Cambridge Assessment
International Education

Cambridge International AS & A Level

CANDIDATE NAME			
CENTRE NUMBER		CANDIDATE NUMBER	

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2023**

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 **24** pages.

1 **(a)** Group 2 carbonates decompose when heated to form the metal oxide and carbon dioxide.

(i) Suggest a mechanism for the decomposition of the carbonate ion by adding **two** curly arrows in Fig. 1.1.

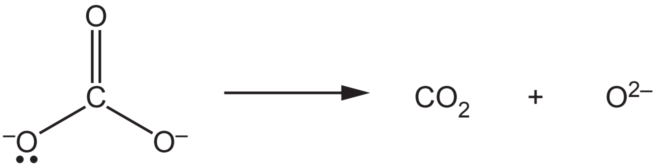

Fig. 1.1

[1]

(ii) Describe the variation in the thermal stability of Group 2 carbonates. Explain your answer.

....

....

....

....

.... [3]

(b) **(i)** Define lattice energy.

....

....

.... [2]

(ii) The lattice energy of the Group 2 carbonates, $\Delta H^{\ominus}_{latt}(MCO_3)$, becomes less exothermic down the group.

The lattice energy of the Group 2 oxides, $\Delta H^{\ominus}_{latt}(MO)$, also becomes less exothermic down the group.

$\Delta H^{\ominus}_{latt}(MCO_3)$ and $\Delta H^{\ominus}_{latt}(MO)$ change by **different** amounts going down the group.

Suggest how the standard enthalpy change of the decomposition reaction for Group 2 carbonates changes down the group.

Explain your reasoning in terms of the relative sizes of the anions and the relative changes in lattice energy down the group.

....

....

....

....

.... [2]

(c) Potassium sulfite, K_2SO_3, is used as a food additive.

The concentration of sulfite ions, SO_3^{2-}, can be determined by titration using aqueous acidified manganate(VII) ions, MnO_4^-.

- A 250 cm^3 solution contains 3.40 g of impure K_2SO_3.
- 25.0 cm^3 of this solution requires 22.40 cm^3 of 0.0250 mol dm^{-3} acidified MnO_4^- to reach the end-point. All the SO_3^{2-} ions are oxidised. None of the other species in the impure K_2SO_3 are oxidised.

The reaction occurs as shown by the two half-equations.

$$H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^+ + 2e^-$$

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

(i) Give the ionic equation for the reaction between SO_3^{2-} and acidified MnO_4^-.

.... [1]

(ii) Calculate the percentage purity of the sample of K_2SO_3.
Show your working.

percentage purity of K_2SO_3 = ... [3]

(d) Potassium disulfite, $K_2S_2O_5$, is another food additive. The disulfite ion, $S_2O_5^{2-}$, has the displayed formula shown in Fig. 1.2.

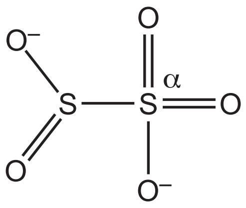

Fig. 1.2

Deduce the geometry (shape) around the S(α) atom in $S_2O_5^{2-}$.

geometry around S(α) .... [1]

[Total: 13]

2 **(a)** State **two** typical chemical properties of a transition element.

1 ....

2 .... [1]

(b) Aqueous solutions of cobalt(II) salts contain the complex ion $[Co(H_2O)_6]^{2+}$.

(i) Define complex ion.

....

.... [1]

(ii) Samples of $[Co(H_2O)_6]^{2+}$ are reacted separately with an excess of aqueous ammonia, with an excess of concentrated HC*l* and with an excess of aqueous sodium hydroxide, as shown in Fig. 2.1.

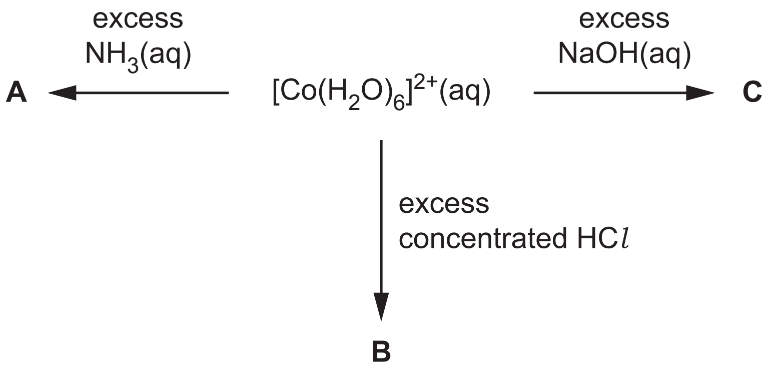

Fig. 2.1

Complete Table 2.1 about the reactions shown by $[Co(H_2O)_6]^{2+}$.

