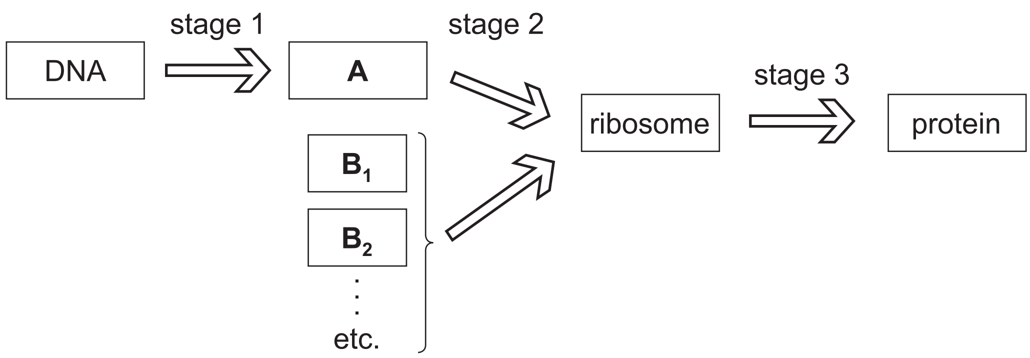
[3]

[Total: 12]

Section B

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

8 **(a)** The sequence of bases in DNA is a code for the order of amino acids in the primary structure of proteins.
The diagram represents the stages involved in the formation of a protein from DNA.



(i) Identify the biochemical structures, **A** and $\mathbf{B_1}$, $\mathbf{B_2}$ etc.

biochemical structure	identity
A	
$\mathbf{B_1}$, $\mathbf{B_2}$ etc.	

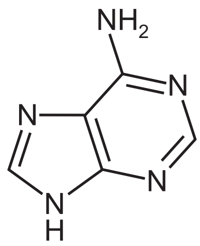
[2]

(ii) Name the biochemical processes involved in stages 1 and 3.

process	name of biochemical process
stage 1	
stage 3	

[1]

(b) Adenine is an integral part of DNA.



adenine

(i) State the molecular formula of adenine.

.... [1]

(ii) Identify the three **other** nitrogenous bases in DNA.

.... [1]

(iii) DNA has a double helical structure that consists of two strands linked together.

What type of bonding exists between the

phosphate and sugar groups within a DNA strand, ...

different bases on the two strands? ....
[2]

(c) The breakdown of adenosine triphosphate, ATP, provides the energy for many cellular reactions.

$$ATP + H_2O \rightarrow ADP + P_i$$

What *type of chemical reaction* is this?

.... [1]

(d) X-ray crystallography can be useful in obtaining information about the structures of large organic molecules, such as ATP. The technique involves X-rays interacting with the electrons within the molecule.

(i) Which element in the molecule of ATP will interact most strongly with the X-ray beam?

.... [1]

(ii) Explain why X-ray crystallography will **not** detect hydrogen atoms.

....

.... [1]

[Total: 10]

9 **(a)** Some metals are essential to biochemical processes.

Complete the following table naming one metal in each case.

biochemical process	metal
haemoglobin in oxygen transport	
transmission of nerve impulses	
enzyme cofactor	

[2]

(b) Enzymes are a special type of protein molecule that catalyse biochemical reactions.

Explain briefly the mechanism by which an enzyme breaks down a substrate molecule.

....

....

....

....

.... [3]

(c) Disulfide bonds play an important role in the stability of some proteins such as the keratin in human hair.
The amino acid involved in the formation of a disulfide bond is cysteine, $H_2NCH(CH_2SH)CO_2H$.

(i) At which level of protein structure (primary, secondary, tertiary) are disulfide bonds formed?

.... [1]

(ii) Use a functional group in cysteine to show how disulfide bonds are formed.

[1]

(iii) What *type of chemical reaction* is this?

.... [1]

(d) The NMR spectrum of cysteine, $H_2NCH(CH_2SH)CO_2H$, shows five absorptions.

After shaking a solution of cysteine with a few drops of D_2O, the NMR spectrum shows **only two** absorptions, **E** and **F**, shown below.

E **F**

(i) Identify the **two** types of protons responsible for the absorptions **E** and **F**.

E ....

F ....
[1]

(ii) State and explain the splitting patterns of the absorptions **E** and **F**.

E ....

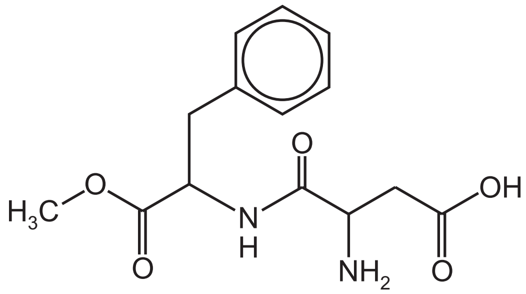
....

F ....

.... [2]

[Total: 11]

10 **(a)** Aspartame is an artificial sweetener that has the structure shown below.



aspartame

(i) Draw a circle around each chiral centre in aspartame. [1]

In the stomach, aspartame is hydrolysed by acid to form three organic products.

(ii) On the diagram above, use arrows to indicate the **two** bonds that would be hydrolysed in the stomach. [2]

(iii) Draw the structures of the **three** products formed after complete acid hydrolysis of aspartame.

[3]

(b) Aspartame is soluble in water.

By referring to the structure of aspartame, explain why it is soluble in water.

....

....

.... [2]

(c) Recently, nanotechnology has been involved in the development of a new natural sweetener, *Nano Sugar*, extracted from sugar cane.

What is the approximate width of a nanoparticle?

.... [1]

[Total: 9]

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Cambridge International A Level

Cambridge International Examinations
Cambridge International Advanced Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

5287725339

CHEMISTRY **9701/42**

Paper 4 Structured Questions **May/June 2014**

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.
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Section A
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Section B
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CAMBRIDGE International Examinations

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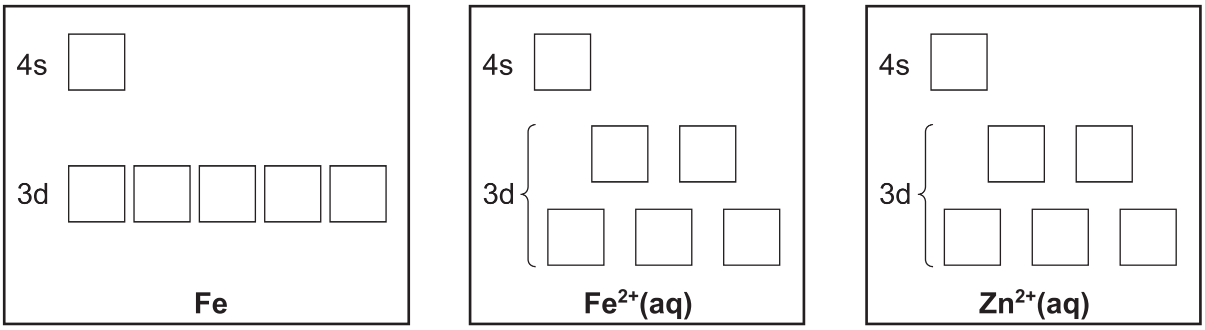
Section A

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

1 (a) (i) On the diagrams below, show the outer electron arrangements of the atoms and ions indicated. (Use the symbol ↑↓ to represent a pair of electrons in an orbital.)



(ii) Use the above diagrams to explain why $Fe^{2+}(aq)$ ions are coloured, whereas $Zn^{2+}(aq)$ ions are colourless.

....

....

....

....

[4]

(b) When concentrated HCl is added to a solution of $Cu^{2+}(aq)$ ions, the solution turns yellow.

(i) State the formula of the species responsible for the yellow colour and name the *type of reaction* that has occurred.

....

....

(ii) Ammonia can react as a base or as a ligand.
Describe the colour changes that occur when $NH_3(aq)$ is **gradually** added, with stirring, to the yellow solution, until the $NH_3(aq)$ is in excess.
Identify the **three** ions or compounds responsible for the new colours.

....

....

....

....

....

....

[7]

(c) When aqueous solutions of KI and $K_2S_2O_8$ are mixed almost no reaction occurs, but when a few drops of Fe^{2+}(aq) or Fe^{3+}(aq) are added, iodine, I_2(aq), is produced at a steady rate.

(i) Write an equation for the overall reaction.

....

(ii) State the precise role of the iron ions during this reaction.

....

(iii) By means of equations or otherwise, explain why the presence of *either* Fe^{2+} *or* Fe^{3+} is able to speed up the reaction.

....

....

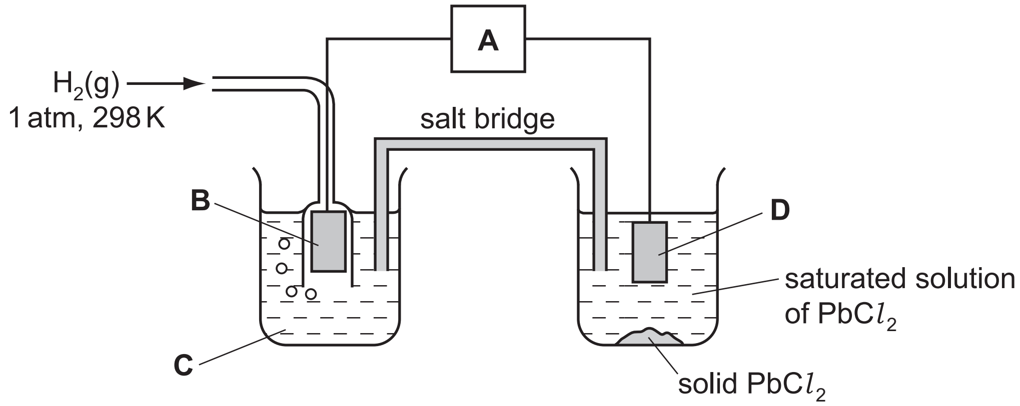
....

[3]

[Total: 14]

2 Lead(II) chloride, $PbCl_2$, can be used in the manufacture of some types of coloured glass.

$PbCl_2$ is only sparingly soluble in water. The $[Pb^{2+}]$ in a saturated solution of $PbCl_2$ can be estimated by measuring the cell potential, E_{cell}, of the following cell.



(a) In the spaces below, identify what the four letters **A-D** in the above diagram represent.

A .... **B** ....

C .... **D** ....

[4]

(b) In a saturated solution of $PbCl_2$, $[PbCl_2(aq)] = 3.5 \times 10^{-2}\,mol\,dm^{-3}$.

(i) The $E^\ominus$ for the Pb^{2+}/Pb electrode is $-0.13\,V$. Predict the potential of the right-hand electrode in the diagram above. Indicate this by placing a tick in the appropriate box in the table below.

electrode potential / V	place **one tick only** in this column
−0.17	
−0.13	
−0.09	
0.00	

Explain your answer.

....

....

(ii) Write an expression for the solubility product, K_{sp}, of $PbCl_2$.

....

(iii) Calculate the value of K_{sp}, including units.

K_{sp} = ... units ....

[5]

(c) The behaviours of $PbCl_2$ and $SnCl_2$ towards reducing agents are similar, but their behaviours towards oxidising agents are very different.

(i) Illustrate this comparison by quoting and comparing relevant $E^{\ominus}$ values for the two metals and their ions. Explain what the relative $E^{\ominus}$ values mean in terms of the ease of oxidation or reduction of these compounds.

....

....

....

....

....

....

(ii) Writing a balanced molecular or ionic equation in each case, suggest a reagent to carry out each of the following reactions.

the reduction of $PbCl_2$

....

the oxidation of $SnCl_2$

....

[5]

(d) (i) Write an equation to represent the lattice energy of $PbCl_2$. Show state symbols.

....

(ii) Use the following data, together with appropriate data from the *Data Booklet*, to calculate a value for the lattice energy of $PbCl_2$.

electron affinity of chlorine	=	$-349\,kJ\,mol^{-1}$
enthalpy change of atomisation of lead	=	$+195\,kJ\,mol^{-1}$
enthalpy change of formation of $PbCl_2(s)$	=	$-359\,kJ\,mol^{-1}$

lattice energy = ... $kJ\,mol^{-1}$

(iii) How might the lattice energy of $PbCl_2$ compare to that of $PbBr_2$? Explain your answer.

....

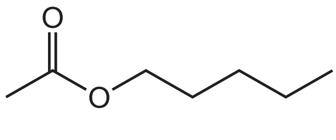
....

....

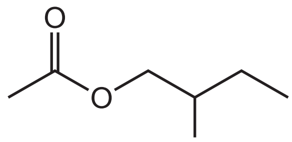
[6]

[Total: 20]

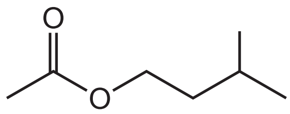
3 The following four isomeric esters with the molecular formula $C_7H_{14}O_2$ are used as artificial flavours in drinks and sweets to give a pear, banana or plum taste to foodstuffs.



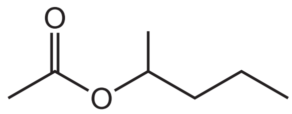
A



B



C



D

(a) In each of the spaces below, write one or more of the letters **A-D**, as appropriate.

(i) Which of these compounds can exist as optical isomers?

....

(ii) On hydrolysis, which of these compounds produce(s) a secondary alcohol?

....

[3]

(b) The hydrolysis of all these compounds produces ethanoic acid, CH_3CO_2H, as one of the products.

State the reagents and conditions needed for this hydrolysis.

.... [1]

(c) The acid dissociation constant, K_a, of ethanoic acid is 1.75×10^{-5} mol dm^{-3}.

(i) Explain why this value of K_a is

- much larger than that of ethanol, CH_3CH_2OH,

....

....

- smaller than that of chloroethanoic acid, $ClCH_2CO_2H$.

....

....

(ii) Calculate the pH of a 0.100 mol dm^{-3} solution of ethanoic acid.

[4]

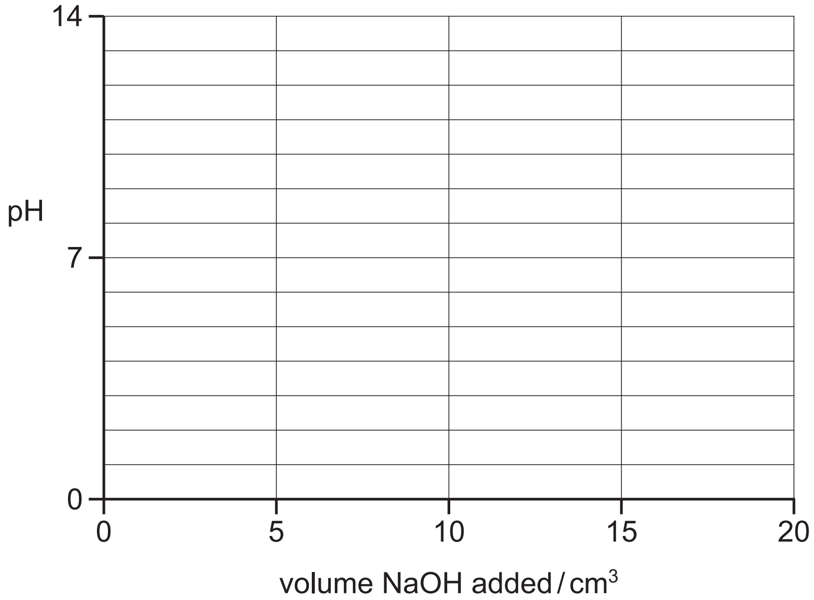
(d) 20.0 cm^3 of 0.100 mol dm^{-3} NaOH were slowly added to a 10.0 cm^3 sample of 0.100 mol dm^{-3} ethanoic acid, and the pH was measured throughout the addition.

(i) Calculate the number of moles of NaOH remaining at the end of the addition.

(ii) Calculate the $[OH^-]$ at the end of the addition.

(iii) Using the expression $K_w = [H^+][OH^-]$ and your value in **(ii)**, calculate $[H^+]$ and the pH of the solution at the end of the addition.

(iv) On the following axes, sketch how the pH will change during the addition of a total of 20.0 cm^3 of 0.100 $mol\,dm^{-3}$ NaOH. Mark clearly where the end point occurs.



(v) From the following list of indicators, put a tick in the box by the side of the indicator you consider most suitable for this titration.

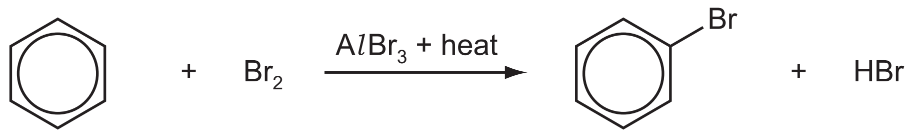
indicator	pH at which colour changes	place **one tick only** in this column
malachite green	0 - 1	
thymol blue	1 - 2	
bromophenol blue	3 - 4	
thymolphthalein	9 - 10	

[7]

[Total: 15]

4 Both ethene and benzene react with bromine.

$$H_2C{=}CH_2 \quad + \quad Br_2 \xrightarrow{\text{room temperature}} BrCH_2CH_2Br$$



(a) What *type of reaction* is the reaction of bromine with

(i) ethene,

....

(ii) benzene?

....

[1]

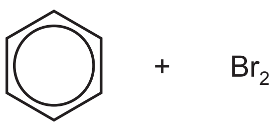
(b) Write an equation to show the formation of the electrophile during the reaction between bromine and benzene.

.... [1]

(c) Each of these reactions involves an intermediate.

(i) Draw the structure of the intermediate in each reaction.

$H_2C{=}CH_2 \quad + \quad Br_2 \quad \rightarrow$



(ii) Suggest why the product of the reaction between bromine and benzene, bromobenzene, is still unsaturated.

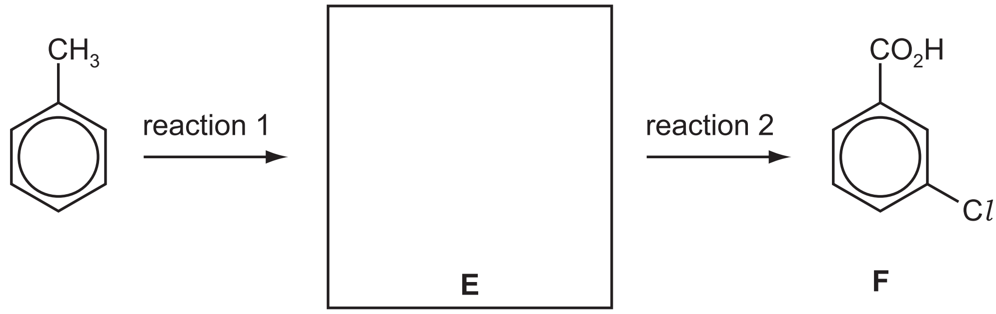
....

[3]

(d) When methylbenzene is nitrated, 4-nitromethylbenzene is formed, but when benzoic acid is nitrated, 3-nitrobenzoic acid is produced.

Consider the following synthesis of 3-chlorobenzoic acid, **F**, from methylbenzene.
Use the information given above to suggest

- the structure of the intermediate **E**,
- the reagents and conditions needed for reactions 1 and 2.



reagents and conditions for reaction 1

....

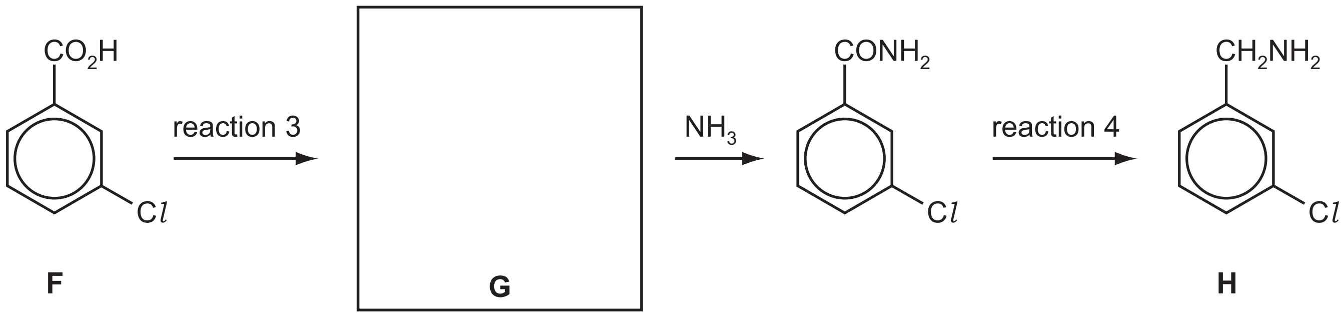
reagents and conditions for reaction 2

....

[3]

(e) Consider the following synthesis of 3-chlorophenylmethylamine, **H**, from **F**.
Suggest

- the structure of the intermediate **G**,
- the reagents for reactions 3 and 4.



reagents for reaction 3

....

reagents for reaction 4

....

[3]

[Total: 11]

5 Although now remembered for his music, the Russian composer Alexander Borodin was a chemist. He is credited with the discovery of the *aldol reaction*, a product of which is compound **J**. **J** shows the following properties:

- its molecular formula is $C_4H_8O_2$,
- it is neutral,
- it reacts with sodium metal,
- it reacts with Fehling's solution,
- it does not react with aqueous bromine.

(a) Suggest which functional groups are responsible for the reactions with

(i) sodium,

....

(ii) Fehling's solution.

....

[2]

(b) The result of the bromine test shows a functional group is absent from compound **J**. Suggest the identity of this functional group.

.... [1]

(c) In the boxes below, draw three possible **straight-chain** structures for **J** that fit the above results, and that are structural isomers of each other.

K

L

M

[3]

(d) Compound **J** reacts with alkaline aqueous iodine to give a pale yellow precipitate.

(i) Which functional group does this reaction show that **J** contains?

....

(ii) Which of your three structures **K**, **L** or **M** contains this group and is therefore **J**?

....
[2]

(e) Compound **J** exists as stereoisomers.

(i) Name the type of stereoisomerism shown by **J**.

....

(ii) Draw two structures of **J** to illustrate this stereoisomerism.

[2]

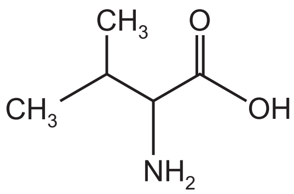
[Total: 10]

Section B

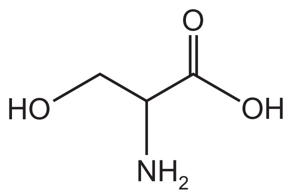
Answer **all** the questions in the spaces provided.

6 This question looks at the formation and breakdown of protein chains in the body.

(a) Proteins are formed from chains of amino acid monomers joined together.
The structures of two amino acids, valine and serine are shown.



valine (val)



serine (ser)

(i) Draw the structure of the dipeptide val-ser, showing the peptide bond in displayed form.

(ii) What *type of reaction* has taken place in order to form this dipeptide?

....

(iii) Identify the other molecule produced in this reaction.

....

[4]

(b) Both DNA and RNA are involved in protein synthesis.

Complete the table to show **three** differences between the structures of DNA and RNA.

	DNA	RNA
1		
2		
3		

[3]

(c) In protein synthesis, sections of the DNA are copied by mRNA and this, in turn, is read by the ribosome in order to assemble the amino acids for the new protein chain. Each group of three bases codes for one amino acid, with some amino acids having several codes. The codes are summarised in the table.

UUU	phe	UCU	ser	UAU	tyr	UGU	cys
UUC	phe	UCC	ser	UAC	tyr	UGC	cys
UUA	leu	UCA	ser	UAA	stop	UGA	stop
UUG	leu	UCG	ser	UAG	stop	UGG	trp
CUU	leu	CCU	pro	CAU	his	CGU	arg
CUC	leu	CCC	pro	CAC	his	CGC	arg
CUA	leu	CCA	pro	CAA	gln	CGA	arg
CUG	leu	CCG	pro	CAG	gln	CGG	arg
AUU	ile	ACU	thr	AAU	asn	AGU	ser
AUC	ile	ACC	thr	AAC	asn	AGC	ser
AUA	ile	ACA	thr	AAA	lys	AGA	arg
AUG	met/ start	ACG	thr	AAG	lys	AGG	arg
GUU	val	GCU	ala	GAU	asp	GGU	gly
GUC	val	GCC	ala	GAC	asp	GGC	gly
GUA	val	GCA	ala	GAA	glu	GGA	gly
GUG	val	GCG	ala	GAG	glu	GGG	gly

In general the amino acid chains start with the code AUG, and end with one of the three 'stop' codes shown in the table.

(i) Use the abbreviations to show the sequence of amino acids in the peptide for the base sequence shown.

– AUGCUAACACCGGAGUAA –

....

(ii) Sometimes an error can occur in the base sequence.

What are these errors called?

....

(iii) This type of error can lead to the formation of a protein with a different structure from the original, as in *sickle cell anaemia*. In this case the amino acid glutamic acid (glu) is replaced by valine (val) in the protein as a result of one base being changed in a three base code.

Use the table to suggest the change of base that causes this.

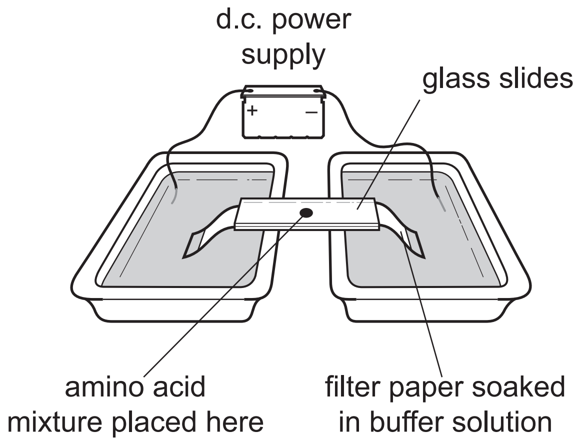
....

[3]

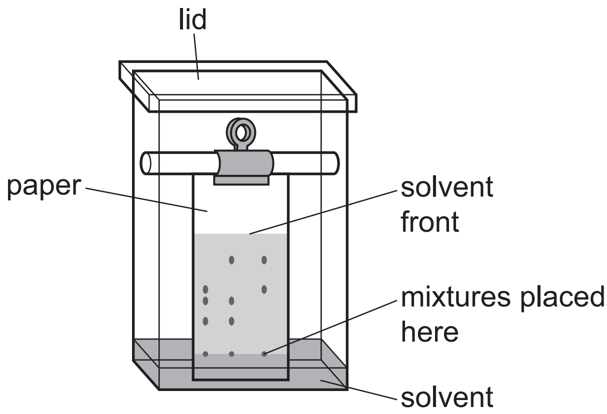
[Total: 10]

7 Modern methods of chemical analysis often rely on the interpretation of data gathered from instrumental techniques.

(a) Electrophoresis and paper chromatography can both be used to separate amino acids from a mixture obtained from polypeptides.



electrophoresis



paper chromatography

In each case, give **one** property of the amino acids that causes their separation.

electrophoresis ....

....

paper chromatography ....

.... [2]

(b) Amino acids are colourless.

How are the positions of the different amino acids made visible so that measurements can be made?

....

.... [1]

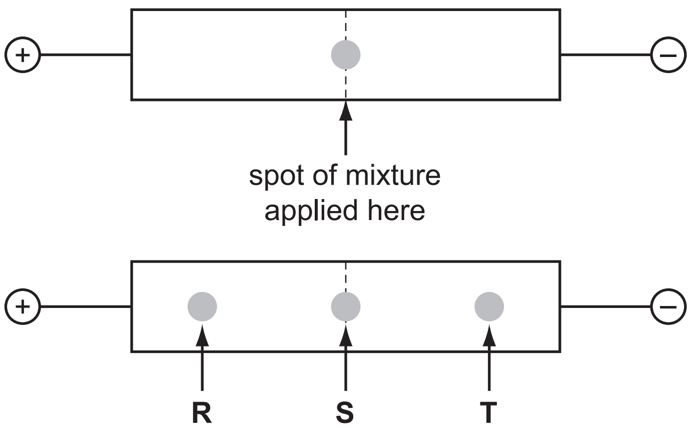
(c) Which **measurements** need to be made in order to identify individual amino acids in paper chromatography?

....

