Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

0529598277

CHEMISTRY **9701/43**

Paper 4 A Level Structured Questions **May/June 2024**

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.

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1 **(a)** **(i)** Describe the trend in the solubility of the hydroxides of magnesium, calcium and strontium.

Explain your answer.

..... > ..... > .....
most soluble least soluble

.....

.....

.....

.....

.....

.....
[4]

(ii) Suggest the variation in pH of saturated solutions of the hydroxides of magnesium, calcium and strontium.

Explain your answer.

.....

.....

..... [1]

(b) Barium hydroxide, $Ba(OH)_2$, is a strong base.

A 250.0 cm^3 solution of $Ba(OH)_2$ with a pH of 12.2 is made by dissolving $Ba(OH)_2$ in distilled water.

Calculate the mass of $Ba(OH)_2$ required to make this solution.

Show your working.

[M_r: $Ba(OH)_2$, 171.3]

mass of $Ba(OH)_2$ = ... g [4]

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(c) The solubility of iron(II) hydroxide, $Fe(OH)_2$, is 5.85×10^{-6} mol dm^{-3} at 298 K.

(i) Write the expression for the solubility product, K_{sp}, of $Fe(OH)_2$.

K_{sp} =

[1]

(ii) Calculate the value of K_{sp} of $Fe(OH)_2$. Include its units.

K_{sp} = ...

units = ...

[2]

[Total: 12]

2 **(a)** **(i)** Define transition element.

.....

.....

..... [1]

(ii) Explain why transition elements can form complex ions.

.....

..... [1]

(b) The 3d orbitals in an isolated Ag^+ ion are degenerate.

(i) Define degenerate d orbitals.

.....

..... [1]

(ii) Sketch the shape of a $3d_{xy}$ orbital in Fig. 2.1.

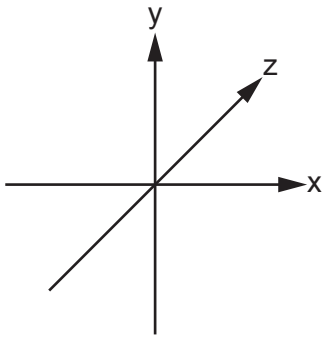

Fig. 2.1

[1]

(c) Tollens' reagent can be used to distinguish between aldehydes and ketones. Tollens' reagent contains $[Ag(NH_3)_2]OH$, which can be prepared in a two-step process.

step 1 Aqueous NaOH is added dropwise to aqueous $AgNO_3$ to form Ag_2O as a brown precipitate.

step 2 Aqueous NH_3 is added dropwise to Ag_2O to form a colourless solution containing $[Ag(NH_3)_2]OH$.

Construct equations for each of the steps in the preparation of $[Ag(NH_3)_2]OH$.

step 1 .....

step 2 .....

[2]

(d) Name the shape of the complex ion $[Ag(NH_3)_2]^+$.

State the bond angle for H-N-Ag and for N-Ag-N.

shape .....

bond angle for H-N-Ag = ... °

bond angle for N-Ag-N = ... °

[2]

(e) An electrochemical cell uses Ag_2O as the positive electrode and Zn as the negative electrode immersed in an alkaline electrolyte.

The overall cell reaction is shown.

$$Ag_2O + Zn + H_2O \rightarrow 2Ag + Zn(OH)_2$$

Complete the half-equation for the reaction at each electrode.

at the positive electrode Ag_2O + ...

at the negative electrode Zn + ...

[2]

(f) Coordination polymers are made when a bidentate ligand acts as a bridge between different metal ions.

Under certain conditions $Ru^{3+}(aq)$ and the bidentate ligand *dps* can form a coordination polymer containing $([Ru(dps)Cl_4]^-)_n$ chains.

dps

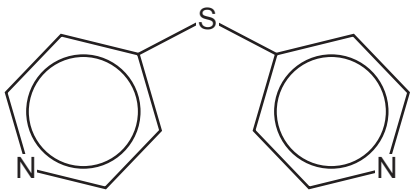

Fig. 2.2

The bidentate ligand *dps* uses each of the nitrogen atoms to bond to a different Ru^{3+}.

Complete Fig. 2.3 by drawing the structure for the coordination polymer $([Ru(dps)Cl_4]^-)_n$. Show **two** repeat units.

The *dps* ligand can be represented using 

.

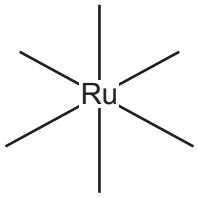

Fig. 2.3

[2]

[Total: 12]

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3 **(a)** When a sample of hydrated lithium ethanedioate, $Li_2C_2O_4 \cdot H_2O$, is gently heated, two gaseous products are formed and a white solid residue remains.

The residue is added to $HNO_3(aq)$. A gas is produced that turns limewater milky.

Complete the equation for the decomposition of $Li_2C_2O_4 \cdot H_2O$.

$Li_2C_2O_4 \cdot H_2O \rightarrow$ ..... + ... + ...

[1]

(b) The trend in the decomposition temperatures of the Group 2 ethanedioates is similar to that of the Group 2 nitrates.