Table 2.1

reagent added to $[Co(H_2O)_6]^{2+}(aq)$	formula of cobalt species formed	colour and state of cobalt species formed	type of reaction
an excess of $NH_3(aq)$	**A** =		
an excess of concentrated HC*l*	**B** =		
an excess of NaOH(aq)	**C** =		

[4]

(c) The ethanedioate ion, $C_2O_4^{2-}$, can act as a bidentate ligand.

(i) Explain what is meant by a bidentate ligand.

....

....

.... [2]

(ii) The complex $[Co(H_2O)_2(C_2O_4)BrCl]^-$ exists as stereoisomers.

Complete the three-dimensional diagrams in Fig. 2.2 to show **four** stereoisomers of $[Co(H_2O)_2(C_2O_4)BrCl]^-$.

The $C_2O_4^{2-}$ ligand is represented using O⌒O .

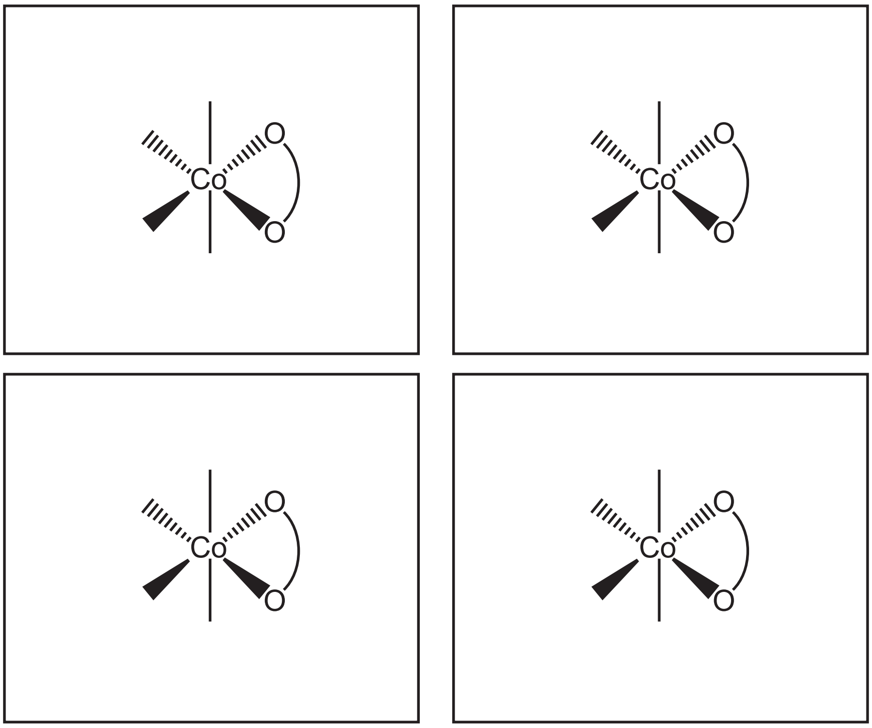

Fig. 2.2

[3]

(iii) State the oxidation state of cobalt in this complex and a type of stereoisomerism shown.

oxidation state of cobalt ....

type of stereoisomerism ....
[1]

[Total: 12]

3 **(a)** Complete Table 3.1 by placing **one** tick (✓) in each row to indicate the sign of each type of energy change under standard conditions.

Table 3.1

energy change	always positive	always negative	can be either negative or positive
bond energy			
enthalpy change of atomisation			
enthalpy change of formation			

[1]

(b) Define standard enthalpy change of atomisation.

....

....

.... [2]

(c) Table 3.2 shows some energy changes.

