Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

9491884931

CHEMISTRY **9701/43**

Paper 4 A Level Structured Questions **October/November 2022**

2 hours

You must answer on the question paper.

No additional materials are needed.

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 and use appropriate units.

INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].
- The Periodic Table is printed in the question paper.
- Important values, constants and standards are printed in the question paper.

This document has **28** pages. Any blank pages are indicated.

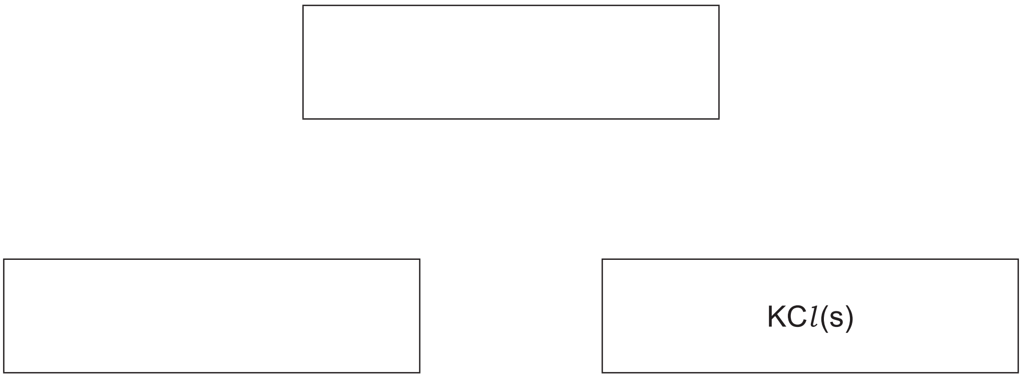
1 Potassium chloride, KCl, and magnesium chloride, $MgCl_2$, are both ionic solids.

Table 1.1

energy change	value / kJ mol^{-1}
standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of KCl	+15
lattice energy, $\Delta H^{\ominus}_{latt}$, of $KCl(s)$	–701
standard enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, of K^+	–322
standard enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, of Cl^-	–364
standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of $MgCl_2$	–155
lattice energy, $\Delta H^{\ominus}_{latt}$, of $MgCl_2(s)$	–2493

(a) Complete the energy cycle involving the enthalpy change of solution and the lattice energy of potassium chloride, KCl, and the relevant enthalpy changes of hydration. Label your diagram.

State symbols should be used.



[2]

(b) Use the data in Table 1.1 to calculate the enthalpy change of hydration of magnesium ions, Mg^{2+}. Show your working.

$\Delta H^{\ominus}_{hyd}$ of magnesium ions, Mg^{2+} = ... kJ mol^{-1} [2]

(c) Explain the reasons why the lattice energy of $MgCl_2$ is more exothermic than the lattice energy of KCl.

....

....

....

.... [2]

(d) Define the following terms.

(i) enthalpy change of atomisation ....

.... [1]

(ii) first electron affinity ....

.... [1]

(e) **(i)** Explain what is meant by entropy, *S*.

....

.... [1]

(ii) Potassium chloride is very soluble in water at 20 °C.

Explain the solubility of potassium chloride by reference to change in entropy, ΔS.

....

.... [1]

(iii) Use the Gibbs equation and your answer to **(e)(ii)** to predict whether potassium chloride is more soluble in water at 20 °C or at 80 °C. Explain your answer.

....

....

.... [1]

[Total: 11]

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

homogeneous catalyst ....

....

heterogeneous catalyst ....

....
[1]

(ii) Iodide ions react with peroxydisulfate ions.

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

This reaction is slow, but it is catalysed by Fe^{2+} ions.

Write two equations to explain how this reaction is catalysed by Fe^{2+} ions.

1 ....

2 ....
[2]

(iii) Suggest why the alternative route in the presence of Fe^{2+} ions has a lower activation energy than the route in the absence of a catalyst.

....

.... [1]

(b) Nitrogen monoxide reacts with oxygen.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

This reaction is second order with respect to nitrogen monoxide and first order with respect to oxygen.

Under certain conditions the value of the rate constant, *k*, is $8.60 \times 10^6\,mol^{-2}\,dm^6\,s^{-1}$.

