



## Cambridge International AS & A Level

CANDIDATE  
NAME

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CENTRE  
NUMBER

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CANDIDATE  
NUMBER

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**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 [ ].
- 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. 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<sup>3</sup> sample from the trichloromethane layer requires 13.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HCl to reach the end-point.
- A 10.0 cm<sup>3</sup> sample from the aqueous layer requires 12.5 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HCl to reach the end-point.

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

$$K_{pc} = \dots\dots\dots [2]$$

(iii) Butylamine, C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub>, 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<sub>3</sub>H<sub>7</sub>CONH<sub>2</sub>, 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.



Standard entropies are shown in Table 2.1.

**Table 2.1**

substance	MgCO <sub>3</sub> (s)	MgO(s)	CO <sub>2</sub> (g)
S <sup>°</sup> / J K <sup>-1</sup> mol <sup>-1</sup>	+65.7	+26.9	+214

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

$\Delta G^\ominus = \dots\dots\dots \text{ kJ mol}^{-1}$  [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, $K_{sp} / \text{mol}^2 \text{dm}^{-6}$
$\text{MgCO}_3$	$1.0 \times 10^{-5}$
$\text{CaCO}_3$	$5.0 \times 10^{-9}$
$\text{SrCO}_3$	$1.1 \times 10^{-10}$

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  $\text{MgCO}_3$ . Include state symbols.

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

- (ii) With reference to your equation in (d)(i), suggest what is observed when a few  $\text{cm}^3$  of concentrated  $\text{Na}_2\text{CO}_3(\text{aq})$  are added to a saturated solution of  $\text{MgCO}_3$ . Explain your answer.

.....  
 .....  
 ..... [2]

- (e) Use the data in Table 2.2 to calculate the solubility of  $\text{MgCO}_3$  in water at 298 K, in  $\text{g dm}^{-3}$ . Show your working.

solubility of  $\text{MgCO}_3 = \dots\dots\dots \text{g dm}^{-3}$  [2]

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

.....

.....

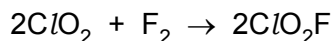
.....

.....

..... [3]

[Total: 16]

- 3 (a) The initial rate of the reaction of chlorine dioxide,  $\text{ClO}_2$ , and fluorine,  $\text{F}_2$ , is measured in a series of experiments at a constant temperature.



The results obtained are shown in Table 3.1.

**Table 3.1**

experiment	$[\text{ClO}_2] / \text{mol dm}^{-3}$	$[\text{F}_2] / \text{mol dm}^{-3}$	initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.010	0.060	$2.20 \times 10^{-3}$
2	0.025	0.060	to be calculated
3	to be calculated	0.040	$7.04 \times 10^{-3}$

The rate equation is  $\text{rate} = k[\text{ClO}_2][\text{F}_2]$ .

- (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  $k$ .

$k = \dots\dots\dots$  units  $\dots\dots\dots$  [2]

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

initial rate =  $\dots\dots\dots$   $\text{mol dm}^{-3} \text{s}^{-1}$  [1]

- (iv) Use the data in Table 3.1 to calculate  $[\text{ClO}_2]$  in experiment 3.

$[\text{ClO}_2] = \dots\dots\dots$   $\text{mol dm}^{-3}$  [1]

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

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

(ii) The mechanism of the reaction between  $\text{ClO}_2$  and  $\text{F}_2$  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]





