Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

3767926625

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **February/March 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.

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1 Iodine is found naturally in compounds in many different oxidation states.

(a) Iodide ions, I^-, react with acidified $H_2O_2(aq)$ to form iodine, I_2, and water.
This reaction mixture is shaken with cyclohexane, C_6H_{12}, to extract the I_2.
Cyclohexane is immiscible with water.

(i) Identify the role of $H_2O_2(aq)$ in its reaction with I^- ions in acidic conditions.

Write an ionic equation for the reaction.

role .....

ionic equation .....

.....
[2]

(ii) 15.0 cm^3 of C_6H_{12} is shaken with 20.0 cm^3 of an aqueous solution containing I_2 until no further change is seen.
It is found that 0.390 g of I_2 is extracted into the C_6H_{12}.
The partition coefficient of I_2 between C_6H_{12} and water, K_{pc}, is 93.8.

Calculate the mass of I_2 that remains in the aqueous layer.
Show your working.

mass of I_2 in aqueous layer = ... g [2]

(iii) Suggest how the value of K_{pc} of I_2 between hexan-2-one, $CH_3(CH_2)_3COCH_3$, and water compares to the value given in **(a)(ii)**.
Explain your answer.

.....

.....

.....

..... [2]

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(b) The Group 1 iodides all form stable ionic lattices and are soluble in water.

(i) Define enthalpy change of solution.

.....

.....

..... [1]

(ii) Use the data in Table 1.1 to calculate the enthalpy change of solution of potassium iodide, KI.

Table 1.1

process	enthalpy change, ΔH / kJ mol^{-1}
$K^+(g) + I^-(g) \rightarrow KI(s)$	–629
$K^+(g) \rightarrow K^+(aq)$	–322
$I^-(g) \rightarrow I^-(aq)$	–293

enthalpy change of solution = ... kJ mol^{-1} [1]

(iii) Suggest the trend in the magnitude of the lattice energies of the Group 1 iodides, LiI, NaI, KI.
Explain your answer.

.....

.....

.....

..... [2]

(c) The concentration of $Cu^{2+}(aq)$ in a solution can be determined by the reaction of Cu^{2+} ions with I^- ions.

reaction 1 $\quad 2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

The I_2 produced in reaction 1 is titrated against a solution containing thiosulfate ions, $S_2O_3^{2-}$, using a suitable indicator.

reaction 2 $\quad 2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

(i) A 25.0 cm^3 portion of a $Cu^{2+}(aq)$ solution reacts with an excess of $I^-(aq)$.
The end-point of the titration occurs when 22.30 cm^3 of 0.150 mol dm^{-3} $S_2O_3^{2-}(aq)$ is added.

Calculate the concentration of $Cu^{2+}(aq)$ in the original solution.

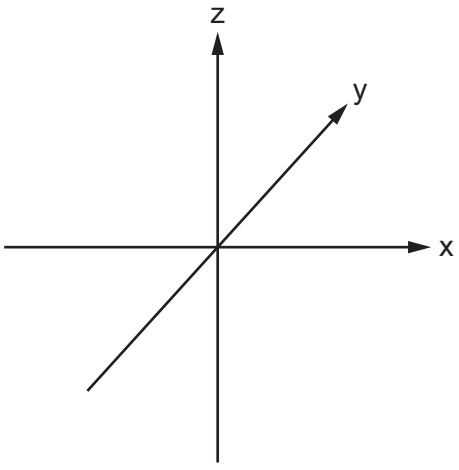
concentration of $Cu^{2+}(aq)$ = ... mol dm^{-3} [2]

(ii) Identify a suitable indicator for the titration.

..... [1]

(iii) Copper(I) and copper(II) both contain electrons in all five 3d orbitals.

Sketch the shape of a $3d_{xy}$ orbital on the axes provided.



[1]

(d) The reaction of I^- ions with persulfate ions, $S_2O_8^{2-}$, can be catalysed by Fe^{3+} ions.

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

Write equations to show how Fe^{3+} catalyses this reaction.

.....