(i) Construct the rate equation for this reaction.

rate =

[1]

(ii) Calculate the initial rate of the reaction under these conditions when the initial concentration of nitrogen monoxide is $7.20 \times 10^{-4}\,mol\,dm^{-3}$ and the initial concentration of oxygen is $1.90 \times 10^{-3}\,mol\,dm^{-3}$.

rate of reaction = ... $mol\,dm^{-3}\,s^{-1}$ [1]

(c) The drug cisplatin, $Pt(NH_3)_2Cl_2$, hydrolyses in water.

$$Pt(NH_3)_2Cl_2 + H_2O \rightarrow [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-$$

The rate equation is shown.

$$\text{rate} = k[Pt(NH_3)_2Cl_2]$$

The value of k is $2.50 \times 10^{-5}\,s^{-1}$ under certain conditions.

(i) This reaction has a constant half-life.

Explain why this is the case.

....

.... [1]

(ii) Use the information in this question to show that the half-life of this reaction is 2.77×10^4 s.

[1]

(iii) 8.00×10^{-6} moles of $Pt(NH_3)_2Cl_2$ are added to $100\,cm^3$ of water.

Calculate the time taken for the concentration of $Pt(NH_3)_2Cl_2$ to fall to $2.50 \times 10^{-6}\,mol\,dm^{-3}$.

time taken = ... s [2]

[Total: 10]

3 Data should be selected from Table 3.1 in order to answer some parts of this question.

Table 3.1

electrode reaction	$E^\ominus$ / V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O$	+1.64
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	+0.89
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.15
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	–0.14
$V^{2+} + 2e^- \rightleftharpoons V$	–1.20
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.26
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00

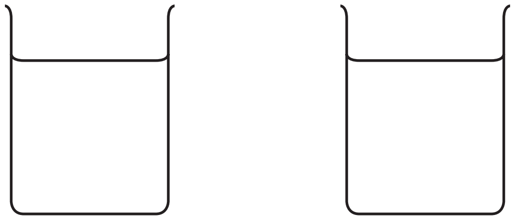
(a) Standard electrode potentials are measured under standard conditions.

(i) Describe the standard conditions used in the Sn^{4+}/Sn^{2+} half-cell.

....

.... [1]

(ii) Complete the diagram below to show how $E^\ominus(Sn^{4+}/Sn^{2+})$ can be measured experimentally. Your diagram should be fully labelled to identify all apparatus and substances.



[3]

(iii) Equal volumes of 1.0 mol dm^{-3} Sn^{2+}(aq) and 1.0 mol dm^{-3} Cl^{-}(aq) are mixed.

Use relevant $E^{\ominus}$ values to explain whether a reaction occurs between these two ions.

....

....

....

.... [2]

(iv) Equal volumes of 1.0 mol dm^{-3} of Sn^{2+}(aq) and acidified 1.0 mol dm^{-3} VO^{2+}(aq) are mixed.

Write an equation for the reaction that takes place in the resulting mixture.

.... [2]

(b) A solution of $SnCl_2$(aq) is electrolysed for a measured time using a steady current.

A mass of 2.95 g of tin metal is produced at the cathode.

Al_2O_3(l) is electrolysed for the same time by the same current.

Calculate the mass of aluminium metal produced at the cathode. Give your answer to **three** significant figures. Show your working.

mass of aluminium metal = ... g [2]

[Total: 10]

4 **(a)** A sample of butanoic acid, $CH_3(CH_2)_2COOH$, is shaken with a mixture of two immiscible solvents, ethoxyethane and water. The solvents form two layers. The butanoic acid is distributed between the two layers, its concentration in ethoxyethane being higher than its concentration in water.

(i) State what is meant by partition coefficient.

....

.... [1]

(ii) The partition coefficient, K_{pc}, for butanoic acid between ethoxyethane and water is 3.50.

A solution of 2.00 g of butanoic acid in 100 cm^3 ethoxyethane is added to water. This mixture is left until there is no further change in the concentration of butanoic acid in either solvent. The mass of butanoic acid dissolved in the ethoxyethane layer is now 1.62 g.