Table 3.2

energy change	value / kJ mol^{-1}
standard enthalpy change of atomisation of silver	+285
first ionisation energy of silver	+731
second ionisation energy of silver	+2074
bond energy of O=O	+496
bond energy of O–O	+150
first electron affinity of oxygen	–141
second electron affinity of oxygen	+798
first ionisation energy of oxygen	+1314
standard enthalpy change of formation of silver oxide, $Ag_2O(s)$	–31

Calculate the lattice energy, $\Delta H^{\ominus}_{latt}$, of $Ag_2O(s)$ using relevant data from Table 3.2.

It may be helpful to draw a labelled energy cycle.

Show your working.

$\Delta H^{\ominus}_{latt}$ of $Ag_2O(s)$ = ... kJ mol^{-1} [3]

(d) Suggest the trend in the magnitude of the lattice energies of the silver compounds Ag_2S, Ag_2O and Ag_2Se.

Explain your answer.

....	....	....
least exothermic		most exothermic

....

....

....
[2]

(e) Silver sulfite, $Ag_2SO_3(s)$, is sparingly soluble in water.

(i) Give an expression for the solubility product, K_{sp}, of Ag_2SO_3.

K_{sp} =

[1]

(ii) Calculate the equilibrium concentration of Ag^+ in a saturated solution of Ag_2SO_3 at 298 K.

[K_{sp}: Ag_2SO_3, 1.50×10^{-14} $mol^3\,dm^{-9}$ at 298 K]

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

(f) The standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of $AgNO_3(s)$ in water is +22.6 $kJ\,mol^{-1}$.

Suggest how the feasibility of dissolving $AgNO_3(s)$ in water changes with temperature.

Explain your answer.

....

....

....

.... [2]

[Total: 12]

4 **(a)** In aqueous solution, iron(III) ions react with iodide ions, as shown.

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$

A series of experiments is carried out using different concentrations of Fe^{3+} and I^-, as shown in Table 4.1.

Table 4.1

experiment	$[Fe^{3+}]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.0400	0.0200	2.64×10^{-4}
2	0.1200	0.0200	7.92×10^{-4}
3	0.0800	0.0400	2.11×10^{-3}

(i) Explain what is meant by overall order of reaction.

....

....

.... [1]

(ii) Use the data in Table 4.1 to deduce the order of reaction with respect to Fe^{3+} and with respect to I^-.

Explain your reasoning.

....

....

....

.... [2]

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

rate = [1]

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

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

(v) Describe qualitatively the effect of an increase in temperature on the rate constant and on the rate of this reaction.

....

.... [1]

(b) In aqueous solution, iodide ions react with acidified hydrogen peroxide, as shown.

$$2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2H_2O$$

The initial rate of reaction is found to be first order with respect to I^-, first order with respect to H_2O_2 and zero order with respect to H^+.

Fig. 4.1 shows a possible four-step mechanism for this reaction.

step 1 $H_2O_2 + I^- \rightarrow IO^- + H_2O$

step 2 $H^+ + IO^- \rightarrow HIO$

step 3 $HIO + I^- \rightarrow I_2 + OH^-$

step 4 $OH^- + H^+ \rightarrow H_2O$

Fig. 4.1

(i) Suggest which of the steps, 1, 2, 3 or 4, in this mechanism is the rate-determining step.

Explain your answer.

....

....

.... [1]

(ii) Identify a step in Fig. 4.1 that involves a redox reaction.

Explain your answer in terms of oxidation numbers.

....

....

.... [1]

(iii) Suggest the role of HIO in this mechanism.

Explain your reasoning.

....

....

.... [1]

[Total: 10]

5 **(a)** Methylbenzene can undergo different reactions, as shown in Fig. 5.1.