Suggest which of CaC_2O_4 and BaC_2O_4 will decompose at the **lower** temperature. Explain your answer.

.....

.....

.....

..... [2]

(c) Potassium iron(III) ethanedioate, $K_3[Fe(C_2O_4)_3]$, dissolves in water to form a green solution.

Explain why transition elements can form coloured complexes.

.....

.....

.....

.....

.....

..... [3]

(d) The anhydrous iron(III) compound $K_3[Fe(C_2O_4)_3]$ decomposes on heating to form a mixture of $K_2[Fe(C_2O_4)_2]$, $K_2C_2O_4$ and CO_2.

Complete the equation for the decomposition of $K_3[Fe(C_2O_4)_3]$.

..... $K_3[Fe(C_2O_4)_3] \rightarrow$ ..... $K_2[Fe(C_2O_4)_2]$ + ... $K_2C_2O_4$ + ... CO_2

[1]

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(e) The $[Fe(C_2O_4)_3]^{3-}$ complex ion shows stereoisomerism.

Complete the three-dimensional diagrams in Fig. 3.1 to show the **two** stereoisomers of $[Fe(C_2O_4)_3]^{3-}$.

The $C_2O_4^{2-}$ ligand can be represented using O O.

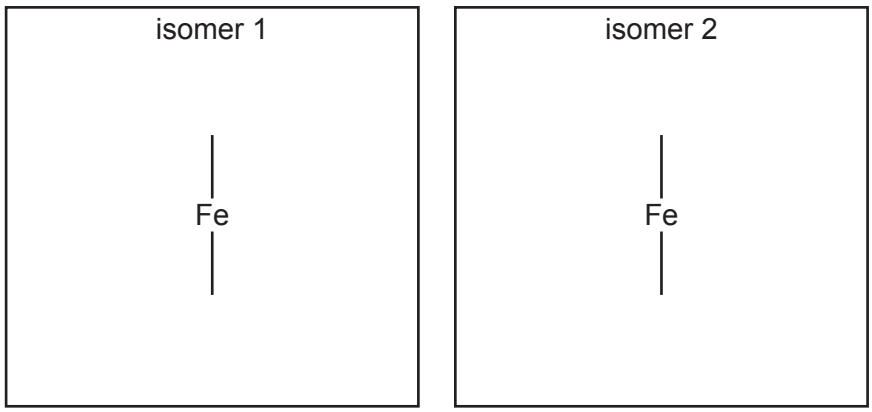

Fig. 3.1

[2]

(f) Buffer solutions are used to regulate pH.
Write **two** equations to describe how a solution containing $HC_2O_4^-$ ions acts as a buffer solution when small amounts of acid or alkali are added.

.....

..... [2]

(g) A fuel cell is an electrochemical cell that can be used to generate electrical energy by using oxygen to oxidise a fuel.

Ethanedioic acid, $(COOH)_2$, dissolved in an alkaline electrolyte is being investigated as a fuel.

The relevant standard electrode potentials, $E^{\ominus}$, for the cell are shown.

$$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq) \qquad E^{\ominus} = +0.40\,V$$

$$2CO_2(g) + 2e^- \rightleftharpoons C_2O_4^{2-}(aq) \qquad E^{\ominus} = -0.59\,V$$

Use these equations to deduce the overall cell reaction. Calculate the value of $E^{\ominus}_{cell}$.

overall cell reaction .....

$E^{\ominus}_{cell}$ = ... V
[2]

[Total: 13]

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4 **(a)** Define standard electrode potential, $E^{\ominus}$, including a description of standard conditions.

.....

.....

..... [2]

(b) **(i)** An electrochemical cell is set up to measure $E^{\ominus}$ of the $Ag^+(aq)/Ag(s)$ electrode.

Draw a labelled diagram of this electrochemical cell.

Include all necessary substances. It is **not** necessary to state conditions used.

[3]

(ii) A separate electrochemical cell is set up using a **lower** concentration of $Ag^+(aq)$ than that used in **(b)(i)**.

Suggest how the electrode potential, E, for the $Ag^+(aq)/Ag(s)$ electrode would change from its $E^{\ominus}$ value. Explain your answer.

.....

.....

..... [1]

(c) Define enthalpy change of solution, $\Delta H^{\ominus}_{sol}$.

.....

..... [1]

(d) Some relevant energy changes for $AgNO_3$ are shown in Table 4.1.

Table 4.1

energy change	value / kJ mol^{-1}
enthalpy change of solution of $AgNO_3$(s)	+22.6
enthalpy change of hydration of silver ions	–475
enthalpy change of hydration of nitrate ions	–314

(i) Complete the energy cycle in Fig. 4.1 to show the relationship between the lattice energy, $\Delta H^{\ominus}_{latt}$, of $AgNO_3$(s) and the energy changes shown in Table 4.1.

Include state symbols for all the species.