..... [2]

(e) An orange precipitate of HgI_2 forms when Hg^{2+} ions are added to KI(aq).
The solubility of HgI_2 at 25 °C is 1.00×10^{-7} g dm^{-3}.

Calculate the solubility product, K_{sp}, of HgI_2.
Include units in your answer.

[M_r: HgI_2, 454.4]

value of K_{sp} = ...

units = ...
[3]

[Total: 19]

2 Silicon is the second most abundant element by mass in the Earth's crust.

(a) In industry, silicon is extracted from SiO_2 by reaction with carbon at over 2000 °C.

reaction 1 $SiO_2(s) + 2C(s) \rightarrow Si(l) + 2CO(g)$

(i) Explain why the entropy change, ΔS, of reaction 1 is positive.

.....

..... [1]

(ii) Reaction 1 is highly endothermic.

Suggest the effect of an increase in temperature on the feasibility of this reaction. Explain your answer.

.....

.....

..... [2]

(b) Silicon is purified by first heating it in a stream of $HCl(g)$ to form $SiHCl_3$. The $SiHCl_3$ formed is then distilled to remove other impurities.

reaction 2 $Si(s) + 3HCl(g) \rightarrow SiHCl_3(g) + H_2(g)$

(i) Table 2.1 shows some standard entropy data.

Table 2.1

compound	standard entropy, $S^\ominus$ / J K^{-1} mol^{-1}
Si(s)	19
$HCl(g)$	187
$SiHCl_3(g)$	314
$H_2(g)$	131

Use the data in Table 2.1 to calculate $\Delta S^\ominus$ for reaction 2.

$\Delta S^\ominus$ = ... J K^{-1} mol^{-1} [2]

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(ii) Reaction 3 is the reverse of reaction 2 and is used to obtain pure silicon.

reaction 3 $SiHCl_3(g) + H_2(g) \rightarrow Si(s) + 3HCl(g)$ $\Delta H = +219.3\,kJ\,mol^{-1}$

Use this information and your answer to **(b)(i)** to calculate the temperature, in K, at which reaction 3 becomes feasible.
Show your working.

[If you were unable to answer **(b)(i)**, you should use $\Delta S^{\ominus} = -150\,J\,K^{-1}\,mol^{-1}$ for reaction 2. This is not the correct answer to **(b)(i)**.]

temperature = ... K [2]

(c) Silicon can also be produced by electrolysis of SiO_2 dissolved in molten $CaCl_2$.
The relevant half-equation for the cathode is shown.

$$SiO_2 + 4e^- \rightarrow Si + 2O^{2-}$$

Calculate the time, in seconds, required to produce 1.00 g of Si by this electrolysis, using a current of 6.00 A.
Assume no other substances are produced at the cathode.

time = ... s [2]

[Total: 9]

3 Titanium is a transition element in Period 4. It is commonly found as TiO_2 in minerals.

(a) (i) Define transition element.

.....

.....

..... [1]

(ii) Identify **two** typical properties of transition elements.

1 .....

2 .....
[1]

(b) The TiO^{2+} ion forms when TiO_2 reacts with an excess of sulfuric acid.

TiO^{2+} can be reduced by zinc metal in acidic conditions to form a purple solution containing $Ti^{3+}(aq)$.

(i) $TiO^{2+}(aq)$ is a colourless ion.

Suggest why.

.....

.....

..... [2]

(ii) Give the electronic configuration of an isolated Ti^{3+} ion.

$1s^2$ ..... [1]

(iii) Write an ionic equation for the reduction of TiO^{2+} by zinc metal in acidic conditions.

..... [1]

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(c) Acidified $Ti^{3+}(aq)$ reacts with oxygen dissolved in water as shown.

$$4Ti^{3+} + O_2 + 2H_2O \rightarrow 4TiO^{2+} + 4H^+ \qquad \Delta G^{\ominus} = -436.1\,kJ\,mol^{-1}$$

The standard reduction potential, $E^{\ominus}$, of $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ is +1.23 V.

(i) Calculate the standard reduction potential, $E^{\ominus}$, in V, of the $TiO^{2+}(aq)/Ti^{3+}(aq)$ half-cell. Show your working.