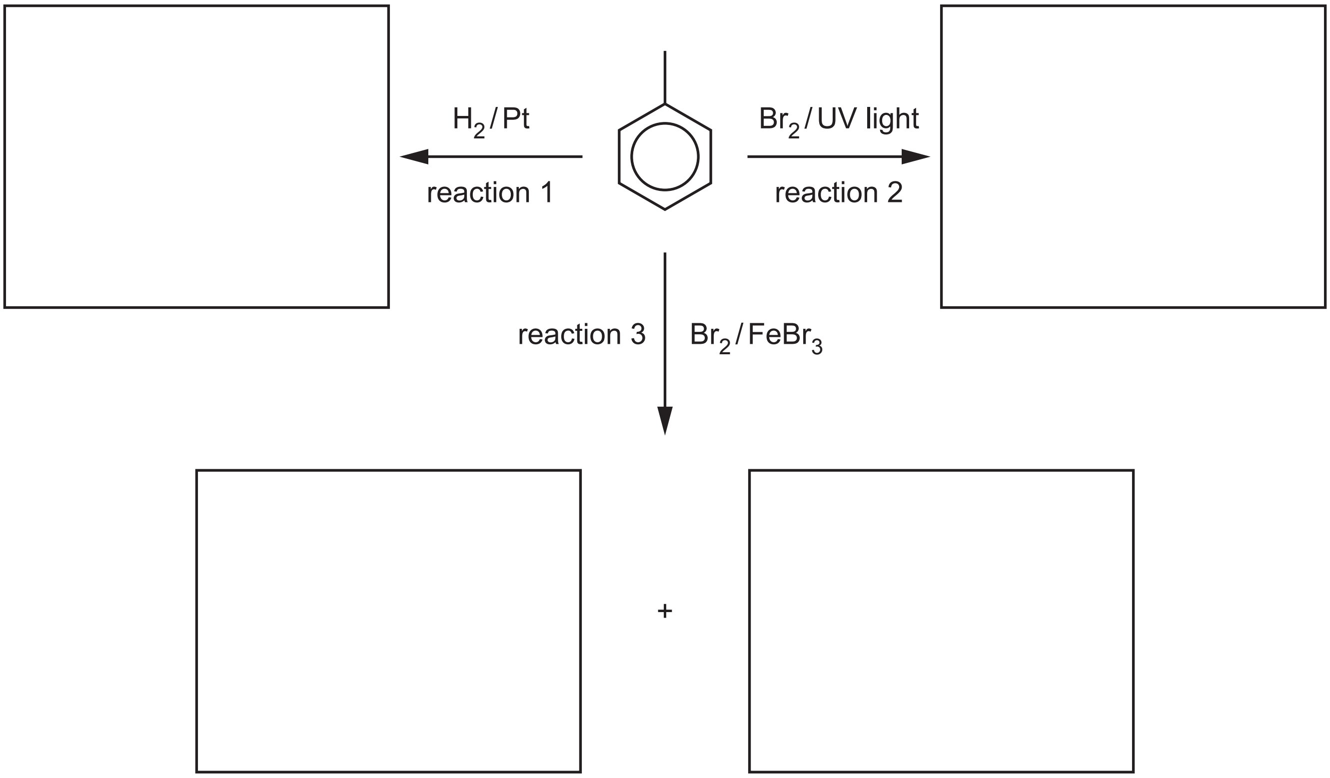

Fig. 5.1

(i) Draw structures in Fig. 5.1 for the possible organic products of the three reactions shown. [3]

(ii) Complete Table 5.1.

Table 5.1

	type of reaction	mechanism
reaction 1		☒
reaction 2	☒	

[2]

(b) When methylbenzene reacts with an electrophile, a substitution reaction occurs. No addition reaction takes place under these conditions.

Explain why no addition reaction takes place.

....

.... [1]

(c) The reaction of methylbenzene with thionyl bromide, $SOBr_2$, in the presence of an iron(III) bromide catalyst, $FeBr_3$, is shown in Fig. 5.2.

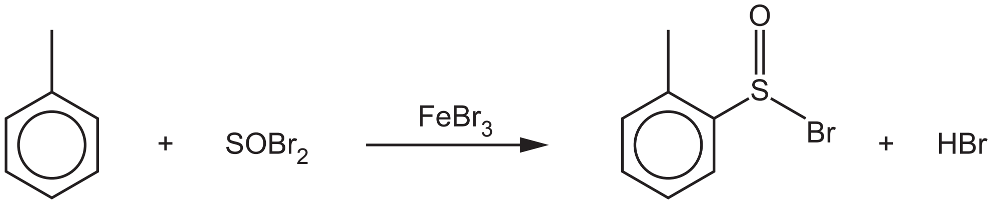

Fig. 5.2

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

The first step of the mechanism generates the $SOBr^+$ electrophile, as shown.

$$SOBr_2 + FeBr_3 \rightarrow SOBr^+ + FeBr_4^-$$

(i) The reaction of methylbenzene with $SOBr^+$ ions is shown in Fig. 5.3. Complete the mechanism in Fig. 5.3.

