Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME			
CENTRE NUMBER		CANDIDATE NUMBER	

0123456789

CHEMISTRY **9701/04**

Paper 4 A Level Structured Questions **For examination from 2022**

SPECIMEN PAPER **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 [ ].

This document has **24** pages. Blank pages are indicated.

1 **(a)** **(i)** State what is meant by partition coefficient.

....

....

.... [2]

Ammonia is soluble in both water and organic solvents.
An aqueous solution of ammonia is shaken with the immiscible organic solvent trichloromethane. The mixture is left to reach equilibrium.

Samples are taken from each layer and titrated with dilute hydrochloric acid.

- A 25.0 cm^3 sample from the trichloromethane layer requires 13.0 cm^3 of 0.100 mol dm^{-3} HCl to reach the end-point.
- A 10.0 cm^3 sample from the aqueous layer requires 12.5 cm^3 of 0.100 mol dm^{-3} HCl to reach the end-point.

(ii) Calculate the partition coefficient, K_{pc}, of ammonia between trichloromethane and water.
Show your working.

K_{pc} = ... [2]

(iii) Butylamine, $C_4H_9NH_2$, is also soluble in both water and organic solvents.

Suggest how the numerical value of K_{pc} of butylamine between trichloromethane and water would compare to the value of K_{pc} calculated in **(a)(ii)**. Explain your answer.

....

....

....

.... [2]

(b) Butanamide, $C_3H_7CONH_2$, is much less basic than butylamine. Explain why.

....

.... [1]

[Total: 7]

2 The feasibility of a chemical reaction depends on the standard Gibbs free energy change, $\Delta G^{\ominus}$. This is dependent on the standard enthalpy and entropy changes, and the temperature.

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

(i) the reaction of magnesium with hydrochloric acid

entropy change ....

explanation .... [1]

(ii) the dissolving of solid potassium chloride in water

entropy change ....

explanation .... [1]

(iii) the condensing of water from steam

entropy change ....

explanation .... [1]

(b) Magnesium carbonate can be decomposed on heating.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g) \qquad \Delta H^{\ominus} = +117\,\text{kJ mol}^{-1}$$

Standard entropies are shown in Table 2.1.

Table 2.1

substance	$MgCO_3$(s)	MgO(s)	CO_2(g)
$S^{\ominus}$ / J K^{-1} mol^{-1}	+65.7	+26.9	+214

(i) Calculate $\Delta G^{\ominus}$ for this reaction at 298 K.
Show your working.

$\Delta G^{\ominus}$ = ... kJ mol^{-1} [3]

(ii) Explain why this reaction is feasible only at high temperatures.

....

.... [1]

(c) Table 2.2 lists values of solubility products, K_{sp}, of some Group 2 carbonates.

Table 2.2

	solubility product in water at 298 K, K_{sp} / $mol^2\,dm^{-6}$
$MgCO_3$	1.0×10^{-5}
$CaCO_3$	5.0×10^{-9}
$SrCO_3$	1.1×10^{-10}

Deduce the trend in the solubility of the Group 2 carbonates down the group. Justify your answer using the data given.

....

.... [1]

(d) **(i)** Write an equation to show the equilibrium for the solubility product of $MgCO_3$. Include state symbols.

.... $\rightleftharpoons$ .... [1]

(ii) With reference to your equation in **(d)(i)**, suggest what is observed when a few cm^3 of concentrated $Na_2CO_3(aq)$ are added to a saturated solution of $MgCO_3$. Explain your answer.

....

....

.... [2]

(e) Use the data in Table 2.2 to calculate the solubility of $MgCO_3$ in water at 298 K, in $g\,dm^{-3}$. Show your working.

solubility of $MgCO_3$ = ... $g\,dm^{-3}$ [2]

(f) Describe and explain the variation in the thermal stabilities of the carbonates of the Group 2 elements.

....

....

....

....