Calculate the volume of water used.

volume of water used = ... cm^3 [2]

(b) An aqueous solution of butanoic acid can be used to make a buffer solution.

(i) Define buffer solution.

....

.... [1]

(ii) Suggest one organic compound, and one inorganic compound, that can be added to two different samples of aqueous butanoic acid to produce buffer solutions.

organic compound ....

inorganic compound ....
[1]

(c) The solubility of aluminium hydroxide, $Al(OH)_3$, in water is 2.47×10^{-9} mol dm^{-3}.

(i) Give the expression for the solubility product, K_{sp}, of aluminium hydroxide.

K_{sp} =

[1]

(ii) Calculate the numerical value of the K_{sp} of aluminium hydroxide. Include the units of K_{sp} in your answer.

K_{sp} = ...

units = ...

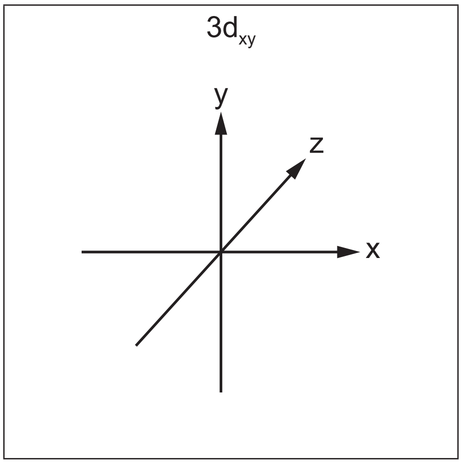
[3]

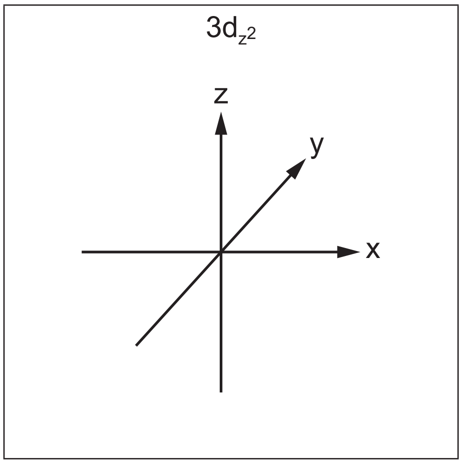
[Total: 9]

5 A transition element is a d-block element which forms one or more stable ions with incomplete d-orbitals.

(a) Two of the 3d orbitals are the $3d_{xy}$ orbital and the $3d_{z^2}$ orbital.

Sketch the shapes of these two orbitals.





[1]

(b) The Ni^{2+} ion forms many different complexes. A solution containing the $[Ni(H_2O)_6]^{2+}$ complex ion is green. When an excess of 1,2-diaminoethane, *en*, $H_2NCH_2CH_2NH_2$, is added, the colour of the solution changes to blue. This is due to the formation of the $[Ni(en)_3]^{2+}$ complex ion.

(i) Explain why the two solutions are coloured, and why the colours are different.

....

....

....

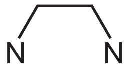
....

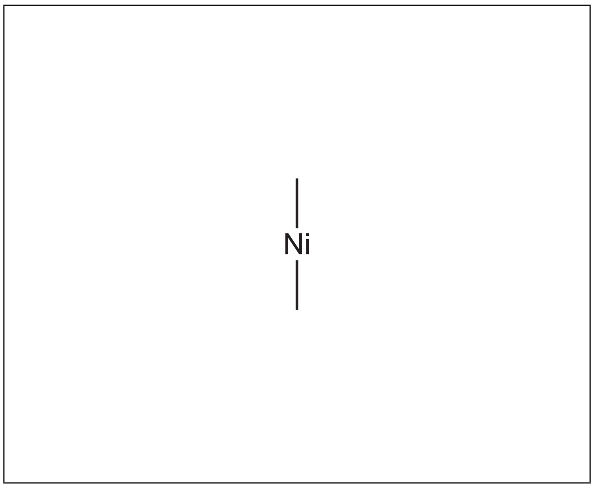
....