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

4-nitromethylbenzene

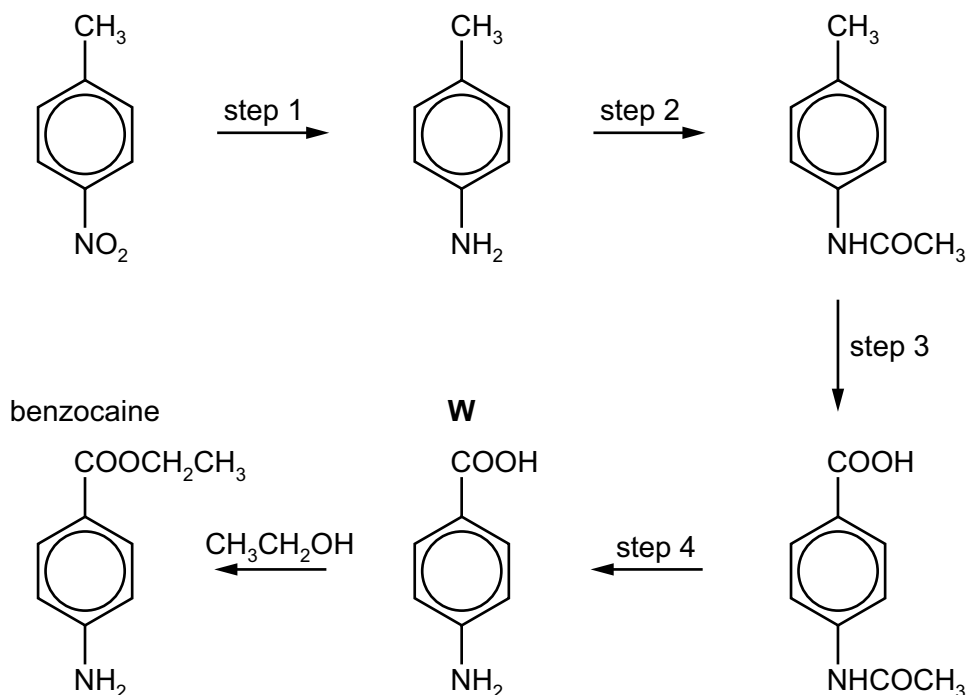


Fig. 4.2

- (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 .....

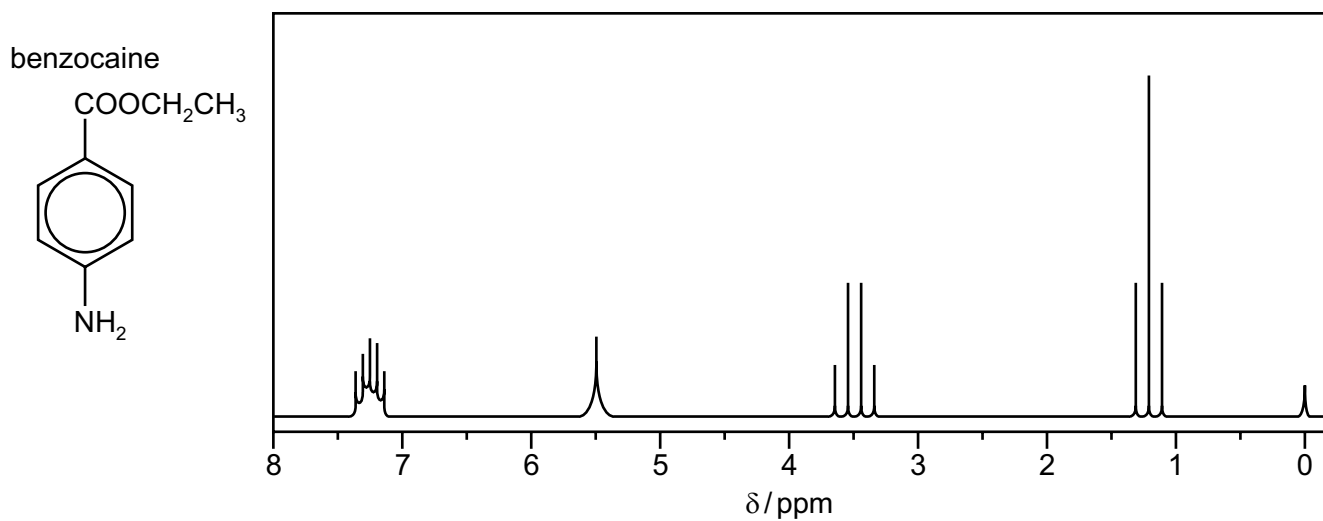
[2]

- (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  $\text{CDCl}_3$  and the proton NMR spectrum of this solution was recorded as shown in Fig. 4.3.



**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  $\delta$  1.2 ppm, 3.5 ppm and 5.5 ppm.

**Table 4.1**

$\delta/\text{ppm}$	environment of proton	number of $^1\text{H}$ 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]