.... [3]

[Total: 16]

3 **(a)** The initial rate of the reaction of chlorine dioxide, ClO_2, and fluorine, F_2, is measured in a series of experiments at a constant temperature.

$$2ClO_2 + F_2 \rightarrow 2ClO_2F$$

The results obtained are shown in Table 3.1.

Table 3.1

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) Explain what is meant by 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*.

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

(iii) Use the data in Table 3.1 to calculate the initial rate in experiment 2.

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

(iv) Use the data in Table 3.1 to calculate $[ClO_2]$ in experiment 3.

$[ClO_2]$ = ... mol dm^{-3} [1]

(b) **(i)** Explain what is meant by rate-determining step.

....

.... [1]

(ii) The mechanism of the reaction between $C\mathit{l}O_2$ and F_2 has two steps.

Suggest equations for the two steps of this mechanism.

step 1 ....

step 2 ....
[1]

(iii) State and explain which of the two steps is the rate-determining step.

rate-determining step = ...

....

.... [1]

(c) Describe the effect of temperature change on the rate of a reaction and the rate constant.

....

.... [1]

[Total: 9]

4 **(a)** 4-nitromethylbenzene can be prepared via an electrophilic substitution reaction as shown in Fig. 4.1.

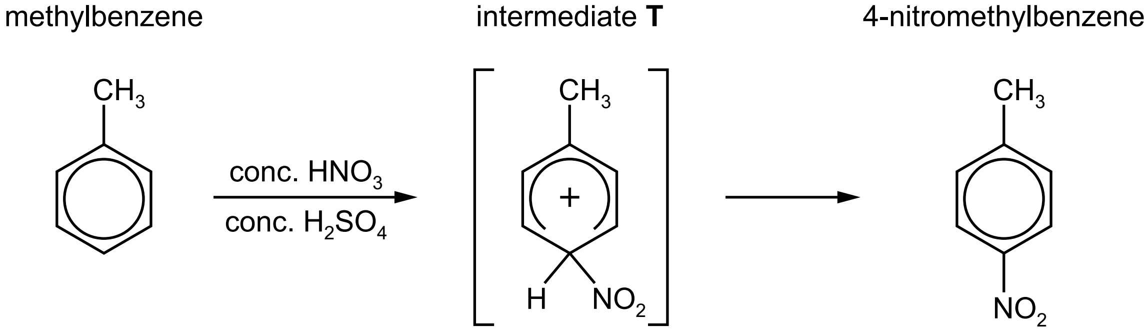


Fig. 4.1

(i) This reaction also forms an isomer of 4-nitromethylbenzene as a by-product. Draw the structure of this by-product.

[1]

(ii) Write an equation for the reaction between HNO_3 and H_2SO_4 that forms the electrophile for this reaction.

.... [1]

(iii) Describe how the structure and bonding of the six-membered ring in intermediate **T** differ from those in methylbenzene. In your answer refer to the hybridisation, the π bonding and the bond angles in the ring system.

....

....

....

....

....

.... [3]

(b) Benzocaine is used as a local anaesthetic. It can be synthesised from 4-nitromethylbenzene by the route shown in Fig. 4.2.