Include all relevant curly arrows and charges.

Draw the structure of the organic intermediate.

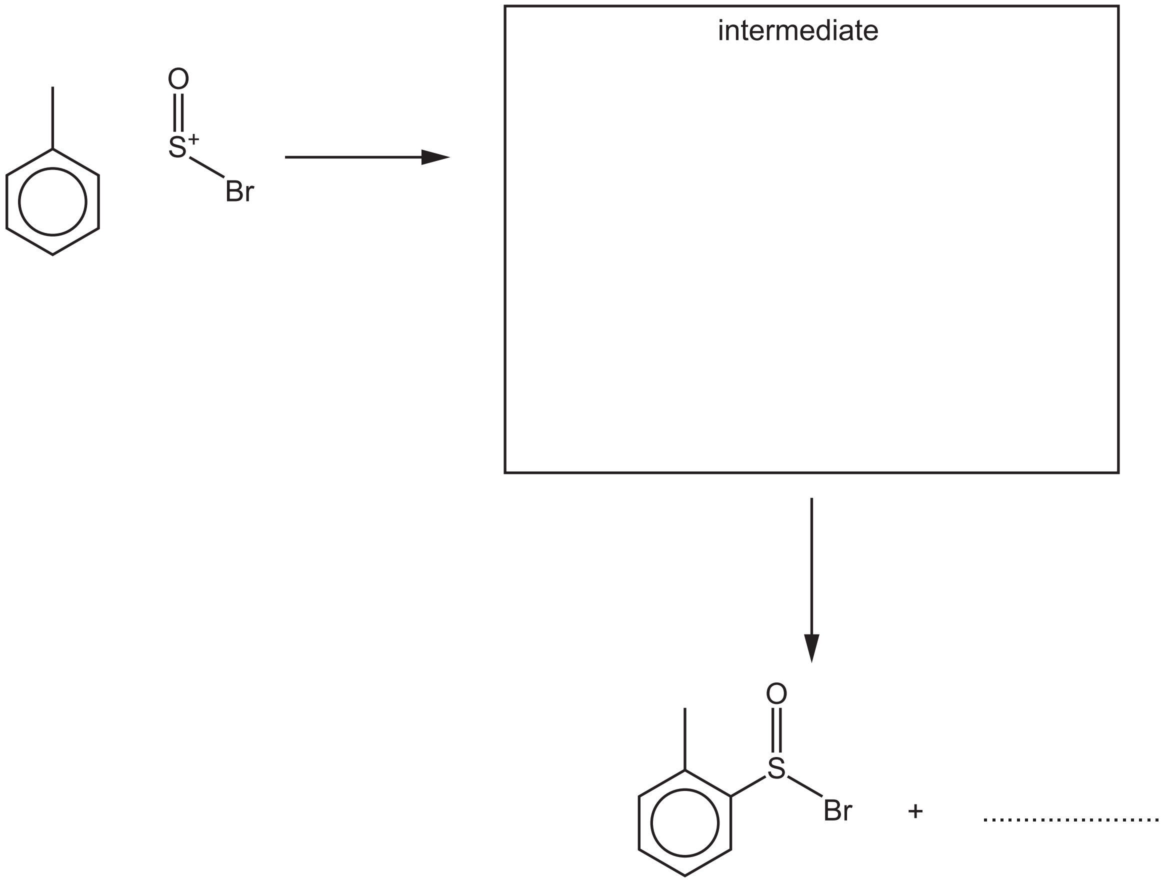

Fig. 5.3

[3]

(ii) The reaction shown in Fig. 5.2 produces a small amount of a by-product, **P**, with the molecular formula $C_{14}H_{14}OS$.

Suggest a structure for by-product **P**.

[1]

(d) Acyl bromides, RCOBr, can be synthesised by the reaction of a carboxylic acid and $SOBr_2$.

This is a similar reaction to the synthesis of acyl chlorides using $SOCl_2$.

(i) Give an equation for the reaction between ethanoic acid and $SOBr_2$.