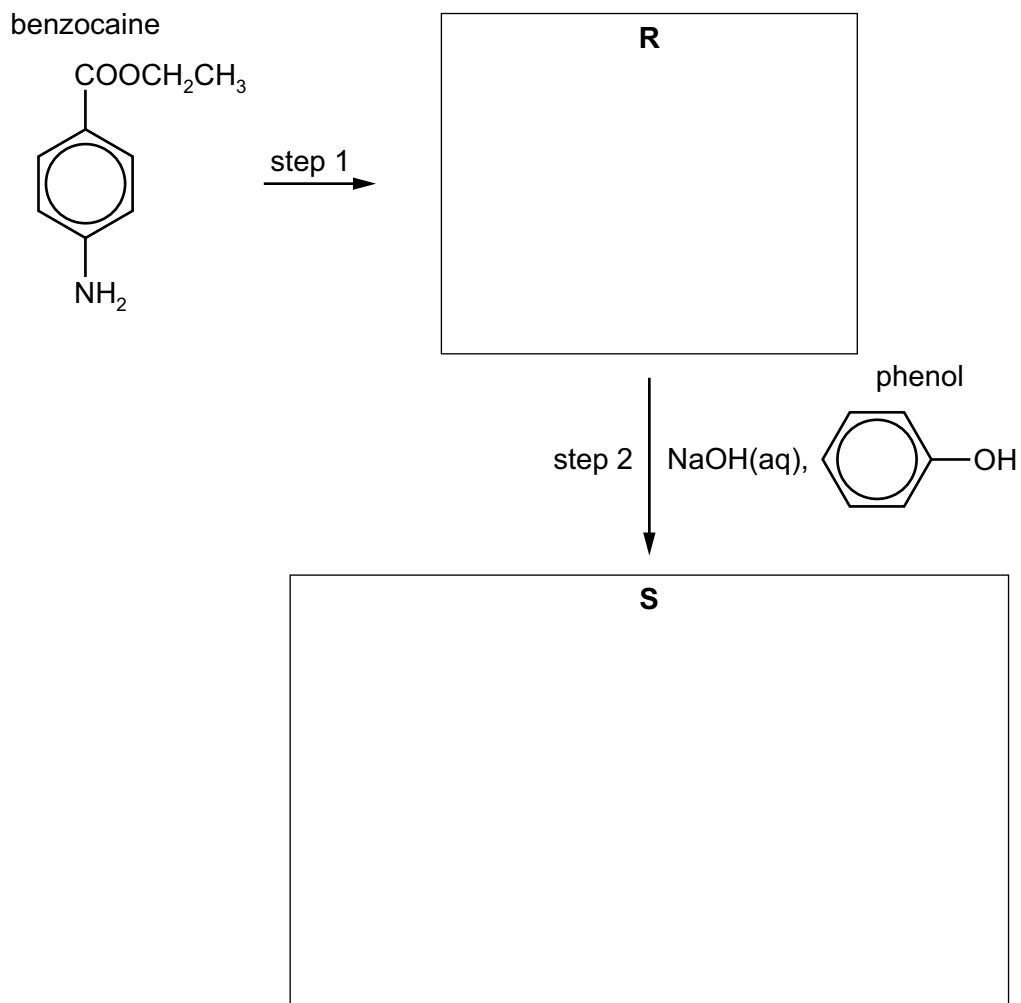
(iii) Explain the splitting pattern for the absorption at  $\delta$ 1.2 ppm.

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

Table 4.2

Environment of proton	Example	chemical shift range, $\delta$ / ppm
alkane	$-\text{CH}_3$ , $-\text{CH}_2-$ , $>\text{CH}-$	0.9–1.7
alkyl next to C=O	$\text{CH}_3-\text{C}=\text{O}$ , $-\text{CH}_2-\text{C}=\text{O}$ , $>\text{CH}-\text{C}=\text{O}$	2.2–3.0
alkyl next to aromatic ring	$\text{CH}_3-\text{Ar}$ , $-\text{CH}_2-\text{Ar}$ , $>\text{CH}-\text{Ar}$	2.3–3.0
alkyl next to electronegative atom	$\text{CH}_3-\text{O}$ , $-\text{CH}_2-\text{O}$ , $-\text{CH}_2-\text{Cl}$	3.2–4.0
attached to alkene	$=\text{CHR}$	4.5–6.0
attached to aromatic ring	$\text{H}-\text{Ar}$	6.0–9.0
aldehyde	$\text{HCOR}$	9.3–10.5
alcohol	$\text{ROH}$	0.5–6.0
phenol	$\text{Ar}-\text{OH}$	4.5–7.0
carboxylic acid	$\text{RCOOH}$	9.0–13.0
alkyl amine	$\text{R}-\text{NH}-$	1.0–5.0
aryl amine	$\text{Ar}-\text{NH}_2$	3.0–6.0
amide	$\text{RCONHR}$	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 <sup>-1</sup>
standard enthalpy change of atomisation of potassium	+89
electron affinity of O(g)	-141
electron affinity of O <sup>-</sup> (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,  $\Delta H_{\text{latt}}^{\ominus}$ , of potassium oxide, K<sub>2</sub>O(s).  
 Show your working.

$$\Delta H_{\text{latt}}^{\ominus} \text{ of K}_2\text{O(s)} = \dots\dots\dots \text{ kJ mol}^{-1} \text{ [3]}$$

(ii) State how  $\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$  differs from  $\Delta H_{\text{latt}}^{\ominus} \text{K}_2\text{O}(\text{s})$ .