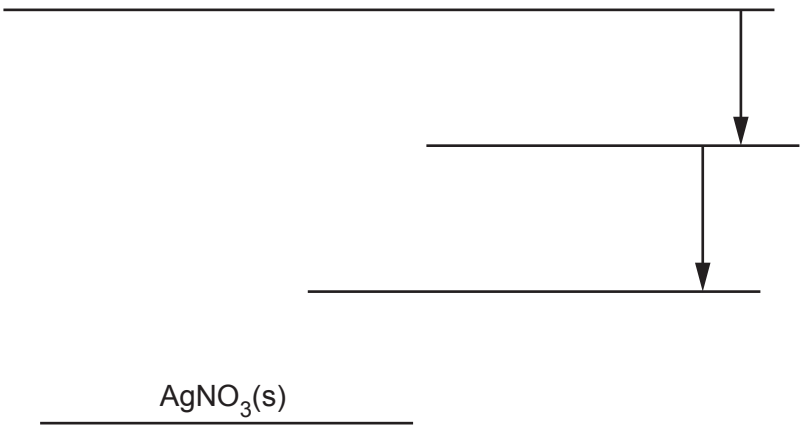

Fig. 4.1

[2]

(ii) Calculate the lattice energy, $\Delta H^{\ominus}_{latt}$, of $AgNO_3$(s).

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

(e) Suggest the trend in the magnitude of the lattice energies of the metal nitrates, $NaNO_3(s)$, $Mg(NO_3)_2(s)$ and $RbNO_3(s)$.

Explain your answer.

....
most exothermic least exothermic

.....

.....

.....

.....

.....
[3]

[Total: 13]

5 **(a)** In aqueous solution, persulfate ions, $S_2O_8^{2-}$, react with iodide ions, as shown in reaction 1.

reaction 1 $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

The rate of reaction 1 is investigated.

A sample of $S_2O_8^{2-}$ is mixed with a large excess of iodide ions of known concentration. The graph in Fig. 5.1 shows the results obtained.

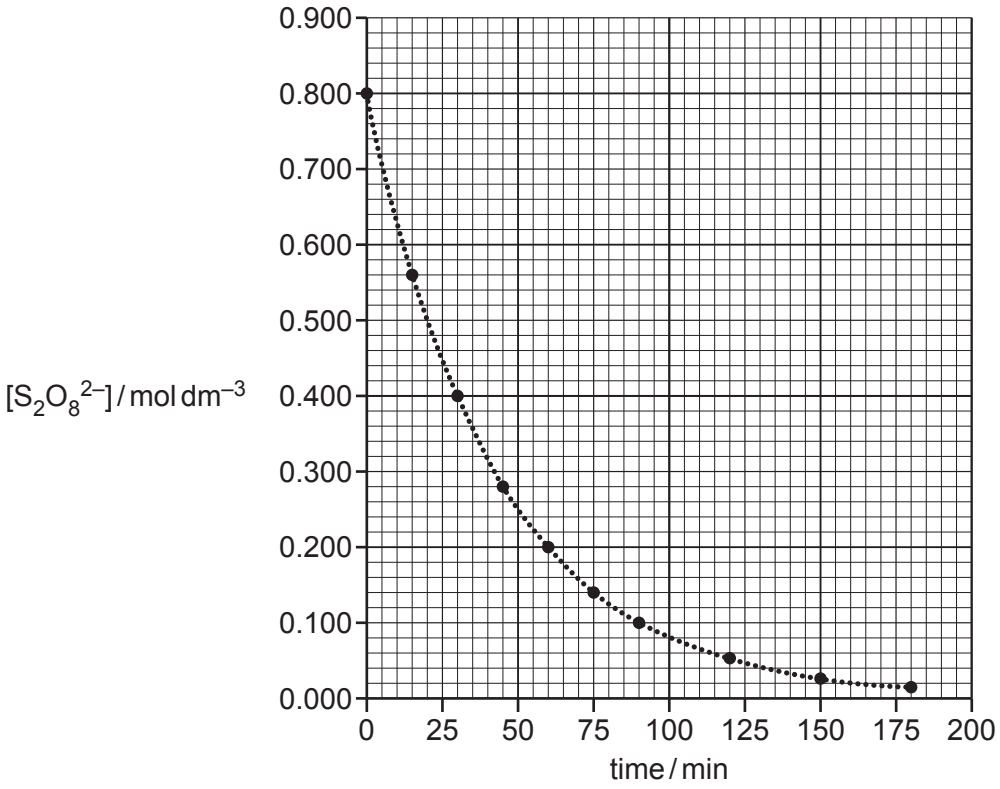

Fig. 5.1

(i) Use Fig. 5.1 to determine the initial rate of reaction 1. Show your working.

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

(ii) The rate equation for reaction 1 is rate = $k\,[S_2O_8^{2-}]\,[I^-]$.

Suggest why a large excess of iodide ions allows the rate constant to be determined from the half-life in this investigation.

.....

.....

..... [1]

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(b) The reaction of persulfate ions, $S_2O_8^{2-}$, with iodide ions is catalysed by Fe^{2+} ions.

Write **two** equations to show how Fe^{2+} catalyses reaction 1.

equation 1 .....

equation 2 .....

[2]

(c) Describe the effect of an increase in temperature on the rate constant and the rate of reaction 1.

.....

..... [1]

(d) In aqueous solution, thiosulfate ions, $S_2O_3^{2-}$, react with hydrogen ions, as shown in reaction 2.

reaction 2 $S_2O_3^{2-} + 2H^+ \rightarrow SO_2 + S + H_2O$

The rate of reaction is first order with respect to $[S_2O_3^{2-}]$ and zero order with respect to $[H^+]$ under certain conditions.