.... [1]

(d) The diagram shows the results of electrophoresis on a mixture of the amino acids glycine, lysine and glutamic acid at pH 7.0. The structures of the amino acids at pH 7.0 are shown.

glycine: $H_3N^+CH_2CO_2^-$
lysine: $H_3N^+CH(CH_2CH_2CH_2CH_2NH_3^+)CO_2^-$
glutamic acid: $H_3N^+CH(CH_2CH_2CO_2^-)CO_2^-$



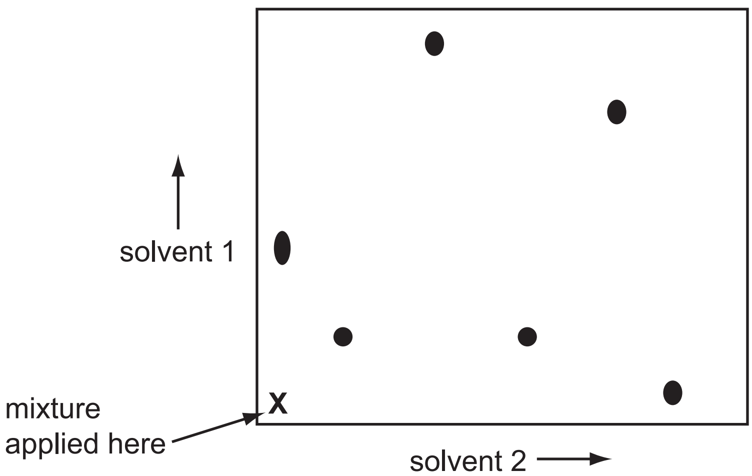
Identify the amino acids responsible for the spots labelled **R**, **S** and **T**.

R ....

S ....

T ....
[3]

(e) This diagram shows the results of two-way paper chromatography of a mixture of amino acids.



To answer these questions you need to indicate clearly on the diagram above as directed in the questions.

(i) Put a **U** next to the amino acid that travelled furthest in solvent 2.

(ii) Put a ring around the **two** amino acids that were **not** separated in solvent 1.

(iii) Put a **W** next to the amino acid that was very soluble in **both** solvents.

[3]

[Total: 10]

8 Polymers consist of monomers joined by either addition or condensation reactions.

(a) Name an example of a synthetic addition polymer and a synthetic condensation polymer.

addition polymer ....

condensation polymer ....
[2]

(b) Addition polymers are long-term pollutants in the environment but condensation polymers are often biodegradable.

(i) What *type of reaction* occurs when condensation polymers biodegrade?

....

(ii) Identify **two** functional groups that could undergo this type of reaction.

....
[2]

(c) Petroleum is a non-renewable resource from which a wide range of useful polymers is currently produced. Current polymer research is looking at renewable plant material as a potential source of monomers.

Two monomers obtained from plants are shown.

$CH_3CH(OH)COOH$ $HOCH_2COOH$

Draw the displayed formula of the repeat unit of a polymer using **both** monomers.

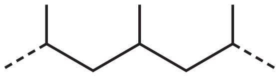
[2]

(d) Monomers obtained from plant sources do not usually form addition polymers.
Suggest why this is.

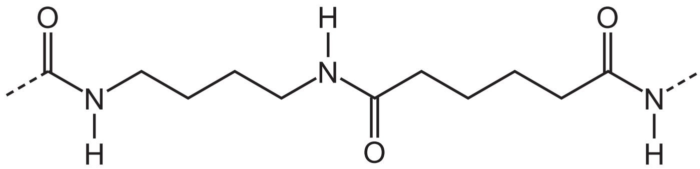
....

.... [1]

(e) The diagrams show sections of two polymers **Y** and **Z**.



Y



Z

(i) What would be the main force between the chains in each polymer?

Y ....

Z ....

(ii) Which is likely to be the more hydrophilic of these two polymers? Explain your answer.

....

....

[3]

[Total: 10]

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Cambridge International A Level

Cambridge International Examinations
Cambridge International Advanced Level

CANDIDATE NAME

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CANDIDATE NUMBER

3272601861

CHEMISTRY **9701/42**

Paper 4 Structured Questions **October/November 2014**

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.

Section A
Answer **all** questions.

Section B
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.

For Examiner's Use	
1	
2	
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8	
Total	

This document consists of **19** printed pages and **1** blank page.

IB14 11_9701_42/FP

CAMBRIDGE International Examinations

Section A

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

1 **(a)** The oxidation of nitrogen(II) oxide is shown in the equation.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The initial rate of this reaction was measured, starting with different concentrations of the two reactants. The following results were obtained.

experiment number	[NO] / $mol\,dm^{-3}$	[O_2] / $mol\,dm^{-3}$	initial rate / $mol\,dm^{-3}\,s^{-1}$
1	0.032	0.012	4.08×10^{-3}
2	0.032	0.024	8.15×10^{-3}
3	0.064	0.024	3.28×10^{-2}
4	0.096	0.036	

(i) Use the data in the table to determine the order with respect to each reactant. Show your reasoning.

....

....

....

....

(ii) Calculate the initial rate in experiment 4. Give your answer to **two** significant figures.

initial rate = ... $mol\,dm^{-3}\,s^{-1}$

(iii) Write the rate equation for this reaction.

....

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

rate constant, *k* = ... units ....

[6]

(b) **(i)** On the following axes

- draw two Boltzmann distribution curves, at two different temperatures, T_1 and T_2 ($T_2 > T_1$),
- label the curves and the axes.

(ii) State and explain, using your diagram, the effect of increasing temperature on the rate of reaction.

....

....

....

[5]

(c) The compound nitrosyl fluoride, NOF, can be formed by the following reaction.

$$2NO(g) + F_2(g) \rightleftharpoons 2NOF(g)$$

The rate is first order with respect to NO and F_2.
The reaction mechanism has **two** steps.

Suggest equations for the two steps of this mechanism, stating which is the rate determining slower step.

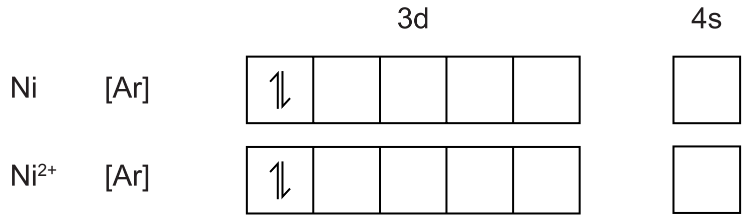
....

....

.... [2]

[Total: 13]

2 **(a)** Complete the electron configurations for Ni and Ni^{2+}.



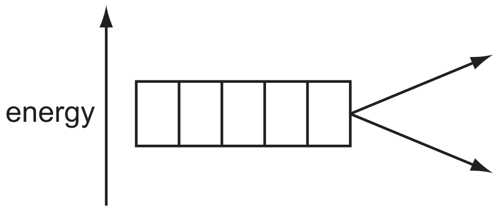
[2]

(b) The presence of electrons in d orbitals is responsible for the colours of transition element compounds.

(i) The d orbitals in an isolated transition metal atom or ion are all at the same energy level. What term is used to describe orbitals that are at the same energy level?

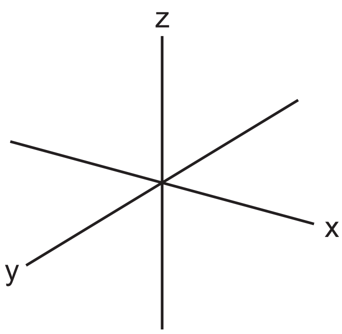
....

(ii) Complete the diagram to show the splitting of the d orbital energy levels in an octahedral complex ion.

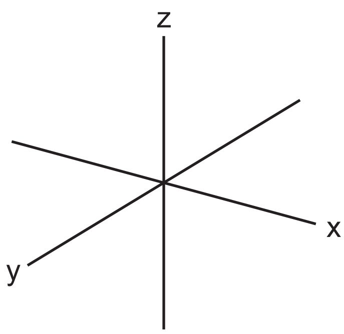


(iii) On the axes below, sketch the shapes of one d orbital from the lower energy level and one d orbital from the higher energy level.

lower energy level



higher energy level



[4]

(c) The octahedral complex $[Ni(H_2O)_6]^{2+}$ is green. Explain the origin of the colour of this complex.

....

....

....

....

.... [3]

(d) When $NH_3(aq)$ is added to the green solution containing $[Ni(H_2O)_6]^{2+}$, a grey-green precipitate, **A**, is formed. This precipitate dissolves in an excess of $NH_3(aq)$ to give a blue-violet solution, **B**. Suggest formulae for **A** and **B** and write equations for the two reactions producing **A** and **B**.

....

....

....

.... [4]

[Total: 13]

3 **(a)** Natural phosphorus consists of one isotope, ^{31}P. Chlorine exists naturally as two isotopes, ^{35}Cl and ^{37}Cl, in the relative abundance ratio of 3 : 1.

(i) The mass spectrum of PCl_3 contains several peaks corresponding to a number of molecular fragments.

Suggest the isotopic composition of the fragments with the following mass numbers.

mass number	isotopic composition
101	
103	
105	

(ii) Predict the relative ratios of the peak heights of the three peaks corresponding to these fragments.

....

[4]

(b) Phosphorus reacts with chlorine to form a variety of chlorides.
PCl_5 is an example of a compound that exists as two structures depending on the conditions.

$$2PCl_5(g) \rightleftharpoons [PCl_4]^+[PCl_6]^-(s)$$

(i) Draw a 'dot-and-cross' diagram to show the bonding in PCl_5. Show the outer electrons only.

(ii) Draw diagrams to suggest the shapes of $[PCl_4]^+$ and $[PCl_6]^-$.

$[PCl_4]^+$ $[PCl_6]^-$

[3]

(c) **(i)** Phosphorus(III) oxide, P_4O_6, contains no P–P or O–O bonds.
In the P_4O_6 molecule, all oxygen atoms are divalent and all phosphorus atoms are trivalent.

Sketch a structure for P_4O_6.

(ii) P_4O_6 can act as a ligand.

What is meant by the term *ligand*?

....

....
[2]

(d) Phosphate ions in water can be removed by adding a solution containing $Ca^{2+}(aq)$ ions, which form a precipitate of calcium phosphate, $Ca_3(PO_4)_2$.

(i) Write an expression for the K_{sp} of $Ca_3(PO_4)_2$.

K_{sp} =

(ii) The solubility of $Ca_3(PO_4)_2$ is $2.50 \times 10^{-6}\,mol\,dm^{-3}$ at 298 K.

Calculate the solubility product, K_{sp}, of $Ca_3(PO_4)_2$ at this temperature. Include the units.

K_{sp} = ... units ....
[4]

  [Turn over

(e) (i) What is meant by the term *lattice energy*?

....

....

(ii) Explain why the lattice energy of calcium phosphate is **less** exothermic than that of magnesium phosphate.

....

....

[3]

[Total: 16]

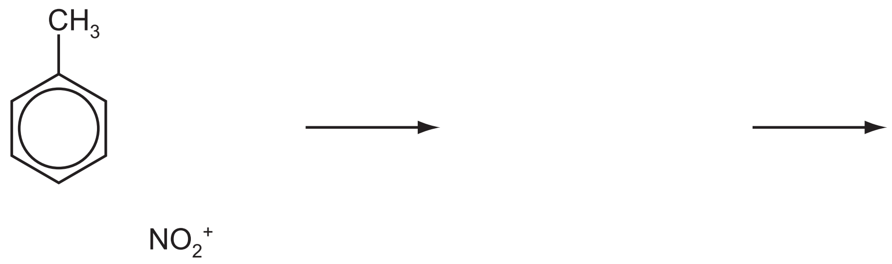
Question 4 starts on the next page.

4 **(a)** Methylbenzene undergoes electrophilic substitution with nitronium ions, NO_2^+.
Nitronium ions are generated by the reaction between concentrated sulfuric acid and concentrated nitric acid.

(i) Construct an equation for the formation of nitronium ions, NO_2^+, by this method.

....

(ii) Complete the scheme to show the mechanism for this reaction. Use curly arrows to show the movement of electron pairs.



[4]

(b) **(i)** Describe and explain the relative acidities of chloroethanoic acid and ethanoic acid.

....

....

....

(ii) Describe and explain the relative acidities of phenol and ethanol.

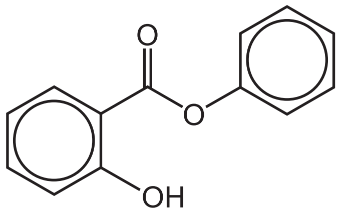
....

....

....

[3]

(c) Phenyl 2-hydroxybenzoate is an antiseptic.



phenyl 2-hydroxybenzoate

Complete the following table about the reactions of phenyl 2-hydroxybenzoate with the three reagents.

reagent	structure of product(s)		type of reaction
Na			
excess $Br_2(aq)$			
excess hot NaOH(aq)			

[6]

[Total: 13]

5 **(a)** Organohalogen compounds can undergo hydrolysis.

$$R\text{–}Cl + H_2O \rightarrow R\text{–}OH + HCl$$

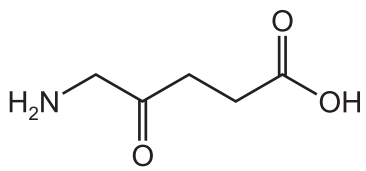
State the relative rates of hydrolysis of the following compounds.

$$CH_3CH_2CH_2Cl \qquad CH_3CH_2COCl \qquad C_6H_5Cl$$

Explain your answer.

[3]

(b) Aminolaevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.



aminolaevulinic acid

Name the **three** functional groups in aminolaevulinic acid.

[2]

(c) Aminolaevulinic acid reacts readily with bromoethane.

(i) Show the mechanism of the **first step** of this reaction on the diagram. Include all necessary curly arrows, lone pairs and relevant dipoles.

$H_3C—CH_2—Br$

(ii) Name the mechanism in **(c)(i)**.

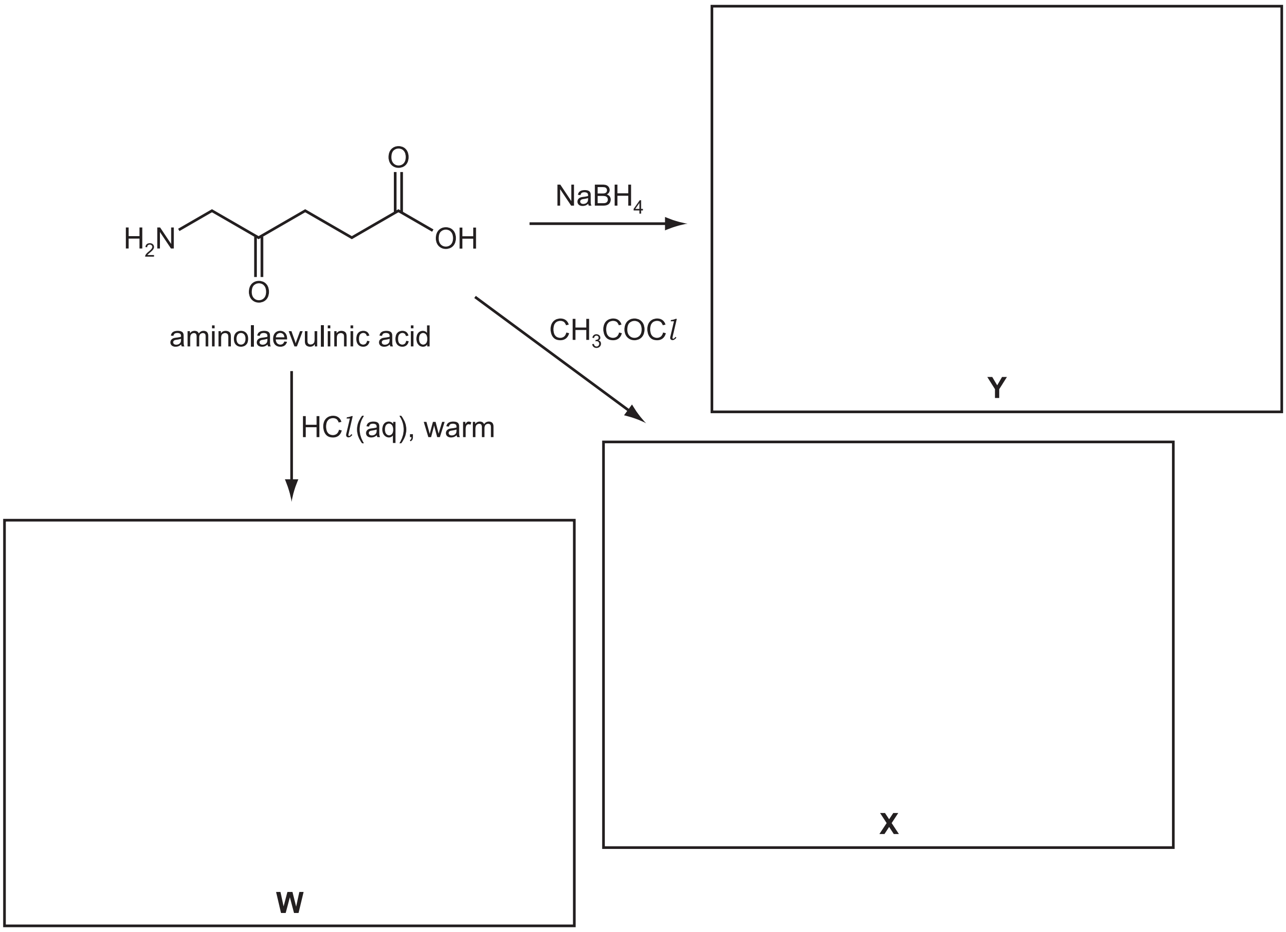
....

(iii) Identify the non-organic product formed in this reaction.

....

[5]

(d) Three reactions of aminolaevulinic acid are shown. Draw the structures of the products **W**, **X** and **Y** in the boxes below.



[3]

(e) Aminolaevulinic acid can undergo polymerisation.

Draw the structure of the polymer showing **two** repeat units. The linkages between the monomer units should be shown fully displayed.

[2]

[Total: 15]

Section B

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

6 **(a)** A mixture of amino acids can be separated by electrophoresis. During an electrophoresis experiment,

- different amino acids move in different directions,
- different amino acids move at different speeds,
- some amino acids do not move at all.

Explain these observations.

....

....

....

.... [3]

(b) **(i)** A mixture of amino acids can also be separated by thin-layer chromatography. Identify the mobile and the stationary phases in this type of chromatography.

mobile phase ....

stationary phase ....

(ii) What is the process by which thin-layer chromatography can separate a mixture?

....
[3]

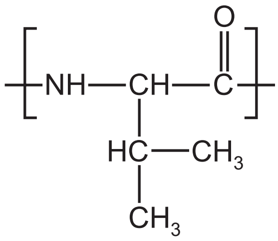
(c) State **three** structural features of DNA.

....

....

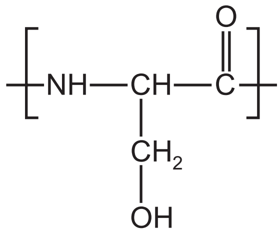
.... [3]

(d) Some diseases are caused by a mutation in the DNA base sequence which results in one amino acid being replaced by another during protein synthesis.
Suggest what changes in the interactions that form the tertiary structure would result from a mutation that replaced a valine residue with a serine residue.



val

replaced by



ser

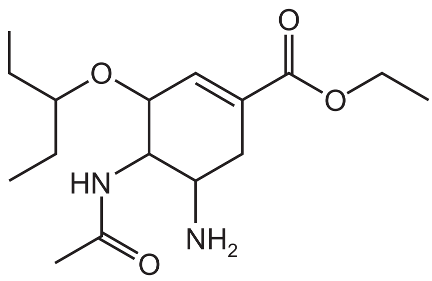
....

....

.... [2]

[Total: 11]

7 (a) Oseltamivir is an antiviral drug that slows the spread of the influenza (flu) virus.



oseltamivir

Circle **two** bonds, each in a different functional group, that could be easily hydrolysed in the body. [2]

(b) Oseltamivir is a chiral drug. This drug is usually taken as a single optical isomer rather than as a mixture of isomers.

Suggest **one** benefit of taking a drug in this way.

....

.... [1]

(c) Oseltamivir is a competitive inhibitor of an enzyme produced by the flu virus.

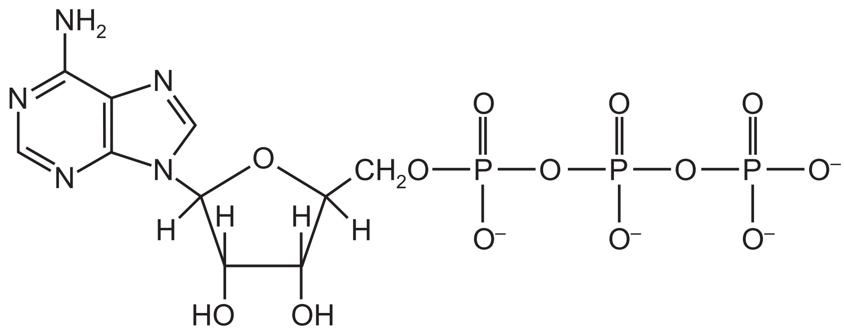
Explain the meaning of the term *competitive inhibitor* and state how its action could be overcome.

....

....

.... [3]

(d) ATP plays an important role in metabolic reactions in living organisms.



ATP

What is the function of ATP in living organisms?

....

.... [1]

[Total: 7]

8 **T** is a saturated alcohol. It was analysed by mass spectroscopy and NMR spectroscopy.
In the mass spectrum, the molecular ion peak, M, was at an m/e value of 74 and the ratio of the heights of the M and M+1 peaks was 20.4 : 0.9.

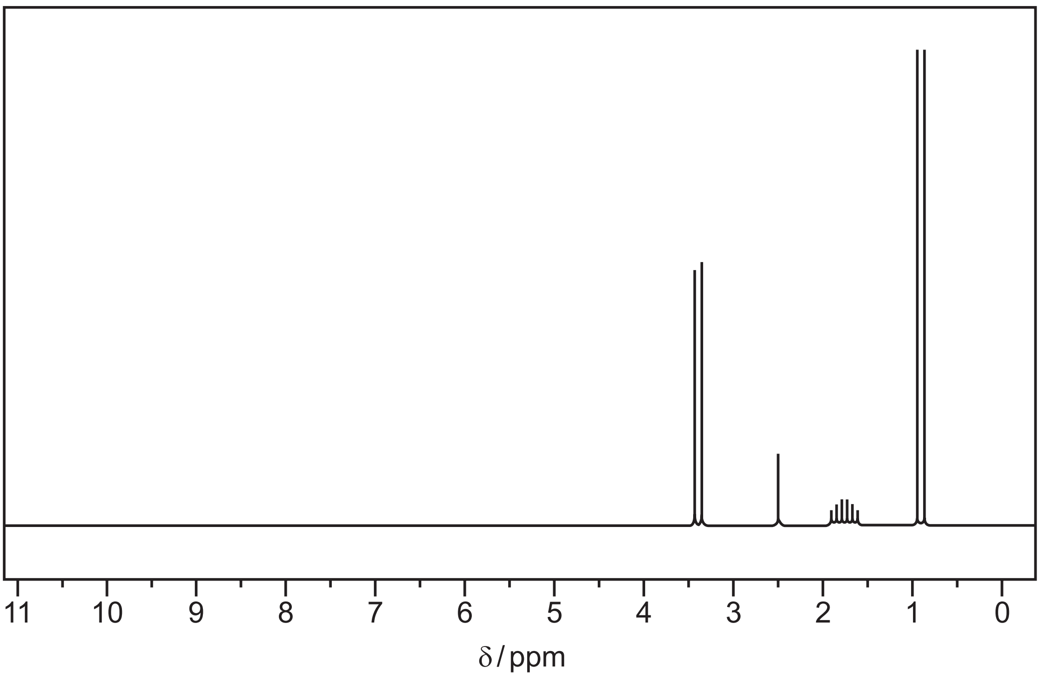
(a) **(i)** Use the ratio of the heights of the M and M+1 peaks to calculate the number of carbon atoms in a molecule of **T**.

(ii) What is the molecular formula of **T**?

molecular formula = ...

[3]

(b) The NMR spectrum of **T** given below shows four absorptions. The absorption at 1.8 ppm is a multiplet and that at 2.5 ppm is a singlet.



(i) Use this information and your answer to **(a)(ii)** to deduce the structure of **T**.

T

(ii) Describe and explain which type of proton is responsible for each of the absorptions.

....

....

....

....

(iii) The absorption at 1.8 ppm is a multiplet and that at 2.5 is a singlet.
State and explain the splitting patterns of the other absorptions, at 0.9 and 3.4 ppm.

....

....

....

(iv) Describe and explain how the NMR spectrum of **T** dissolved in D_2O would differ from the one shown.

....

....

....
[9]

[Total: 12]

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UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CANDIDATE NAME	

CENTRE NUMBER						CANDIDATE NUMBER					

CHEMISTRY **9701/42**

Paper 4 Structured Questions **May/June 2013**

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 a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Section A
Answer **all** questions.

Section B
Answer **all** questions.

You may lose marks if you do not show your working or if you do not use appropriate units.
A Data Booklet is provided.
Electronic calculators may be used.

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.

For Examiner's Use	
1	
2	
3	
4	
5	
6	
7	
8	
Total	

This document consists of **16** printed pages and **4** blank pages.

UNIVERSITY *of* CAMBRIDGE
International Examinations

Section A

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

1 A bromoalkane, R–Br, is hydrolysed by aqueous sodium hydroxide.

(a) **(i)** Write a balanced equation for this reaction.

....

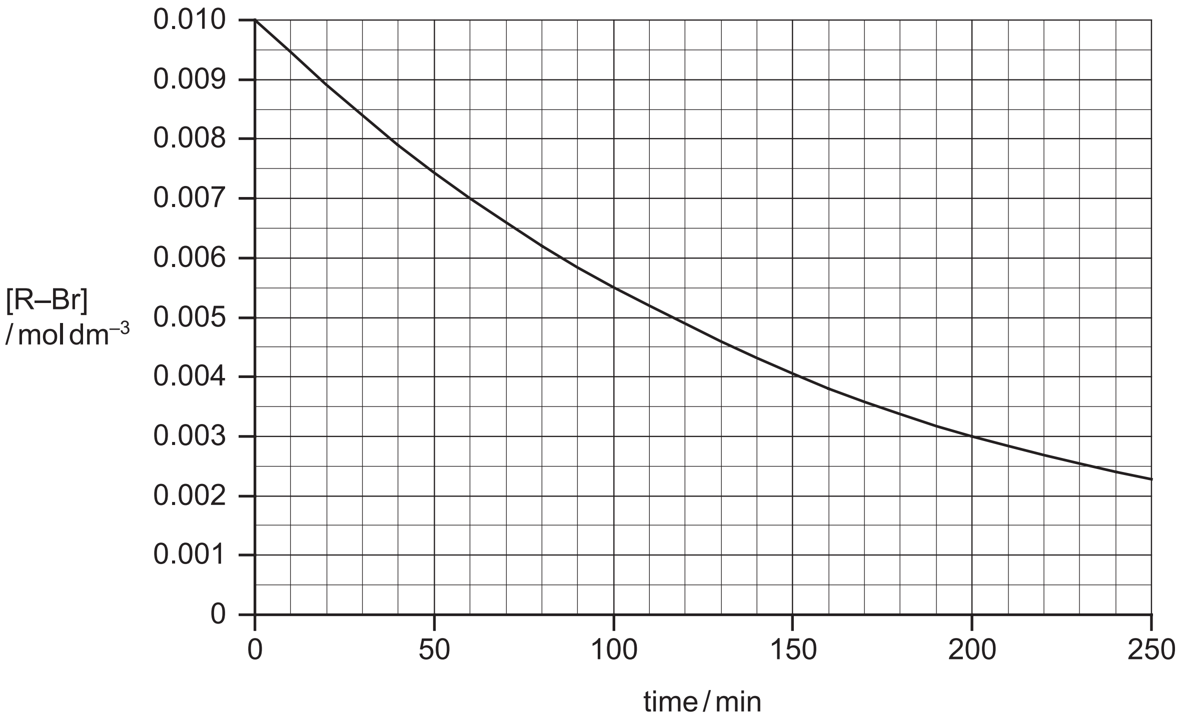
(ii) What *type of reaction* is this?

....

[2]

(b) The concentration of bromoalkane was determined at regular time intervals as the reaction progressed.

Two separate experiments were carried out, with different NaOH concentrations. The graph below shows the results of an experiment using [NaOH] = 0.10 mol dm^{-3}.



When the experiment was repeated using [NaOH] = 0.15 mol dm^{-3}, the following results were obtained.

time / min	[R–Br] / mol dm^{-3}
0	0.0100
40	0.0070
80	0.0049
120	0.0034
160	0.0024
200	0.0017
240	0.0012

(i) Plot these data on the axes above, and draw a line of best fit.

For Examiner's Use

(ii) Use one of the graphs to confirm that the reaction is first order with respect to R–Br. Show all your working, and show clearly any construction lines you draw.

(iii) Use the graphs to calculate the order of reaction with respect to NaOH. Show all your working, and show clearly any construction lines you draw on the graphs.