Indicate this by placing **one** tick (✓) in the appropriate box in Table 5.2.

**Table 5.2**

$\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$ is less negative than $\Delta H_{\text{latt}}^{\ominus} \text{K}_2\text{O}(\text{s})$	$\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$ is the same as $\Delta H_{\text{latt}}^{\ominus} \text{K}_2\text{O}(\text{s})$	$\Delta H_{\text{latt}}^{\ominus} \text{Na}_2\text{O}(\text{s})$ is more negative than $\Delta H_{\text{latt}}^{\ominus} \text{K}_2\text{O}(\text{s})$

Explain your answer.

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

[Total: 7]

6 (a) Define a transition element.

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

(b) (i)  $\text{NH}_3$  acts as a monodentate ligand. State what is meant by monodentate ligand.

.....  
.....  
..... [2]

(ii) Aqueous silver ions,  $\text{Ag}^+(\text{aq})$ , react with aqueous ammonia,  $\text{NH}_3(\text{aq})$ , 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  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ . One is green and the other is violet.

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

..... [1]

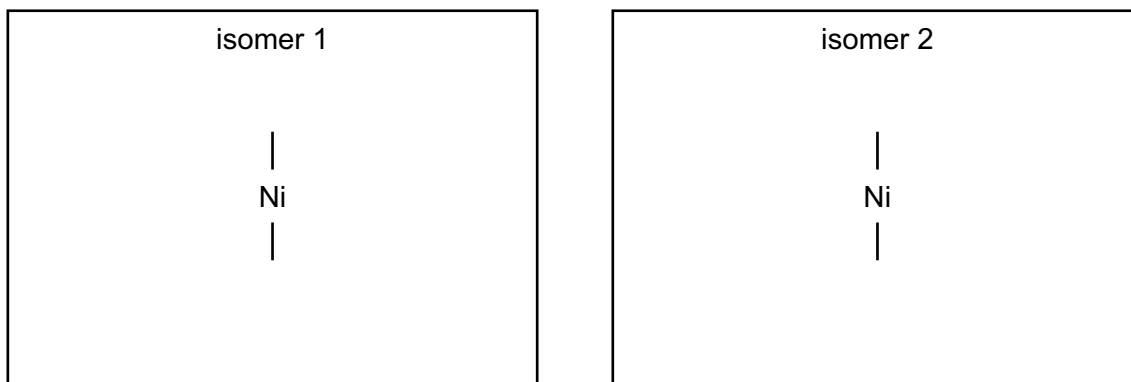
(ii) Explain why these two complex ions are coloured and why they have different colours.

.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....  
..... [4]

(d) The ligand ethane-1,2-diamine,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ , is represented by *en*.

Nickel forms the complex ion  $[\text{Ni}(\text{en})_3]^{2+}$  in which it is surrounded octahedrally by six nitrogen atoms.

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



[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,  $\text{HOOC}\text{COOH}$ , to form the polymer **Z**.

Draw the structure of polymer **Z**, showing two repeat units.

[2]

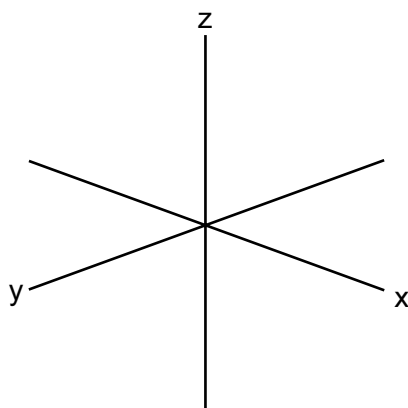
(ii) Name the type of reaction occurring during this polymerisation.

..... [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		
$\text{Fe}^{2+}$ in the $\text{I}^- / \text{S}_2\text{O}_8^{2-}$ reaction		
$\text{NO}_2$ in the oxidation of $\text{SO}_2$		

[1]

- (c) A solution containing a mixture of  $\text{Sn}^{2+}(\text{aq})$  and  $\text{Sn}^{4+}(\text{aq})$  is added to a solution containing a mixture of  $\text{Fe}^{2+}(\text{aq})$  and  $\text{Fe}^{3+}(\text{aq})$ .