The rate constant, k, for this reaction is $1.58 \times 10^{-2}\,s^{-1}$.

Calculate the half-life, $t_{\frac{1}{2}}$, for reaction 2.

$t_{\frac{1}{2}}$ = ... s [1]

(e) The compound nitrosyl bromide, NOBr, can be formed as shown in reaction 3.

reaction 3 $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$

The rate is first order with respect to [NO] and first order with respect to $[Br_2]$.

The reaction mechanism has two steps.

Suggest equations for the **two** steps of this mechanism. State which is the rate-determining step.

step 1 .....

step 2 .....

rate-determining step = ...

[2]

[Total: 8]

6 (a) (i) State what is meant by partition coefficient, K_{pc}.

.....

.....

..... [1]

(ii) The partition coefficient, K_{pc}, for a compound, **X**, between carbon disulfide, CS_2, and water is 10.5.

1.85 g of **X** is dissolved in water and made up to 100.0 cm^3 in a volumetric flask.
40.0 cm^3 of this aqueous solution is shaken with 25.0 cm^3 of CS_2.
The mixture is left to reach equilibrium.

Calculate the mass of **X**, in g, extracted into the CS_2 layer.

mass of **X** = ... g [2]

(b) The compound C_6H_6 has many structural isomers. Four suggested structures of C_6H_6 are shown in Fig. 6.1.

Kekulé benzene Dewar benzene Ladenburg benzene delocalised benzene



Fig. 6.1

Using Fig. 6.1, complete Table 6.1 to predict the number of carbon atoms that have sp, sp^2 and sp^3 hybridisation in Kekulé benzene, Dewar benzene and Ladenburg benzene.

Table 6.1

C_6H_6 structure	sp hybridised	sp^2 hybridised	sp^3 hybridised
Kekulé benzene			
Dewar benzene			
Ladenburg benzene			

[2]

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(c) Describe the shape of delocalised benzene.

Include the geometry of each carbon, the C-C-H bond angle and the type of bond(s) between the carbon atoms and between the carbon and hydrogen atoms.

.....

.....

.....

.....

..... [2]

(d) Suggest why Dewar benzene and Ladenburg benzene are unstable isomers of C_6H_6.

.....

..... [1]

(e) Complete Table 6.2 to predict the number of peaks in the proton (^1H) NMR spectrum for Dewar benzene, Ladenburg benzene and delocalised benzene.

Table 6.2

	number of peaks
Dewar benzene	
Ladenburg benzene	
delocalised benzene	

[1]

(f) The reaction of phenylethanone with 1,4-dibromobutane, $BrCH_2CH_2CH_2CH_2Br$, in the presence of $FeBr_3$ is shown in Fig. 6.2.

phenylethanone

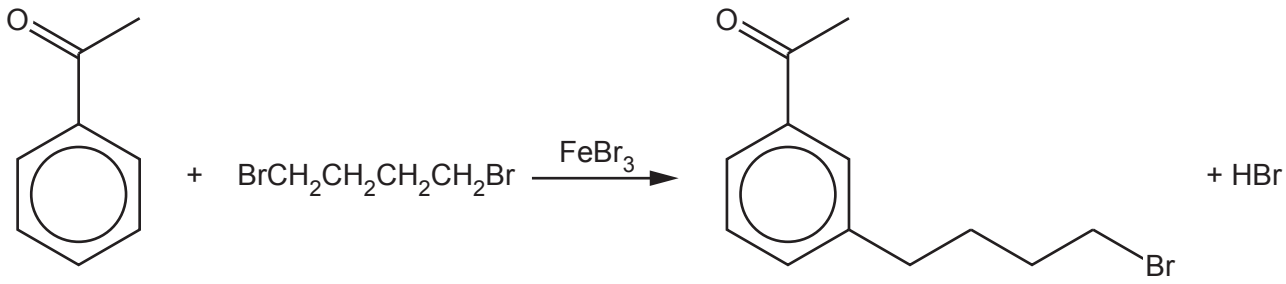

Fig. 6.2

The mechanism of this reaction is similar to that of the alkylation of benzene.

(i) Construct an equation for the formation of the electrophile, $BrCH_2CH_2CH_2CH_2^+$.

..... [1]

(ii) Complete the mechanism in Fig. 6.3 for the reaction of phenylethanone with $BrCH_2CH_2CH_2CH_2^+$ ions.

Include all relevant curly arrows and charges.
Draw the structure of the organic intermediate.