.... [4]

(ii) The $[Ni(en)_3]^{2+}$ complex can exist as a mixture of two stereoisomers.

Complete the three-dimensional diagram to show one of the stereoisomers.

Each *en* ligand can be represented using  .



[1]

(iii) Name the geometry of the complex ion drawn in **(b)(ii)** and the type of stereoisomerism shown by $[Ni(en)_3]^{2+}$.

geometry ....

stereoisomerism shown .... [1]

(c) Iron(II) carbonate, $FeCO_3$, and nickel(II) carbonate, $NiCO_3$, both decompose when heated.

$FeCO_3$ decomposes at a lower temperature than $NiCO_3$.

Suggest a possible reason for this difference. Explain your answer.

....

....

....

....

.... [2]

(d) **A** is a pale green salt containing Fe^{2+} ions. A sample of 2.62 g of **A** is dissolved in water and the solution is made up to exactly 100 cm^3 with water. 25.0 cm^3 samples of this solution are placed in conical flasks and titrated against 0.0100 mol dm^{-3} acidified potassium manganate(VII).

The equation for the only reaction that occurs is shown.

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

The average titre value is 35.0 cm^3 of 0.0100 mol dm^{-3} acidified potassium manganate(VII).

(i) Describe the colour change that is seen in the conical flask at the end-point of this titration.

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

(ii) Calculate the percentage by mass of iron in **A**.

[A_r: Fe, 55.8]

percentage by mass of iron = ... % [2]

[Total: 12]

Question 6 starts on the next page.

6 An aqueous solution of copper(II) sulfate is a blue colour due to the presence of $[Cu(H_2O)_6]^{2+}$ complex ions.

(a) **(i)** Write an equation for the reaction between $[Cu(H_2O)_6]^{2+}$ ions and NaOH(aq).

.... [1]

(ii) Write an equation for the reaction between $[Cu(H_2O)_6]^{2+}$ ions and an excess of conc. HCl.

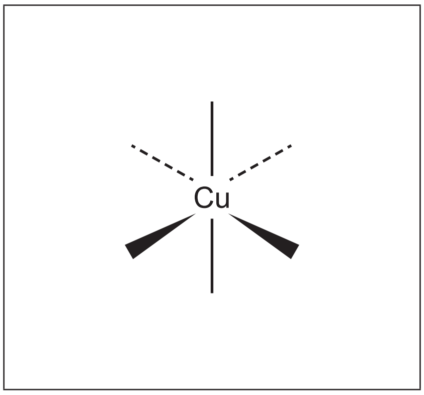
.... [1]

(b) If an excess of ammonia is added to a solution of $[Cu(H_2O)_6]^{2+}$ a deep blue solution containing $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ions is formed.

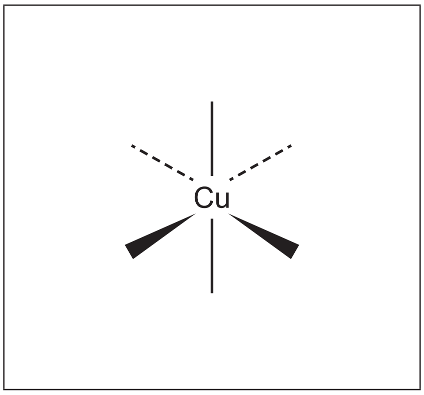
(i) There are two possible stereoisomers with the formula $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

Complete the diagrams to show the two stereoisomers in the boxes below.

isomer 1



isomer 2



[1]

(ii) Use your answer in **(b)(i)** to deduce whether each of these isomers is polar or non-polar.

polarity of isomer 1 ....

polarity of isomer 2 ....
[1]

(c) The numerical value of the stability constant, K_{stab}, of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is 1.40×10^{13}.

(i) Define stability constant.

....

.... [1]

(ii) Compare the stabilities of the $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ions. Explain your answer.

....

.... [1]

(iii) Write an expression for the stability constant, K_{stab}, of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion. State the units of the stability constant.

K_{stab} =

units = ...

[2]

(iv) In a particular solution the concentration of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is 0.0074 mol dm^{-3} and the concentration of NH_3 is 0.57 mol dm^{-3}.