$E^{\ominus}$ = ... V [3]

(ii) When aqueous citrate ions, $C_6H_5O_7^{3-}$, are added to $Ti^{3+}(aq)$, the $[Ti(C_6H_5O_7)_2]^{3-}(aq)$ complex forms.

Explain, in terms of d-orbitals, why Ti^{3+} is able to form complex ions.

.....

..... [1]

(iii) Acidified $[Ti(C_6H_5O_7)_2]^{3-}(aq)$ does not react with oxygen dissolved in water, unlike acidified $Ti^{3+}(aq)$.

Suggest what this means for the value of the standard reduction potential, $E^{\ominus}$, of the following half-cell.

$$[Ti(C_6H_5O_7)_2]^{2-}(aq) + e^- \rightleftharpoons [Ti(C_6H_5O_7)_2]^{3-}(aq)$$

Explain your answer.

.....

..... [1]

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(d) Some reactions of TiO_2 are shown in Fig. 3.1.

The anion, $acac^-$, is a bidentate ligand.

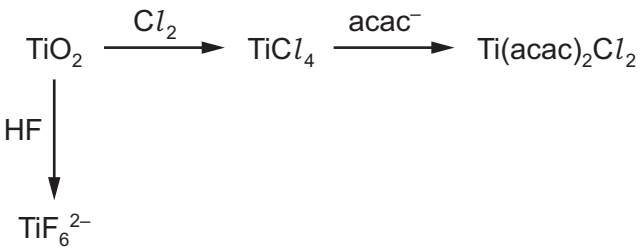

Fig. 3.1

(i) The titanium ions in TiF_6^{2-} and $Ti(acac)_2Cl_2$ have a coordination number of 6.

State what is meant by coordination number.

.....

..... [1]

(ii) Write an equation for the formation of TiF_6^{2-} from TiO_2.

..... [1]

(iii) State what is meant by bidentate ligand.

.....

.....

..... [2]

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(iv) $Ti(acac)_2Cl_2$ shows both optical and geometrical (cis/trans) isomerism.

$Ti(acac)_2Cl_2$ exists as three stereoisomers.

The structure of one stereoisomer of $Ti(acac)_2Cl_2$ is shown in Fig. 3.2.

stereoisomer 1

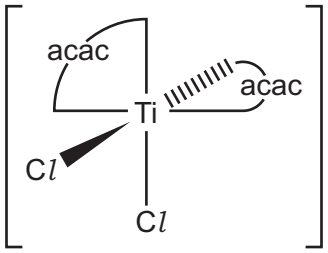
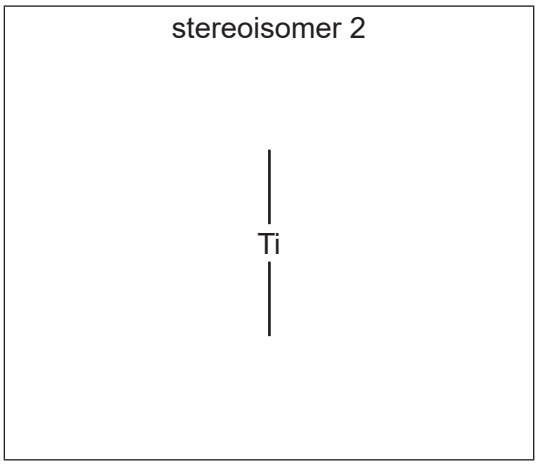


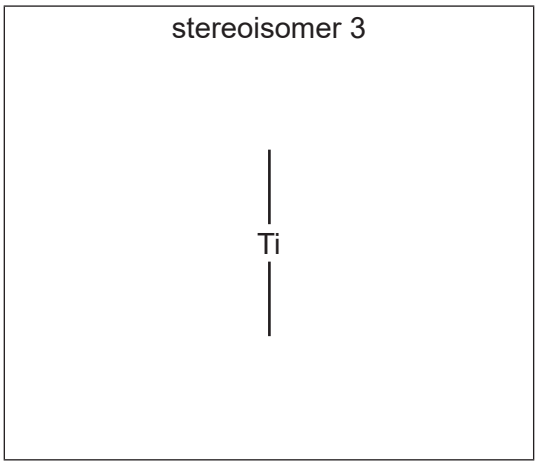
Fig. 3.2

Complete the structures of the other two stereoisomers of $Ti(acac)_2Cl_2$.

stereoisomer 2



stereoisomer 3



[2]

(v) The $acac^-$ anion is symmetrical.