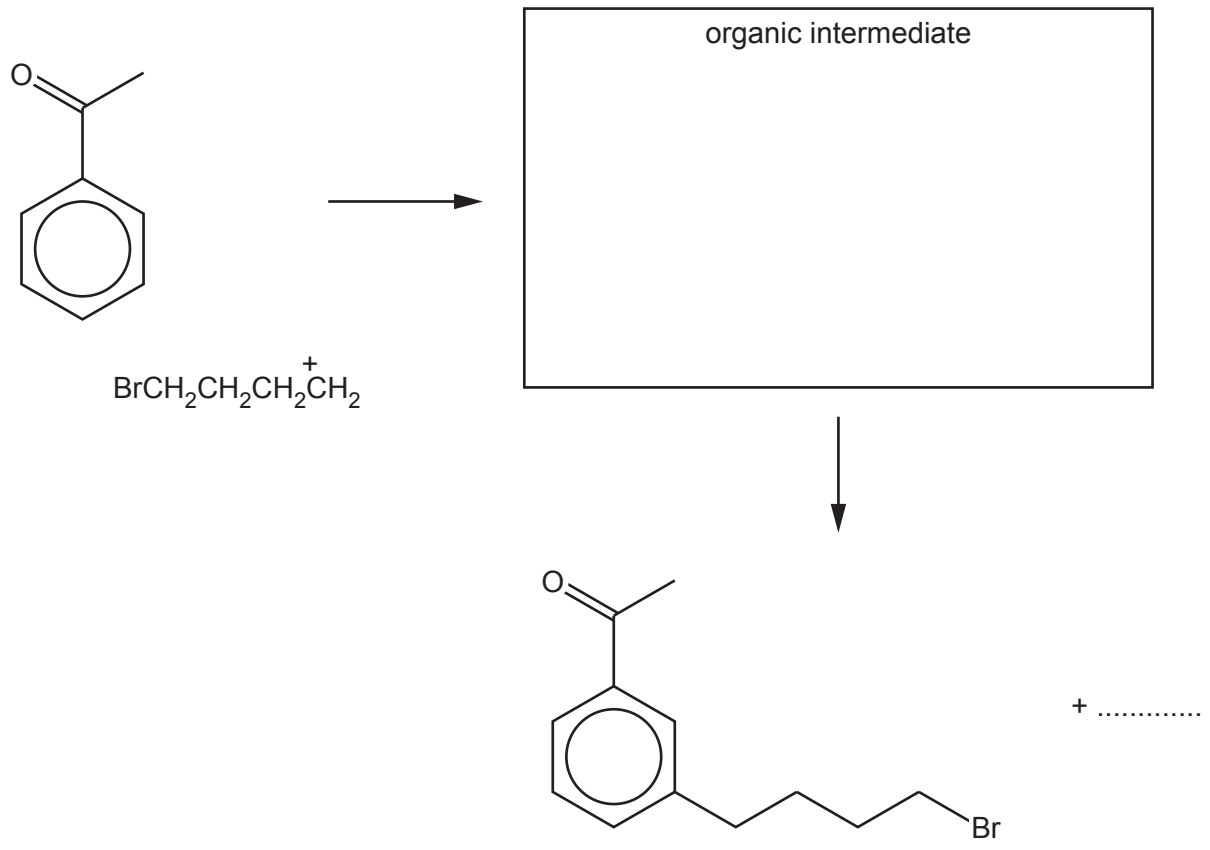

Fig. 6.3

[3]

(iii) The reaction shown in Fig. 6.2 forms small amounts of two by-products, **Y** ($C_{20}H_{22}O_2$) and **Z** ($C_{12}H_{14}O$).

Suggest structures for **Y** and **Z** in the boxes in Fig. 6.4.

Y ($C_{20}H_{22}O_2$)	**Z** ($C_{12}H_{14}O$)

Fig. 6.4

[2]

[Total: 15]

7 Four esters, **A**, **B**, **C** and **D**, with the molecular formula $C_6H_{12}O_2$ are shown in Fig. 7.1.

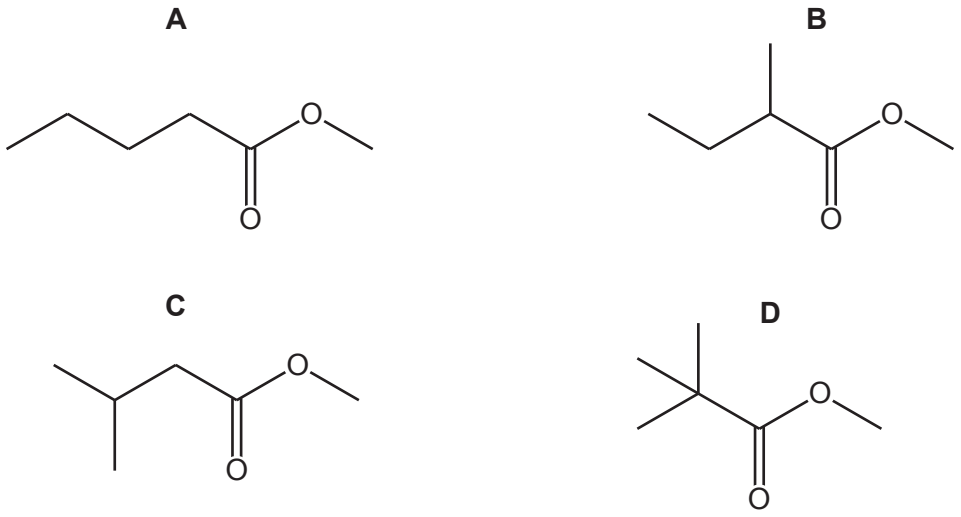

Fig. 7.1

(a) Give the systematic name of ester **A**.