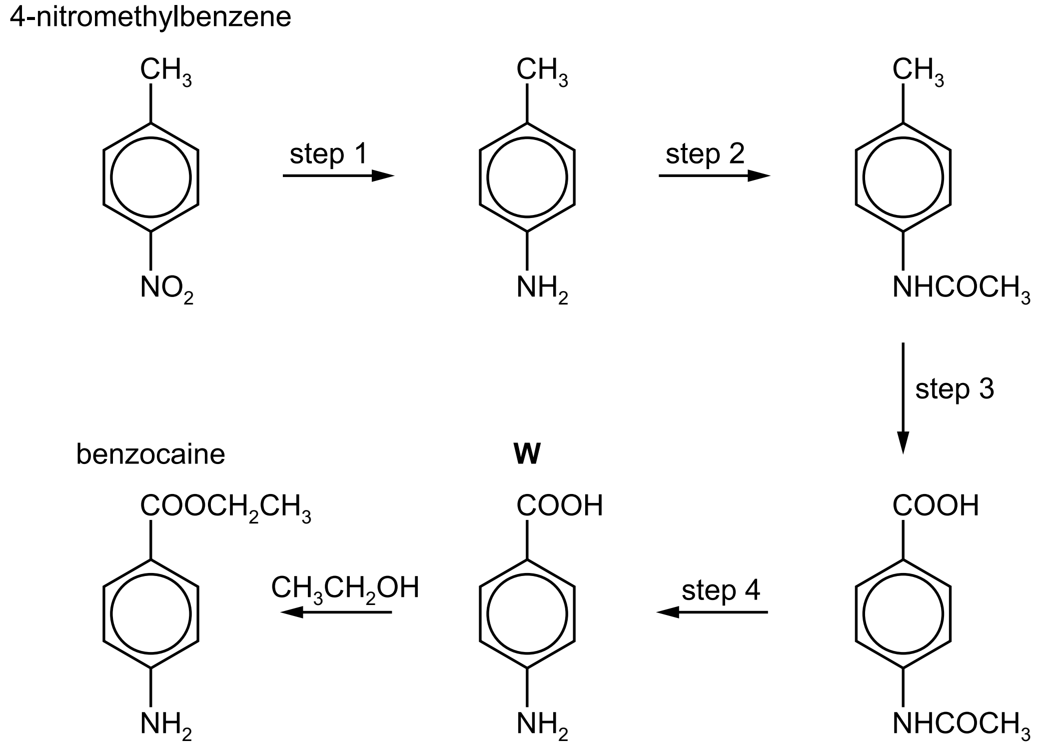


Fig. 4.2

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

.... [1]

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

step 1 .... [2]

(iii) Suggest the reagent for step 2.

step 2 .... [1]

(iv) Suggest the reagents and conditions for step 3 and step 4.

step 3 ....

step 4 ....
[2]

(c) A sample of benzocaine was analysed by carbon-13 NMR and proton NMR spectroscopy.

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

.... [1]

Benzocaine was dissolved in $CDCl_3$ and the proton NMR spectrum of this solution was recorded as shown in Fig. 4.3.

benzocaine

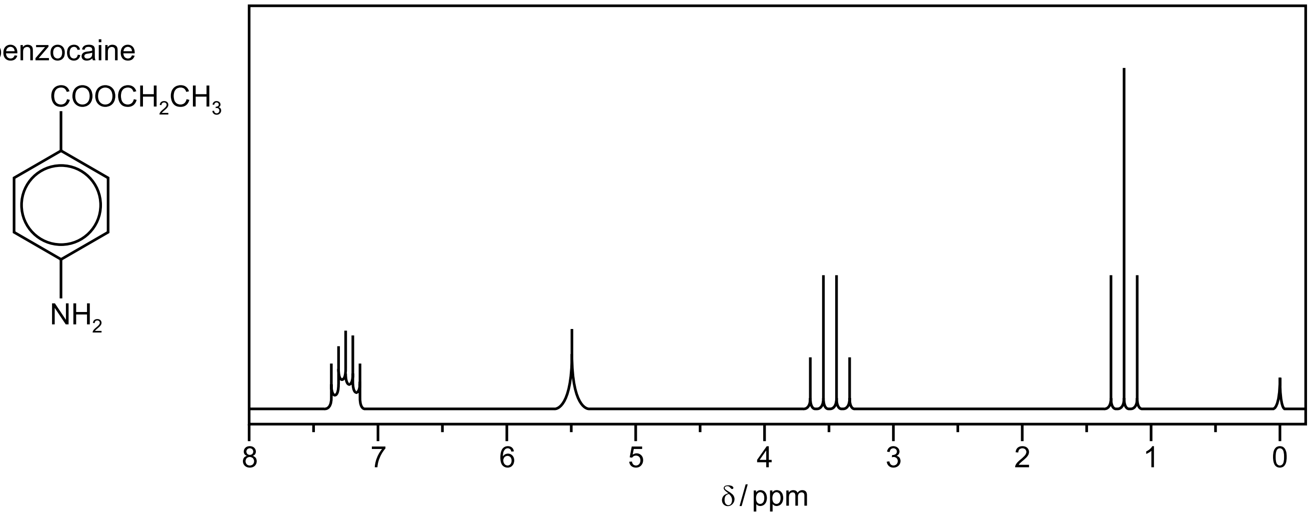


Fig. 4.3

(ii) The data in Table 4.2 should be used in answering this question.