Deduce which, if any, of stereoisomers 1, 2 and 3 in **(d)(iv)** are polar.
Explain your answer.

.....

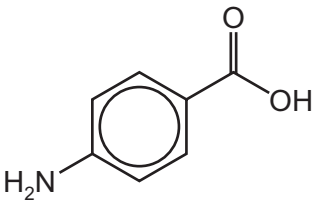
.....

..... [2]

[Total: 19]

4 Compounds **F** and **J** are shown in Fig. 4.1.

F



J

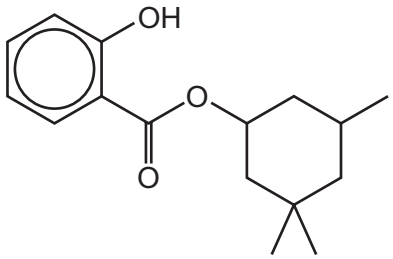


Fig. 4.1

(a) **F** and **J** both contain the arene functional group.

(i) Identify the other functional groups in **F** and **J**.

F: .....

J: .....
[2]

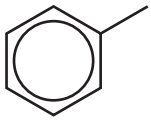
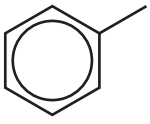
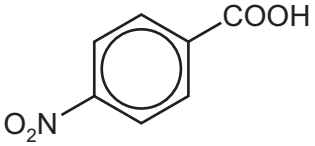
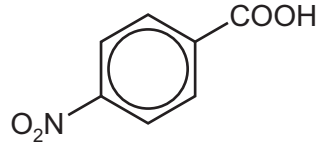
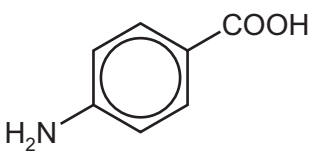
(ii) State the number of chiral centres in a molecule of **F** and in a molecule of **J**.

number of chiral centres in: **F** = ... **J** = ...
[1]

(b) A student proposes a multi-step synthesis of **F** from benzene, as shown in Table 4.1.

(i) Complete Table 4.1 by providing relevant details of the reagents and conditions for steps 1 and 4, and the structure of product **D**.

Table 4.1

step	organic reactant	reagent(s) and conditions	organic product
1		.....	
2		concentrated HNO_3 and concentrated H_2SO_4	**D**
3	**D**	hot alkaline $KMnO_4$ then dilute H_2SO_4	**E** 
4		.....	**F** 

[3]

(ii) In a second multi-step synthesis, the student changes the order in which the reagents and conditions are used.
The reaction scheme is shown in Fig. 4.2.
G is the major product of this synthesis.

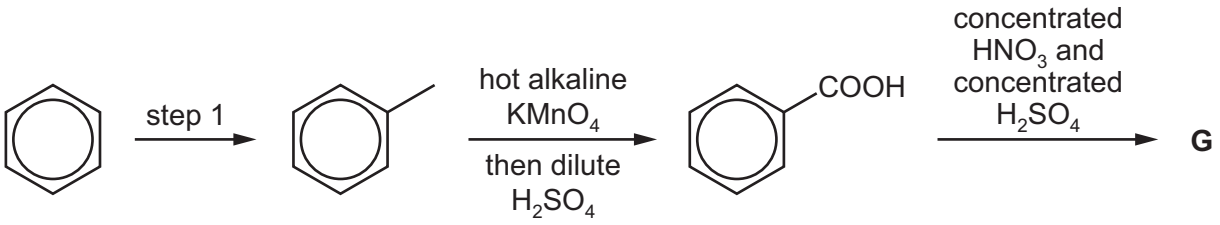


Fig. 4.2

Draw the structure of **G**.
Explain why **G** is the major product of the synthesis rather than **E**.