..... [1]

(b) A mixture of these esters, **A**, **B**, **C** and **D**, is analysed by gas–liquid chromatography.

The chromatogram produced is shown in Fig. 7.2. The number above each peak represents the area under the peak.

The area under each peak is proportional to the mass of the respective ester in the mixture.

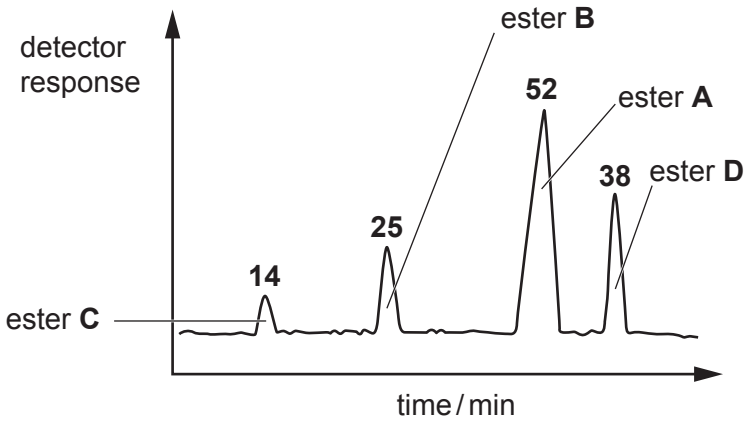

Fig. 7.2

(i) State what is meant by retention time.

.....

..... [1]

(ii) Calculate the percentage by mass of ester **D** in the original mixture.

percentage by mass of ester **D** = ... % [1]

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(c) Separate samples of the esters, **A**, **B**, **C** and **D**, are analysed using proton (^{1}H) NMR and carbon-13 NMR spectroscopy.

(i) Complete Table 7.1 to show the number of peaks in each NMR spectrum for esters **B** and **C**.

Table 7.1

ester	number of peaks in proton (^{1}H) NMR spectrum	number of peaks in carbon-13 NMR spectrum
B		
C		

[2]

(ii) Identify **all** of the esters from **A**, **B**, **C** and **D** that have at least one triplet peak in their proton (^{1}H) NMR spectrum.

..... [1]

Question 7 continues on page 20.

(d) Compound **F**, $C_6H_8O_3$, shows stereoisomerism and effervesces with Na_2CO_3(aq).

Compound **F** reacts with alkaline I_2(aq) to form yellow precipitate **G** and compound **H**.

Compound **F** reacts with $LiAlH_4$ to form compound **J**, $C_6H_{12}O_2$.

Compound **F** reacts with $SOCl_2$ to form compound **K**, $C_6H_7O_2Cl$.

Compound **K** reacts with propan-2-ol to form compound **L**.

Draw the structures of compounds **F**, **G**, **H**, **J**, **K** and **L** in the boxes in Fig. 7.3.