Complete Table 4.1 for the chemical shifts δ 1.2 ppm, 3.5 ppm and 5.5 ppm.

Table 4.1

δ / ppm	environment of proton	number of ^{1}H atoms responsible for the peak	splitting pattern
1.2			
3.5			
5.5			
7.1–7.4	attached to aromatic ring	4	two doublets

[3]

(iii) Explain the splitting pattern for the absorption at δ1.2 ppm.

....

.... [1]

Table 4.2

Environment of proton	Example	chemcial shift range, δ / ppm
alkane	–C**H**$_3$, –C**H**$_2$–, >C**H**–	0.9–1.7
alkyl next to C=O	C**H**$_3$–C=O,–C**H**$_2$–C=O, >C**H**–C=O	2.2–3.0
alkyl next to aromatic ring	C**H**$_3$–Ar, –C**H**$_2$–Ar, >C**H**–Ar	2.3–3.0
alkyl next to electronegative atom	C**H**$_3$–O,–C**H**$_2$–O, –C**H**$_2$–C*l*	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–N**H**$_2$	3.0–6.0
amide	RCON**H**R	5.0–12.0

(d) Benzocaine can also be used to synthesise the azo compound **S** by the following route.

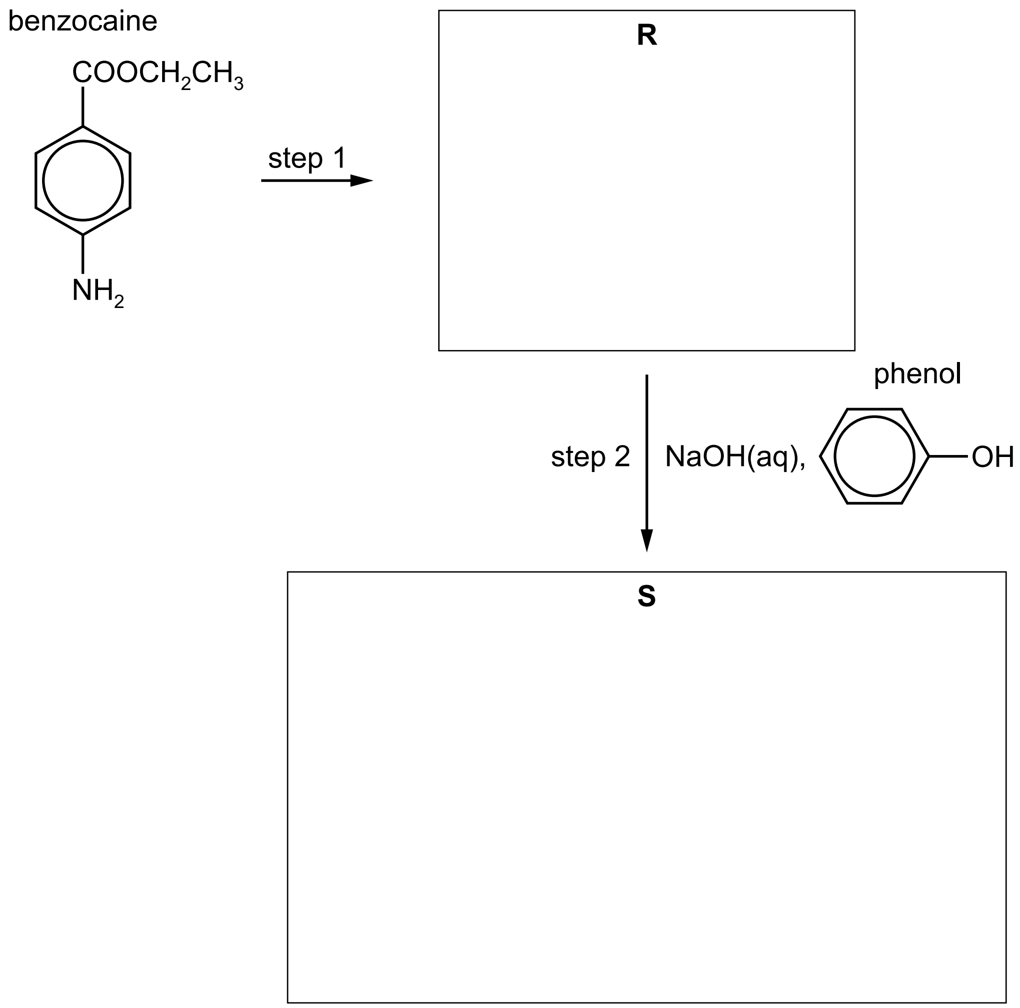


Fig. 4.4

(i) Suggest the reagent(s) used for step 1.

.... [1]

(ii) Suggest structures for compounds **R** and **S** and draw them in the boxes in Fig. 4.4. [2]

[Total: 19]

5 **(a)** Lattice energies are always negative showing that they represent exothermic changes.

(i) Explain what is meant by lattice energy.

....

....

.... [2]

(ii) Explain why lattice energy is an exothermic process.

....

.... [1]

Table 5.1

energy change	value / kJ mol^{-1}
standard enthalpy change of atomisation of potassium	+89
electron affinity of O(g)	–141
electron affinity of O^-(g)	+798
standard enthalpy change of formation of potassium oxide	–361
first ionisation energy of potassium	+418