(iv) Write the rate equation for this reaction, and calculate the value of the rate constant.

rate =

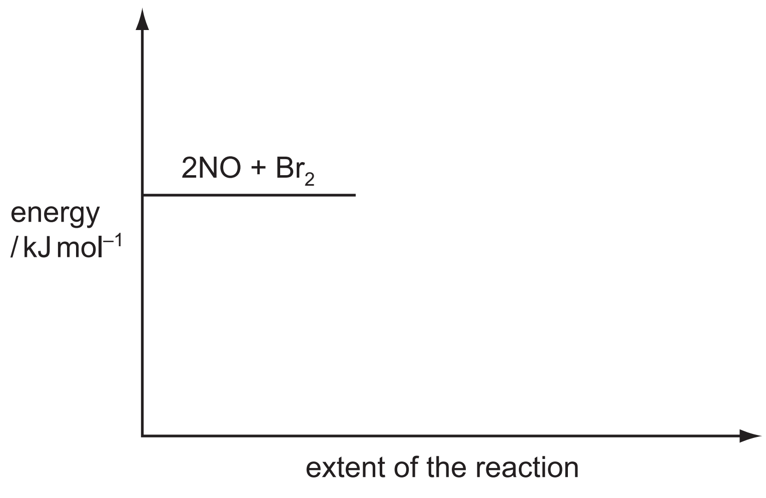
[7]

(c) Nitric oxide, NO, and bromine vapour react together according to the following equation.

$$2NO(g) + Br_2(g) \rightarrow 2NOBr(g) \qquad \Delta H = -23\,kJ\,mol^{-1}$$

The reaction has an activation energy of $+5.4\,kJ\,mol^{-1}$.

Use the following axes to sketch a fully-labelled reaction pathway diagram for this reaction.
Include all numerical data on your diagram.



[2]

[Total: 11]

For Examiner's Use

2 **(a)** **(i)** With the aid of a fully-labelled diagram, describe the standard hydrogen electrode.

(ii) Use the *Data Booklet* to calculate the standard cell potential for the reaction between Cr^{2+} ions and $Cr_2O_7^{2-}$ ions in acid solution, and construct a balanced equation for the reaction.

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

equation ....

(iii) Describe what you would see if a blue solution of Cr^{2+} ions was added to an acidified solution of $Cr_2O_7^{2-}$ ions until reaction was complete.

....

....

[8]

For Examiner's Use

(b) A buffer solution is to be made using 1.00 mol dm^{-3} ethanoic acid, CH_3CO_2H, and 1.00 mol dm^{-3} sodium ethanoate, CH_3CO_2Na.
Calculate to the nearest 1 cm^3 the volumes of each solution that would be required to make 100 cm^3 of a buffer solution with pH 5.50.
Clearly show all steps in your working.
K_a (CH_3CO_2H) = 1.79 × 10^{-5} mol dm^{-3}

volume of 1.00 mol dm^{-3} CH_3CO_2H = ... cm^3

volume of 1.00 mol dm^{-3} CH_3CO_2Na = ... cm^3

[4]

(c) Write an equation to show the reaction of this buffer solution with each of the following.

(i) added HCl ....

(ii) added NaOH ....

[2]

(d) Choose **one** reaction in organic chemistry that is catalysed by an acid, and write the structural formulae of the reactants and products in the boxes below.

$$\boxed{} \xrightarrow{H^+} \boxed{}$$

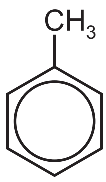
[3]

[Total: 17]

For Examiner's Use

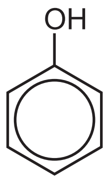
3 **(a)** Describe the reagents and conditions required to form a nitro compound from the following.

(i) methylbenzene



....

(ii) phenol



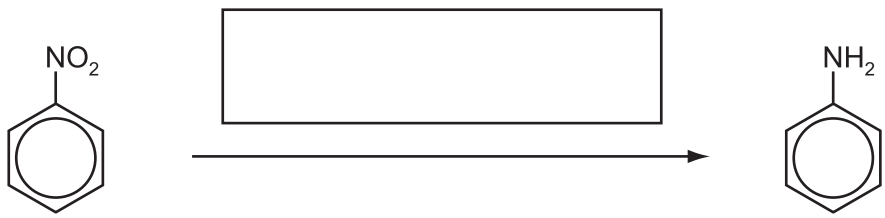
....

[3]

(b) Draw the structure of the intermediate organic ion formed during the nitration of benzene.

[1]

(c) In the box over the arrow below, write the reagents needed to convert nitrobenzene into phenylamine.



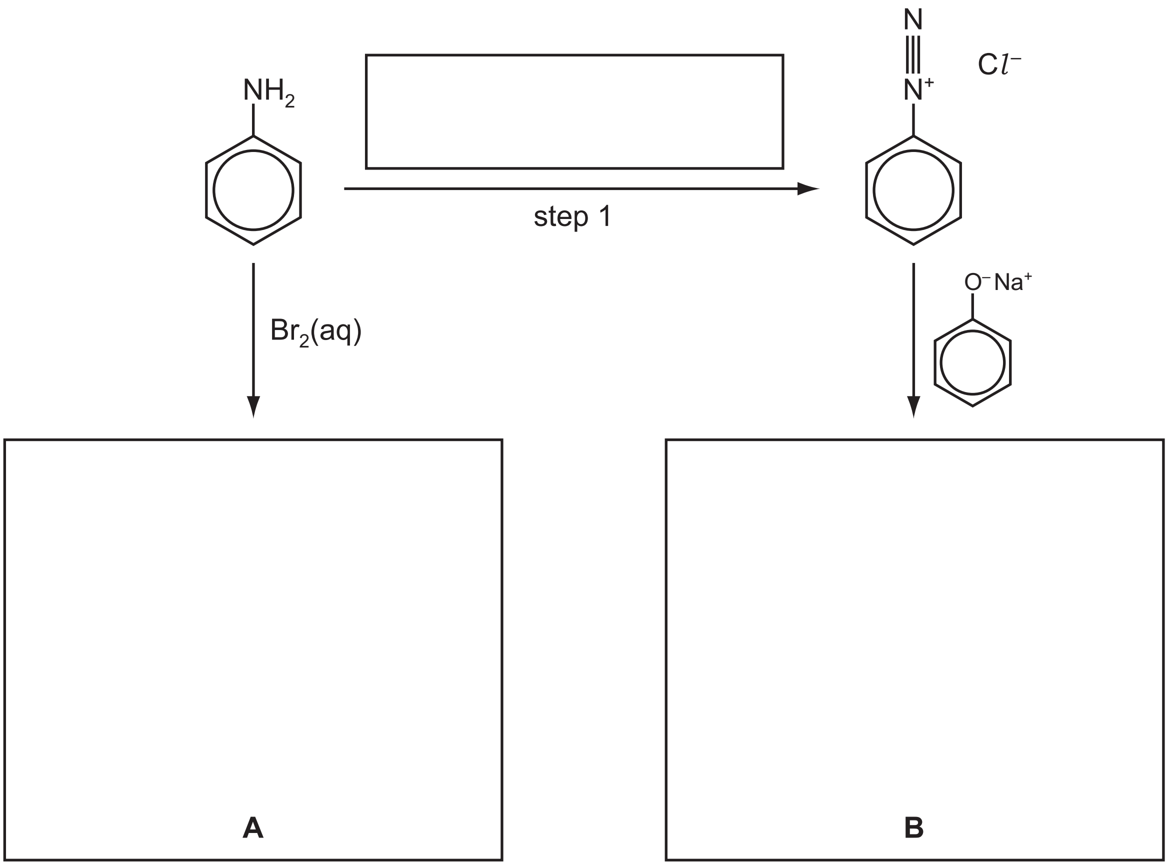
[1]

For Examiner's Use

(d) Phenylamine can be converted into the organic compounds **A** and **B**.

(i) Suggest the structural formulae of **A** and **B** in the boxes below.

(ii) Suggest suitable reagents and conditions for step 1, and write them in the box over the arrow.



[3]

(e) When phenylamine is treated with propanoyl chloride a white crystalline compound, **C**, $C_9H_{11}NO$, is formed.

(i) Name the functional group formed in this reaction. ....

(ii) Calculate the percentage by mass of nitrogen in **C**.

percentage = ... %

(iii) Draw the structural formula of **C**.

[3]

[Total: 11]

For Examiner's Use

4 **(a)** **(i)** Suggest why transition elements show variable oxidation states in their compounds whereas s-block elements like calcium do not.

....

....

(ii) Calculate the oxidation number of the metal in each of the following ions.

VO_2^{+} ....

CrF_6^{2-} ....

MnO_4^{2-} ....

[4]

(b) Explain why transition element complexes are often coloured whereas compounds of s-block elements such as calcium and sodium are not.

....

....

....

....

....

....

[4]

(c) SO_2 and MnO_4^{-} react together in acidic solution.

(i) Use the *Data Booklet* to construct a balanced equation for this reaction.

....

(ii) Describe the colour change you would see when SO_2(aq) is added to a sample of acidified $KMnO_4$ until the SO_2 is in excess.

from .... to ....

[3]

(d) Describe the observations you would make when NH_3(aq) is added gradually to a solution containing Cu^{2+} ions, until the NH_3 is in an excess.

....

....

....

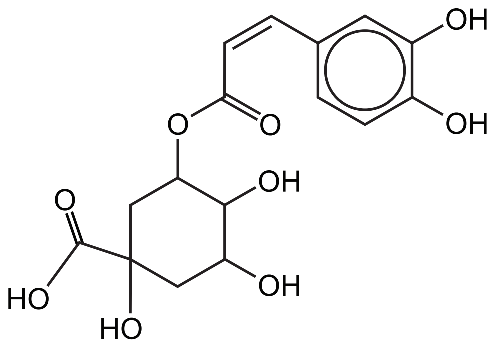
....

[3]

[Total: 14]

For Examiner's Use

5 Coffee beans contain chlorogenic acid.



chlorogenic acid

(a) (i) Draw circles around any chiral centres in the above structure.

(ii) Write down the molecular formula of chlorogenic acid.

....

(iii) How many moles of $H_2(g)$ will be evolved when 1 mol of chlorogenic acid reacts with an excess of sodium metal?

....

(iv) How many moles of NaOH(aq) will react with 1 mol of chlorogenic acid under each of the following conditions?

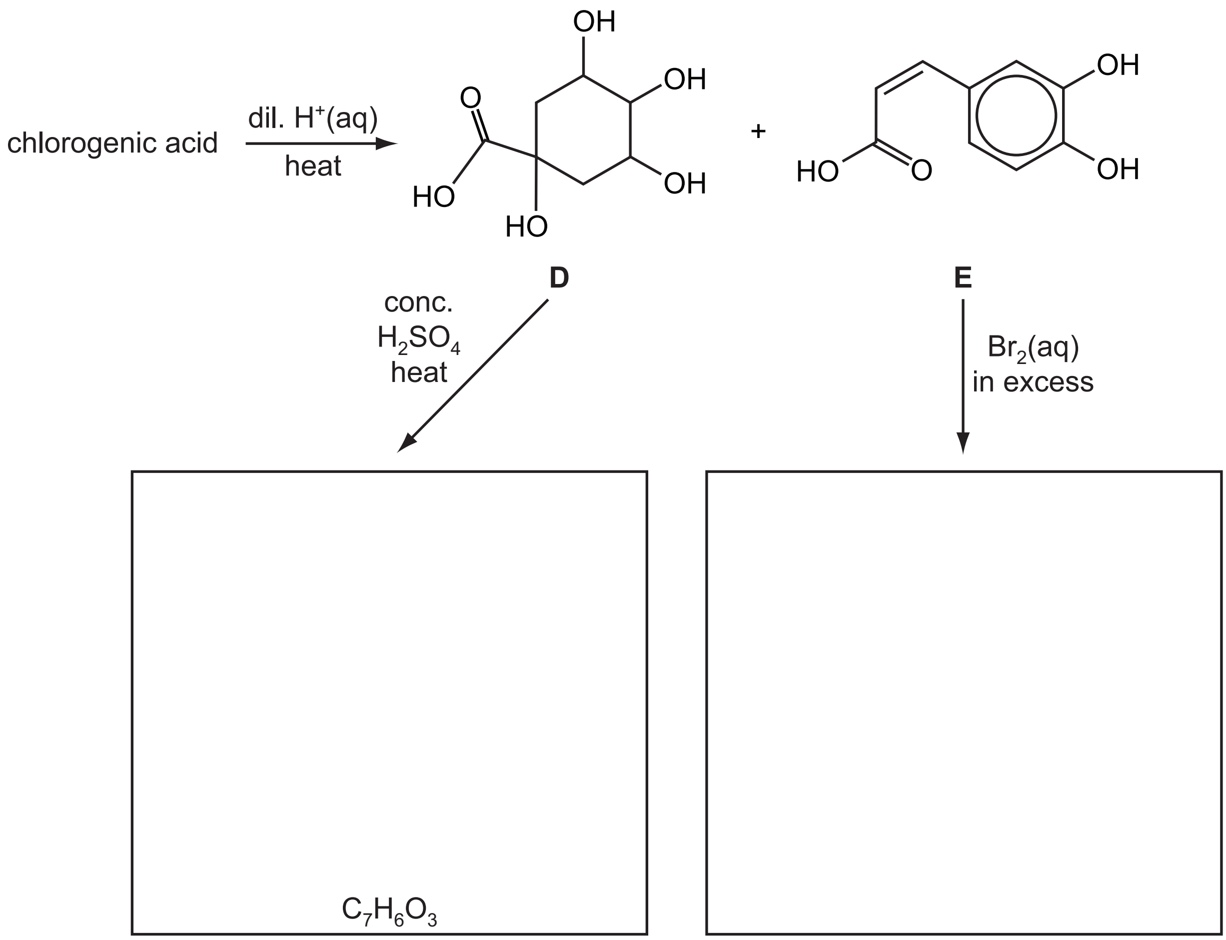
in the cold ....

on heating ....

[6]

For Examiner's Use

(b) On heating with dilute aqueous acid, chlorogenic acid produces two compounds, **D** and **E**.



F **G**

(i) What *type of reaction* is chlorogenic acid undergoing when **D** and **E** are formed?

....

When compound **D** is heated with concentrated H_2SO_4, compound **F**, $C_7H_6O_3$, is formed.

Compound **F** evolves CO_2(g) when treated with Na_2CO_3(aq), and decolourises Br_2(aq), giving a white precipitate. It does not, however, decolourise cold dilute acidified $KMnO_4$.

When compound **E** is treated with an excess of Br_2(aq), compound **G** is produced.

(ii) If the test with cold dilute acidified $KMnO_4$ had been positive, which functional group would this have shown to be present in **F**?

....

(iii) **Name** the functional groups in compound **F** that would react with the following.

Na_2CO_3(aq) .... Br_2(aq) ....

(iv) Suggest structures for compounds **F** and **G** and draw them in the relevant boxes above.

For Examiner's Use

(v) Compound **E** is one of a pair of stereoisomers.

What type of stereoisomerism is shown by compound **E**?

....

(vi) Draw the structure of the other stereoisomer in the box below.

[8]

(c) Calculate the volume of 0.1 $mol\,dm^{-3}$ NaOH that is needed to react completely with 0.1 g of compound **E**.

volume = ... cm^3
[3]

[Total: 17]

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For Examiner's Use

Section B

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

6 There are two important polymerisations that occur within living organisms – protein synthesis and the formation of DNA.

(a) Complete the table by placing a tick (✓) in the correct column to indicate in which process each substance could be used.

substance	protein synthesis	formation of DNA
cysteine		
cytosine		
glutamine		
guanine		

[3]

(b) DNA consists of a double helical structure.

(i) Describe the bonding between the two strands in DNA and state which part of each strand is joined by it.

....

....

(ii) How does the strength of this bonding relate to the mechanism of the replication of DNA?

....

....

[4]

(c) Some diseases are caused by changes in the structure of proteins. Explain the genetic basis of these changes.

....

....

....

....

[3]

[Total: 10]

For Examiner's Use

7 The techniques of mass spectrometry and NMR spectroscopy are useful in determining the structures of organic compounds.

(a) The three peaks of highest mass in the mass spectrum of organic compound **L** correspond to masses of 142, 143 and 144.
The ratio of the heights of the M : M+1 peaks is 43.3 : 3.35, and the ratio of heights of the M : M+2 peaks is 43.3 : 14.1.

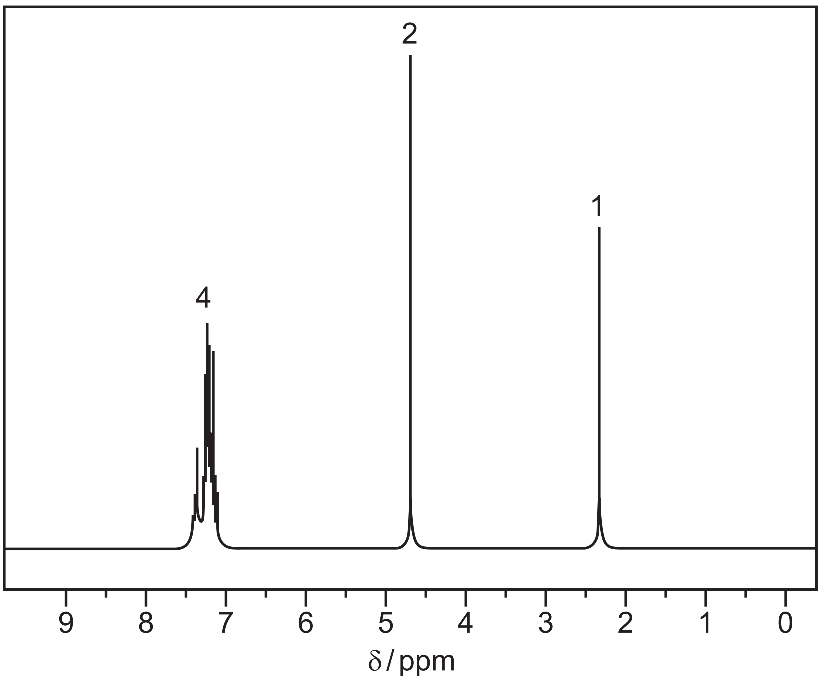
(i) Use the data to calculate the number of carbon atoms present in **L**.

(ii) Explain what element is indicated by the M+2 peak.

....

....

Compound **L** reacts with sodium metal. The NMR spectrum of compound **L** is given below.



(iii) What does the NMR spectrum tell you about the number of protons in **L** and their chemical environments?

....

....

For Examiner's Use

(iv) Use the information given and your answers to **(i)**, **(ii)** and **(iii)** to deduce a structure for **L**.
Explain how you arrive at your answer.

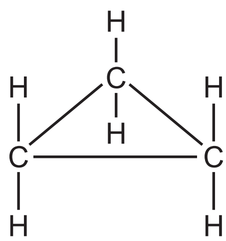
structure of **L**

[7]

(b) The molecular formula C_3H_6 represents the compounds propene and cyclopropane.

$CH_3CH{=}CH_2$

propene



cyclopropane

(i) Suggest **one** difference in the fragmentation patterns of the mass spectra of these compounds.

....

....

(ii) Suggest **two** differences in the NMR spectra of these compounds.

....

....

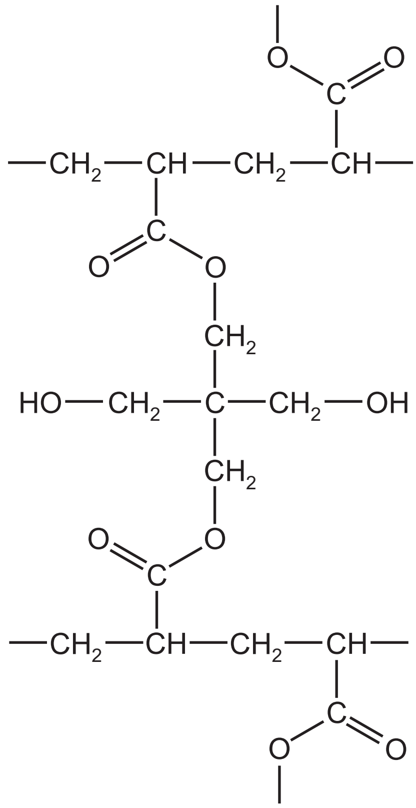
....

[3]

[Total: 10]

8 In recent years there has been considerable interest in a range of polymers known as 'hydrogels'. These polymers are hydrophilic and can absorb large quantities of water.

(a) The diagram shows part of the structure of a hydrogel.



The hydrogel is formed from chains of one polymer which are cross-linked using another molecule.

(i) Draw the structure of the monomer used in the polymer chains.

(ii) State the type of polymerisation used to form these chains.

....

....

(iii) Draw the structure of the molecule used to cross-link the polymer chains.

For Examiner's Use

(iv) During the cross-linking, a small molecule is formed as a by-product. Identify this molecule.

....

[5]

(b) Once a hydrogel has absorbed water, it can be dried and re-used many times. Explain why this is possible, referring to the structure on the opposite page.

....

....

....

[2]

(c) Not every available side chain in the polymer is cross-linked, and the amount of cross-linking affects the properties of the hydrogel.

(i) The amount of cross-linking has little effect on the ability of the gel to absorb water. Suggest why this is the case.

....

....

....

(ii) Suggest **one** property of the hydrogel that will change if more cross-linking takes place. Explain how the increased cross-linking brings about this change.

....

....

....

[3]

[Total: 10]

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UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CANDIDATE NAME	

CENTRE NUMBER							CANDIDATE NUMBER					

5507470235

CHEMISTRY **9701/42**

Paper 4 Structured Questions **October/November 2013**

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.
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Section A
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Section B
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For Examiner's Use	
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UNIVERSITY of CAMBRIDGE International Examinations

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For Examiner's Use

Section A

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

1 **(a)** Gaseous ammonia reacts with gaseous hydrogen chloride to form solid ammonium chloride.

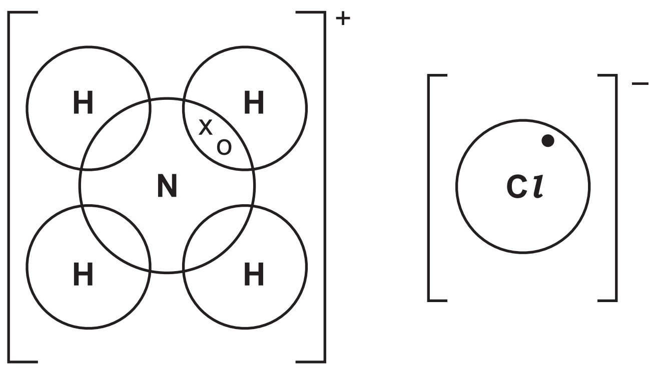
$$NH_3 + HCl \rightarrow NH_4Cl$$

The bonding in ammonium chloride includes ionic, covalent and co-ordinate (dative covalent) bonds.

Complete the following 'dot-and-cross' diagram of the bonding in ammonium chloride. For **each** of the six atoms show **all** the electrons in its outer shell. Three electrons have already been included.

Use the following code for your electrons.

● electrons from chlorine
x electrons from hydrogen
o electrons from nitrogen



[3]

(b) When a sample of dry ammonia is needed in the laboratory, the gas is passed through a tower containing lumps of solid calcium oxide, CaO.

(i) Suggest why the usual drying agent for gases, concentrated H_2SO_4, is **not** used for ammonia.

....

(ii) Write an equation for the reaction between CaO and H_2O.

....

(iii) Suggest why CaO rather than MgO is used to dry ammonia.

....

[3]

For Examiner's Use

(c) (i) Write an equation showing the thermal decomposition of calcium nitrate, $Ca(NO_3)_2$.

....

(ii) State and explain how the thermal stabilities of the nitrates vary down Group II.

....

....

....

....

[4]

[Total: 10]

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For Examiner's Use

2 **(a)** The melting points of some Group IV elements are given below.

element	melting point / K
C	3925
Si	1683
Ge	1210
Sn	505

Suggest an explanation for each of the following.

(i) The melting point of silicon is less than that of carbon.

....

....

(ii) The melting point of tin is less than that of germanium.

....

....
[2]

(b) Using data from the *Data Booklet* where appropriate, write equations for the following reactions of compounds of Group IV elements.

(i) $SiCl_4(l) + H_2O(l)$

....

(ii) the action of heat on $PbCl_4(l)$

....

(iii) $SnCl_2(aq) + FeCl_3(aq)$

....

(iv) $SnO_2(s) + NaOH(aq)$

....
[4]

[Total: 6]

For Examiner's Use

3 **(a) (i)** Using the symbol **HZ** to represent a Brønsted-Lowry acid, write equations which show the following substances acting as Brønsted-Lowry bases.

NH_3 + $\rightarrow$

CH_3OH + $\rightarrow$

(ii) Using the symbol **B⁻** to represent a Brønsted-Lowry base, write equations which show the following substances acting as Brønsted-Lowry acids.

NH_3 + $\rightarrow$

CH_3OH + $\rightarrow$

[4]

(b) State briefly what is meant by the following terms.

(i) reversible reaction

....

(ii) dynamic equilibrium

....

....

[2]

(c) (i) Explain what is meant by a *buffer solution*.

....

....

....

(ii) Explain how the working of a buffer solution relies on a reversible reaction involving a Brønsted-Lowry acid such as **HZ** and a Brønsted-Lowry base such as **Z⁻**.

....

....

....

....

[4]

For Examiner's Use

(d) Propanoic acid, $CH_3CH_2CO_2H$, is a weak acid with $K_a = 1.34 \times 10^{-5}$ mol dm^{-3}.

(i) Calculate the pH of a 0.500 mol dm^{-3} solution of propanoic acid.

Buffer solution **F** was prepared by adding 0.0300 mol of sodium hydroxide to 100 cm^3 of a 0.500 mol dm^{-3} solution of propanoic acid.

(ii) Write an equation for the reaction between sodium hydroxide and propanoic acid.

....

(iii) Calculate the concentrations of propanoic acid and sodium propanoate in buffer solution **F**.

[propanoic acid] = ... mol dm^{-3}

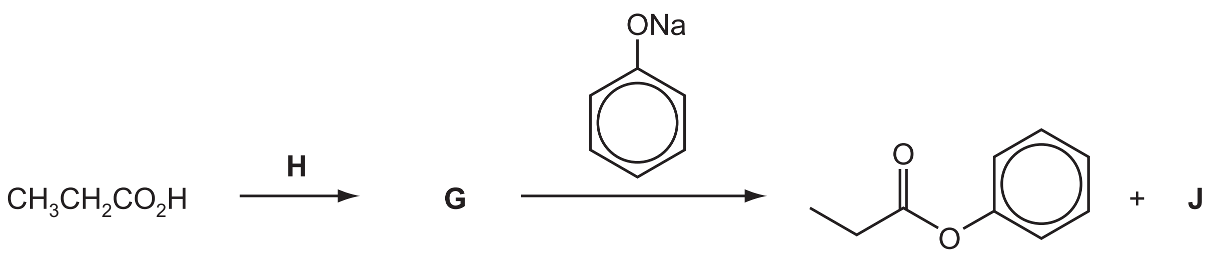
[sodium propanoate] = ... mol dm^{-3}

(iv) Calculate the pH of buffer solution **F**.

pH = ...

[6]

(e) Phenyl propanoate cannot be made directly from propanoic acid and phenol.
Suggest the identities of the intermediate **G**, the reagent **H** and the by-product **J** in the following reaction scheme.



G is ....

H is ....

J is ....

[2]

[Total: 18]

For Examiner's Use

4 (a) Explain what is meant by the term *bond energy*.

[2]

(b) (i) Describe and explain the trend in bond energies of the C–X bond in halogenoalkanes, where X = F, C*l*, Br or I.

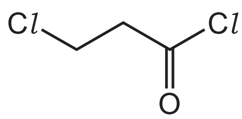
(ii) Describe the relationship between the reactivity of halogenoalkanes, RX, and the bond energies of the C–X bond.

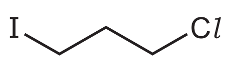
[3]

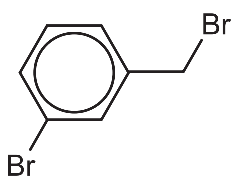
(c) Use the *Data Booklet* to suggest an explanation as to why CFCs such as CF_2Cl_2 are much more harmful to the ozone layer than fluorocarbons such as CF_4 or hydrocarbons such as butane, C_4H_{10}.

[3]

(d) Predict the products of the following reactions and draw their structures in the boxes below. The molecular formula of each product is given, where X = C*l*, Br or I.

H_2O +  ⟶ $C_3H_5O_2X$

H_2O +  ⟶ C_3H_7OX

H_2O +  ⟶ C_7H_7OX

[3]

For Examiner's Use

(e) Ethane reacts with chlorine according to the following equation.

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

(i) State the conditions needed for this reaction.

....

(ii) State the *type of reaction* occurring here.

....

One of the steps during this reaction is the following process.

$$Cl^\bullet + CH_3CH_3 \rightarrow HCl + CH_3CH_2^\bullet$$

(iii) Use the *Data Booklet* to calculate the enthalpy change, ΔH, of this step.