.....

.....

.....
[2]

(c) **J** reacts under suitable conditions with NaOH(aq).
After acidification of the reaction mixture, compounds **K** and **L** form.

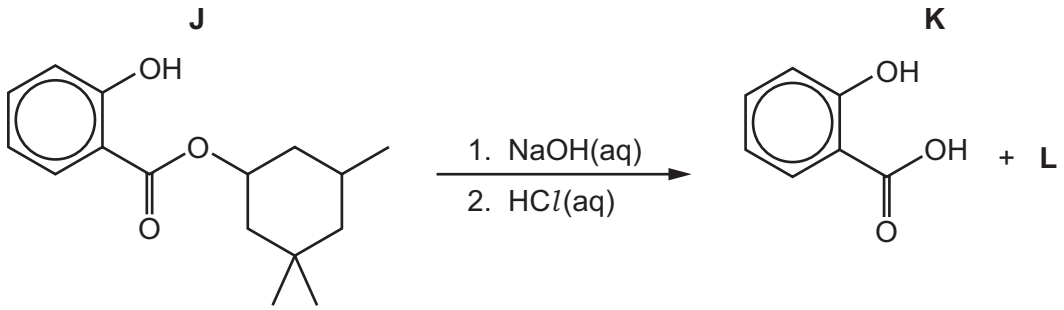


Fig. 4.3

(i) Give the molecular formula of **L**.

..... [1]

(ii) State the **two** types of reaction that occur when **J** reacts with NaOH(aq).

1 .....

2 .....
[2]

(d) **K** can also be synthesised from phenol, C_6H_5OH.

Fig. 4.4 shows several reactions of phenol.

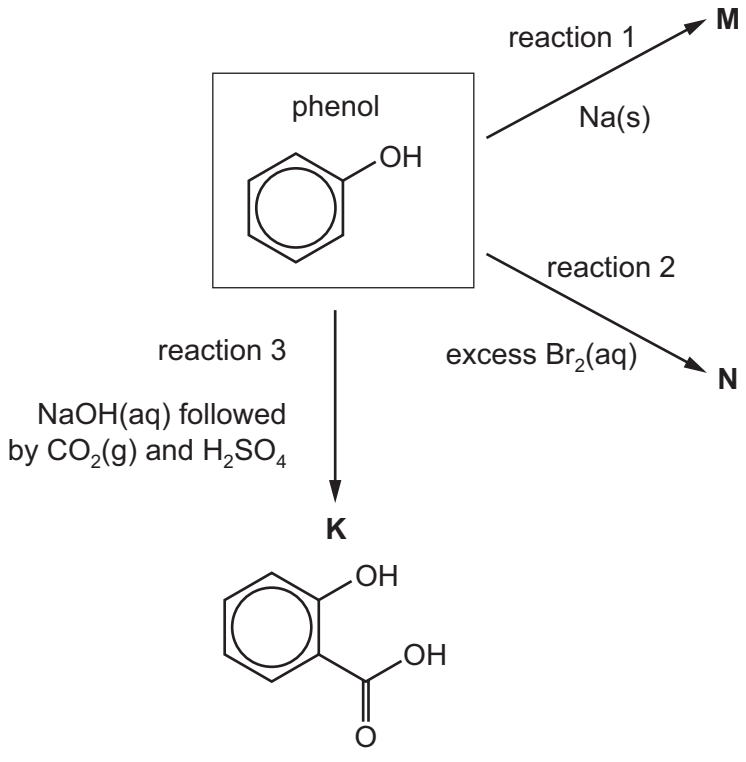


Fig. 4.4

(i) Write an equation for the formation of **M** in reaction 1.

..... [1]

(ii) Draw **N**, the product of reaction 2.

[1]

(iii) Explain why phenol is a weaker acid than **K**.

.....

.....

.....

..... [2]

(e) Phenol and benzene both react with nitric acid, as shown in Fig. 4.5.