Use your expression in **(c)(iii)** and the K_{stab} value of 1.40×10^{13} to calculate the concentration of the $[Cu(H_2O)_6]^{2+}$ complex ion in this solution.

concentration of $[Cu(H_2O)_6]^{2+}$ = ... mol dm^{-3} [1]

(d) Phenanthroline, $C_{12}H_8N_2$, and ethanedioate ions, $C_2O_4^{2-}$, are bidentate ligands.

Ruthenium(III) ions, Ru^{3+}, form an octahedral complex with phenanthroline and chloride ions. The complex ion contains two phenanthroline molecules.

Iron(III) ions, Fe^{3+}, form an octahedral complex with ethanedioate ions only.

Deduce the formula and charge of each of these complex ions.

Ru^{3+} complex ....

Fe^{3+} complex ....

[2]

[Total: 11]

7 **(a)** The structure of compound **P** is shown in Fig. 7.1.

P

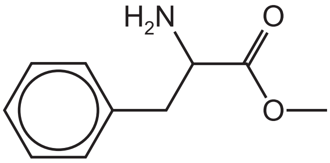


Fig. 7.1

(i) **P** is optically active.

Use an asterisk (*) to identify all chiral carbon atoms on the structure of **P** in Fig. 7.1. [1]

(ii) Plane polarised light is passed through a pure sample of one enantiomer of **P**. This is then repeated with a pure sample of the other enantiomer of **P**.

Describe the results of these two experiments, stating the similarities and differences of the results.

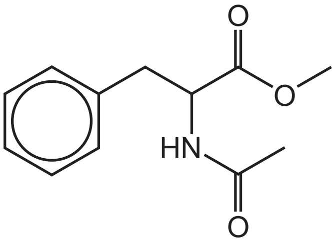
....

....

.... [2]

(b) **P** can be used to make compound **Q** in a single step reaction.

Q



(i) Give the structural formula of the compound that is added to **P** to make **Q** and give the formula of the other product of this reaction.

compound added to **P** ....

other product ....
[1]

(ii) When an ester is treated with $LiAlH_4$ in dry ether the ester linkage is cleaved by the addition of four hydrogen atoms and two alcohols are produced.

Draw the structures of the compounds formed when **Q** is treated with an **excess** of $LiAlH_4$ in dry ether.

[3]

(iii) Compare the relative basicities of compound **P**, compound **Q** and phenylamine.

.... < .... < ....
least basic most basic

Explain your answer.

....

....

....

....
[3]

(c) **P** can be used to make compound **R** in a two-step reaction, shown in Fig. 7.2.

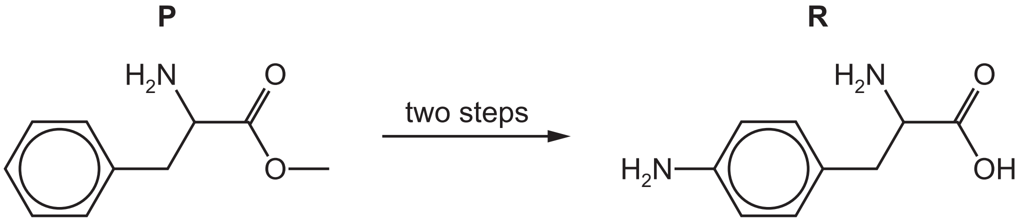


Fig. 7.2

(i) Identify the reagents and conditions used for the two steps of the reaction.

step 1 ....

step 2 ....
[2]

(ii) Complete Table 7.1 by drawing the structures of the organic products formed when **R** is treated separately with the reagents given.

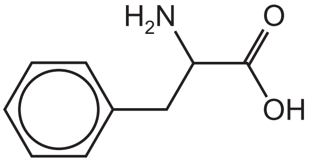
Table 7.1

reagent	product
HNO_2(aq) at 4 °C	
an excess of Br_2(aq) at room temperature	

[2]

(d) **P** can be used to produce compound **T**.

T



(i) In aqueous solution, **T** has a property called an isoelectric point.

Explain what is meant by isoelectric point.

....