second ionisation energy of potassium	+3070
first ionisation energy of oxygen	+1310
second ionisation energy of oxygen	+3390
O=O bond energy (diatomic molecule)	+496
O–O bond energy (polyatomic molecule)	+150

(b) **(i)** Use relevant data from Table 5.1 to calculate the lattice energy, $\Delta H^{\ominus}_{latt}$, of potassium oxide, K_2O(s).
Show your working.

$\Delta H^{\ominus}_{latt}$, of K_2O(s) = ... kJ mol^{-1} [3]

(ii) State how $\Delta H^{\ominus}_{latt}Na_2O(s)$ differs from $\Delta H^{\ominus}_{latt}K_2O(s)$.
Indicate this by placing **one** tick (✓) in the appropriate box in Table 5.2.

Table 5.2

$\Delta H^{\ominus}_{latt}Na_2O(s)$ is less negative than $\Delta H^{\ominus}_{latt}K_2O(s)$	$\Delta H^{\ominus}_{latt}Na_2O(s)$ is the same as $\Delta H^{\ominus}_{latt}K_2O(s)$	$\Delta H^{\ominus}_{latt}Na_2O(s)$ is more negative than $\Delta H^{\ominus}_{latt}K_2O(s)$

Explain your answer.

....

.... [1]

[Total: 7]

6 **(a)** Define a transition element.

....

.... [1]

(b) **(i)** NH_3 acts as a monodentate ligand. State what is meant by monodentate ligand.

....

....

.... [2]

(ii) Aqueous silver ions, $Ag^+(aq)$, react with aqueous ammonia, $NH_3(aq)$, to form a linear complex.

Suggest the formula of this complex, including its charge.

.... [1]

(c) There are two isomeric complex ions with the formula $[Cr(NH_3)_4Cl_2]^+$. One is green and the other is violet.

(i) Suggest the type of isomerism shown by these two complex ions.

.... [1]

(ii) Explain why these two complex ions are coloured and why they have different colours.

....

....

....

....

....