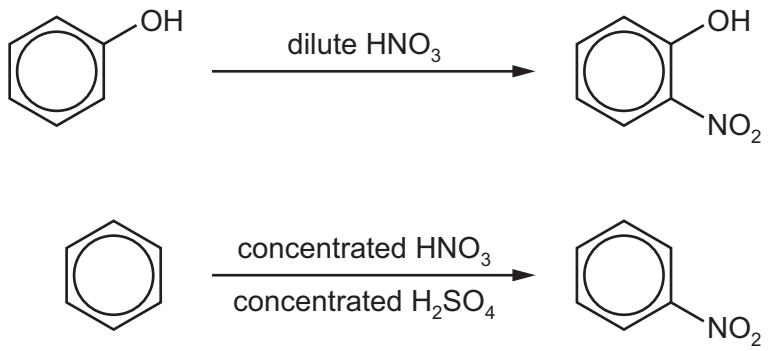


Fig. 4.5

Explain why the reagents and conditions for these two reactions are different.

.....

.....

.....

.....

..... [3]

[Total: 18]

5 2-Chloropropanoic acid, $CH_3CHCl COOH$, is used in many chemical syntheses.

(a) (i) An equilibrium is set up when $CH_3CHCl COOH$ is added to water.

Write the equation for this equilibrium.

..... [1]

(ii) 0.150 mol of $CH_3CHCl COOH$ dissolves in 250 cm^3 of distilled water to produce a solution of pH 1.51.

Calculate the pK_a of $CH_3CHCl COOH$.

pK_a = ... [2]

(iii) An equal concentration of aqueous propanoic acid has pH 2.55.

Explain the difference in the pH of solutions of equal concentration of $CH_3CHCl COOH$ and propanoic acid.

.....

.....

.....

..... [2]

(b) When $CH_3CHCl COOH$ reacts with aqueous NH_3, alanine forms.

alanine

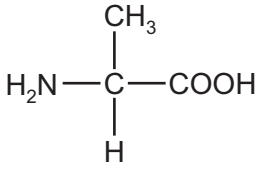


Fig. 5.1

Alanine is an amino acid. Its isoelectric point is 6.1.

(i) State what is meant by isoelectric point.

.....

..... [1]

(ii) Give the structural formula of alanine at pH 2.

..... [1]

(iii) Alanine exists as a pair of optical isomers. The structure of one optical isomer is shown in Fig. 5.2.

Draw the three-dimensional structure of the other optical isomer of alanine.

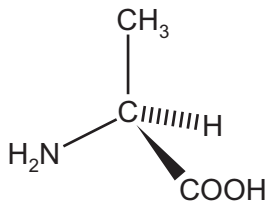
optical isomer 1	optical isomer 2
	

Fig. 5.2

[1]

(iv) Polymer **C** forms from the reaction between alanine and 4-aminobutanoic acid, $H_2N(CH_2)_3COOH$.

Draw a repeat unit of **C**. The functional group formed should be displayed.

[2]

(v) State the type of polymerisation shown in **(b)(iv)**.

..... [1]

(vi) Scientists are investigating **C** as a replacement for poly(propene) in packaging.

Suggest an advantage of using **C** instead of poly(propene).

.....

..... [1]

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[Turn over

(c) A student studies the reaction of $CH_3CHCl COOH$ with aqueous NH_3 to determine the reaction mechanism.

The student finds that when $CH_3CHCl COOH$ and NH_3 are added in a 1 : 1 stoichiometric ratio, the conjugate acid and base of the reactants are quickly formed.

reaction 1 $CH_3CHCl COOH + NH_3 \rightarrow CH_3CHCl COO^- + NH_4^+$

(i) Identify the conjugate acid–base pairs in reaction 1.

conjugate acid–base pair I ..... and .....

conjugate acid–base pair II ..... and .....

[1]

In an excess of NH_3, $CH_3CHCl COO^-$ undergoes a nucleophilic substitution reaction.

reaction 2 $CH_3CHCl COO^- + NH_3 \rightarrow CH_3CH(NH_2)COO^- + H^+ + Cl^-$

A student investigates the rate of reaction 2. The student mixes $CH_3CHCl COO^-$ with a large excess of NH_3. The graph in Fig. 5.3 shows the results obtained.