.... [1]

(ii) **T** can polymerise under suitable conditions. No other monomer is involved in this reaction.

Draw a section of the polymer chain formed that includes three **T** monomers. Identify the repeat unit on your diagram.

[2]

[Total: 17]

8 Benzene, C_6H_6, is an aromatic molecule.

(a) State the C–C–C bond angle and the hybridisation shown by the carbon atoms in benzene.

bond angle ....

hybridisation ....
[1]

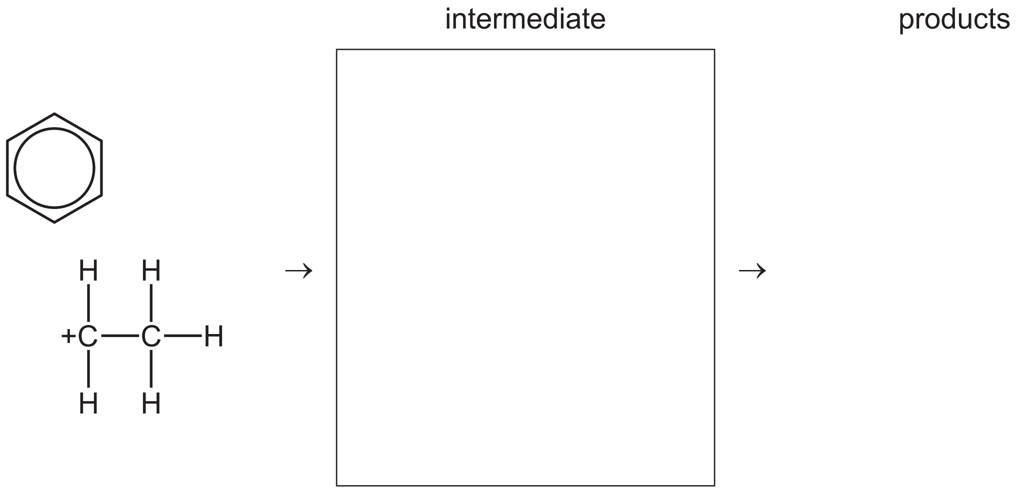
(b) Benzene reacts with chloroethane in the presence of a catalyst. The reaction mechanism is called electrophilic substitution.

(i) The first step in the reaction is the generation of the $^+CH_2CH_3$ electrophile.

Write an equation for the reaction that generates this electrophile.

.... [1]

(ii) Describe the mechanism for the reaction between benzene and the $^+CH_2CH_3$ electrophile. Include all relevant curly arrows and charges.



[3]

(c) Chlorobenzene and chloroethane have different reactivities in nucleophilic substitution reactions.

(i) Identify a suitable reagent to illustrate this difference in reactivity.

The reagent chosen should give **visibly** different results with chlorobenzene and chloroethane.

.... [1]

(ii) Write equations to describe any reactions that occur.

[1]

(iii) Explain the difference in the reactivities of chlorobenzene and chloroethane in nucleophilic substitution reactions.

....

.... [1]

[Total: 8]

9 **(a)** Gas-liquid chromatography involves a stationary phase and a mobile phase.

(i) Name, or describe in detail, a suitable substance that could be used for each phase.

stationary ....

mobile .... [1]

A mixture of three organic compounds is separated by gas-liquid chromatography. The chromatogram obtained is shown in Fig. 9.1. The amount of each substance is proportional to the area under its peak.