.... [1]

(ii) Suggest the relative ease of hydrolysis of acyl bromides, RCOBr, acyl chlorides, RCOC*l*, and alkyl chlorides, RC*l*.

Explain your answer.

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

easiest to hydrolyse hardest to hydrolyse

....

....

....

....

....

[3]

[Total: 14]

6 **(a)** Perindopril is a drug used to treat heart disease.

perindopril

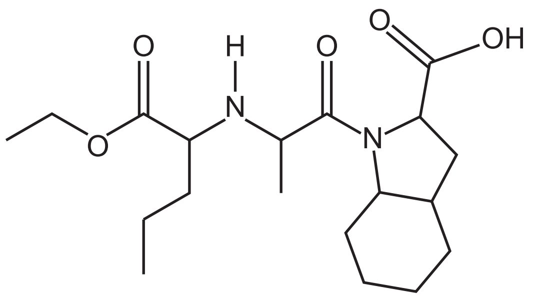

Fig. 6.1

(i) State the number of chiral carbon atoms present in one molecule of perindopril.

.... [1]

(ii) Suggest **one** benefit and **one** disadvantage of producing a drug such as perindopril as a single pure optical isomer.

benefit ....

....

disadvantage ....

.... [2]

(b) **(i)** Name all the functional groups in perindopril.

....

.... [2]

(ii) A sample of perindopril is hydrolysed with hot aqueous acid.

Draw the structures of the **three** organic products of the **complete** acid hydrolysis of perindopril.

[3]

[Total: 8]

7 **(a)** Explain why phenol is brominated much more easily than benzene is brominated.

....

....

....

....

.... [3]

(b) Iodine monobromide, I–Br, reacts with benzene in the presence of an $AlBr_3$ catalyst.

Predict whether the organic product will be bromobenzene or iodobenzene.
Explain your answer.

....

....

.... [1]

(c) Fig. 7.1 shows some reactions of phenol.

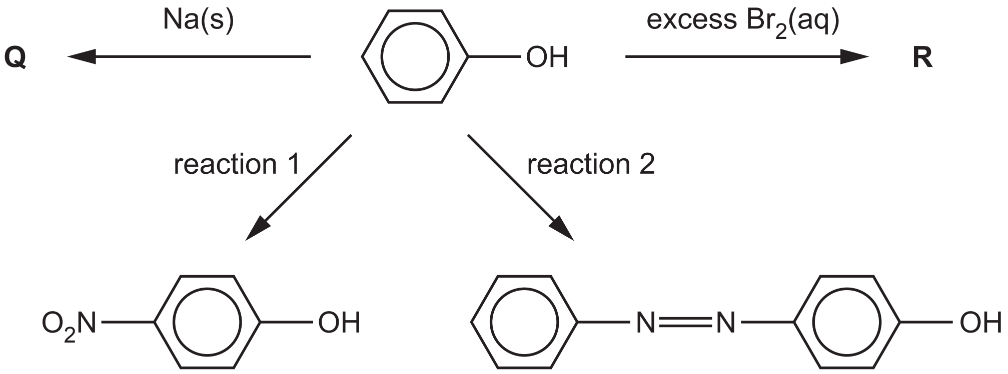

Fig. 7.1

(i) Give an equation for the reaction of phenol with Na(s).

.... [1]

(ii) Draw the structure of the organic product, **R**, formed when phenol reacts with an excess of Br_2(aq).

[1]

(iii) State the reagents and conditions for reaction 1 and reaction 2 in Fig. 7.1.

reaction 1 ....

reaction 2 ....
[2]

[Total: 8]

8 **(a)** Describe the difference in reactivity between chloroethane and chlorobenzene with $OH^-(aq)$.

Explain your answer.

....

....

....

.... [2]

(b) Compound **T**, $C_5H_9O_2Cl$, is a useful synthetic intermediate.

Fig. 8.1 shows some reactions of **T**.