ΔH = ... kJ mol^{-1}

(iv) Use the *Data Booklet* to calculate the enthalpy change, ΔH, of the similar reaction:

$$I^\bullet + CH_3CH_3 \rightarrow HI + CH_3CH_2^\bullet$$

ΔH = ... kJ mol^{-1}

(v) Hence suggest why it is **not** possible to make iodoethane by reacting together iodine and ethane.

....

(vi) Complete the following equations of some possible steps in the formation of chloroethane.

$Cl_2 \rightarrow$ ....

$Cl^\bullet + CH_3CH_3 \rightarrow HCl + CH_3CH_2^\bullet$

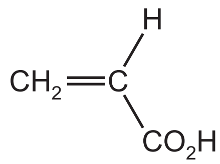
$CH_3CH_2^\bullet$ + ... $\rightarrow$ .... + ...

.... + ... $\rightarrow CH_3CH_2Cl$

[8]

[Total: 19]

5 Super-absorbent polymers have the ability to absorb 200-300 times their own mass of water. They are classified as hydrogels and they are widely used in personal disposable hygiene products such as babies' nappies (diapers).
These polymers are commonly made by the polymerisation of compound **K** mixed with sodium hydroxide in the presence of an initiator.



K

(a) (i) Explain what is meant by the term *polymerisation*.

....

....

(ii) What type of polymerisation is involved in the formation of hydrogels?

....

(iii) Describe the changes in chemical bonding that occur during the polymerisation of **K**.

....

....

[3]

(b) *Acrylic acid* is the common name for compound **K**.
Suggest the systematic (chemical) name of **K**.

....

[1]

(c) (i) Draw the structure of at least **two** repeat units of the polymer formed by the above method from acrylic acid, **K**, when mixed with NaOH.

(ii) The C–C–C bond angle in compound **K** changes when the polymer is formed.
State and explain how the C–C–C bond angle differs between a molecule of **K** and the polymer.

angle changes from .... to ....

explanation ....

....

[4]

For Examiner's Use

(d) (i) Draw a detailed diagram of a portion of the polymer you have drawn in **(c)(i)** to explain how it can absorb a large volume of water.

(ii) A student added 0.10 g of the polymer to 10 cm^3 of aqueous copper(II) sulfate solution.
Predict, with a reason, what you expect to observe.

....

....
[4]

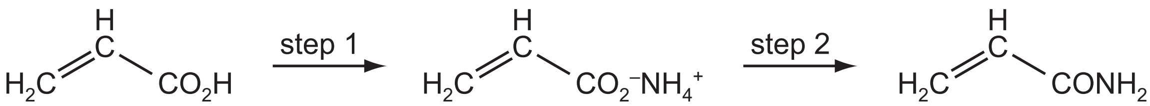
(e) Compound **L**, CH_2=CHCONH_2, can also be polymerised to form a super-absorbent polymer.

(i) Name the **two** functional groups in compound **L**.

....

....

Compound **K** can be converted into compound **L** by the following two-step route.



K **L**

(ii) Suggest a reagent for step 1.

....

(iii) What other product is formed in step 2?

....

(iv) State the reagents and conditions necessary to re-form **K** from **L**.

....
[5]

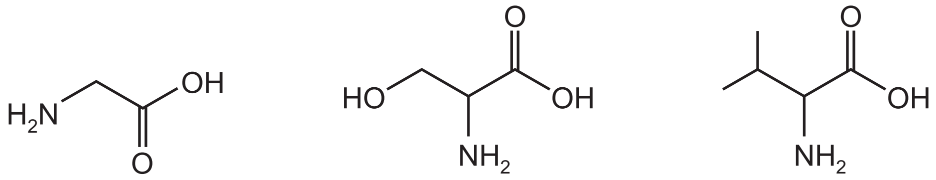
[Total: 17]

[Turn over

Section B

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

6 **(a)** Protein molecules are formed by the polymerisation of amino acids in the body. The structures of three amino acids are given.



glycine (*gly*) serine (*ser*) valine (*val*)

(i) How many different tripeptides can be made using **one** molecule of **each** of the amino acids shown?

....

(ii) Draw the tripeptide *ser*-*gly*-*val*, showing the peptide bonds in displayed form.

(iii) Within the tripeptide, which amino acid provides a hydrophobic side chain?

....

(iv) Polypeptide chains can form bonds giving proteins their *secondary* and *tertiary* structures.
Using the tripeptide in **(ii)**, state **two** types of bonding that can be formed and the groups in the tripeptide that are involved in this bonding.

bond .... groups ....

bond .... groups ....

[6]

For Examiner's Use

(b) Enzymes are particular types of proteins that catalyse chemical reactions. The efficiency of enzymes can be reduced by the presence of other molecules known as inhibitors. Explain how both *competitive* and *non-competitive* inhibitors prevent enzymes from working efficiently.

(i) competitive inhibitors ....

....

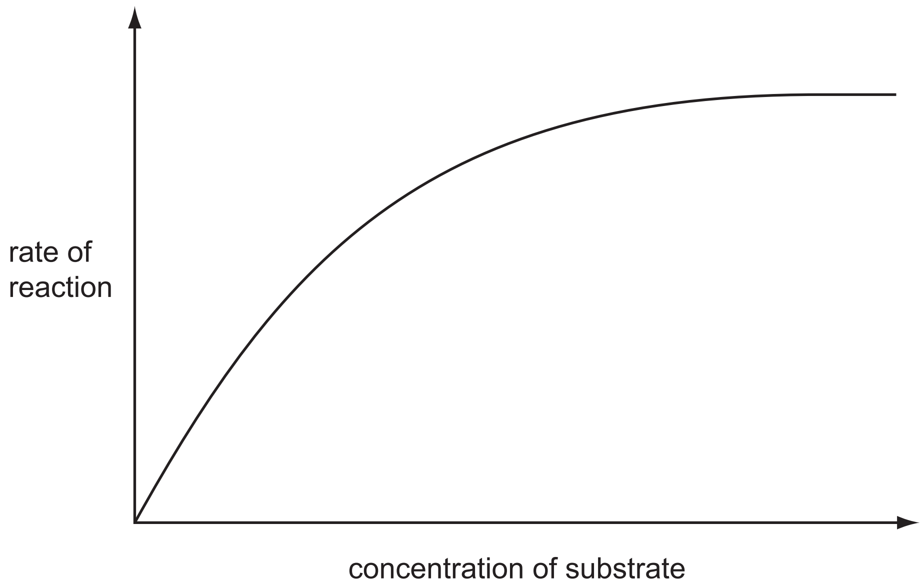
....

(ii) non-competitive inhibitors ....

....

....

(iii) The graph shows the rate of an enzyme-catalysed reaction against the substrate concentration in the absence of an inhibitor.



On the same axes, sketch a graph showing the rate of this reaction if a *non-competitive inhibitor* was present.

[4]

[Total: 10]

For Examiner's Use

7 Electrophoresis is a technique which can be used to separate amino acids or peptide fragments present in a mixture.

(a) Draw a diagram to show the apparatus used to carry out electrophoresis. You should label each of the relevant parts of the apparatus.

[4]

(b) How far an amino acid will travel during electrophoresis depends on the pH of the solution. For a given potential difference, state **two other** factors that will affect how far a given amino acid travels in a fixed time during electrophoresis.

1. ....

....

2. ....

....
[2]

(c) A number of analytical and separation techniques rely on substances having different partition coefficients.

State what is meant by the term *partition coefficient*.

....

....

....
[1]

For Examiner's Use

(d) The partition coefficient of **X** between ethoxyethane and water is 40.0.
A solution contains 4.00 g of **X** dissolved in 0.500 dm^3 of water.

Calculate the mass of **X** that can be extracted from this aqueous solution by shaking it with

(i) 0.050 dm^3 of ethoxyethane,

(ii) two successive portions of 0.025 dm^3 of ethoxyethane.

[4]

[Total: 11]

For Examiner's Use

8 In a world with a rapidly increasing population, access to clean drinking water is critical. For many countries, groundwater sources, rather than stored rainwater or river-water, are vital. *Groundwater* is water that exists in the pore spaces and fractures in rock and sediment beneath the Earth's surface. The World Health Organisation (WHO) provides maximum recommended concentrations for different ions present in drinking water.

(a) The geological nature of the soil determines the chemical composition of the groundwater. The table shows some ions which may contaminate groundwater.

ion present	WHO maximum permitted concentration / $mg\,dm^{-3}$
Ba^{2+}	0.30
Cl^-	250.00
NO_3^-	50.00
Pb^{2+}	0.01
Na^+	20.00
SO_4^{2-}	500.00

(i) Nitrate, NO_3^-, ions are difficult to remove from groundwater. What is the reason for this?

....

(ii) State which ions in the table above are likely to be removed from the water by treatment with powdered limestone, $CaCO_3$, giving reasons for each of your answers.

....

....

.... [4]

(b) Nitrates and phosphates can enter water courses such as rivers or streams as a result of human activity. Both of these ions are nutrients for algae.

(i) What is the origin of these nitrates?

....

For Examiner's Use

(ii) Suggest an origin for the phosphates found in water courses.

....

(iii) What effect do nitrates and phosphates have on water courses?

....

....

[3]

(c) Acid rain can have a major impact on natural waters, particularly lakes. In recent years there has been a worldwide effort to reduce the amount of acid rain produced.

(i) Write equations to show the production of acid rain from sulfur dioxide, SO_2.

....

....

(ii) The use of fossil fuels is one major source of sulfur dioxide.
Name another major industrial source.

....

[2]

[Total: 9]

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UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

7179900853

CHEMISTRY **9701/42**

Paper 4 Structured Questions **May/June 2012**

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 a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Section A
Answer **all** questions.

Section B
Answer **all** questions.

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.

For Examiner's Use	
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8	
Total	

This document consists of **17** printed pages and **3** blank pages.

UNIVERSITY *of* CAMBRIDGE International Examinations
[Turn over

Section A

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

1 (a) (i) What is meant by the term *enthalpy change of hydration*, $\Delta H^{\ominus}_{hyd}$?

....

....

(ii) Write an equation that represents the $\Delta H^{\ominus}_{hyd}$ of the Mg^{2+} ion.

....

(iii) Suggest a reason why $\Delta H^{\ominus}_{hyd}$ of the Mg^{2+} ion is greater than $\Delta H^{\ominus}_{hyd}$ of the Ca^{2+} ion.

....

....

(iv) Suggest why it is impossible to determine the enthalpy change of hydration of the oxide ion, O^{2-}.

....

....
[5]

(b) The enthalpy change of solution for $MgCl_2$, $\Delta H^{\ominus}_{sol}(MgCl_2(s))$, is represented by the following equation.

$$MgCl_2(s) + aq \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

Describe the simple apparatus you could use, and the measurements you would make, in order to determine a value for $\Delta H^{\ominus}_{sol}(MgCl_2(s))$ in the laboratory.

....

....

....

....

....

.... [4]

For Examiner's Use

For Examiner's Use

(c) The table below lists data relevant to the formation of $MgCl_2(aq)$.

enthalpy change	value / $kJ\,mol^{-1}$
$\Delta H^{\ominus}_{f}(MgCl_2(s))$	–641
$\Delta H^{\ominus}_{f}(MgCl_2(aq))$	–801
lattice energy of $MgCl_2(s)$	–2526
$\Delta H^{\ominus}_{hyd}(Mg^{2+}(g))$	–1890

By constructing relevant thermochemical cycles, use the above data to calculate a value for

(i) $\Delta H^{\ominus}_{sol}(MgCl_2(s))$,

$\Delta H^{\ominus}_{sol}$ = ... $kJ\,mol^{-1}$

(ii) $\Delta H^{\ominus}_{hyd}(Cl^{-}(g))$.

$\Delta H^{\ominus}_{hyd}$ = ... $kJ\,mol^{-1}$

[3]

(d) Describe and explain how the solubility of magnesium sulfate compares to that of barium sulfate.

....

....

....

....

.... [4]

[Total: 16]

For Examiner's Use

2 Carbon monoxide, CO, occurs in the exhaust gases of internal combustion engines.

(a) **(i)** Suggest a dot-and-cross diagram for CO.

(ii) Suggest **one** reason why CO is produced in addition to CO_2 in some internal combustion engines.

....

....

(iii) Carbon monoxide can be removed from the exhaust gases by a catalytic converter. Write an equation for a reaction that occurs in a catalytic converter that removes CO.

....

[3]

(b) The standard enthalpy change of formation, $\Delta H_f^\ominus$, of CO is –111 kJ mol^{-1}, and that of CO_2 is –394 kJ mol^{-1}.
Calculate the standard enthalpy change of the following reaction.

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$

$\Delta H^\ominus$ = ... kJ mol^{-1}

[2]

(c) Carbon monoxide reacts with a ruthenium(II) chloride complex according to the equation

$$[Ru(H_2O)_2Cl_4]^{2-} + CO \rightarrow [Ru(H_2O)(CO)Cl_4]^{2-} + H_2O.$$

(i) Describe the *type of reaction* that is occurring here.

....

(ii) During the reaction, the colour of the solution changes from deep blue to green. Explain the origin of colour in transition element complexes, and why different complexes often have different colours.

....

....

....

....

....

....

....

For Examiner's Use

The following table shows how the initial rate of this reaction varies with different concentrations of reactants.

$[[Ru(H_2O)_2Cl_4]^{2-}]$ / mol dm^{-3}	[CO] / mol dm^{-3}	rate / mol dm^{-3} s^{-1}
1.1×10^{-2}	1.7×10^{-3}	1.6×10^{-7}
1.6×10^{-2}	3.6×10^{-3}	2.3×10^{-7}
2.2×10^{-2}	2.7×10^{-3}	3.2×10^{-7}

(iii) Use these data to determine the order of reaction with respect to each reagent, and write the rate equation for the reaction.

....

....

....

....

....

....

There are three possible mechanisms for this reaction, which are described below.

mechanism 1 $\quad [Ru(H_2O)_2Cl_4]^{2-} + CO \xrightarrow{\text{slow}} [Ru(H_2O)(CO)Cl_4]^{2-} + H_2O$

mechanism 2 $\quad [Ru(H_2O)_2Cl_4]^{2-} \xrightarrow{\text{slow}} [Ru(H_2O)Cl_4]^{2-} + H_2O$

$[Ru(H_2O)Cl_4]^{2-} + CO \xrightarrow{\text{fast}} [Ru(H_2O)(CO)Cl_4]^{2-}$

mechanism 3 $\quad [Ru(H_2O)_2Cl_4]^{2-} + CO \xrightarrow{\text{slow}} [Ru(H_2O)_2(CO)Cl_4]^{2-}$

$[Ru(H_2O)_2(CO)Cl_4]^{2-} \xrightarrow{\text{fast}} [Ru(H_2O)(CO)Cl_4]^{2-} + H_2O$

(iv) Deduce which of these three mechanisms is consistent with the rate equation you suggested in part **(iii)**. Explain your answer.

....

....

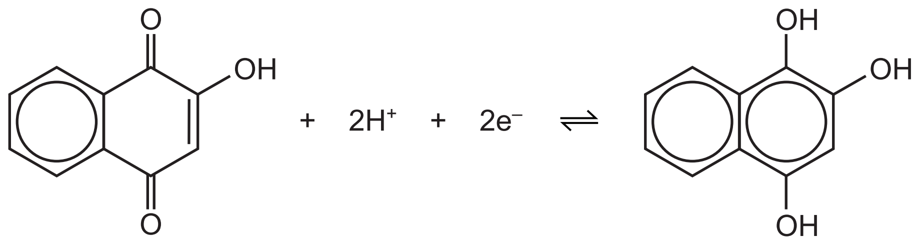
....
[10]

[Total: 15]

For Examiner's Use

3 Lawsone is the dye that is extracted from the henna plant, *Lawsonia inermis*. Although its natural colour is yellow, lawsone reacts with the proteins in hair and skin to produce the characteristic brown henna colour.

Lawsone can readily be reduced to 1,2,4-trihydroxynaphthalene, compound **A**.



$E^{\ominus} = +0.36\,V$

lawsone 1,2,4-trihydroxynaphthalene, **A**

(a) **(i)** Name **three** functional groups in lawsone.

....

....

(ii) Describe a reaction (reagent with conditions) that you could use to distinguish lawsone from compound **A**.
Describe the observations you would make with **both** compounds.

....

....

....

....

(iii) Suggest a reagent that could be used to convert lawsone into compound **A** in the laboratory.

....

....

(iv) Draw the structural formula of the compound formed when lawsone is reacted with Br_2(aq).

[6]

For Examiner's Use

(b) Compound **A** can be oxidised to lawsone by acidified $K_2Cr_2O_7$.

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

....

(ii) Construct an equation for this reaction. Use the molecular formulae of lawsone, $C_{10}H_6O_3$, and compound **A**, $C_{10}H_8O_3$, in your equation.

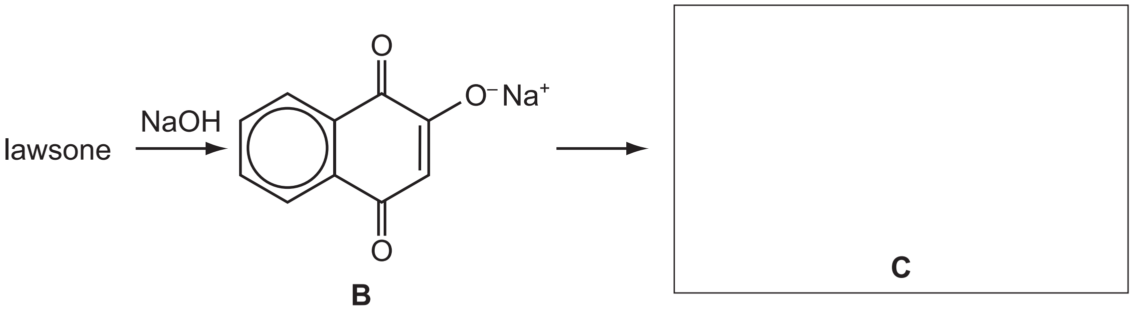
....

(iii) When 20.0 cm^3 of a solution of compound **A** was acidified and titrated with 0.0500 $mol\,dm^{-3}$ $K_2Cr_2O_7$, 7.50 cm^3 of the $K_2Cr_2O_7$ solution was needed to reach the end-point.
Calculate [**A**] in the solution.

[**A**] = ... $mol\,dm^{-3}$
[5]

[Turn over

(c) When lawsone is reacted with NaOH(aq), compound **B** is produced.



B

Reacting **B** with ethanoyl chloride, CH_3COCl, produces compound **C**, with the molecular formula $C_{12}H_8O_4$.

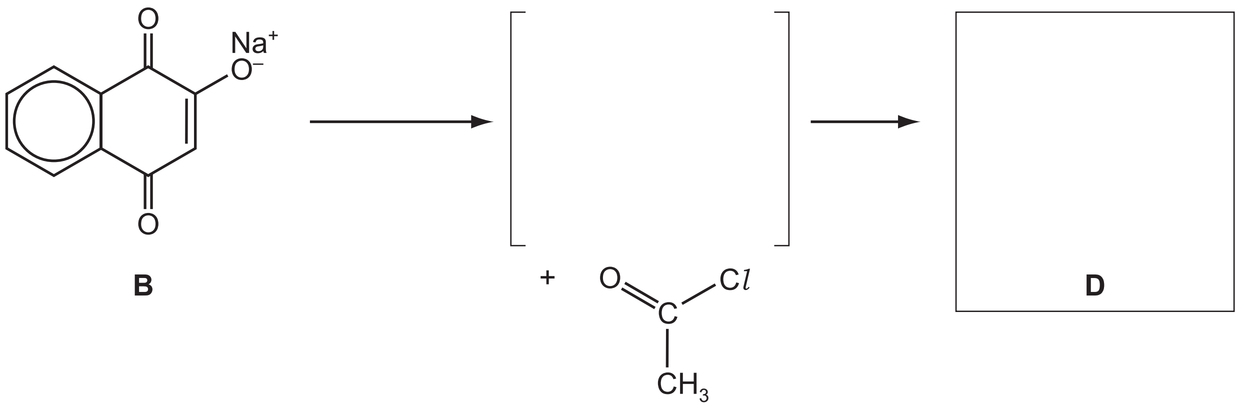
(i) Suggest the identity of compound **C**, and draw its structure in the box above.

Another compound, **D**, in addition to **C**, is produced in the above reaction. **D** is an isomer of **C** which contains the same functional groups as **C**, but in different positions.

(ii) Suggest a possible structure for **D**.

D

(iii) Suggest a mechanism for the formation of **D** from **B** and ethanoyl chloride by drawing relevant structures and curly arrows in the following scheme.



[3]

[Total: 14]

For Examiner's Use

4 **(a)** Describe and explain the trend in the volatilities of the halogens Cl_2, Br_2 and I_2.

....

....

....

.... [3]

(b) For each of the following pairs of compounds, predict which compound has the higher boiling point, and explain the reasons behind your choice.
Use diagrams in your answers where appropriate.

(i) H_2O and H_2S

(ii) $CH_3-CH_2-CH_3$ and CH_3-O-CH_3

[4]

(c) Briefly explain the shape of the SF_6 molecule, drawing a diagram to illustrate your answer.

[2]

[Total: 9]

For Examiner's Use

5 **(a)** Describe and explain how the acidities of $CHCl_2CO_2H$ and CH_2ClCO_2H compare to each other, and to the acidity of ethanoic acid.

....

....

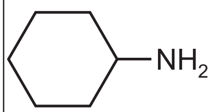
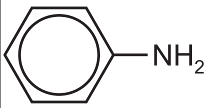
....

....

....

[3]

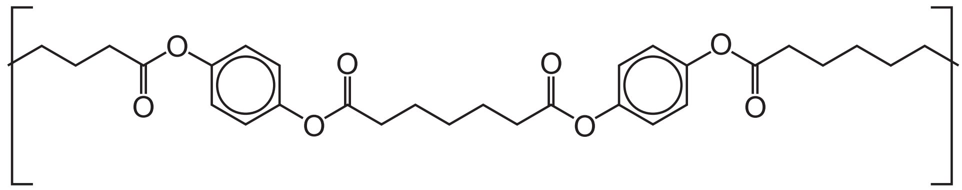
(b) For each of the following pairs of compounds, suggest one chemical test (reagents and conditions) that would distinguish between them.
State the observations you would make with each compound, writing 'none' if appropriate.

first compound	second compound	test (reagents and conditions)	observation with first compound	observation with second compound
				
CH_3CH_2COCl	CH_3COCH_2Cl			
CH_3CH_2CHO	CH_3COCH_3			

[7]

For Examiner's Use

(c) The following diagram shows a section (not a repeat unit) of a polymer, **G**, that can be made from the two monomers **E** and **F**.

E + **F** ⟶ 

polymer **G**

(i) What *type of polymerisation* made this polymer?

....

(ii) Draw the structures of the two monomers **E** and **F**.

E	**F**

(iii) Suggest the conditions needed to make polymer **G** from **E** and **F** in the laboratory.

....

....

....

(iv) One of the monomers, **E** or **F**, could be changed to make a more rigid polymer of a similar chemical type to **G**.
Suggest which of your two monomers could be changed, and suggest a structure for the new monomer.

Monomer to be changed (**E** or **F**) ....

Structural formula of the new monomer

[6]

[Total: 16]

Section B

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

6 **(a)** The table shows the structures of four amino acids found in proteins in the human body. Complete the table by indicating the type of tertiary interaction each side-chain is most likely to have when its amino acid is present in a protein chain.

amino acid	structure	type of interaction
alanine	$H_2NCH(CH_3)CO_2H$	
cysteine	$H_2NCH(CH_2SH)CO_2H$	
lysine	$H_2NCH((CH_2)_4NH_2)CO_2H$	
serine	$H_2NCH(CH_2OH)CO_2H$	

[3]

(b) Metal ions play an important role in the biochemistry of the human body. For each of the following metal ions, outline one of the places in the body it can be found and its main role there.

iron ....

....

....

potassium ....

....

....

zinc ....

....

....

[3]

For Examiner's Use

(c) Many chemical reactions at a cellular level require energy in order to take place. This energy is largely provided by the breakdown of one particular compound.

(i) Write an equation showing the breakdown of this compound.

....

(ii) What type of chemical reaction is this?

....

[2]

(d) Cystic fibrosis is a genetic disease caused by a mutation in the DNA sequence resulting in the production of a faulty version of an important protein which acts as an ion pump in the cell membrane. This pump controls the flow of ions into and out of cells.
People with the faulty protein show two major symptoms.

- water is retained in cells in the lungs resulting in the formation of a thick, sticky mucous outside the cells;
- their sweat is very salty.

Based on the information given for people with cystic fibrosis,

(i) suggest which ions are involved in the ion flow,

....

....

(ii) suggest and explain what type of bonding might result in thick or sticky mucous.

....

....

[2]

[Total: 10]

For Examiner's Use

7 NMR and X-ray crystallography are two important analytical techniques which can be used to study the structure and function of molecules.

(a) Nuclear magnetic resonance, NMR, arises because protons possess spin which generates a small magnetic moment. When an external magnetic field is applied the protons can align with or against the external field. If they are given a small amount of energy in the radio frequency range each can be 'promoted' so that their magnetic moment opposes the external field.

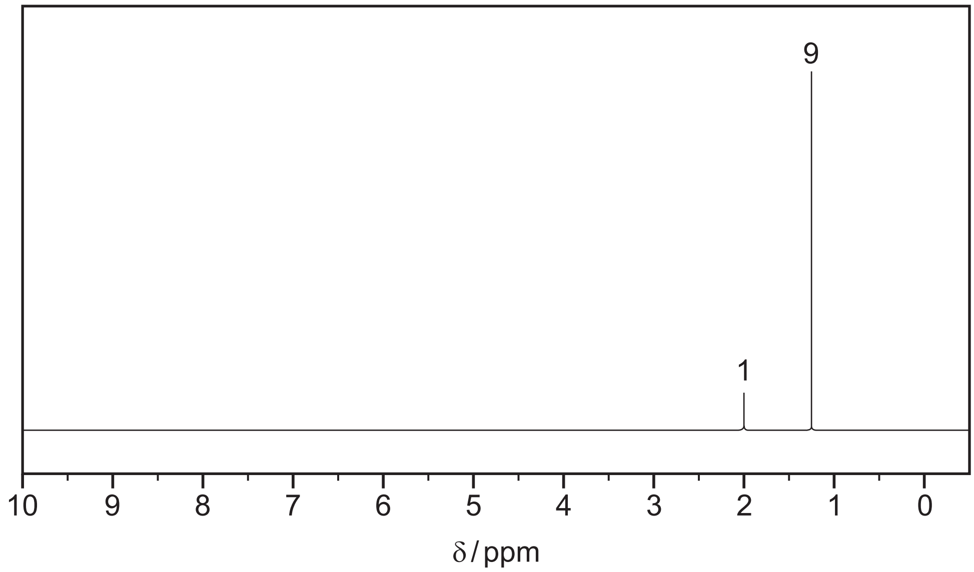
Two factors can influence the energy required for this promotion. What are they?

(i) ....

(ii) ....

[2]

(b) A compound, **J**, has the formula $C_4H_{10}O$. The NMR spectrum of **J** is shown.



(i) Indicate the groups responsible for each peak and hence deduce the structure of **J**.

peak at 1.26 δ .... peak at 2.0 δ ....

structure of **J**

For Examiner's Use

(ii) There are three other isomers of **J** containing the same functional group as **J**. Draw the structures of two of these three isomers and indicate how many different chemical shifts each would show in its NMR spectrum.

isomer 1 isomer 2

number of groups of peaks .... number of groups of peaks ....

[6]

(c) X-ray crystallography can be useful in gathering information about the structure of large organic molecules, such as nucleic acids.

(i) Which element will show up most strongly in the X-ray crystallography of a nucleic acid? Explain your answer.

....

....

(ii) X-ray crystallography will **not** detect hydrogen atoms. Explain why this is so.

....

....

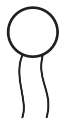
[2]

[Total: 10]

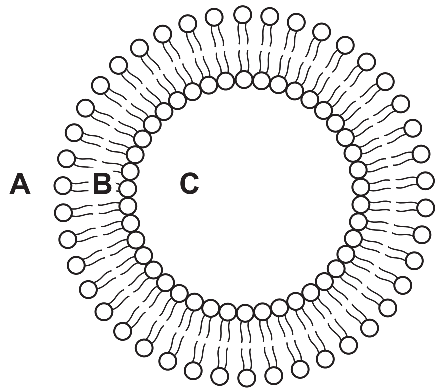
For Examiner's Use

8 The developments in nanotechnology and drug delivery over the past 20 years have been wide-ranging.

(a) One of the most widespread developments for delivering a range of pharmaceutical products has been the use of liposomes. These are artificially created spheres made from phospholipids which have an ionic phosphate 'head' and two hydrocarbon 'tails'.



phospholipid



liposome

Liposomes have also been used to carry pharmaceuticals such as vitamins and moisturisers used in cosmetic anti-ageing creams. Otherwise these pharmaceuticals may be oxidised or dehydrated if exposed to air.