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

**Table 7.2**

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

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

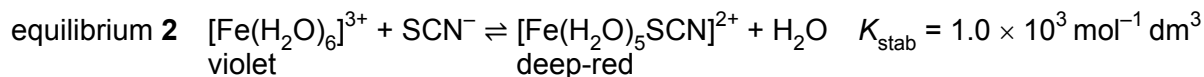
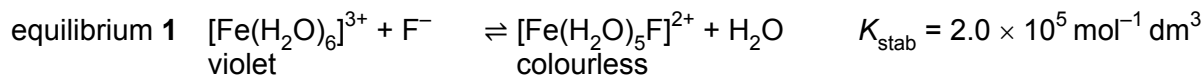
- (i) Write an equation for this reaction.

..... [1]

- (ii) Calculate  $E^\ominus_{\text{cell}}$  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.



The following two experiments are carried out.

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

Experiment 2: A few drops of  $KF(aq)$  are added to  $5 \text{ cm}^3$  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 .....

.....

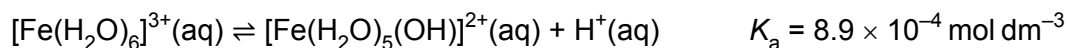
.....

[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.

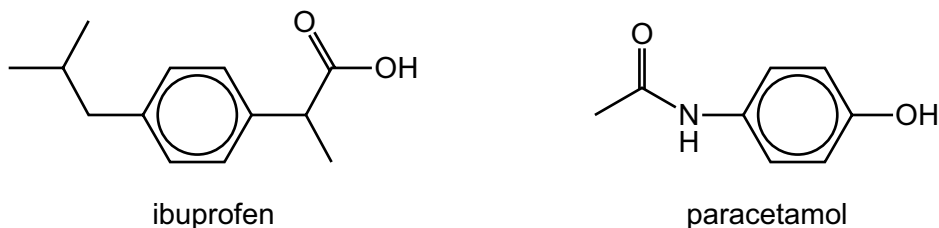


Calculate the pH of a  $0.25 \text{ mol dm}^{-3} FeCl_3$  solution.  
Show your working.

pH = ..... [2]

[Total: 13]

8 Ibuprofen and paracetamol are pain-relief drugs.



**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:

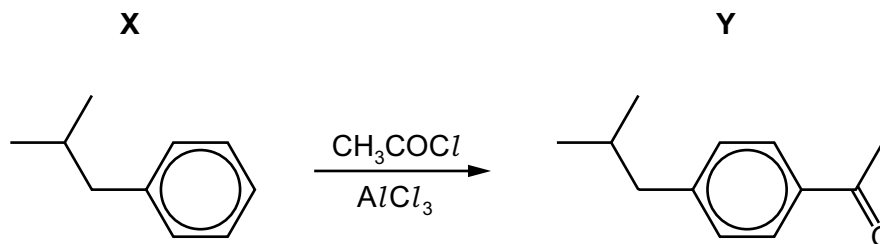
- drawing the structures of the organic products formed,
- stating the types of reaction.

**Table 8.1**

reagent	organic product structure	type of reaction
$\text{LiAlH}_4$		
an excess of $\text{Br}_2(\text{aq})$		

[3]

(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	$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
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 J g <sup>-1</sup> K <sup>-1</sup> )

## The Periodic Table of Elements

Group																																			
1	2	1										13	14	15	16	17	18																		
		<div style="display: flex; justify-content: space-between;"> <div style="border: 1px solid black; padding: 5px;"> <b>Key</b>            atomic number            atomic symbol            name            relative atomic mass         </div> <div style="border: 1px solid black; padding: 5px;">           H            hydrogen            1.0         </div> </div>																																	
		<div style="display: flex; justify-content: space-between;"> <div style="border: 1px solid black; padding: 5px;">           4  <b>Be</b>            beryllium            9.0         </div> <div style="border: 1px solid black; padding: 5px;">           10  <b>Ne</b>            neon            20.2         </div> </div>																																	
3	Li	4	Be	5	B	6	C	7	N	8	O	9	F	10	Ne																				
11	Na	12	Mg	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar																				
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
55	Cs	56	Ba	57–71	lanthanoids	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn
87	Fr	88	Ra	89–103	actinoids	104	Rf	105	Db	106	Sg	107	Bh	108	Hs	109	Mt	110	Ds	111	Rg	112	Cn	113	Nh	114	Fl	115	Mc	116	Lv	117	Ts	118	Og

lanthanoids	57	La	58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu
actinoids	89	Ac	90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr

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