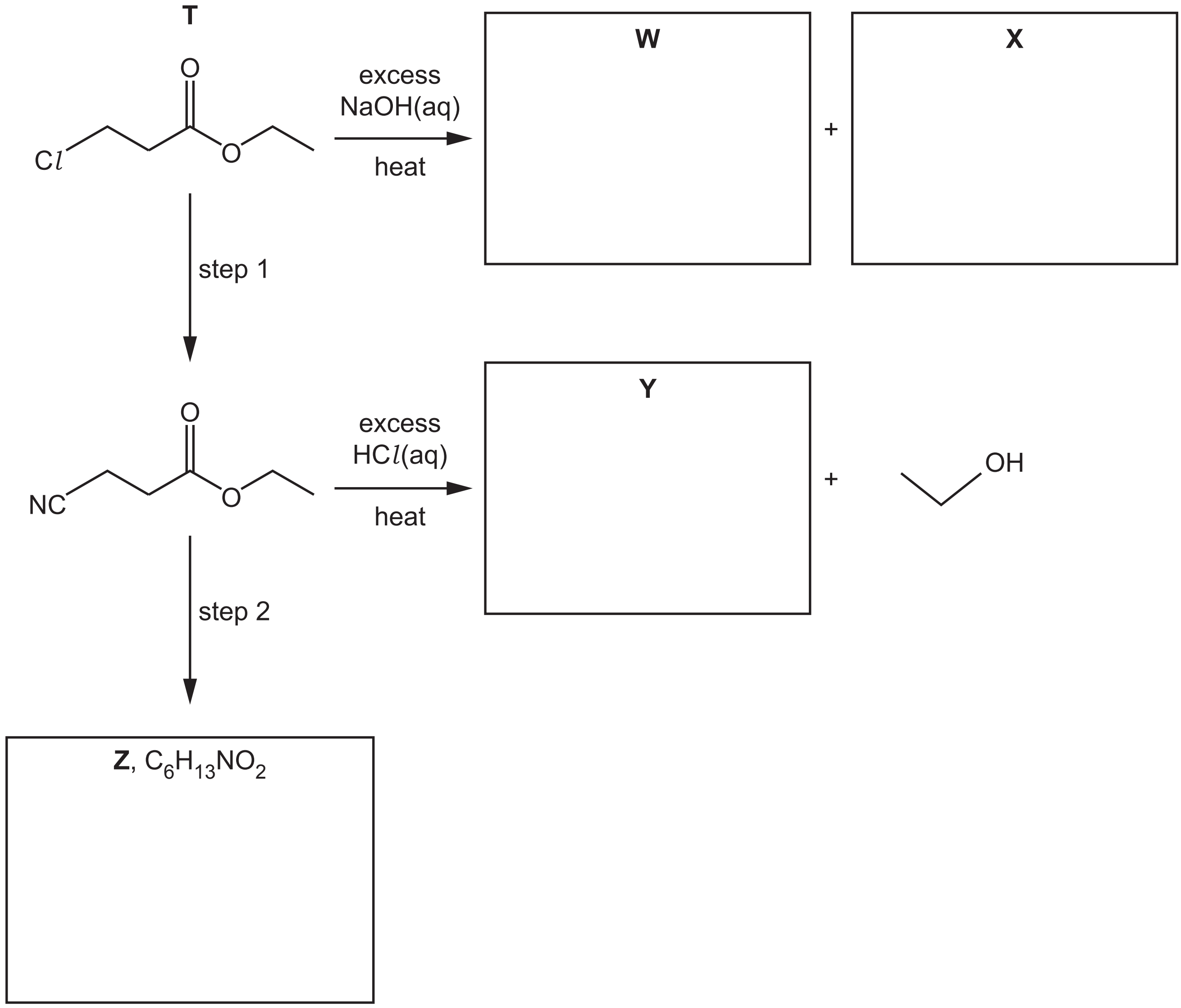

Fig. 8.1

(i) Give the systematic name for **T**.

.... [1]

(ii) Draw the structures of **W**, **X**, **Y** and **Z** in Fig. 8.1. [4]

(iii) State the reagents and conditions for steps 1 and 2 in Fig. 8.1.

step 1 ....

step 2 ....

[2]

(c) The proton (^1H) NMR spectrum of compound **T**, $C_5H_9O_2Cl$, in $CDCl_3$ is shown in Fig. 8.2.