(i) State in which area of the liposome, **A**, **B** or **C**, each of the following types of molecule would be carried.

a hydrophilic moisturiser ....

a fat-soluble vitamin ....

(ii) For one of the areas, **A**, **B** or **C**, suggest why this would **not** be an appropriate place to carry either molecule.

....

....

....
[3]

(b) When liposomes are used to carry drugs, their main purpose is to prevent the drug molecules from being broken down on passage through the digestive system.

(i) Name a functional group present in drug molecules that might be broken down by acid in the stomach.

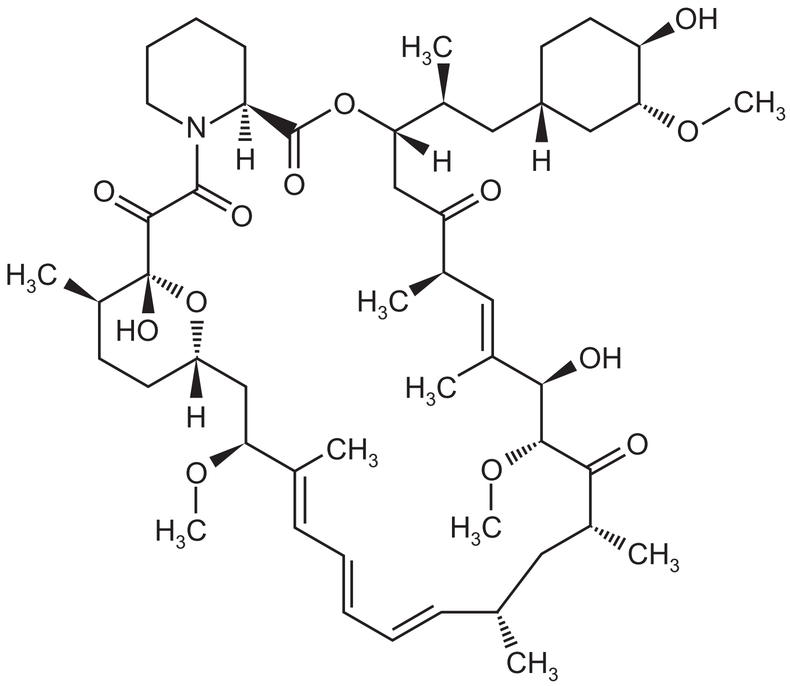
....

For Examiner's Use

(ii) Name the *type of reaction* that would cause such a breakdown.

....

(iii) The drug *Sirolimus* is used to suppress possible rejection by the body after kidney transplants.



Sirolimus

Circle **two bonds**, each in a **different** functional group that could be broken down in the digestive system.

[4]

(c) *Sirolimus* is not very soluble in water, greatly reducing its effectiveness when given by mouth or by injection. To increase its effectiveness when taken by mouth nano-sized crystals of the drug combined with poly(ethylene glycol) or PEG (shown below) are produced.

$$HO—(CH_2—CH_2—O)_n—H$$

(i) Suggest what is meant by the term *nano-sized*.

....

(ii) Suggest where on the molecule of PEG the drug would be attached.

....

(iii) Why would bonding the drug to a PEG molecule improve its solubility in water?

....

[3]

[Total: 10]

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UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education
Advanced Subsidiary Level and Advanced Level

CANDIDATE NAME

CENTRE NUMBER | CANDIDATE NUMBER

6738575012

CHEMISTRY **9701/42**

Paper 4 Structured Questions **October/November 2012**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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Section A
Answer **all** questions.

Section B
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UNIVERSITY of CAMBRIDGE International Examinations

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For Examiner's Use

Section A

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

1 **(a)** Write down what you would see, and write equations for the reactions that occur, when silicon(IV) chloride and phosphorus(V) chloride are separately mixed with water.

silicon(IV) chloride

....

....

phosphorus(V) chloride

....

....
[4]

(b) Iron(III) chloride, $FeCl_3$, is used to dissolve unwanted copper from printed circuit boards (PCBs) by the following reaction.

$$2FeCl_3(aq) + Cu(s) \rightarrow 2FeCl_2(aq) + CuCl_2(aq)$$

A solution in which $[Fe^{3+}(aq)]$ was originally equal to $1.50\,mol\,dm^{-3}$ was re-used several times to dissolve copper from the PCBs, and was then titrated as follows.

A $2.50\,cm^3$ sample of the partially-used-up solution was acidified and titrated with $0.0200\,mol\,dm^{-3}$ $KMnO_4$.
This oxidised any $FeCl_2$ in the solution back to $FeCl_3$.
It was found that $15.0\,cm^3$ of $KMnO_4(aq)$ was required to reach the end point.

(i) Construct an ionic equation for the reaction between Fe^{2+} and MnO_4^- in acid solution.

....

(ii) State here the $Fe^{2+} : MnO_4^-$ ratio from your equation in **(i)**. ....

(iii) Calculate the number of moles of MnO_4^- used in the titration.

(iv) Calculate the number of moles of Fe^{2+} in $2.50\,cm^3$ of the partially-used-up solution.

For Examiner's Use

(v) Calculate the $[Fe^{2+}]$ in the partially-used-up solution.

(vi) Calculate the mass of copper that could still be dissolved by 100 cm^3 of the partially-used-up solution.

mass of copper = ... g
[6]

(c) When $SiCl_4$ vapour is passed over Si at red heat, Si_2Cl_6 is formed. Si_2Cl_6 contains a Si-Si bond.
The reaction of Si_2Cl_6 and Cl_2 re-forms $SiCl_4$.

$$Si_2Cl_6(g) + Cl_2(g) \rightarrow 2SiCl_4(g)$$

Use bond energy data from the *Data Booklet* to calculate $\Delta H^{\ominus}$ for this reaction.

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

(d) Calcium forms three calcium silicides, Ca_2Si, CaSi and $CaSi_2$. The first of these reacts with water as follows.

$$.........Ca_2Si + ...H_2O \rightarrow ....Ca(OH)_2 + ...SiO_2 + ...H_2$$

(i) Balance this equation. You may find the use of oxidation numbers helpful.

(ii) During this reaction, state

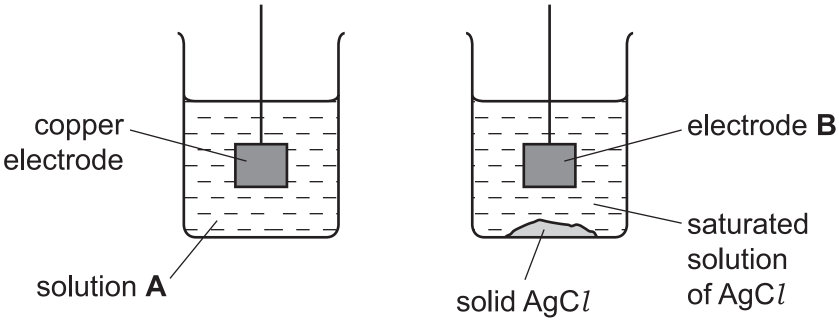
which element(s) have been oxidised, ...

which element(s) have been reduced. ....
[2]

[Total: 14]

For Examiner's Use

2 **(a)** The diagram below shows an incomplete experimental set-up needed to measure the E_{cell} of a cell composed of the standard Cu^{2+}/Cu electrode and an Ag^{+}/Ag electrode.



(i) State the chemical composition of

solution **A**, ...

electrode **B**. ....

(ii) Complete the diagram to show the whole experimental set-up.

[4]

(b) The above cell is not under standard conditions, because the $[Ag^{+}]$ in a saturated solution of AgC*l* is much less than 1.0 mol dm^{-3}. The $E_{electrode}$ is related to $[Ag^{+}]$ by the following equation.

equation 1 $$E_{electrode} = E^{\ominus}_{electrode} + 0.06 \log[Ag^{+}]$$

(i) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ if the cell was operating under standard conditions.

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

In the above experiment, the E_{cell} was measured at +0.17V.

(ii) Calculate the value of $E_{electrode}$ for the Ag^{+}/Ag electrode in this experiment.

....

(iii) Use equation 1 to calculate $[Ag^{+}]$ in the saturated solution.

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

[3]

For Examiner's Use

(c) **(i)** Write an expression for K_{sp} of silver sulfate, Ag_2SO_4, including units.

K_{sp} = ... units ....

Using a similar experimental set-up to that illustrated opposite, it is found that $[Ag^+]$ in a saturated solution of Ag_2SO_4 is 1.6×10^{-2} mol dm^{-3}.

(ii) Calculate the value of K_{sp} of silver sulfate.

K_{sp} = ...

[3]

(d) Describe how the colours of the silver halides, and their relative solubilities in NH_3(aq), can be used to distinguish between solutions of the halide ions Cl^-, Br^- and I^-.

....

....

....

....

....

....

.... [4]

(e) Describe and explain the trend in the solubilities of the sulfates of the elements in Group II.

....

....

....

....

....

....

.... [4]

[Total: 18]

3 **(a)** Catalysts can be described as homogeneous or heterogeneous.

(i) What is meant by the terms *homogeneous* and *heterogeneous*?

....

....

(ii) By using iron and its compounds as examples, outline the different modes of action of homogeneous and heterogeneous catalysis.
Choose **one** example of each type, and for **each** example you should

- state what the catalyst is, and whether it is acting as a homogeneous or a heterogeneous catalyst,
- write a balanced equation for the reaction,
- outline how the catalyst you have chosen works to decrease the activation energy.

....

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....

.... [8]

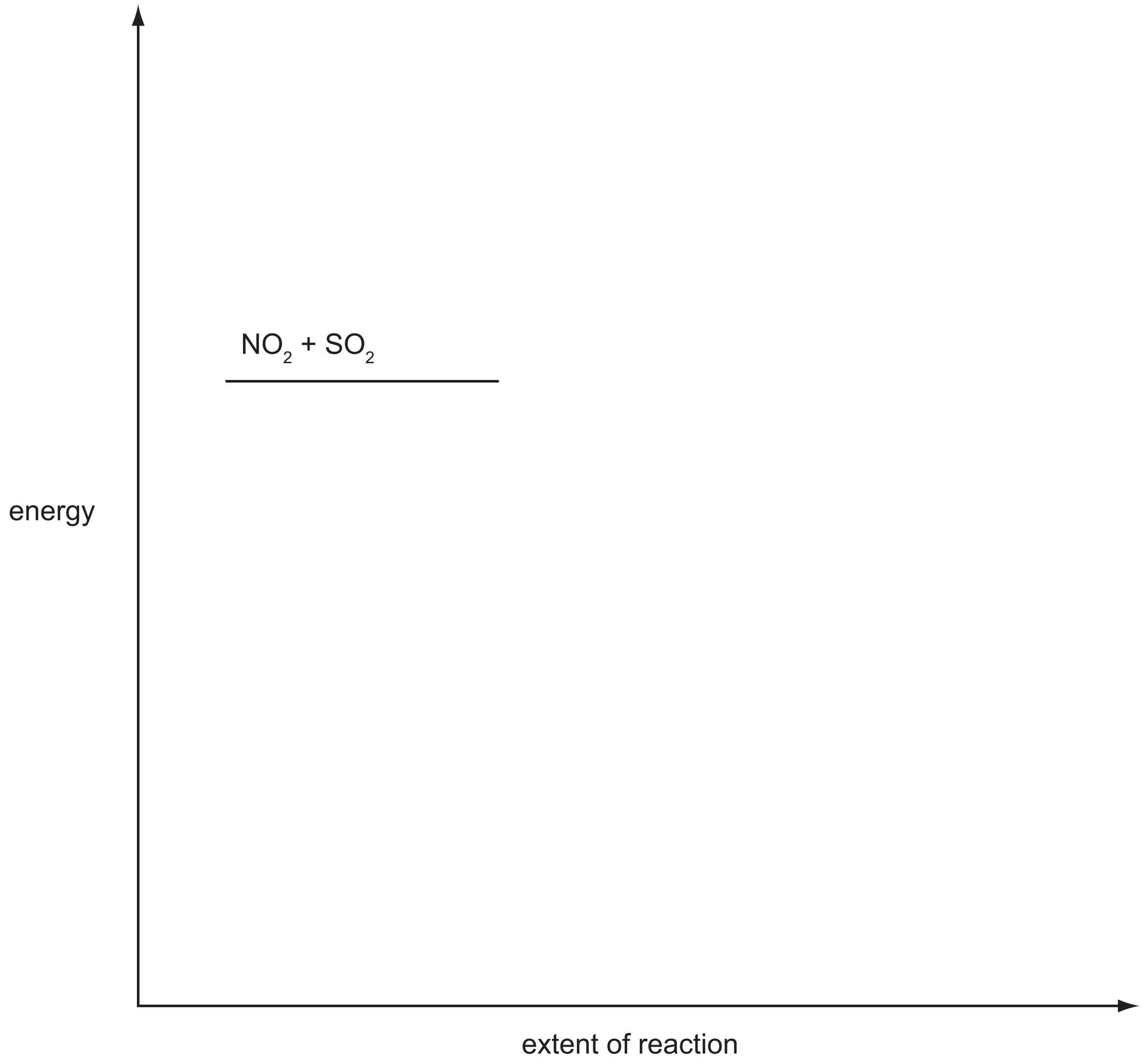
For Examiner's Use

(b) The reaction between SO_2, NO_2 and O_2 occurs in two steps.

$$NO_2 + SO_2 \rightarrow NO + SO_3 \qquad \Delta H_1^\ominus = -88\,\text{kJ mol}^{-1}$$
$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \qquad \Delta H_2^\ominus = -57\,\text{kJ mol}^{-1}$$

The activation energy of the first reaction, E_{a_1}, is higher than that of the second reaction, E_{a_2}.

Use the axes below to construct a fully-labelled reaction pathway diagram for this reaction, labelling E_{a_1}, E_{a_2}, $\Delta H_1^\ominus$ and $\Delta H_2^\ominus$.



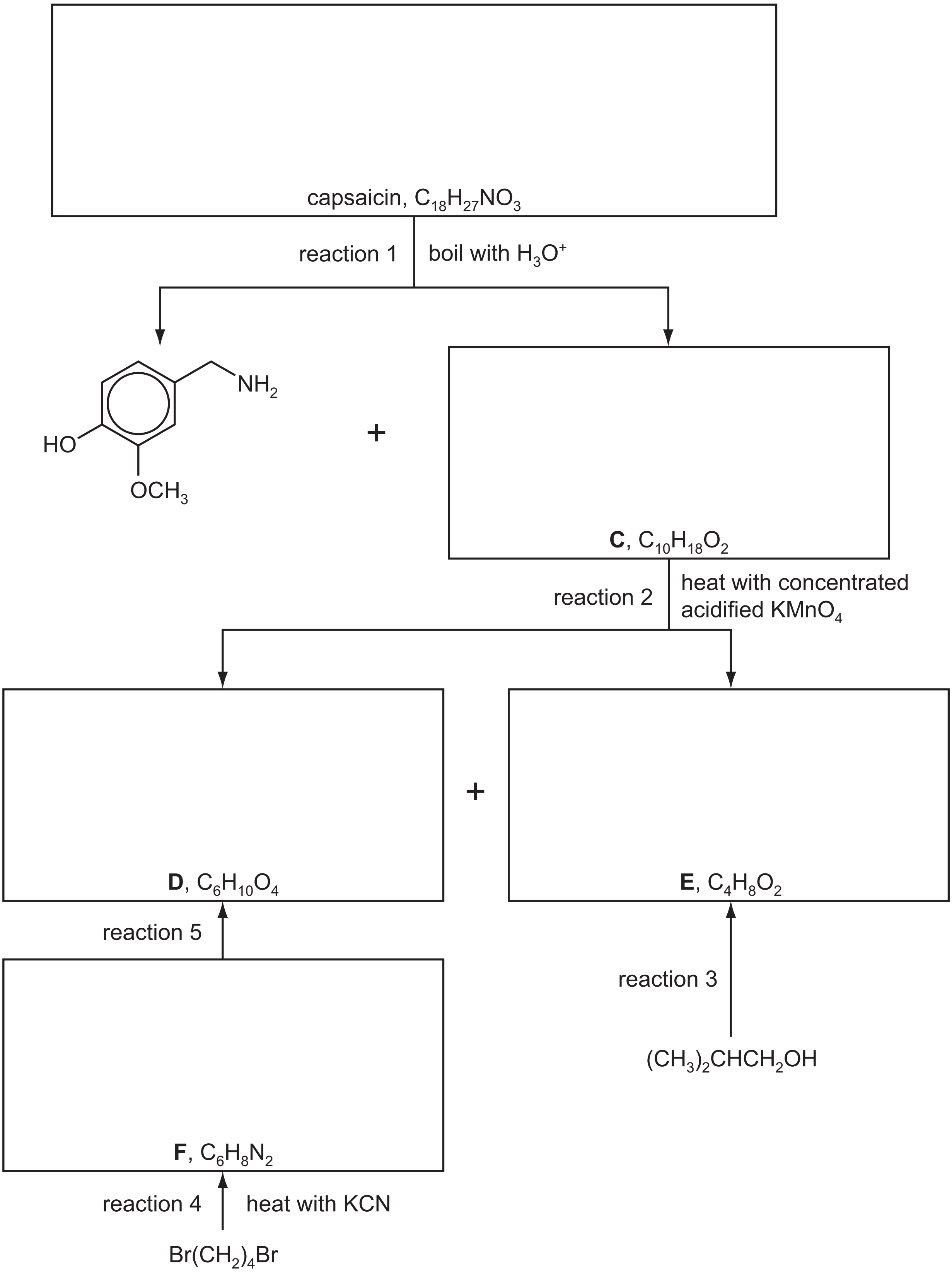
[2]

[Total: 10]

[Turn over

4 The compound responsible for the hot taste of chilli peppers is capsaicin. Its molecular structure can be deduced by the following reaction scheme.

For Examiner's Use



Compounds **C**, **D** and **E** all react with Na_2CO_3(aq).

For Examiner's Use

Answer the following questions.

(a) Suggest reagents and conditions for reaction 3.

.... [1]

(b) What *type of reaction* is reaction 4?

.... [1]

(c) Suggest reagents and conditions for reaction 5.

.... [1]

(d) Name the functional group in **C** that has reacted with hot concentrated acidified $KMnO_4$.

.... [1]

(e) Suggest the name of the functional group in capsaicin that has reacted in reaction 1.

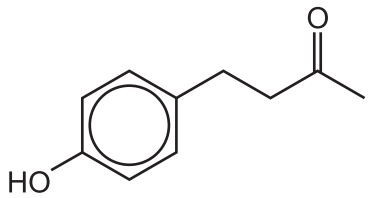
.... [1]

(f) Work out structures for compounds **C**–**F** and capsaicin, and draw their structural formulae in the boxes opposite. [5]

[Total: 10]

For Examiner's Use

5 Compound **G** is a naturally occurring aromatic compound that is present in raspberries.



compound **G**

(a) Identify the functional groups present in compound **G**.

....

.... [2]

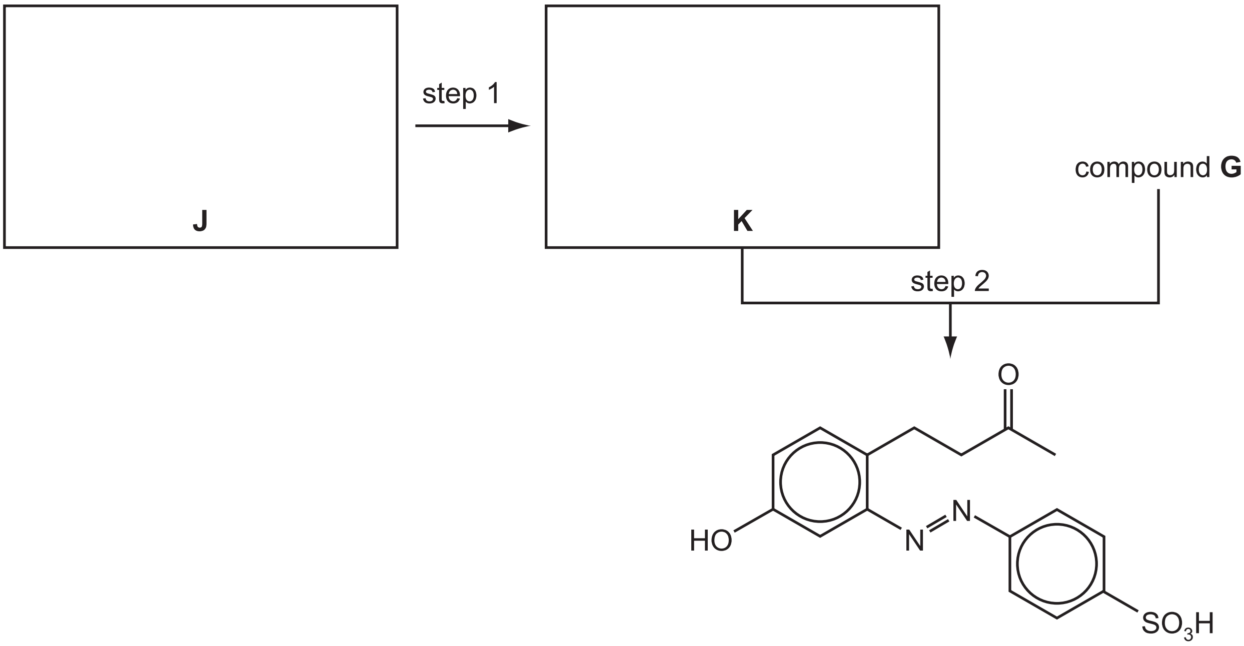
(b) Complete the following table with information about the reactions of the three stated reagents with compound **G**.

reagent	observation	structure of organic product	type of reaction
sodium metal			
aqueous bromine			
aqueous alkaline iodine			

[8]

For Examiner's Use

(c) The dye **H** can be made from compound **G** by the route shown below.



dye **H**

(i) Draw the structures of the amine **J** and the intermediate **K** in the boxes above.

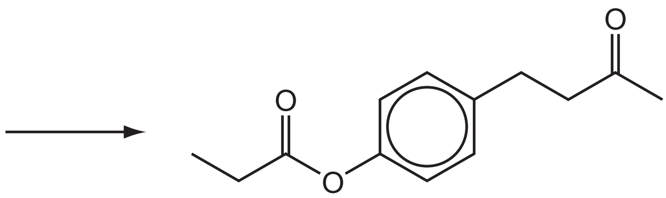
(ii) Suggest reagents and conditions for

step 1, ...

step 2. ....

[5]

(d) Suggest a reaction scheme by which compound **G** and propanoic acid could be converted into compound **L**.



compound **L**

[3]

[Total: 18]

For Examiner's Use

Section B

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

6 Proteins are complex molecules made up from long chains that are folded to give a three-dimensional structure.

(a) Study the table which describes aspects of bonding in proteins. For each description of a bonding type, indicate whether it contributes to the primary, secondary or tertiary structure of a protein.

bonding type	structure involved
disulfide bonds between parts of the chain	
hydrogen bonds in a β-pleated sheet	
ionic bonds between parts of the chain	
peptide links between amino acids	

[3]

(b) Explain, with the use of diagrams as appropriate, the difference between competitive and non-competitive inhibition of enzymes.

....

....

....

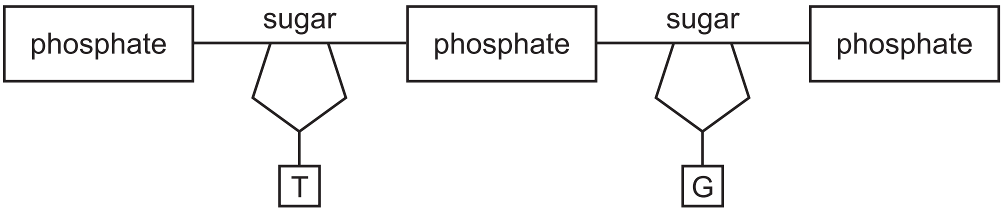
....

....

.... [4]

For Examiner's Use

(c) The diagram shows one strand of DNA. Draw a matching strand showing clearly, with labels, the bonds holding the two strands together.
Name the bases in **your** strand, indicating clearly which base bonds to each base in the strand shown.



names of bases ....

[3]

[Total: 10]

For Examiner's Use

7 DNA fingerprinting has become an important analytical technique, largely due to its use in 'screening' crime suspects. It also has a range of applications in modern analysis including determining family links, medicine and archaeology.

(a) **(i)** DNA fingerprinting uses an analytical technique you have studied. What is the name of that technique?

....

(ii) In order to carry out DNA fingerprinting, the DNA must first be broken down into shorter lengths of polynucleotides. How is this accomplished?

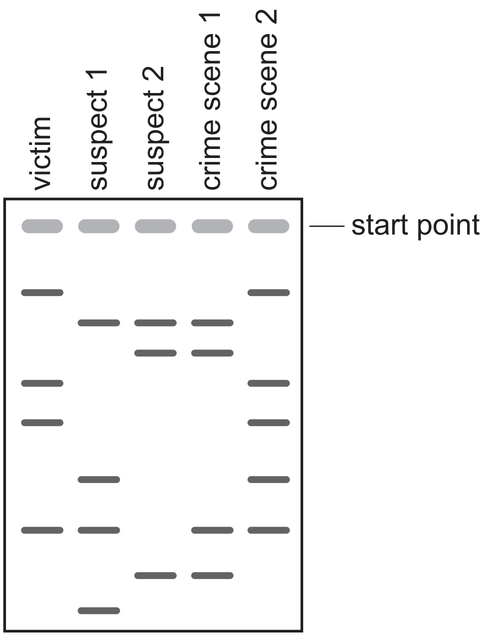
....

(iii) What part of the DNA fragments enables them to move in an electric field?

....

[3]

(b) The DNA fingerprints shown were obtained from a crime scene. DNA samples were recovered from two rooms in the house where the crime took place. The victim's DNA and that of two possible suspects were included in the analysis.



(i) Indicate with an **X** on the diagram, which lines from suspect 1 and from suspect 2 **cannot** distinguish which of them was present in the house.

(ii) Based on this evidence one suspect was arrested. Which suspect would you expect this to be? Explain your reasoning.

....

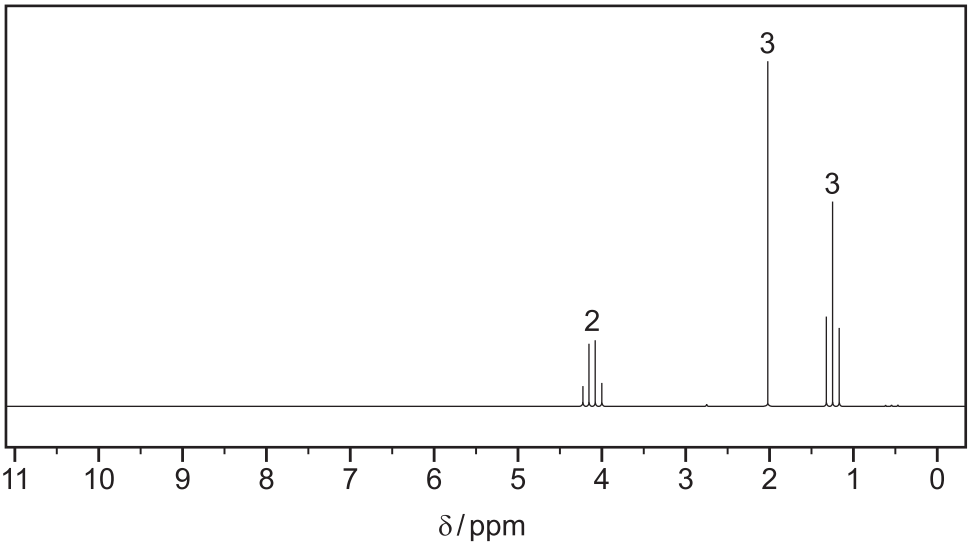
....

[2]

For Examiner's Use

(c) A sample of a liquid, **P**, was found at the scene of the crime and was analysed using mass spectrometry and NMR spectroscopy.

The mass spectrum has M and M+1 peaks in the ratio of 5.1 : 0.22 with the M peak at *m*/*e* = 88.
The NMR spectrum is shown



Use the data to suggest a structure for **P**, explaining your answer.

....

....

....

....

....

....

....

structure of **P**

[5]

[Total: 10]

For Examiner's Use

8 The increasing awareness of the diminishing supply of crude oil has resulted in a number of initiatives to replace oil-based polymers with those derived from natural products. One such polymer, 'polylactide' or PLA, is produced from corn starch and has a range of applications.

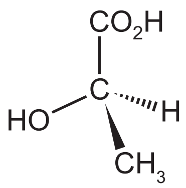
(a) The raw material for the polymer, lactic acid (2-hydroxypropanoic acid), is formed by the fermentation of corn starch using enzymes from bacteria.