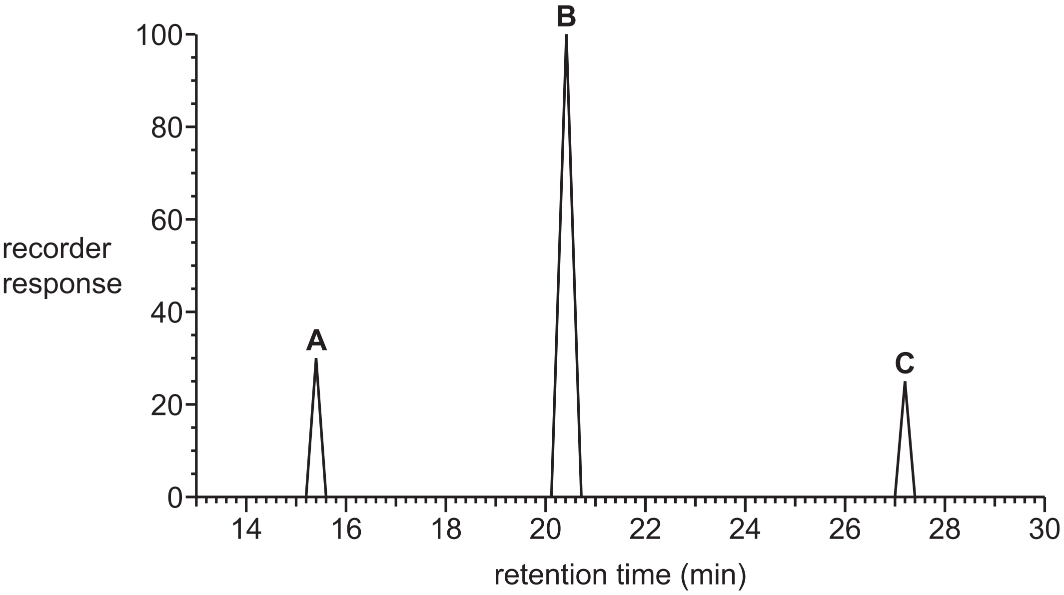


Fig. 9.1

(ii) Explain the meaning of retention time.

....

.... [1]

(iii) Calculate the percentage of **B** in the mixture. Show your working.

percentage of **B** = ... % [2]

(b) Complete Table 9.1 to give the number of peaks in the carbon-13 NMR spectrum of each of the five isomers of $C_5H_{10}O_2$ that has an ester group.

Table 9.1

structural formula	number of peaks
$CH_3CH_2CH_2CO_2CH_3$	
$CH_3CH_2CO_2CH_2CH_3$	
$CH_3CO_2CH_2CH_2CH_3$	
$(CH_3)_2CHCO_2CH_3$	
$CH_3CO_2CH(CH_3)_2$	

[2]

(c) State the number of peaks that would be seen in the proton (^1H) NMR spectrum of methyl butanoate, $CH_3CH_2CH_2CO_2CH_3$. Name all the splitting patterns seen in this spectrum.

number of peaks ....

splitting patterns ....

[2]

(d) **D** and **E** are both esters with the molecular formula $C_5H_{10}O_2$. Their proton (^1H) NMR spectra are shown in Fig. 9.2 and Fig. 9.3.