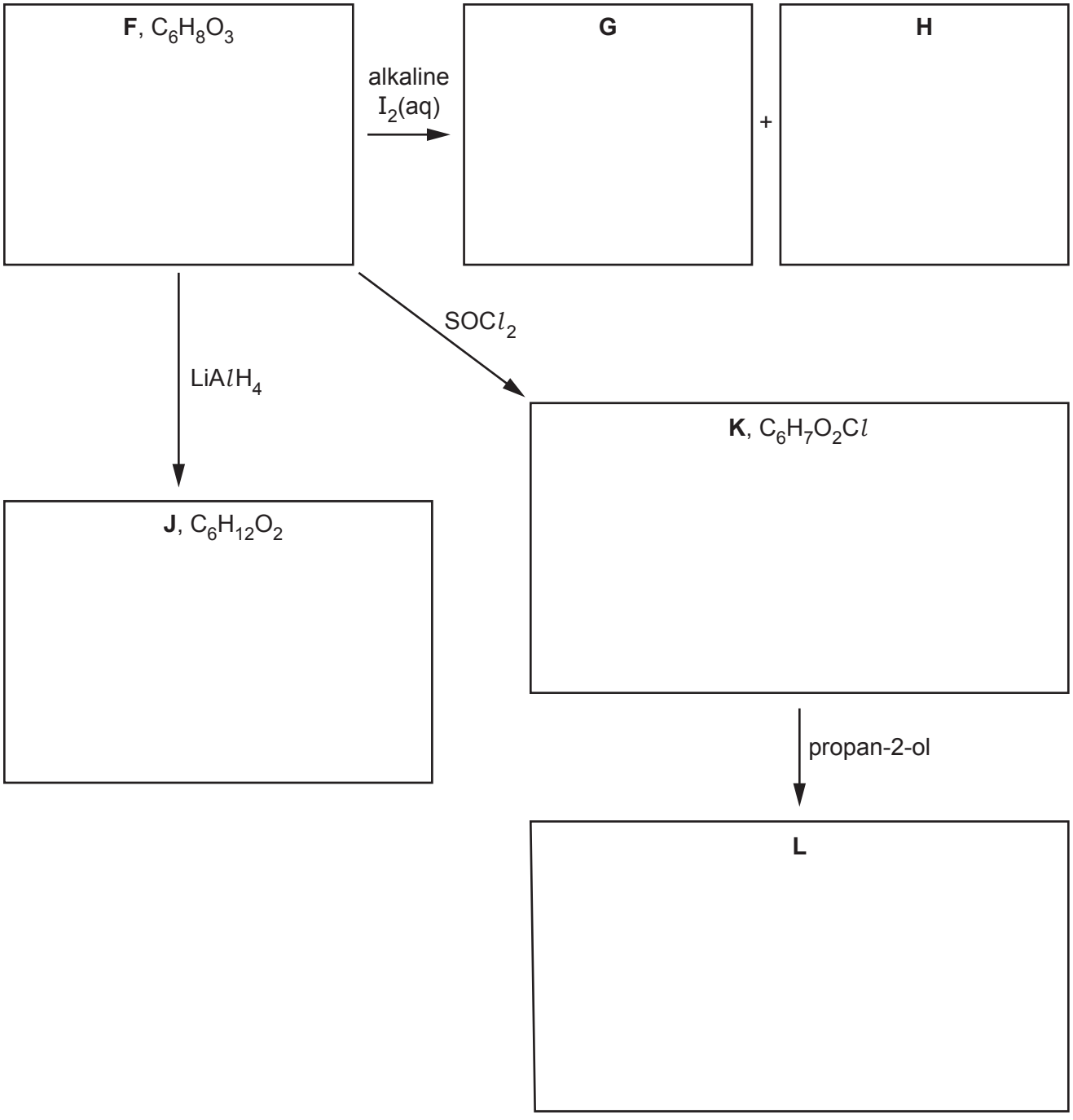

Fig. 7.3

[6]

[Total: 12]

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8 Neotame is an artificial sweetener added to some foods.

neotame

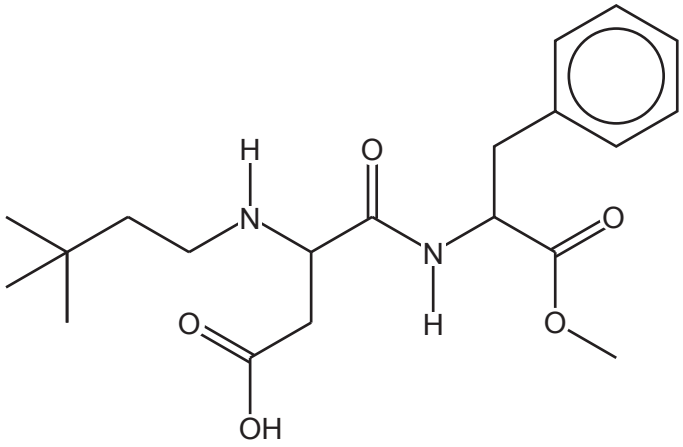

Fig. 8.1

(a) (i) State the number of chiral carbon atoms in a molecule of neotame.

..... [1]

(ii) Neotame contains the arene functional group.

Identify all the **other** functional groups present in neotame.

.....

..... [2]

(b) Neotame reacts with an excess of hot NaOH(aq) to form three organic products.

(i) State the **two** types of reaction that occur when neotame reacts with hot NaOH(aq).

1 .....

2 .....
[2]

neotame

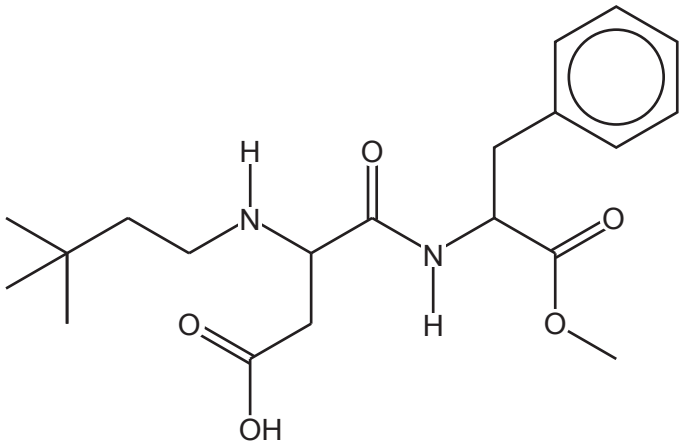

Fig. 8.1

(ii) Draw the structures of the **three** organic products formed from the reaction of neotame with an excess of hot NaOH(aq).

[3]

[Total: 8]

9 **(a)** Samples of phenol, C_6H_5OH, are reacted separately with sodium and with dilute nitric acid.

phenol

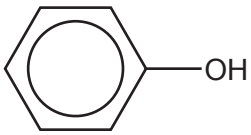

Fig. 9.1

(i) Write the equation for the reaction of C_6H_5OH with Na.

..... [1]

(ii) Draw the structures of the **two** major isomeric organic products formed in the reaction of phenol with dilute HNO_3.

[1]

(b) Salicylic acid can be synthesised from phenol.

salicylic acid

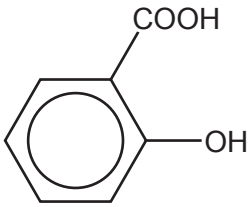

Fig. 9.2

One of the steps in this synthesis is the electrophilic substitution reaction of carbon dioxide with the phenoxide ion, $C_6H_5O^-$.