(i) Calcium hydroxide is added to the fermentation tanks to prevent the production of lactic acid from slowing down.
Why might high acidity reduce the effectiveness of the enzymes?

....

....

(ii) The structure of lactic acid is shown.



What type of reaction takes place in this polymerisation?

....
[2]

(b) Lactic acid exists in two stereoisomeric forms. Draw the other form in the box.

[1]

For Examiner's Use

(c) One of the reasons PLA has attracted so much attention is that it is biodegradeable. This does, however, restrict some potential uses. The simple polymer has a melting point of around 175 °C, but softens between 60-80 °C. However, its thermoplastic properties enable it to have a range of uses in fibres and in food packaging.

(i) Explain why PLA would **not** be a suitable packaging material for foods pickled in vinegar.

....

....

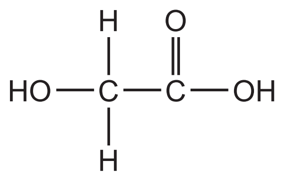
(ii) PLA containers are not used for hot drinks. Suggest why.

....

....

[2]

(d) Lactic acid can also be co-polymerised with glycolic acid.



glycolic acid

(i) Draw a section of the co-polymer showing one repeat unit.

(ii) Suggest what type(s) of bonding will occur between chains of this co-polymer, indicating the groups involved.

....

....

....

(iii) Suggest one property in which the co-polymer differs from PLA.

....

....

[5]

[Total: 10]

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UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CANDIDATE NAME	

CENTRE NUMBER		CANDIDATE NUMBER	

0314640454

CHEMISTRY **9701/42**

Paper 4 Structured Questions **May/June 2011**

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 a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Section A
Answer **all** questions.

Section B
Answer **all** questions.

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.

For Examiner's Use	
1	
2	
3	
4	
5	
6	
7	
8	
Total	

This document consists of **16** printed pages and **4** blank pages.

UNIVERSITY *of* CAMBRIDGE International Examinations

Section A

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

For Examiner's Use

1 **(a)** Hydrogen fluoride, HF, behaves as a weak acid in water, with $K_a = 5.6 \times 10^{-4}\,\text{mol dm}^{-3}$.

Calculate the pH of a $0.050\,\text{mol dm}^{-3}$ solution of HF.

pH = ... [2]

(b) Gaseous ammonia and hydrogen fluoride react together to give solid ionic ammonium fluoride.

$$NH_3(g) + HF(g) \rightleftharpoons NH_4F(s) \qquad \Delta H = -147\,\text{kJ mol}^{-1}$$

(i) What *type of reaction* is this?

....

(ii) Draw dot-and-cross diagrams (outer shells only) describing the bonding in the three compounds involved in this reaction.

NH_3	HF	NH_4F

(iii) There are **three** types of bonding in NH_4F.
Give the names of each of the three types, and state where in the compound each type occurs.

....

....

....

For Examiner's Use

(iv) The reaction between NH_3 and HF is reversible. What conditions of temperature and pressure would favour the **reverse** reaction, i.e. the dissociation of NH_4F? Explain your answer.

....

....

....
[9]

(c) Many commercial copper and brass polishes contain ammonia. The tarnish that forms on the surface of copper is often copper sulfide, CuS. In the presence of O_2 from the air, NH_3 can combine with this copper sulfide to produce the soluble cuprammonium sulfate, $[Cu(NH_3)_4]SO_4$.

(i) Construct an equation for this reaction.

....

(ii) State the colour of cuprammonium sulfate solution.

....

(iii) Describe what you would see if a solution of cuprammonium sulfate was diluted with water. Explain your answer.

....

....
[3]

(d) When sulfuric acid is added to Cu^{2+}(aq), no colour change occurs, but when concentrated hydrochloric acid is added to Cu^{2+}(aq), the solution turns yellow-green. The solution reverts to its original colour when it is diluted with water.

Suggest the type of reaction occurring with HCl(aq), suggest what is formed during the reaction, and write an equation for the change.

....

....

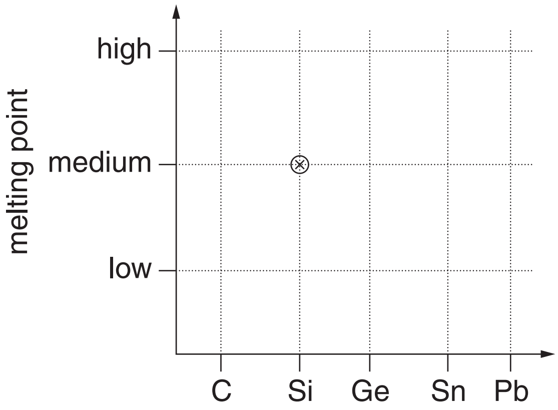
....

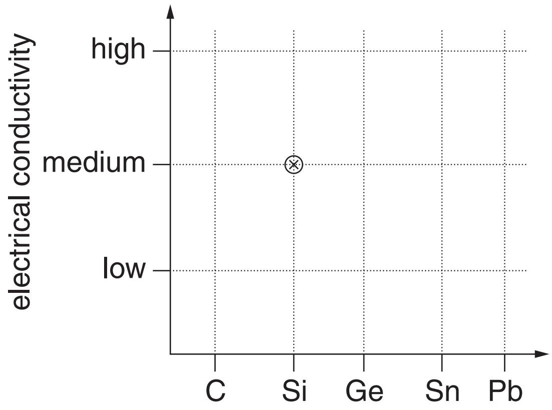
.... [3]

[Total: 17]

2 **(a)** **(i)** On the following grids, plot points showing the variation in the named property of the Group IV elements. Your points should show for each element, whether the melting point/electrical conductivity is 'high', 'medium' or 'low'. The point for silicon has already been plotted in each case.

For Examiner's Use





(ii) Suggest explanations of these trends in terms of the structure and bonding of the Group IV elements.

melting point

....

....

electrical conductivity

....

....

[6]

(b) Choose **one** reaction to illustrate **each** of the following statements. Write an equation for each of your chosen reactions, and describe what you would see as the reaction is carried out.

(i) PbO is more stable than PbO_2.

....

....

(ii) CO is easily oxidised to CO_2.

....

....

(iii) Aqueous $SnCl_2$ is a useful reducing agent.

....

....

[4]

[Total: 10]

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For Examiner's Use

3 **(a)** State the relationship between the Faraday constant, *F*, the charge on the electron, *e*, and the Avogadro number, *L*.

.... [1]

(b) If the charge on the electron, the A_r and the valency of copper are known, the value of the Avogadro number can be determined experimentally. This is done by passing a known current for a known time through a copper electrolysis cell, and weighing the mass of copper deposited onto the cathode.

(i) Draw a diagram of suitable apparatus for carrying out this experiment.
Label the following: power supply (with + and – terminals); anode; cathode; and ammeter.
State the composition of the electrolyte.

The following are the results obtained from one such experiment.

current passed through the cell	=	0.500 A
time current was passed through cell	=	30.0 min
initial mass of copper cathode	=	52.243 g
final mass of copper cathode	=	52.542 g

(ii) Use these data and relevant information from the *Data Booklet* to calculate a value of *L* to **3 significant figures**.

L = ...
[9]

For Examiner's Use

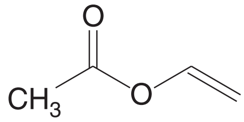
(c) Use relevant information from the *Data Booklet* to identify the substances formed at the anode and at the cathode when aqueous solutions of the following compounds are electrolysed.

compound	product at anode	product at cathode
AgF		
$FeSO_4$		
$MgBr_2$		

[5]

[Total: 15]

4 **(a)** Polyvinyl acetate, PVA, is a useful adhesive for gluing together articles made from wood, paper or cardboard. The monomer of PVA is ethenyl ethanoate, **B**.

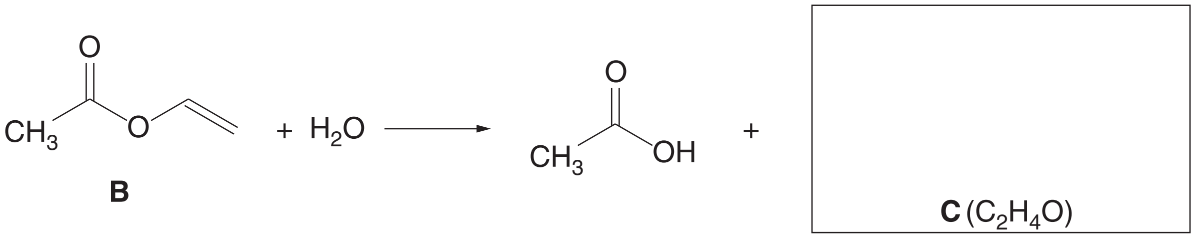


B

PVA is formed from **B** by the process of addition polymerisation.

(i) Draw a section of the PVA molecule containing at least 2 monomer molecules, and identify clearly the repeat unit.

The ester **B** can be hydrolysed in the usual way, according to the following equation.



(ii) Use this information to suggest a possible structure for **C** and draw it in the box above.

When substance **C** is extracted from the product mixture, it is found that it does **not** decolourise Br_2(aq), but it **does** form a pale yellow precipitate with alkaline aqueous iodine.

(iii) Suggest a structure for **C** that fits this new information.

(iv) Suggest a confirmatory test for the functional group in the structure you have drawn in **(iii)**. Your answer should include the reagent you would use and the observation you would make.

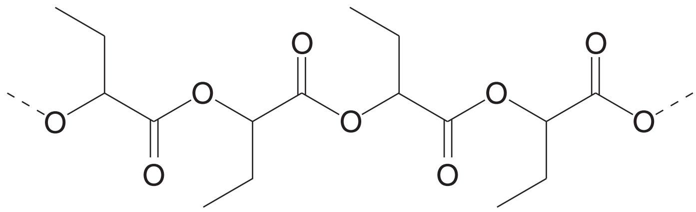
....

....

[6]

For Examiner's Use

(b) The following diagram represents a section of another polymer.



D

(i) On the above formula draw brackets, [ ], around the atoms that make up the repeat unit of this polymer.

(ii) Name the functional group in polymer **D**.

....

(iii) Suggest and draw the structure of the monomer, **E**, that could form this polymer.

(iv) What *type of polymerisation* is involved in making polymer **D** from its monomer?

....

(v) What is the relationship between the repeat unit of polymer **D** and the repeat unit of PVA?

....

[5]

(c) Monomer **E** exists as two stereoisomers. Heating either isomer with Al_2O_3 gives a mixture of two unsaturated carboxylic acids **F** and **G**, which are stereoisomers of each other.

(i) Name the *type of stereoisomerism* shown by compound **E**.

....

(ii) Suggest structures for **F** and **G**, and name the type of stereoisomerism they show.

E $\xrightarrow{Al_2O_3}$ [**F**] + [**G**]

type of isomerism ....

[4]

[Total: 15]

5 **(a)** Describe and explain how the acidities of ethanol and phenol compare to that of water.

For Examiner's Use

....

....

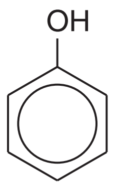
....

....

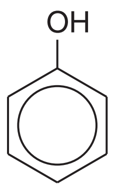
....

....[4]

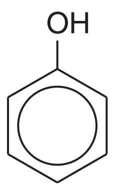
(b) Complete the following equations showing **all** the products of each of these reactions of phenol. Include reaction conditions where appropriate in the boxes over the arrows. If no reaction occurs write ***no reaction*** in the products box.



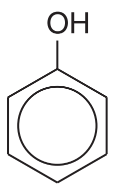
+ Na $\longrightarrow$



+ NaOH $\longrightarrow$



+ CH_3CO_2H $\longrightarrow$

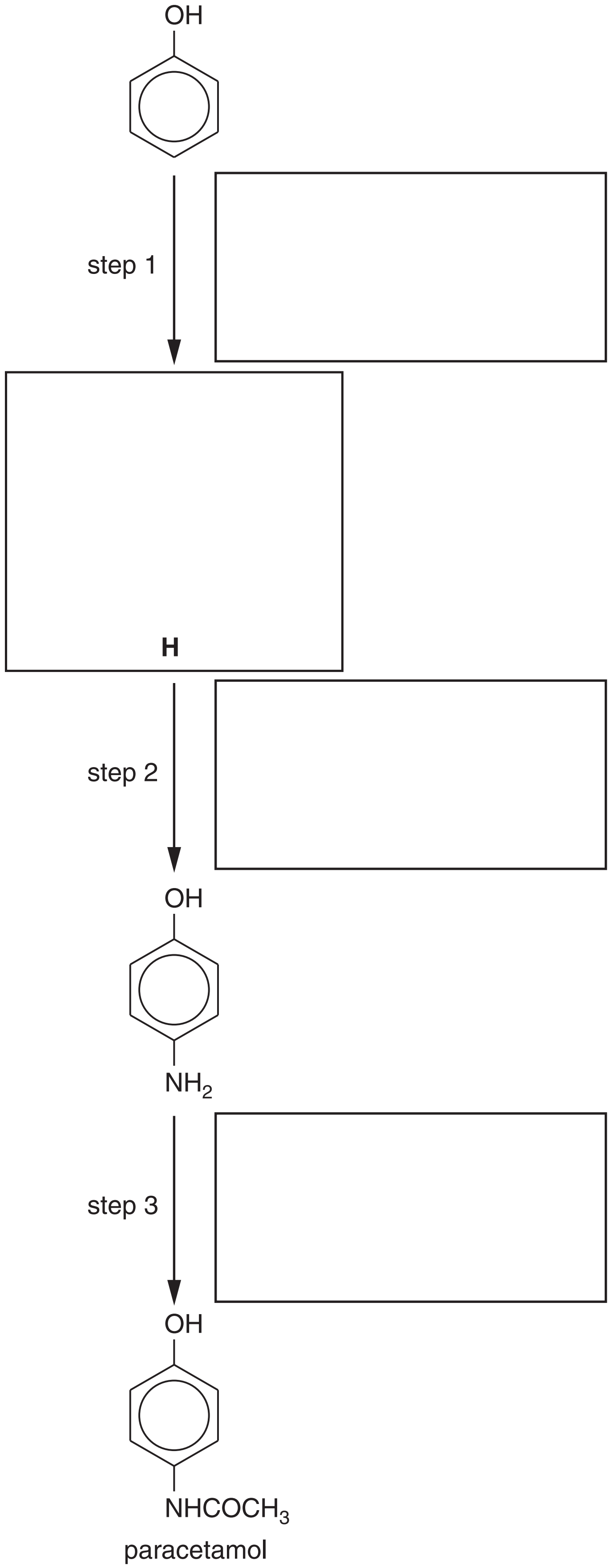


+ Br_2 $\longrightarrow$

[5]

(c) The analgesic drug paracetamol can be synthesised from phenol by the following route. Suggest reagents and conditions for the each of three steps, and suggest the structure of the intermediate **H**. Write your answers in the boxes provided.

For Examiner's Use



[4]

[Total: 13]

Section B

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

For Examiner's Use

6 Enzymes are protein molecules that are highly efficient in catalysing specific chemical reactions in living organisms.

(a) To work in tissues, enzyme molecules generally need to be water-soluble. What does this tell you about the nature of the side-chains on the exterior of the molecules?

....

.... [1]

(b) Enzymes function by a substrate molecule interacting with a particular part of the enzyme known as the 'active site'. The substrate is converted into products that are then released, to be replaced by another substrate molecule.

(i) Describe briefly the primary, secondary and tertiary structures of an enzyme.

....

....

....

....

....

....

(ii) The activity of an enzyme depends upon the tertiary structure of the protein molecule. Explain how the tertiary structure produces an effective active site.

....

....

(iii) Give **two** conditions that can **reduce** the activity of an enzyme, explaining the reason in each case.

I ....

....

....

II ....

....

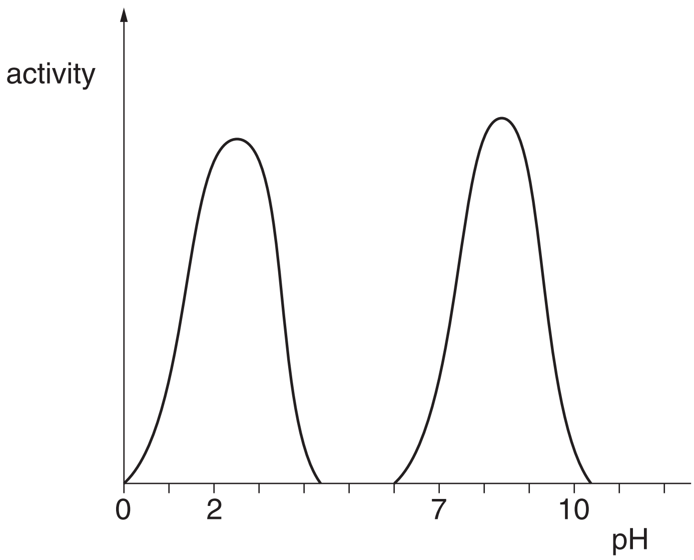
....

[6]

(c) An individual enzyme operates best at a specific pH. Different enzymes operate best under conditions of different pH. Three enzymes involved in the digestion of food are amylase, pepsin and trypsin.

- Amylase, found in saliva, hydrolyses starch to a mixture of glucose and maltose under approximately neutral conditions.
- Pepsin hydrolyses proteins to peptides in the acid conditions of the stomach.
- Trypsin continues the hydrolysis of peptides to amino acids in the mildly alkaline conditions of the small intestine.

The graph below shows the activity of two of the three enzymes mentioned above.



(i) Label each peak shown with the name of the enzyme responsible, either amylase, pepsin or trypsin.

(ii) On the axes above, sketch the graph that the third enzyme would produce, and label it with the name of that enzyme.

[3]

[Total: 10]

7 The technique of DNA fingerprinting has been one of the most important developments in biochemical analysis in recent times. It has enabled enormous advances to be made in forensic science, medicine and archaeology.

(a) The table shows different stages in the production of a genetic fingerprint. Use the numbers 1 to 6 to put the stages in the correct sequence in the blank column.

stages	process	correct sequence (numbers)
A	place samples on agarose gel	
B	use polymerase chain reaction	
C	label with radioactive isotope	
D	extract DNA	
E	use restriction enzyme	
F	carry out electrophoresis	

[3]

(b) One of the stages above uses a radioactive isotope.

(i) What isotope is used? ....

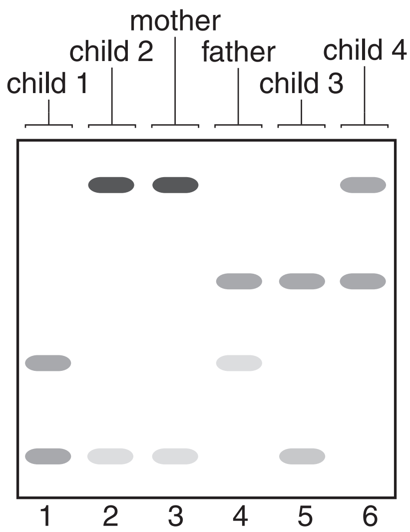
(ii) Why is this isotope chosen?

....

....

[2]

(c) The following DNA fingerprints were taken from a family of mother, father and four children.



For Examiner's Use

(i) Are all of the children related to the mother? State the evidence for your answer.

....

....

(ii) Which child is unlikely to be related to the father? State the evidence for your answer.

....

....

[2]

(d) DNA fingerprinting has been successfully used in archaeological investigations.

(i) Ancient writings were often made on goatskins. Over the centuries these have often become broken into fragments, making reconstruction of the writings almost impossible.

Suggest how the use of DNA fingerprinting might be able to identify which fragments came from a particular skin.

....

....

....

....

(ii) Apart from the examples of human remains and goatskins, state one other material that could be investigated using this technique.

....

....

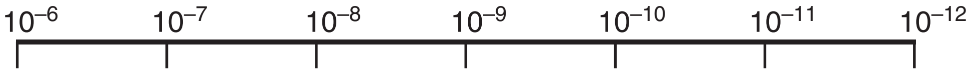
[3]

[Total: 10]

For Examiner's Use

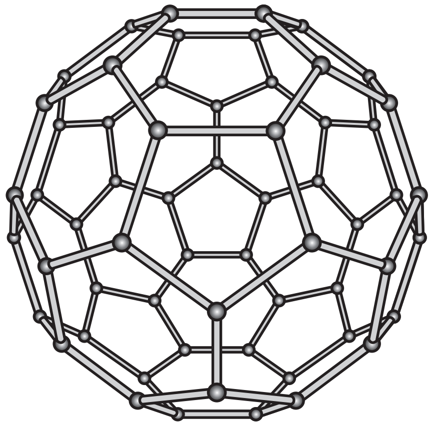
8 Nanotechnology is a fast-developing area of science based on the ability to manipulate materials of very small dimensions.

(a) On the scale shown in metres, mark the upper and lower limits of the range of sizes for nanoparticles.



[2]

(b) One of the most commonly recognised nanoparticles is the 'buckyball', a spherical form of carbon containing 60 carbon atoms. It has been referred to as the third allotrope of carbon.



Diamond and graphite are two other allotropes of carbon. Suggest what is meant by the term *allotrope*.

....

....

.... [2]

(c) Nanoparticles are used to deliver drugs within cells. Suggest what property of nanoparticles enables them to be used in this way. Explain your answer.

....

....

.... [2]

For Examiner's Use

(d) Copper is an important metal that has been used for thousands of years. The problem today is that most of the ores rich in copper compounds have been used up. A century ago ores containing >2% of copper by mass would have been worked; today's mines have to operate at much lower percentages, down to 0.5% of copper by mass.

(i) By what *type of reaction* is the copper present in the ore converted to copper metal?

....

One of the main ores of copper contains the mineral *chalcopyrite*, $CuFeS_2$.

(ii) Calculate the percentage of copper by mass in *chalcopyrite*.

(iii) If the ore contains 2% of *chalcopyrite* by mass, calculate the mass of copper which can be produced from each tonne of ore.

(iv) Certain bacteria are able to extract copper from the 'spoil' heaps of previously mined copper ore. These bacteria are sprayed onto the spoil heaps in an aqueous solution and the resulting solution containing iron(II) sulfate and copper(II) sulfate is collected in tanks.

Suggest how the copper could be recovered as metal.

....

....

....

[4]

[Total: 10]

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UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

0651889794

CHEMISTRY **9701/42**

Paper 4 Structured Questions **October/November 2011**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Centre number and candidate number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs, or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
DO **NOT** WRITE ON ANY BARCODES.

Section A
Answer **all** questions.

Section B
Answer **all** questions.

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.

For Examiner's Use	
1	
2	
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6	
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8	
Total	

This document consists of **17** printed pages and **3** blank pages.

DC (NF/SW) 50350

UNIVERSITY of CAMBRIDGE International Examinations

Section A

For Examiner's Use

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

1 **(a)** The halogens chlorine and bromine react readily with hydrogen.

$$X_2(g) + H_2(g) \longrightarrow 2HX(g) \qquad [X = Cl \text{ or } Br]$$

(i) Describe how you could carry out this reaction using chlorine.

....

(ii) Describe **two** observations you would make if this reaction was carried out with bromine.

....

....

(iii) Use bond energy data from the *Data Booklet* to calculate the $\Delta H^\ominus$ for this reaction when

X = C*l*,

$\Delta H^\ominus$ = ... $kJ\,mol^{-1}$

X = Br.

$\Delta H^\ominus$ = ... $kJ\,mol^{-1}$

(iv) What is the major reason for the difference in these two $\Delta H^\ominus$ values?

....

[8]

For Examiner's Use

(b) Some halogens also react readily with methane.

$$CH_4(g) + X_2(g) \rightarrow CH_3X(g) + HX(g)$$

(i) What conditions are needed to carry out this reaction when X is bromine, Br?

....

(ii) Use bond energy data from the *Data Booklet* to calculate the $\Delta H^{\ominus}$ of this reaction for the situation where X is iodine, I.

$\Delta H^{\ominus}$ = ... $kJ\,mol^{-1}$

(iii) Hence suggest why it is not possible to make iodomethane, CH_3I, by this reaction.

....

[4]

(c) Halogenoalkanes can undergo *homolytic fission* in the upper atmosphere.

(i) Explain the term *homolytic fission*.

....

....

(ii) Suggest the most likely organic radical that would be formed by the homolytic fission of bromochloromethane, CH_2BrCl. Explain your answer.

....

....

....

[3]

(d) The reaction between propane and chlorine produces a mixture of many compounds, four of which are structural isomers with the molecular formula $C_3H_6Cl_2$.
Draw the structural or skeletal formulae of these isomers, and indicate any chiral atoms with an asterisk (*).

[3]

[Total: 18]

2 Acetals are compounds formed when aldehydes are reacted with an alcohol and an acid catalyst. The reaction between ethanal and methanol was studied in the inert solvent dioxan.

For Examiner's Use

$$\underset{\text{ethanal}}{CH_3CHO} + \underset{\text{methanol}}{2CH_3OH} \overset{H^+}{\rightleftharpoons} \underset{\text{acetal } \mathbf{A}}{CH_3CH(OCH_3)_2} + H_2O$$

(a) When the initial rate of this reaction was measured at various starting concentrations of the three reactants, the following results were obtained.

experiment number	$[CH_3CHO]$ / mol dm^{-3}	$[CH_3OH]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	relative rate
1	0.20	0.10	0.05	1.00
2	0.25	0.10	0.05	1.25
3	0.25	0.16	0.05	2.00
4	0.20	0.16	0.10	3.20

(i) Use the data in the table to determine the order with respect to each reactant.

order with respect to $[CH_3CHO]$ ....

order with respect to $[CH_3OH]$ ....

order with respect to $[H^+]$ ....

(ii) Use your results from part **(i)** to write the rate equation for the reaction.

....

(iii) State the units of the rate constant in the rate equation ....

(iv) Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are 0.20 mol dm^{-3}.

relative rate = ...

[6]

For Examiner's Use

(b) The concentration of the acetal product was measured when experiment number 1 was allowed to reach equilibrium. The result is included in the following table.

	$[CH_3CHO]$ / $mol\,dm^{-3}$	$[CH_3OH]$ / $mol\,dm^{-3}$	$[H^+]$ / $mol\,dm^{-3}$	[acetal **A**] / $mol\,dm^{-3}$	$[H_2O]$ / $mol\,dm^{-3}$
at start	0.20	0.10	0.05	0.00	0.00
at equilibrium	(0.20–$\boldsymbol{x}$)			$\boldsymbol{x}$	
at equilibrium				0.025	

(i) Complete the second row of the table in terms of $\boldsymbol{x}$, the concentration of acetal **A** at equilibrium. You may wish to consult the chemical equation opposite.

(ii) Using the [acetal **A**] as given, $0.025\,mol\,dm^{-3}$, calculate the equilibrium concentrations of the other reactants and products and write them in the third row of the table.

(iii) Write the expression for the equilibrium constant for this reaction, K_c, stating its units.

K_c = ... units = ...

(iv) Use your values in the third row of the table to calculate the value of K_c.

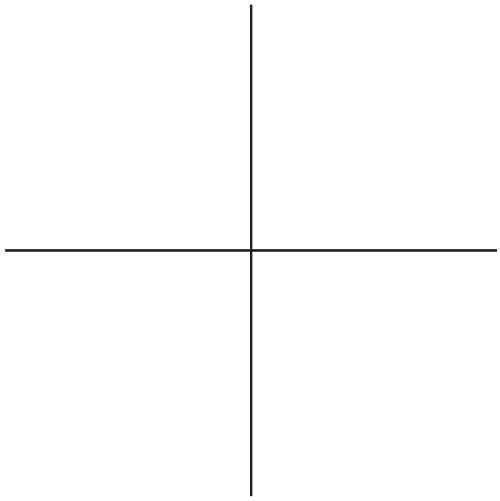
K_c = ...

[9]

[Total: 15]

For Examiner's Use

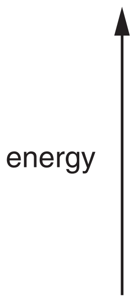
3 **(a)** On the following diagram draw a clear **labelled** sketch to describe the shape and symmetry of a typical d-orbital.



[2]

(b) Although the five d-orbitals are at the same energy in an isolated atom, when a transition element ion is in an octahedral complex the orbitals are split into two groups.

(i) Draw an orbital energy diagram to show this, indicating the number of orbitals in each group.



(ii) Use your diagram as an aid in explaining the following.

- Transition element complexes are often coloured.

....

....

....

....

- The colour of a complex of a given transition element often changes when the ligands around it are changed.

....

....

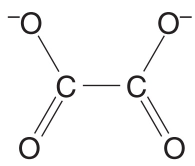
....

[7]

For Examiner's Use

(c) Heating a solution containing potassium ethanedioate, iron(II) ethanedioate and hydrogen peroxide produces the light green complex $K_3Fe(C_2O_4)_3$, which contains the ion $[Fe(C_2O_4)_3]^{3-}$.