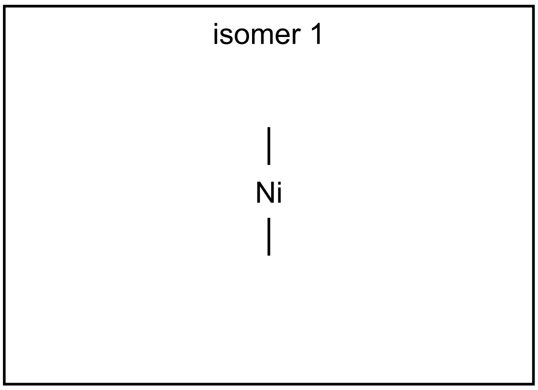
....

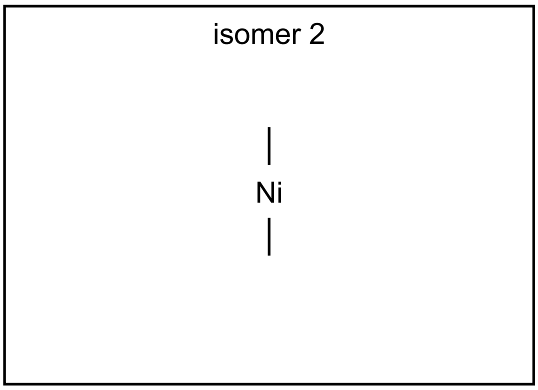
....

.... [4]

(d) The ligand ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$, is represented by *en*.
Nickel forms the complex ion $[Ni(en)_3]^{2+}$ in which it is surrounded octahedrally by six nitrogen atoms.

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





[2]

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

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

....

....

.... [2]

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

.... [1]

(f) **(i)** Under certain conditions ethane-1,2-diamine reacts with ethanedioic acid, HOOCCOOH, to form the polymer **Z**.
Draw the structure of polymer **Z**, showing two repeat units.

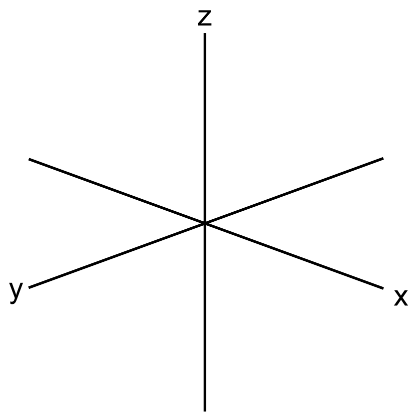
[2]

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

.... [1]

[Total: 17]

7 **(a)** Sketch the shape of a $3d_{xy}$ orbital.



[1]

(b) **(i)** Some transition elements and their compounds behave as catalysts. Explain why transition elements behave as catalysts.

....

....

....

.... [2]

(ii) Catalysis can be classified as heterogeneous or homogeneous.
Complete Table 7.1 by placing **one** tick (✓) in each row to indicate the type of catalysis in each reaction.

Table 7.1

reaction	type of catalysis	
	heterogeneous	homogeneous
Fe in the Haber process		
Fe^{2+} in the I^- / $S_2O_8{}^{2-}$ reaction		
NO_2 in the oxidation of SO_2		

[1]

(c) 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).

Table 7.2 lists electrode potentials for some electrode reactions of these ions.

Table 7.2

electrode reaction	$E^{\ominus}$ / V
$Fe^{2+} + 2e^{-} \rightleftharpoons Fe$	–0.44
$Fe^{3+} + 3e^{-} \rightleftharpoons Fe$	–0.04
$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$	+0.77
$Sn^{2+} + 2e^{-} \rightleftharpoons Sn$	–0.14
$Sn^{4+} + 2e^{-} \rightleftharpoons Sn^{2+}$	+0.15

$E^{\ominus}$ data from the table can be used to predict the reaction that takes place when the two solutions are mixed.

(i) Write an equation for this reaction.

.... [1]

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

....