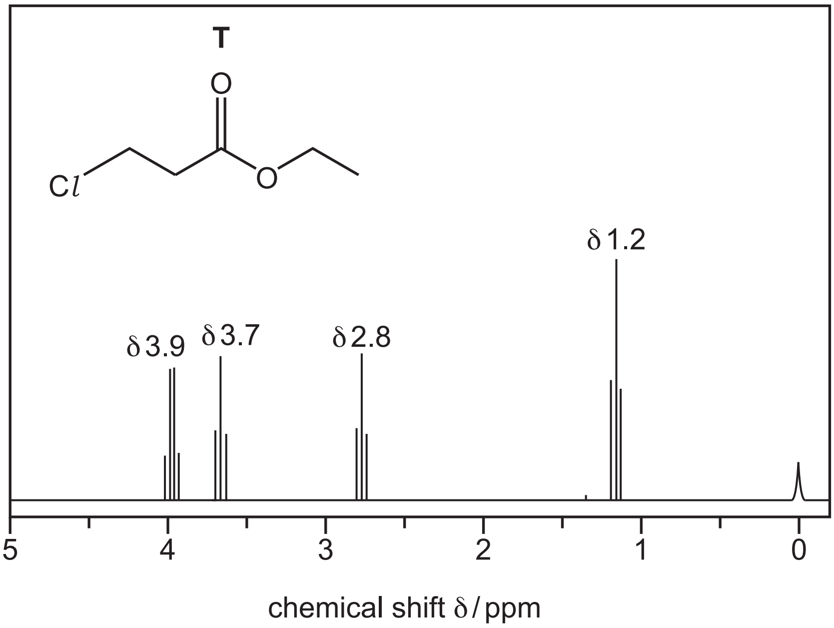

Fig. 8.2

Table 8.1

environment of proton	example	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	=C**H**R	4.5–6.0
attached to aromatic ring	**H**–Ar	6.0–9.0
aldehyde	**H**COR	9.3–10.5
alcohol	RO**H**	0.5–6.0
phenol	Ar–O**H**	4.5–7.0
carboxylic acid	RCOO**H**	9.0–13.0
alkyl amine	R–N**H**–	1.0–5.0
aryl amine	$Ar-NH_2$	3.0–6.0
amide	RCON**H**R	5.0–12.0

(i) Suggest why $CDCl_3$ is used as a solvent instead of $CHCl_3$ for the proton (^1H) NMR spectrum.

....

.... [1]

(ii) Complete Table 8.2 for the proton (^1H) NMR spectrum of **T**.

Table 8.2

chemical shift δ/ppm	environment of proton	splitting pattern	number of ^1H atoms responsible for the peak
1.2			
2.8			
3.7			
3.9			

[4]

(iii) Explain the splitting pattern of the peak at δ 3.9 ppm.

....

.... [1]

[Total: 15]

9 **(a)** Define standard cell potential, $E^{\ominus}_{\text{cell}}$.

....

.... [1]

(b) An electrochemical cell is set up to measure $E^{\ominus}_{\text{cell}}$ of a cell consisting of an $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell and a $\text{C}l_2/\text{C}l^-$ half-cell.

Draw a labelled diagram of this electrochemical cell.

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

[3]

(c) The cell reaction for the electrochemical cell in **(b)** is shown.

$$\text{C}l_2 + 2\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + 2\text{C}l^- \qquad E^{\ominus}_{\text{cell}} = +0.59\,\text{V}$$

Calculate $\Delta G^{\ominus}$, in kJ mol^{-1}, for this cell reaction.

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

(d) Another experiment is set up using the same electrochemical cell.

In this experiment the Fe^{2+} concentration is 0.15 mol dm^{-3}. All other concentrations remain at their standard values.

The Nernst equation is shown.

$$E = E^{\ominus} + (0.059/z)\log\frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

(i) Use the Nernst equation to calculate the electrode potential, *E*, for the Fe^{3+}/Fe^{2+} half-cell in this experiment.

[$E^{\ominus}$: Fe^{3+}/Fe^{2+} = +0.77 V]

E = ... V [1]

(ii) Use your answer to **(d)(i)** to calculate E_{cell} for this electrochemical cell.

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

[Total: 8]

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	$c = 4.18\ \text{kJ kg}^{-1}\text{K}^{-1}$ ($4.18\ \text{J g}^{-1}\text{K}^{-1}$)

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 –