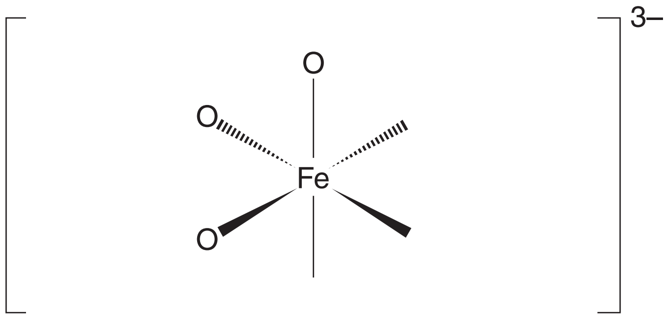
The structure of the ethanedioate ion is as follows.



(i) Calculate the oxidation number of carbon in this ion. ....

(ii) Calculate the oxidation number of iron in $[Fe(C_2O_4)_3]^{3-}$. ....

(iii) The iron atom in the $[Fe(C_2O_4)_3]^{3-}$ ion is surrounded octahedrally by six oxygen atoms. Complete the following **displayed** formula of this ion.



(iv) In sunlight the complex decomposes into potassium ethanedioate, iron(II) ethanedioate and carbon dioxide.

Use oxidation numbers to help you balance the following equation for this decomposition.

$K_3Fe(C_2O_4)_3 \rightarrow$ ....$K_2C_2O_4$ + ...FeC_2O_4 + ...CO_2

[5]

[Total: 14]

For Examiner's Use

4 **(a)** **(i)** Write the equation for a reaction in which ethylamine, $C_2H_5NH_2$, acts as a Brønsted-Lowry base.

....

(ii) Ammonia, ethylamine and phenylamine, $C_6H_5NH_2$, are three nitrogen-containing bases.

Place these three compounds in order of basicity, with the most basic first.

most basic		least basic

(iii) Explain why you have placed the three compounds in this order.

....

....

....

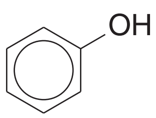
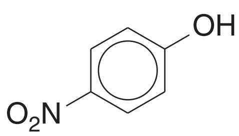
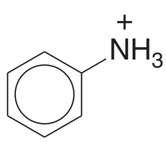
....

[4]

(b) **(i)** Write an equation for a reaction in which phenol, C_6H_5OH, acts as a Brønsted-Lowry acid.

....

The pK_a values for phenol, 4-nitrophenol and the phenylammonium ion are given in the table.

compound	pK_a
	10.0
	7.2
	4.6

(ii) Suggest an explanation for the difference in the pK_a values of phenol and nitrophenol.

....

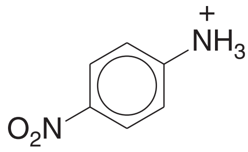
....

....

....

For Examiner's Use

(iii) Using the information in the table opposite, predict which of the following pK_a values is the most likely for the 4-nitrophenylammonium ion.



Place a tick (✓) in the box beside the value you have chosen.

pK_a	
1.0	
4.5	
7.0	
10.0	

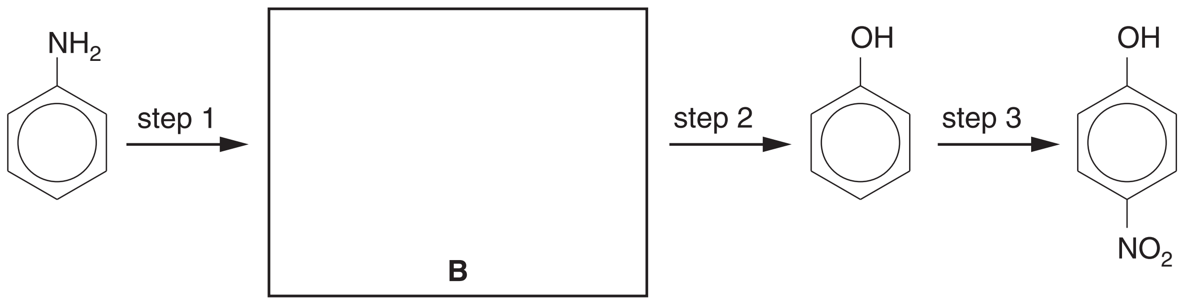
(iv) Explain your answer to part **(iii)**.

....

....

....
[5]

(c) Phenylamine can be converted to 4-nitrophenol by the following steps.



(i) Suggest the identity of intermediate **B** by drawing its structure in the box above.

(ii) Suggest reagents and conditions for the three steps in the above scheme.

	reagent(s)	conditions
step 1		
step 2		
step 3		

[5]

[Total: 14]

5 Compound **C** has the molecular formula $C_7H_{14}O$. Treating **C** with hot concentrated acidified $KMnO_4$(aq) produces two compounds, **D**, C_4H_8O, and **E**, $C_3H_4O_3$. The results of four tests carried out on these three compounds are shown in the following table.

For Examiner's Use

test reagent	result of test with		
	compound **C**	compound **D**	compound **E**
Br_2(aq)	decolourises	no reaction	no reaction
Na(s)	fizzes	no reaction	fizzes
I_2(aq) + OH^-(aq)	no reaction	yellow precipitate	yellow precipitate
2,4-dinitrophenylhydrazine	no reaction	orange precipitate	orange precipitate

(a) State the functional groups which the above four reagents test for.

(i) Br_2(aq)

....

(ii) Na(s)

....

(iii) I_2(aq) + OH^-(aq)

....

(iv) 2,4-dinitrophenylhydrazine

....
[4]

(b) Based upon the results of the above tests, suggest structures for compounds **D** and **E**.

D, C_4H_8O **E**, $C_3H_4O_3$

[2]

(c) Compound **C** exists as two stereoisomers.

For Examiner's Use

Draw the structural formula of **each** of the two isomers, and state the type of stereoisomerism involved.

type of stereoisomerism ....

[3]

[Total: 9]

Section B

For Examiner's Use

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

6 Proteins exist in an enormous variety of sizes and structures in living organisms. They have a wide range of functions which are dependent upon their structures. The structure and properties of an individual protein are a result of the primary structure – the sequence of amino acids that form the protein.

(a) Proteins are described as condensation polymers.

(i) Write a balanced equation for the condensation reaction between two glycine molecules, $H_2NCH_2CO_2H$.

(ii) Draw the skeletal formula for the organic product.

[2]

(b) X-ray analysis has shown that in many proteins there are regions with a regular arrangement within the polypeptide chain. This is called the secondary structure and exists in two main forms.

(i) State the two forms of secondary structure found in proteins.

....

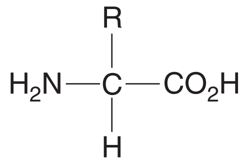
....

(ii) Draw a diagram to illustrate **one** form of secondary structure.

[4]

For Examiner's Use

(c) There are around 20 different common amino acids found in humans most of which have the same general structure.



The nature of the group R affects which bonds are formed as the secondary structure of the protein is further folded to give the tertiary structure.

Complete the table indicating the type of **tertiary** bonding that each pair of the amino acid residues is likely to produce.

residue 1	residue 2	type of tertiary bonding
$–HNCH(CH_2CH_2CH_2CH_2NH_2)CO–$	$–HNCH(CH_2CH_2CO_2H)CO–$	
$–HNCH(CH_3)CO–$	$–HNCH(CH_3)CO–$	
$–HNCH(CH_2SH)CO–$	$–HNCH(CH_2SH)CO–$	
$–HNCH(CH_2OH)CO–$	$–HNCH(CH_2CO_2H)CO–$	

[4]

[Total: 10]

For Examiner's Use

7 One of the key areas of investigation in understanding the structures of polypeptides and proteins is the sequence of amino acids that make up the polypeptide chains.

(a) One of the methods used to determine the amino acids present in a polypeptide chain is electrophoresis.

Sketch and label the apparatus used to carry out electrophoresis.

[4]

(b) In electrophoresis, different amino acids move in different directions and at different speeds.

(i) What factors determine the *direction of travel* of an amino acid?

....

....

....

(ii) What factors determine the *speed of movement* of an amino acid?

....

....

[3]

(c) Another important technique used to examine the structure of proteins is X-ray crystallography. In this technique the position of individual atoms can be determined, and the distances between them measured.

For Examiner's Use

(i) Hydrogen atoms never produce images using X-ray crystallography. Explain why this is the case.

....

....

(ii) Suggest and explain which one of the atoms in a molecule of cysteine, $H_2NCH(CH_2SH)CO_2H$, would show up most clearly using X-ray crystallography.

....

....

[3]

[Total: 10]

8 In today's world we make use of a wide range of different polymers. These polymers are often substitutes for traditional materials, but may have more useful properties.

(a) Complete the table identifying one traditional material that has been replaced by each polymer.

traditional material	modern polymer and its use
	PVC in packaging
	Terylene in fabrics
	polycarbonate bottle

[2]

(b) Throwing away articles made from polymers after use is a major environmental concern for **two** main reasons. Identify **each** of these reasons and suggest a strategy that has been adopted to try to overcome each of these.

reasons : ....

....

....

strategy 1 : ....

....

strategy 2 : ....

....

[3]

For Examiner's Use

(c) One suggestion for the disposal of polymers is to use them as a fuel to provide energy for small-scale power stations or district heating schemes.
Identify one polymer which would be **unsuitable** for this use, explaining the reason behind this.

polymer ....

reason ....

....

.... [2]

(d) Polymers can be either thermoplastic or thermosetting.

Name a thermoplastic polymer. ....

State which type of polymerisation produces thermoplastic polymers, explaining your answer in terms of the structure of the polymer.

....

....

....

.... [3]

[Total: 10]

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UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CANDIDATE NAME	

CENTRE NUMBER		CANDIDATE NUMBER	

4308858825

CHEMISTRY **9701/42**

Paper 4 Structured Questions **May/June 2010**

1 hour 45 minutes

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.
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Section A
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Section B
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For Examiner's Use	
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UNIVERSITY of CAMBRIDGE International Examinations

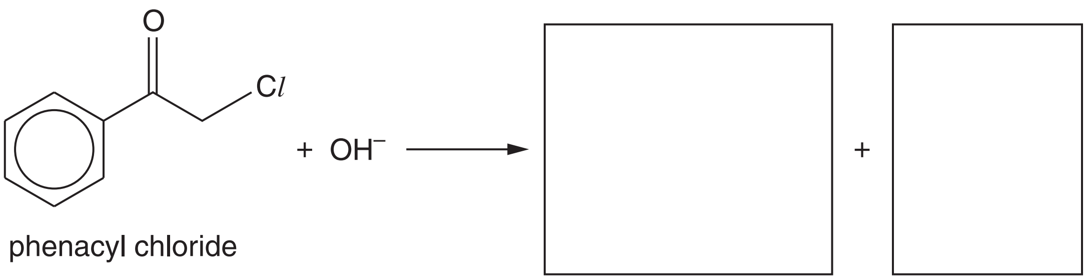
[Turn over

Section A

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

1 Phenacyl chloride has been used as a component of some tear gases. Its lachrymatory and irritant properties are due to it reacting with water inside body tissues to produce hydrochloric acid.

It undergoes a nucleophilic substitution reaction with NaOH(aq).



phenacyl chloride

(a) Write the formulae of the products of this reaction in the two boxes above. [2]

When the rate of this reaction was measured at various concentrations of the two reagents, the following results were obtained.

experiment number	[phenacyl chloride]	[NaOH]	relative rate
1	0.020	0.10	1.0
2	0.030	0.10	1.5
3	0.025	0.20	2.5

(b) **(i)** What is meant by the term *order of reaction*?

....

(ii) Use the above data to deduce the order with respect to each reactant. Explain your reasoning.

....

....

....

....

....

(iii) Write the overall rate equation for the reaction.

....

(iv) Describe the mechanism for this reaction that is consistent with your overall rate equation.
You should show all intermediates and/or transition states and partial charges, and you should represent the movements of electron pairs by curly arrows.

[7]

(c) (i) Describe an experiment that would show that CH_3COCl reacts with water at a much faster rate than phenacyl chloride. Include the reagents you would use, and the observations you would make with each chloride.

....

....

....

....

....

....

....

(ii) Suggest an explanation for this difference in reactivity.

....

....
[4]

[Total: 13]

For Examiner's Use

2 **(a)** Describe and explain how the solubilities of the sulfates of the Group II elements vary down the group.

....

....

....

....

....

.... [3]

(b) The following table lists some enthalpy changes for magnesium and strontium compounds.

enthalpy change	value for magnesium / $kJ\,mol^{-1}$	value for strontium / $kJ\,mol^{-1}$
lattice enthalpy of $\boldsymbol{M}(OH)_2$	–2993	–2467
enthalpy change of hydration of $\boldsymbol{M}^{2+}(g)$	–1890	–1414
enthalpy change of hydration of $OH^-(g)$	–550	–550

(i) Use the above data to calculate values of $\Delta H^\ominus_{solution}$ for $Mg(OH)_2$ and for $Sr(OH)_2$.

$Mg(OH)_2$ ....

....

$\Delta H^\ominus_{solution}$ = ... $kJ\,mol^{-1}$

$Sr(OH)_2$ ....

....

$\Delta H^\ominus_{solution}$ = ... $kJ\,mol^{-1}$

(ii) Use your results in **(i)** to suggest whether $Sr(OH)_2$ is more or less soluble in water than is $Mg(OH)_2$. State any assumptions you make.

....

....

(iii) Suggest whether $Sr(OH)_2$ would be more or less soluble in hot water than in cold. Explain your reasoning.

....

....

[5]

(c) Calcium hydroxide, $Ca(OH)_2$, is slightly soluble in water.

For Examiner's Use

(i) Write an expression for K_{sp} for calcium hydroxide, and state its units.

K_{sp} = units ....

(ii) 25.0 cm^3 of a saturated solution of $Ca(OH)_2$ required 21.0 cm^3 of 0.0500 mol dm^{-3} HCl for complete neutralisation.

Calculate the $[OH^-(aq)]$ and the $[Ca^{2+}(aq)]$ in the saturated solution, and hence calculate a value for K_{sp}.

$[OH^-(aq)]$ = ...

$[Ca^{2+}(aq)]$ = ...

K_{sp} = ...

(iii) How would the solubility of $Ca(OH)_2$ in 0.1 mol dm^{-3} NaOH compare with that in water?
Explain your answer.

....

....

[6]

[Total: 14]

For Examiner's Use

3 **(a)** Fluorine is much more electronegative than both silicon and sulfur, but whereas the molecule of SF_4 has an overall dipole, that of SiF_4 has none.

Suggest a reason for this difference.

....

....[1]

(b) Predict whether or not the following molecules will have an overall dipole. Place a tick in the appropriate column.

compound	molecule has an overall dipole	molecule does not have an overall dipole
BCl_3		
PCl_3		
CCl_4		
SF_6		

[2]

(c) Boron and silicon are two elements adjacent to carbon in the periodic table. CCl_4 does not react with water, whereas BCl_3 and $SiCl_4$ do react.

(i) Suggest a reason for this difference in reactivity.

....

....

(ii) Construct equations showing the reaction of these two chlorides with an excess of water.

BCl_3 ....

$SiCl_4$ ....

[3]

(d) When reacted with a small quantity of water, $SiCl_4$ produces an oxychloride **X**, $Si_xCl_yO_z$. The mass spectrum of **X** shows peaks at mass numbers of 133, 149, 247, 263 and 396. (You should assume that the species responsible for all these peaks contain the ^{16}O, the ^{35}Cl and the ^{28}Si isotopes only.)

For Examiner's Use

(i) Use these data to deduce the molecular formula of **X**.

molecular formula ....

(ii) Suggest the structures of the fragments responsible for the peaks at the following mass numbers.

mass number	structure
133	
247	
263	

(iii) Hence suggest the displayed formula of **X**.

[5]

[Total: 11]

For Examiner's Use

4 **(a)** Complete the electronic structures of the Cr^{3+} and Mn^{2+} ions.

Cr^{3+} $1s^2 2s^2 2p^6$ ....

Mn^{2+} $1s^2 2s^2 2p^6$ ....

[2]

(b) **(i)** Describe what observations you would make when dilute $KMnO_4$(aq) is added slowly and with shaking to an acidified solution of $FeSO_4$(aq) until the $KMnO_4$ is in a large excess.

....

....

....

....

....

....

(ii) Construct an ionic equation for the reaction that occurs.

....

[4]

(c) By selecting relevant $E^{\ominus}$ data from the *Data Booklet* explain why acidified solutions of Fe^{2+}(aq) are relatively stable to oxidation by air, whereas a freshly prepared precipitate of $Fe(OH)_2$ is readily oxidised to $Fe(OH)_3$ under alkaline conditions.

relevant $E^{\ominus}$ values and half equations

....

....

....

....

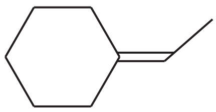
explanation

....

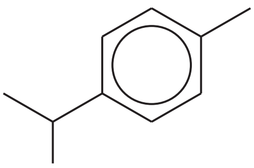
....

[4]

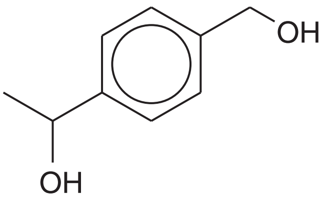
(d) Predict the organic products of the following reactions and draw their structures in the boxes below. You may use structural or skeletal formulae as you wish.



hot conc. $MnO_4^- + H^+$ →



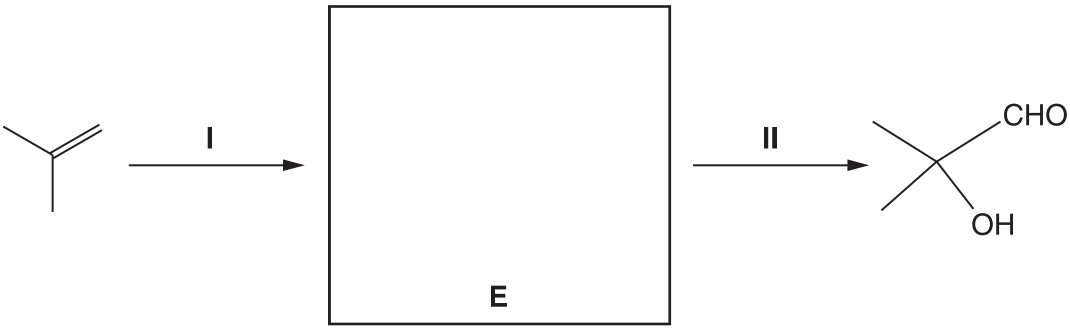
hot conc. $MnO_4^- + H^+$ →



hot $Cr_2O_7^{2-} + H^+$ →

[4]

(e) $KMnO_4$ and $K_2Cr_2O_7$ are the reagents that can be used to carry out the following transformation.



(i) Draw the structure of intermediate **E** in the box above.

(ii) Suggest reagents and conditions for the following.

reaction **I** ....

reaction **II** ....

[3]

[Total: 17]

For Examiner's Use

5 **(a)** **(i)** Briefly explain why the benzene molecule is planar.

....

....

....

(ii) Briefly explain why all the carbon-carbon bonds in benzene are the same length.

....

....

....

[2]

(b) Benzene can be nitrated by warming it with a mixture of concentrated sulfuric and nitric acids.

(i) By means of an equation, illustrate the initial role of the sulfuric acid in this reaction.

....

(ii) Name the type of reaction and describe the mechanism for the nitration reaction, including curly arrows showing the movement of electrons and all charges.

type of reaction ....

mechanism

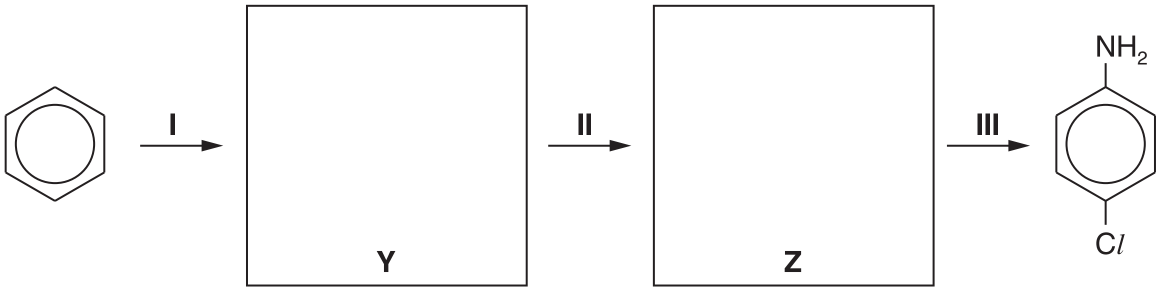
[4]

(c) State the reagents and conditions needed to convert benzene into chlorobenzene.

....[1]

(d) Nitrobenzene undergoes further substitution considerably more slowly than chlorobenzene. In nitrobenzene the incoming group joins to the benzene ring in the 3-position, whereas in chlorobenzene the incoming group joins to the benzene ring in the 4-position.

(i) Use these ideas to suggest the structures of the intermediate compounds **Y** and **Z** in the following synthesis of 4-chlorophenylamine.

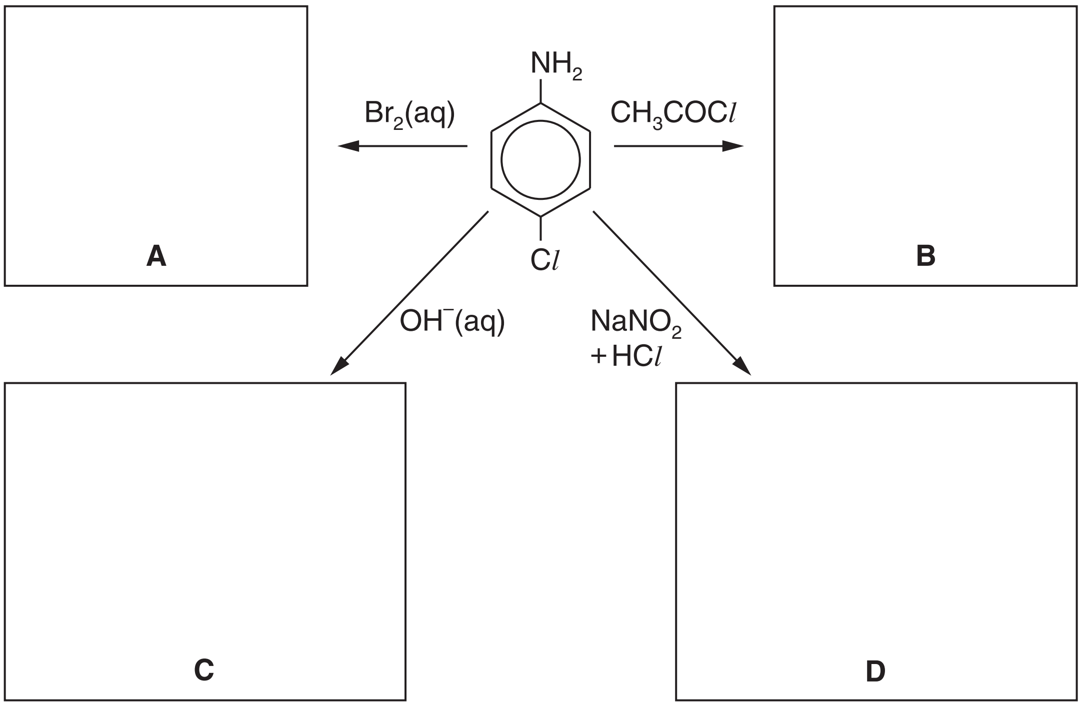


(ii) Suggest the reagents and conditions needed for reaction **III** in the above synthesis.

....

....

(iii) Suggest the structural formulae of the products **A**, **B**, **C** and **D** of the following reactions. If no reaction occurs write "no reaction" in the relevant box.



[8]

[Total: 15]

Section B

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

For Examiner's Use

6 Human hair and silk both consist of proteins. Proteins are described as having three major levels of structure: primary, secondary and tertiary.

(a) Outline what is meant by the terms *primary structure* and *tertiary structure* of a protein.

primary structure ....

....

....

tertiary structure ....

....

.... [2]

(b) In hair, the secondary structure consists of α-helices which are cross-linked by disulfide bonds. The amino acid responsible for this cross-linking is cysteine, $H_2NCH(CH_2SH)CO_2H$.

(i) Show by means of a diagram how the disulfide cross-links are formed.

(ii) What type of reaction is this?

....

(iii) State **three** other interactions that stabilise the tertiary structure of proteins.

....

....

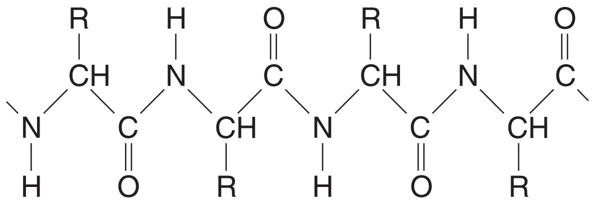
....
[4]

(c) The β-pleated sheet is a different form of secondary structure found in proteins, such as those in silk.

(i) What type of bonding is responsible for stabilising the β-pleated sheet in silk?

....

(ii) On the diagram below, draw a second polypeptide strand and show how bonds would be formed that stabilise this β-pleated sheet.



[3]

(d) The cysteine-containing protein in hair is called α-keratin. A similar sequence of amino acids can produce β-keratin proteins found in the scales, claws and shells of reptiles such as tortoises. In β-keratin the secondary structure of the protein is in the form of a β-pleated sheet.

Suggest what makes the β-pleated sheet in β-keratin so much less flexible than the β-pleated sheet in silk.

....

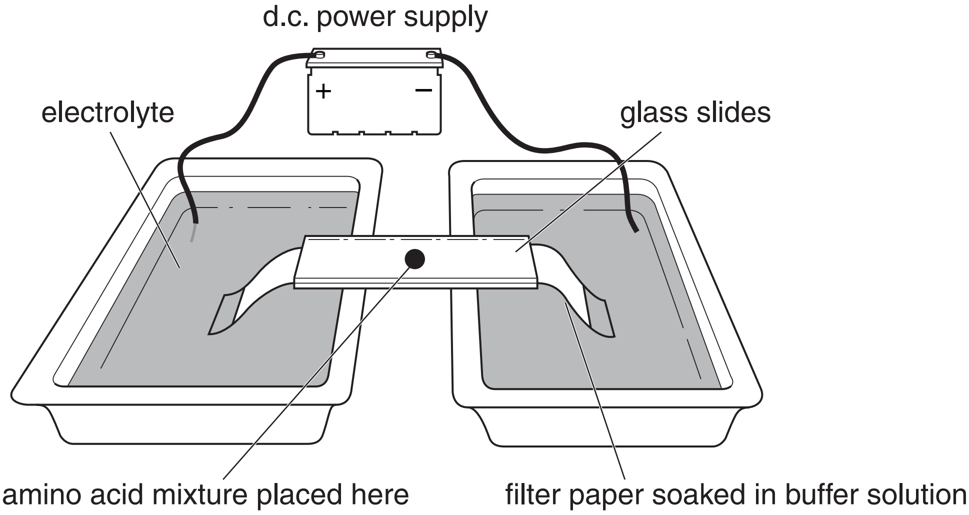
....

....[1]

[Total: 10]

For Examiner's Use

7 A mixture of amino acids may be separated using electrophoresis. A typical practical set-up is shown in the diagram.



(a) When the power supply is switched on, some amino acids may **not** move, but remain stationary. Suggest an explanation for this observation.

....

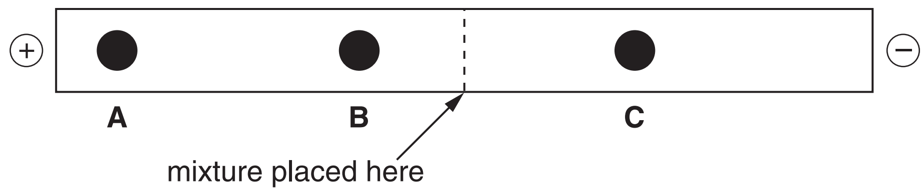
....

....[2]

(b) The amino acid glycine has the formula $H_2NCH_2CO_2H$. Identify the species formed on the filter paper if glycine moves to the left (positive) end of the filter paper.

.... [1]

(c) The following result was obtained from another electrophoresis. What can be deduced about the relative sizes of, and charges on, the amino acid species **A**, **B** and **C**?



amino acid	relative size	charge
A		
B		
C		

[3]

For Examiner's Use

(d) The sequence of amino acids in a polypeptide may be determined by partial hydrolysis of the chain into smaller pieces, often tripeptides.

(i) Following such a partial hydrolysis, the following tripeptides were obtained from a given polypeptide.

ala-gly-asp   gly-ala-gly   lys-val-ser   ser-ala-gly   val-ser-ala

Given that the N-terminal amino acid is lysine (lys) suggest the amino acid sequence of the **shortest** polypeptide that would give the above tripeptides.

....