.... [1]

(d) Hexaaquairon(III) ions are pale violet. They form a colourless complex with fluoride ions, F^-, as shown in equilibrium **1**, and a deep-red complex with thiocyanate ions, SCN^-, as shown in equilibrium **2**.

equilibrium **1** $[Fe(H_2O)_6]^{3+} + F^- \rightleftharpoons [Fe(H_2O)_5F]^{2+} + H_2O$ $K_{stab} = 2.0 \times 10^5\ mol^{-1}\ dm^3$
violet → colourless

equilibrium **2** $[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Fe(H_2O)_5SCN]^{2+} + H_2O$ $K_{stab} = 1.0 \times 10^3\ mol^{-1}\ dm^3$
violet → deep-red

The following two experiments are carried out.

Experiment 1: A few drops of KSCN(aq) are added to $5\ cm^3$ of Fe^{3+}(aq), followed by a few drops of KF(aq).

Experiment 2: A few drops of KF(aq) are added to $5\ cm^3$ of Fe^{3+}(aq), followed by a few drops of KSCN(aq).

(i) Predict and explain the sequence of colour changes you would observe in each of Experiment 1 and Experiment 2.

Experiment 1 ....

....

....

Experiment 2 ....

....

.... [4]

(ii) Name the type of reaction occurring during the experiments in **(d)(i)**.

.... [1]

(e) Solutions of iron(III) salts are acidic due to the equilibrium shown.

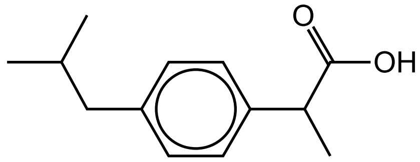
$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$ $K_a = 8.9 \times 10^{-4}\ mol\ dm^{-3}$

Calculate the pH of a $0.25\ mol\ dm^{-3}$ $FeCl_3$ solution.
Show your working.

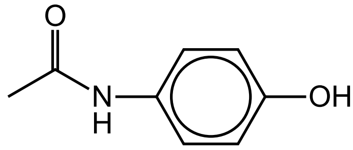
pH = ... [2]

[Total: 13]

8 Ibuprofen and paracetamol are pain-relief drugs.



ibuprofen



paracetamol

Fig. 8.1

(a) Ibuprofen and paracetamol both contain the aryl (benzene) functional group.
Name the other functional groups present in each molecule.

ibuprofen ....

paracetamol ....
[2]

(b) Ibuprofen contains a chiral centre and has two enantiomers.

(i) State one similarity and one difference in the physical or chemical properties between the two enantiomers.

similarity ....

....

difference ....

.... [1]

(ii) Explain what is meant by racemic mixture.

....

.... [1]

(c) Paracetamol reacts separately with the two reagents shown in the table.

Complete Table 8.1 by:
- drawing the structures of the organic products formed,
- stating the types of reaction.

Table 8.1

reagent	organic product structure	type of reaction
$LiAlH_4$		
an excess of $Br_2(aq)$		

[3]

[Turn over

(d) One of the steps in the manufacture of ibuprofen is shown in Fig. 8.2.

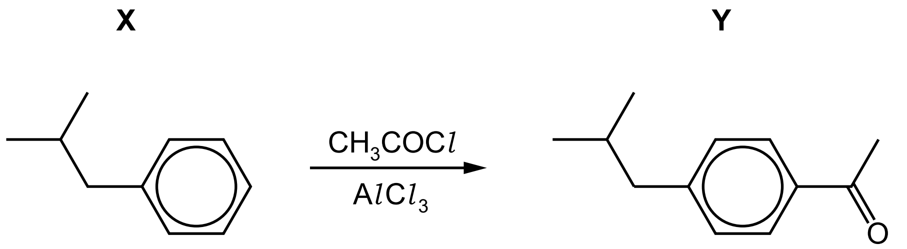


Fig. 8.2

(i) Write an equation to show how $AlCl_3$ generates the electrophile for the conversion of **X** into **Y**.

.... [1]

(ii) Draw the mechanism for the conversion of **X** into **Y**. Include all necessary curly arrows and charges.

[3]

(iii) Write an equation to show how the $AlCl_3$ is regenerated.

....[1]

[Total: 12]

Important values, constants and standards

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