Complete the mechanism in Fig. 9.3 for the reaction of $C_6H_5O^-$ with CO_2.

Include all relevant curly arrows, dipoles and charges. Draw the structure of the organic intermediate.

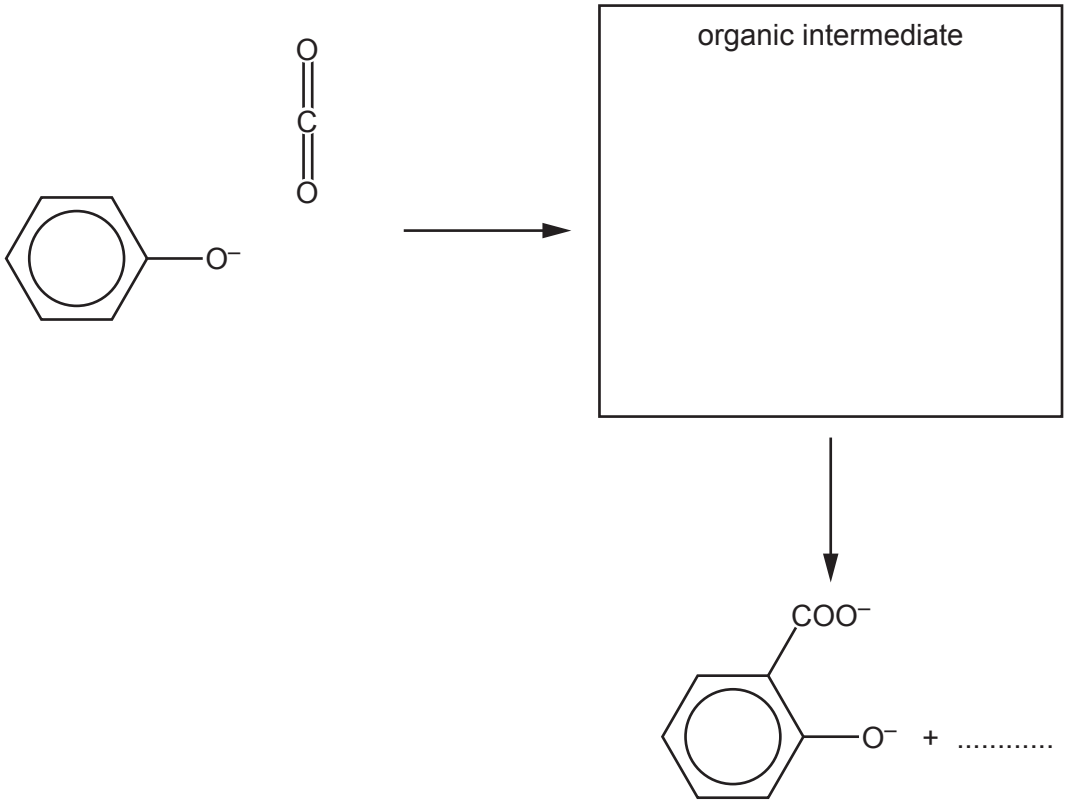

Fig. 9.3

[3]

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(c) Some syntheses use Diels–Alder reactions, which normally involve a diene and an alkene reacting together to form a cyclohexene.

(i) Draw **three** curly arrows in Fig. 9.4 to complete the mechanism for the Diels–Alder reaction between buta-1,3-diene and ethene.

buta-1,3-diene ethene cyclohexene



Fig. 9.4

[1]

(ii) Another Diels–Alder reaction of buta-1,3-diene is shown in Fig. 9.5.

Predict the product formed in this reaction.

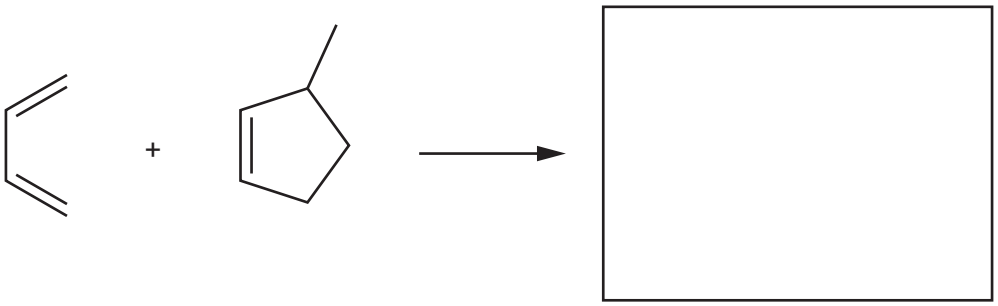

Fig. 9.5

[1]

[Total: 7]

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Important values, constants and standards

molar gas constant	$R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^{4}\,\text{C mol}^{-1}$
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	$c = 4.18\,\text{kJ kg}^{-1}\,\text{K}^{-1}$ ($4.18\,\text{J g}^{-1}\,\text{K}^{-1}$)

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The Periodic Table of Elements

Group																		
1	2											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 –

Key

atomic number
atomic symbol
name
relative atomic mass

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	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 –

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