The structural formulae of the amino acids in the polypeptide are given below.

abbreviation	amino acid	structural formula
ala	alanine	$H_2NCH(CH_3)CO_2H$
asp	aspartic acid	$H_2NCH(CH_2CO_2H)CO_2H$
gly	glycine	$H_2NCH_2CO_2H$
lys	lysine	$H_2NCH(CH_2CH_2CH_2CH_2NH_2)CO_2H$
ser	serine	$H_2NCH(CH_2OH)CO_2H$
val	valine	$H_2NCH(CH(CH_3)_2)CO_2H$

(ii) Which of the tripeptides in **(i)** has the lowest M_r?

....

(iii) Select **one** amino acid **from those listed in the table** which contains an ionic side-chain at pH 8.

....

[4]

[Total: 10]

8 The design and development of batteries has been a major research area in recent years.

For Examiner's Use

(a) Lead-acid batteries, used in cars, are made up of a number of rechargeable cells in series, and were first developed in 1860. They have the disadvantage of a relatively high mass compared to the energy stored. During discharge, the electrode reactions in the cells of these batteries are as follows.

I $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

II $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

State which of these reactions occurs at the positive electrode in a lead-acid cell during discharge, explaining your answer.

....

.... [1]

(b) Use the *Data Booklet* and the equations **I** and **II** above to calculate the voltage produced by a lead-acid cell under standard conditions.

[2]

(c) Nickel-metal hydride batteries were developed in the 1980s and have become increasingly common particularly for small devices such as mobile phones and digital cameras that need near-constant sources of electrical energy. These cells use nickel oxohydroxide (NiO(OH)) as one electrode and a hydrogen-absorbing alloy such as $LiNi_5$ as the other electrode.

One reaction that takes place in these batteries is

$$NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^-$$

(i) State the oxidation state of nickel in NiO(OH). ....

(ii) Suggest a likely advantage of these batteries compared with lead-acid batteries.

....

....
[2]

(d) Hydrogen fuel cells have been suggested as the next major advance in electrically powered vehicles. In these fuel cells hydrogen is oxidized to produce water, using a catalyst and inert electrodes.

For Examiner's Use

(i) Suggest a material for the electrodes.

....

(ii) Use your knowledge of hydrogen to suggest a disadvantage of these fuel cells in powering vehicles.

....

.... [2]

(e) Many of the world's countries are developing ways of recycling materials which are valuable or which require large amounts of energy to produce.

For each of the following recyclable materials, state whether recycling of this material is important in saving energy or in saving resources. Use your knowledge of chemistry to explain each choice.

glass ....

....

....

steel ....

....

....

plastics ....

....

.... [3]

[Total: 10]

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UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CANDIDATE NAME	

CENTRE NUMBER		CANDIDATE NUMBER	

3430056738

CHEMISTRY **9701/42**

Paper 4 Structured Questions **October/November 2010**

1 hour 45 minutes

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Centre number and candidate number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs, or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
DO **NOT** WRITE ON ANY BARCODES.

Section A
Answer **all** questions.

Section B
Answer **all** questions.

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.

For Examiner's Use	
1	
2	
3	
4	
5	
6	
7	
8	
9	
Total	

This document consists of **17** printed pages and **3** blank pages.

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Section A

For Examiner's Use

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

1 **(a)** Write a balanced equation for the reaction of each of the following chlorides with water.

phosphorus(V) chloride ....

silicon(IV) chloride..

[2]

(b) When sulfur is heated under pressure with chlorine, the major product is SCl_2 (Cl-S-Cl).

$$S_8(g) + 8Cl_2(g) \rightarrow 8SCl_2(g)$$

Use data from the *Data Booklet* to calculate the enthalpy change, ΔH, for this reaction. The eight sulfur atoms in the S_8 molecule are all joined in a single ring by single bonds.

ΔH = ...kJ mol^{-1}

[2]

(c) Under suitable conditions, SCl_2 reacts with water to produce a yellow precipitate of sulfur and a solution **A**. Solution **A** contains a mixture of SO_2(aq) and compound **B**.

(i) What is the oxidation number of sulfur in SCl_2? ....

(ii) Work out how the oxidation number of sulfur changes during the reaction of SCl_2 with water.

....

....

(iii) Suggest the identity of compound **B**. ....

(iv) Construct an equation for the reaction between SCl_2 and water.

....

(v) What would you observe when each of the following reagents is added to separate samples of solution **A**?

$AgNO_3$(aq)..

$K_2Cr_2O_7$(aq) ....

[7]

[Total: 11]

For Examiner's Use

2 (a) (i) What is meant by the term *ligand* in the context of transition element chemistry?

....

....

(ii) Decide which of the following species could be a ligand, and which could not be. Place a tick (✓) in the appropriate column.

species	can be a ligand	cannot be a ligand
OH^-		
NH_4^+		
CH_3OH		
CH_3NH_2		

[3]

(b) Read the following description of some reactions of copper(II) sulfate, and answer the questions that follow.

When 0.1 mol of white anhydrous $CuSO_4$ is dissolved in liquid ammonia at –33 °C, a deep blue solution **C** results.
When 0.2 mol of solid NaOH is added to solution **C**, and the ammonia solvent allowed to evaporate, a solid residue is obtained.
Heating this residue to 200 °C produces a dark coloured mixture of two solids.
When water is added to this mixture, a black solid **D** and a colourless solution **E** are formed. Neither **D** nor **E** contains nitrogen.
Adding $BaCl_2$(aq) to solution **E** produces a white precipitate **F**.
Solid **D** dissolves in HNO_3(aq) on warming, without evolution of gas, to give a pale blue solution containing $Cu(NO_3)_2$(aq).

(i) Suggest the formula of the compound contained in each of the following.

solution **C** ....

solid **D** ....

solution **E** ....

white precipitate **F** ....

(ii) Name the type of reaction that is occurring when **D** reacts with HNO_3(aq).

....

[5]

For Examiner's Use

(c) (i) Describe what you would observe when a solid sample of anhydrous $Cu(NO_3)_2$ is strongly heated.

....

....

(ii) Write an equation for this reaction.

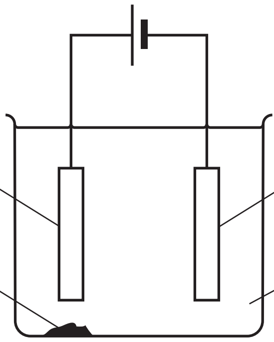
....

[2]

[Total: 10]

For Examiner's Use

3 The electrolytic purification of copper can be carried out in an apparatus similar to the one shown below.



The impure copper anode contains small quantities of metallic nickel, zinc and silver, together with inert oxides and carbon resulting from the initial reduction of the copper ore with coke. The copper goes into solution at the anode, but the silver remains as the metal and falls to the bottom as part of the anode 'sludge'. The zinc also dissolves.

(a) **(i)** Write a half equation including state symbols for the reaction of copper at the anode.

....

(ii) Use data from the *Data Booklet* to explain why silver remains as the metal.

....

(iii) Use data from the *Data Booklet* to predict what happens to the nickel at the anode.

....

....

(iv) Write a half equation including state symbols for the main reaction at the cathode.

....

(v) Use data from the *Data Booklet* to explain why zinc is not deposited on the cathode.

....

....

(vi) Suggest why the blue colour of the electrolyte slowly fades as the electrolysis proceeds.

....

....

[7]

For Examiner's Use

(b) Most of the current passed through the cell is used to dissolve the copper at the anode and precipitate pure copper onto the cathode. However, a small proportion of it is 'wasted' in dissolving the impurities at the anode which then remain in solution.
When a current of 20.0 A was passed through the cell for 10.0 hours, it was found that 225 g of pure copper was deposited on the cathode.

(i) Calculate the following, using appropriate data from the *Data Booklet*.

- number of moles of copper produced at the cathode

- number of moles of electrons needed to produce this copper

- number of moles of electrons that passed through the cell

(ii) Hence calculate the percentage of the current through the cell that has been 'wasted' in dissolving the impurities at the anode.

[4]

(c) Nickel often occurs in ores along with iron. After the initial reduction of the ore with coke, a nickel-iron alloy is formed.
Use data from the *Data Booklet* to explain why nickel can be purified by a similar electrolysis technique to that used for copper, using an impure nickel anode, a pure nickel cathode, and nickel sulfate as the electrolyte. Explain what would happen to the iron during this process.

....

....

....

.... [2]

[Total: 13]

For Examiner's Use

4 The most typical oxides of tin and lead are SnO, SnO_2, PbO and PbO_2.

The following two generalisations can be made about the oxides of the elements in Group IV.

- As the metallic character of the elements increases down the Group, the oxides become more basic.
- The oxides of the elements in their higher oxidation states are more acidic than the oxides of the elements in their lower oxidation states.

(a) Use these generalisations to suggest which of the above oxides of tin or lead is **most likely** to react with each of the following reagents. In each case write a balanced equation for the reaction.

(i) with NaOH(aq)

formula of oxide ....

equation ....

(ii) with HCl(aq)

formula of oxide ....

equation ....

[4]

(b) 'Red lead' is used as a pigment, and as a metal primer paint to prevent the corrosion of steel. It is an oxide of lead that contains 9.30% oxygen by mass.

Calculate to **3 significant figures** the number of moles of oxygen and lead contained in a 100.0 g sample of red lead. Hence calculate its empirical formula.

empirical formula: .... [2]

For Examiner's Use

(c) Lead(II) chloride is slightly soluble in water.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad K_{sp} = 2.0 \times 10^{-5}$$

(i) Write an expression for the solubility product, K_{sp} for lead(II) chloride and state its units.

K_{sp} = ... units ....

(ii) Calculate $[Pb^{2+}(aq)]$ in a saturated solution of $PbCl_2$.

....

....

An excess of $PbCl_2(s)$ is stirred with 0.50 mol dm^{-3} NaCl until equilibrium has been established. The excess $PbCl_2(s)$ is then filtered off.

(iii) Assuming $[Cl^-]$ remains at 0.50 mol dm^{-3} throughout, calculate the $[Pb^{2+}(aq)]$ in the remaining solution.

....

....

(iv) Suggest an explanation for the difference between this value and the value that you calculated in **(ii)**.

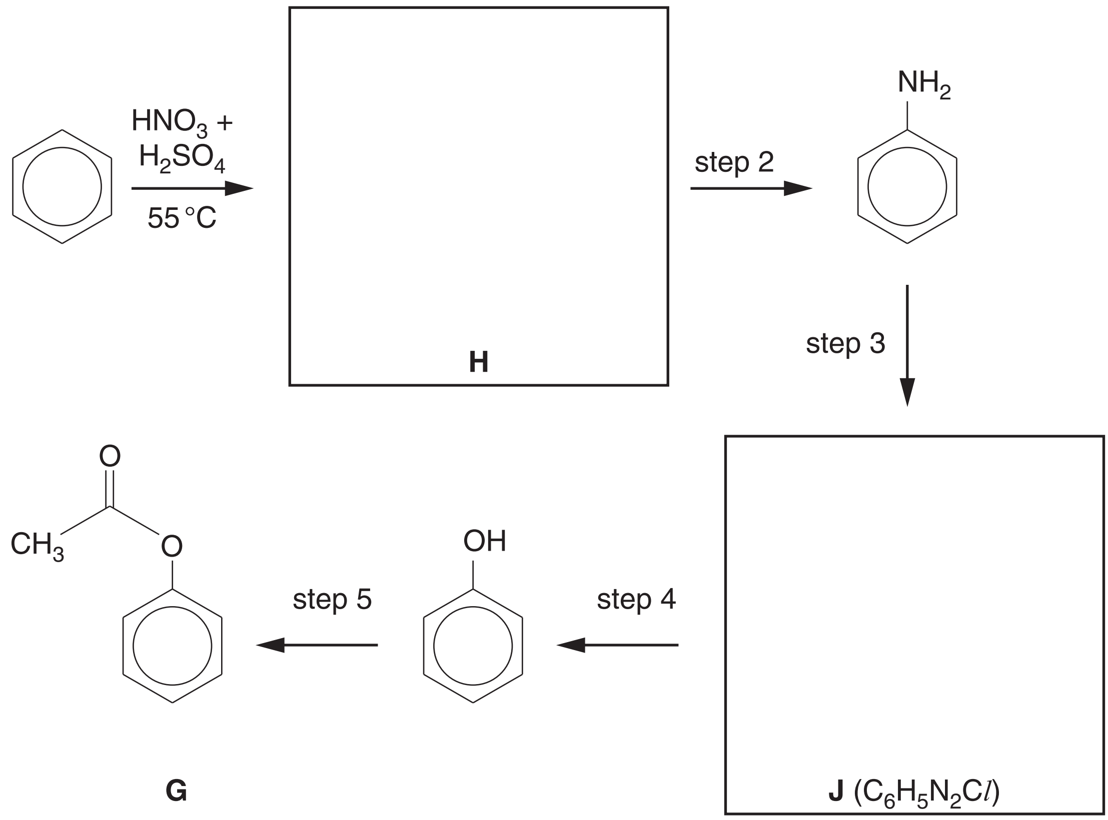
....

[4]

[Total: 10]

For Examiner's Use

5 **(a)** Compound **G** can be synthesised from benzene by the route shown below.



(i) **Name** the functional group formed in step 5.

....

(ii) Draw the structures of the intermediates **H** and **J** in the boxes above.

(iii) Suggest reagents and conditions for the following.

step 2 ....

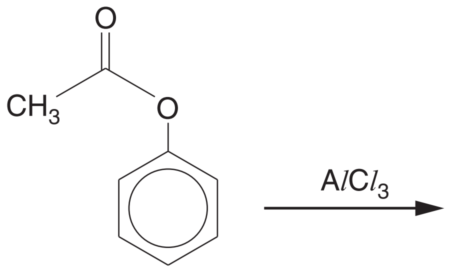
step 3 ....

step 4 ....

step 5 ....

[7]

(b) In a reaction discovered just over 100 years ago by the German chemist Karl Fries, compound **G** is converted into compound **K** when it is heated with $AlCl_3$.
Compound **K** is a structural isomer of **G**.



G

K ($C_8H_8O_2$)

Compound **K** is a 1,4-disubstituted benzene derivative. It is insoluble in water, but dissolves in NaOH(aq). It gives a white precipitate with Br_2(aq), and a yellow precipitate with alkaline aqueous iodine.

(i) What is meant by the term *structural isomerism*?

....

....

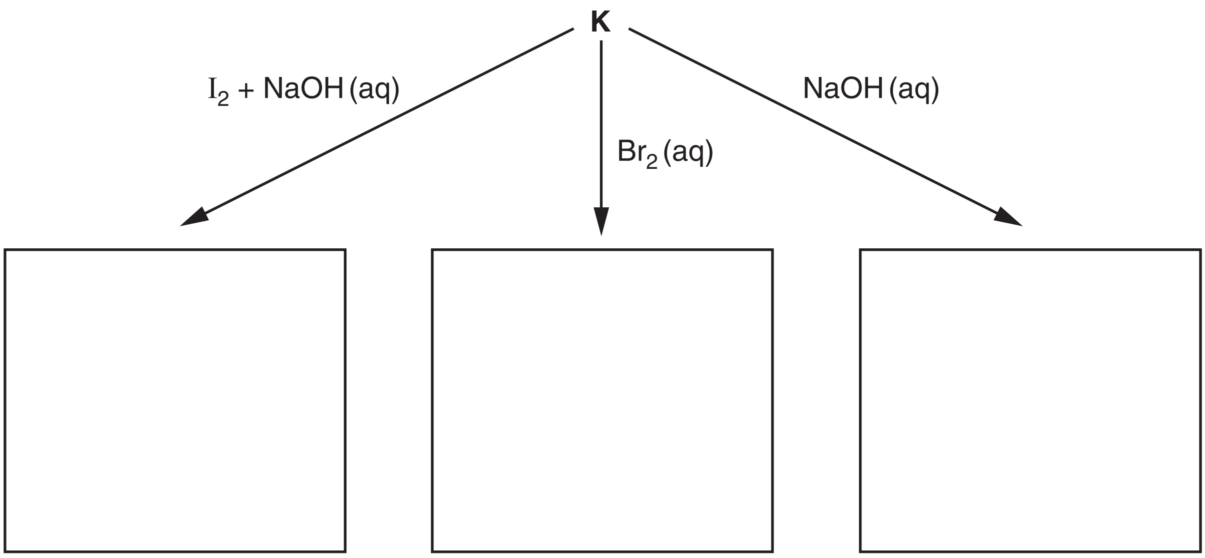
(ii) Use the information given above to **name** two functional groups in compound **K**.

....

....

(iii) Suggest the structural formula of **K**, and draw it in the box above.

(iv) Suggest structures for the aromatic products of the following reactions.

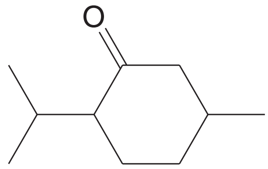


[7]

[Total: 14]

6 Menthone, $C_{10}H_{18}O$, is a cyclic ketone that occurs in oil of peppermint.

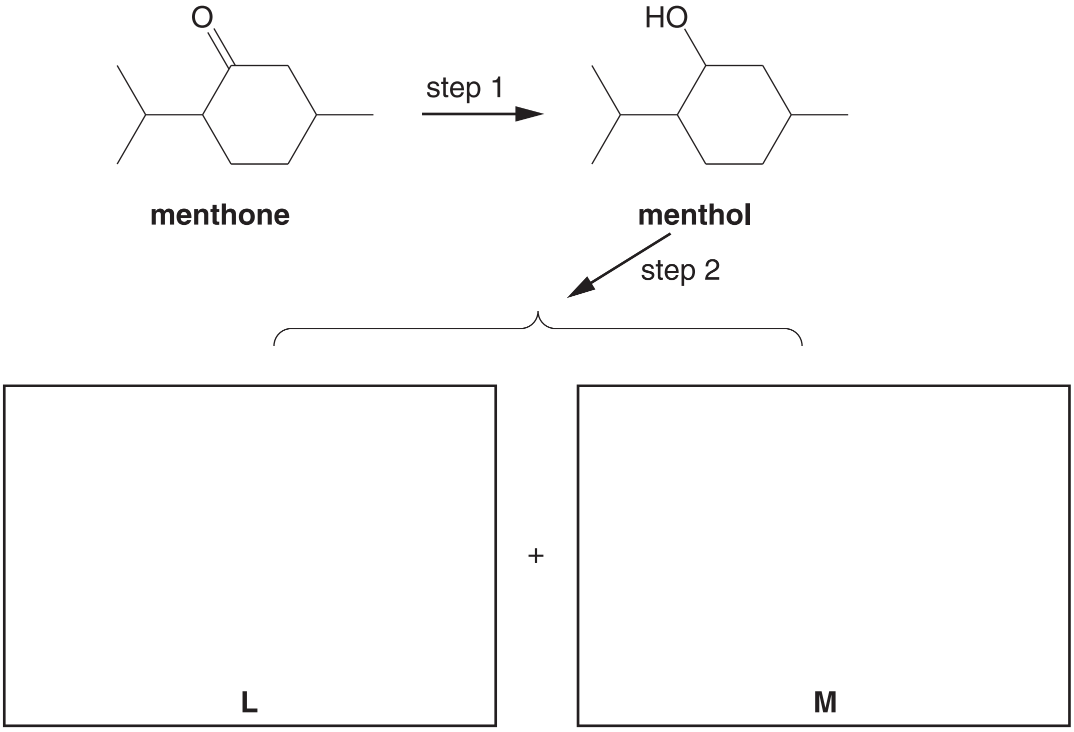
For Examiner's Use



menthone

(a) Use asterisks (*) on the formula above to identify any chiral centres in the molecule of menthone. [2]

(b) Menthone can be reduced to menthol, which can be dehydrated to a mixture of two alkenes, **L** and **M**.



(i) Suggest reagents for

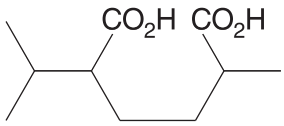
step 1, ...

step 2. ....

(ii) Suggest structures for **L** and **M** and draw them in the boxes above. [4]

For Examiner's Use

(c) When heated with concentrated, acidified $KMnO_4$(aq), one of the two alkenes **L** or **M** produces the dicarboxylic acid **N**.



N

(i) Give the letter of the alkene that produced **N** by this reaction.

....

(ii) Suggest the structure of the product, **P**, of the reaction between the other alkene you have drawn and hot concentrated acidified $KMnO_4$.

P

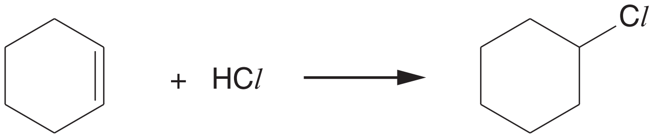
(iii) Suggest **one** chemical test that would enable you to distinguish between **N** and **P**.

reagent(s) ....

observation..

[3]

(d) Chlorocyclohexane can be prepared by bubbling HC*l*(g) through a solution of cyclohexene.



Suggest the mechanism of this 2-stage reaction by means of a diagram. Include all whole or partial charges, and represent the movements of electron pairs by curly arrows.

[3]

[Total: 12]

Section B

For Examiner's Use

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

7 Whilst small amounts of some metal ions are vital in the human body, others can be highly toxic.

(a) Hg^{2+} ions are toxic for a number of reasons. Hg^{2+} ions can react with the R–S–S–R group, which is found in proteins.

$$R–S–S–R + 2Hg^{2+} + H_2 \rightarrow 2\,R–S–Hg^{+} + 2H^{+} \qquad \text{reaction 1}$$

(i) What is the name of the R–S–S–R group in proteins?

....

(ii) Which level of protein structure will be affected by reaction 1?

....

....

(iii) Why will this affect the activity of an enzyme?

....

....

[3]

(b) Ag^{+} ions can combine with free –COOH groups in the side chains of the amino acid residues in proteins to form partially covalent silver carboxylates.

$$RCOOH + Ag^{+} \rightarrow RCOOAg + H^{+} \qquad \text{reaction 2}$$

(i) What type of behaviour is the –COOH group showing in reaction 2?

....

....

(ii) What types of R group interactions will be affected by reaction 2? Explain your answer.

....

....

....

....

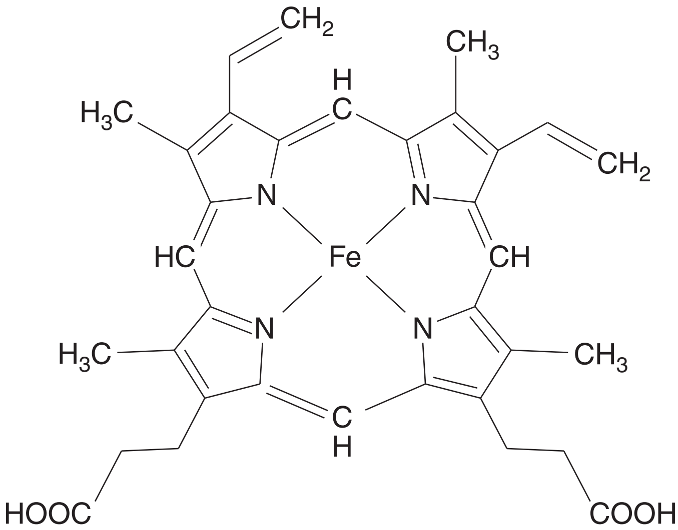
....

[4]

For Examiner's Use

(c) By contrast, iron is an extremely important metal used in haemoglobin to transport oxygen molecules from the lungs to muscle cells and to carry carbon dioxide in the reverse direction.

One haemoglobin molecule contains four haem groups, each of which contains one iron atom. In the haem group four nitrogen atoms are in the same plane as the iron atom. The oxygen molecule is attached above this plane, and the iron atom is joined to a protein chain below this plane.



haem

(i) How many oxygen **atoms** could one haemoglobin molecule transport?

....

(ii) By what type of bonding is the oxygen molecule likely to be held to the iron atom in haem?

....

(iii) What is the geometry of bonding around the iron atom?

....

[3]

[Total: 10]

8 **(a)** NMR spectroscopy and X-ray crystallography are two techniques that use electromagnetic radiation to look at the structures of large molecules.

For Examiner's Use

For each technique state the sub-atomic particle involved, and explain how this particle interacts with the radiation.

NMR..

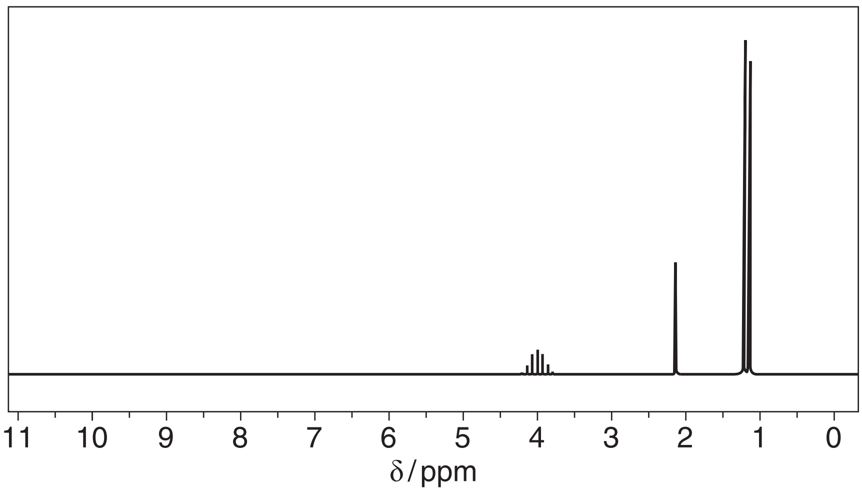
....

X-ray ....

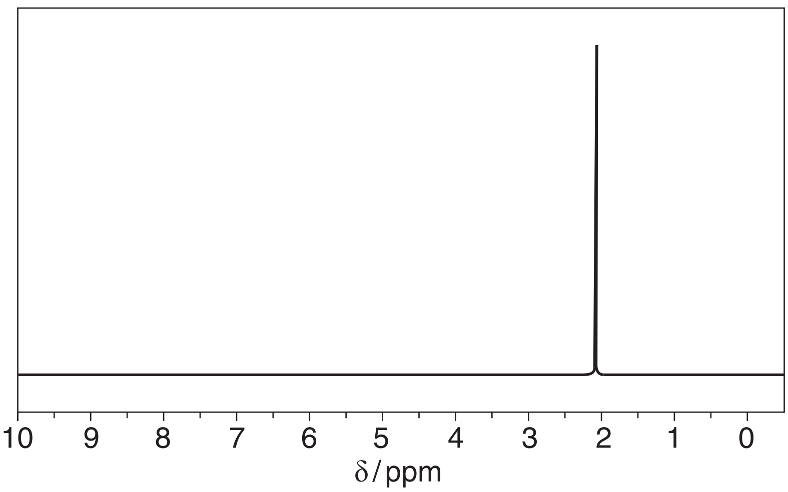
....

[4]

(b) The two NMR spectra **1** and **2** were obtained before and after an alcohol, **Y**, was oxidised to give compound **Z**. The numbers of hydrogen atoms responsible for each peak have **not** been shown. All the peaks have been shown.



1



2

For Examiner's Use

(i) State which spectrum, **1** or **2**, was produced by the alcohol, giving a reason for your answer.

spectrum ....

reason ....

....

(ii) The mass spectrum of **Y** showed an M : M+1 peak ratio of 17.6:0.6.
Use this and other information in the question to suggest the identities of both **Y** and **Z**.

(iii) Draw a displayed formula for **Y** in the box provided

Y is

(iv) Explain why the NMR spectrum of **Z** only shows one peak.

....

....
[7]

[Total: 11]

For Examiner's Use

9 A possible source of energy for the road vehicles of the future is hydrogen. One of the problems still to be solved is the storage of the hydrogen in the vehicle. A conventional tank holding liquid hydrogen would have to be pressurised and refrigerated. In a crash, this type of tank could break resulting in the rapid release of hydrogen and an explosion.

One alternative is to use a fuel tank packed with carbon nanotubes. The hydrogen in the tank would be adsorbed onto the surface of the nanotubes at a pressure of no more than a few atmospheres.

(a) **(i)** What is the approximate width of a carbon nanotube?

....

(ii) In what structural form is the carbon in a nanotube?

....

(iii) What forces could be responsible for holding the hydrogen on the surface of the nanotubes? Explain your answer.

....

....

....

[4]

(b) The hydrogen atoms in a fuel tank packed with nanotubes are closer together than in liquid hydrogen. Suggest **one** advantage of this.

....

.... [1]

(c) When a nanotube-packed fuel tank is full of hydrogen there is a steady pressure of hydrogen in the tank. While hydrogen gas is being removed from the fuel tank to power the car, the pressure in the fuel tank drops very little for some time. State Le Chatelier's principle, and suggest how it explains this observation.

....

....

....

....

....

.... [4]

[Total: 9]

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