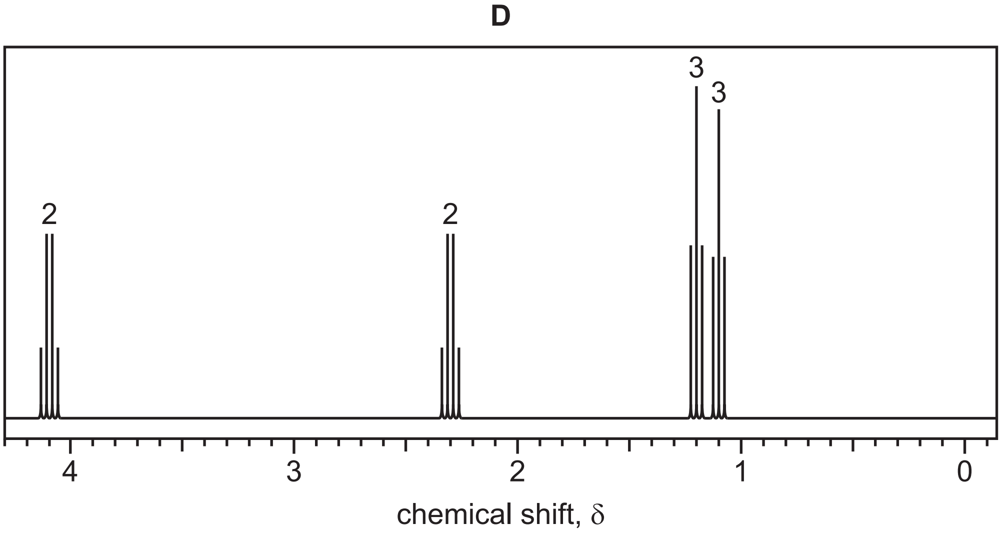


Fig. 9.2

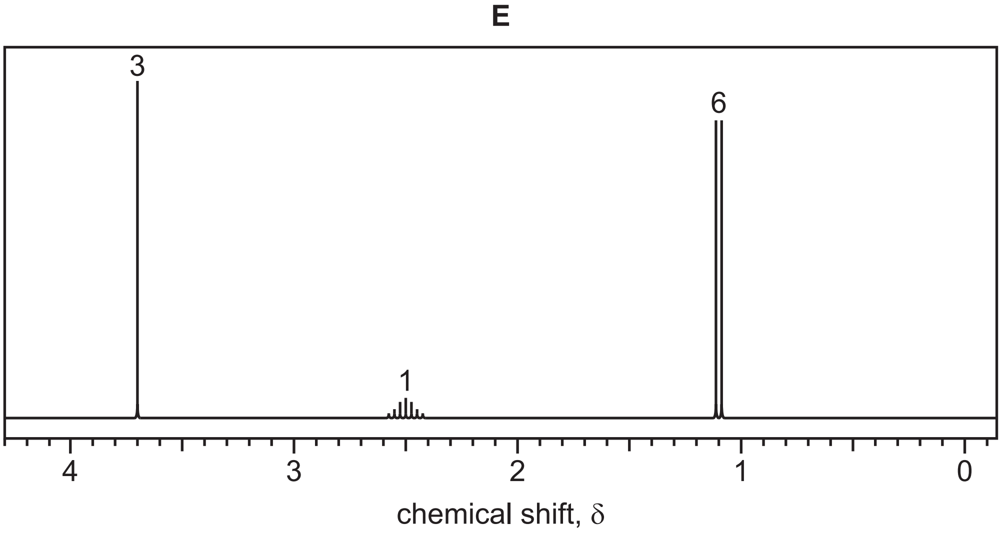


Fig. 9.3

Table 9.2

environment of proton	example	typical chemical shift range, δ/ppm
alkane	$-CH_3$, $-CH_2-$, $>CH-$	0.9–1.7
alkyl next to C=O	$CH_3-C=O$, $-CH_2-C=O$, $>CH-C=O$	2.2–3.0
alkyl next to aromatic ring	CH_3-Ar, $-CH_2-Ar$, $>CH-Ar$	2.3–3.0
alkyl next to electronegative atom	CH_3-O, $-CH_2-O$, $-CH_2-Cl$	3.2–4.0
attached to alkene	$=CHR$	4.5–6.0

(i) Deduce the structures of the two esters **D** and **E** and draw their displayed formulae in the boxes below.

D $C_5H_{10}O_2$	**E** $C_5H_{10}O_2$

[2]

(ii) The spectrum of **D** includes a quartet at δ 4.1.

Identify the protons responsible for this quartet on your structure in **(i)** by labelling these protons with the letter **F**.

Explain why this peak is split into a quartet.

....

....
[1]

(iii) The spectrum of **E** has a doublet at δ 1.1.

Identify the protons responsible for this doublet on your structure in **(i)** by labelling these protons with the letter **G**.

Explain why this peak has a chemical shift of 1.1.

....

....
[1]

[Total: 12]

BLANK PAGE

Important values, constants and standards

molar gas constant	$R = 8.31\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^{4}\,\text{C}\,\text{mol}^{-1}$
Avogadro constant	$L = 6.022 \times 10^{23}\,\text{mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19}\,\text{C}$
molar volume of gas	$V_m = 22.4\,\text{dm}^3\,\text{mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,\text{dm}^3\,\text{mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,\text{kJ}\,\text{kg}^{-1}\,\text{K}^{-1}$ ($4.18\,\text{J}\,\text{g}^{-1}\,\text{K}^{-1}$)

The Periodic Table of Elements

Key

atomic number
atomic symbol
name
relative atomic mass

Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
							1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0											5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3											13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.4	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –