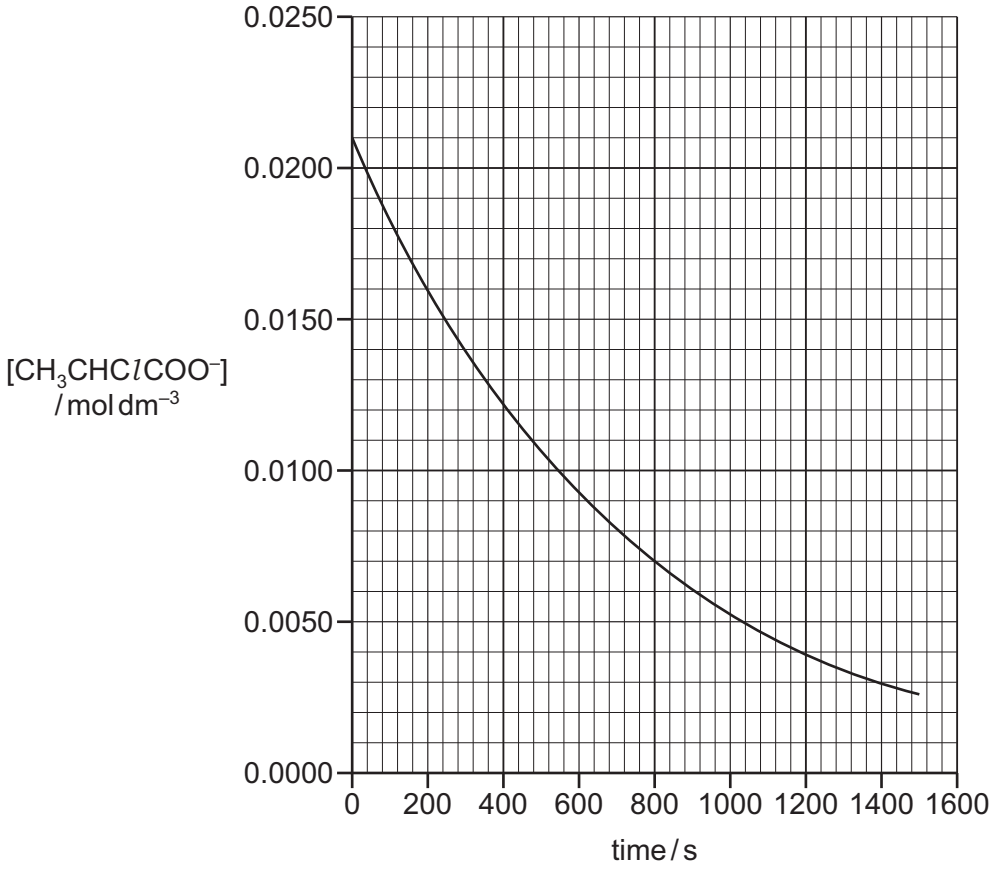


Fig. 5.3

(ii) Use the graph in Fig. 5.3 to show that reaction 2 is first order with respect to $[CH_3CHClCOO^-]$.

.....

.....

.....

..... [2]

(iii) Explain why a **large** excess of NH_3 needs to be used in order to obtain the results in Fig. 5.3.

.....

..... [1]

(iv) The student measures the effect of changing the concentration of NH_3 on the rate of reaction 2. Table 5.1 shows the results obtained.

Table 5.1

experiment	$[CH_3CHClCOO^-]$ / mol dm^{-3}	$[NH_3]$ / mol dm^{-3}	initial rate of reaction / mol dm^{-3} s^{-1}
1	0.00120	0.00300	1.47×10^{-5}
2	0.00120	0.00450	2.21×10^{-5}

Use the information in Table 5.1 and in **(c)(ii)** to determine whether the nucleophilic substitution reaction proceeds via an S_N1 or an S_N2 mechanism.
Explain your answer.

.....

.....

.....

..... [2]

(v) Describe the effect of an increase in temperature on the rate of reaction of $CH_3CHClCOO^-$ and NH_3.
Explain your answer.

.....

.....

.....

..... [2]

(vi) When an excess of $CH_3CHClCOO^-$ is used, further substitution reactions occur. One product has the formula $C_6H_9NO_4^{2-}$.

Suggest the structure of $C_6H_9NO_4^{2-}$.

[1]

[Total: 21]

6 Lidocaine is used as an anaesthetic. A synthesis of lidocaine is shown in Fig. 6.1.

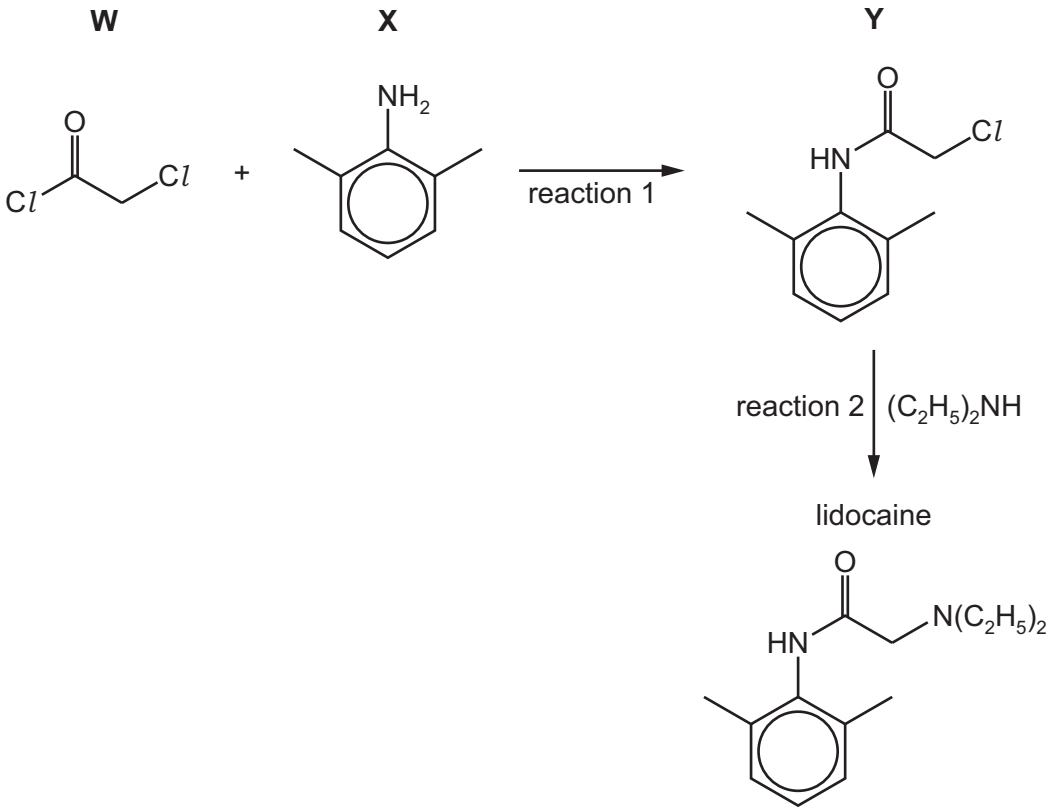


Fig. 6.1

(a) **W** can be formed by reacting $HOCH_2COOH$ with an excess of $SOCl_2$.

Write an equation for this reaction.

..... [1]

(b) After **W** and **X** have reacted together, an excess of $CH_3COONa(aq)$ is added to the reaction mixture.

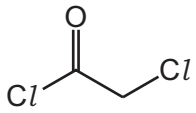
Suggest why.

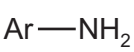
.....

..... [1]

(c) The reaction of **W** with **X**, reaction 1, follows an addition–elimination mechanism.

Complete the mechanism for the reaction of **W** with **X**.
Include all relevant curly arrows, lone pairs of electrons, charges and partial charges.
Use Ar–NH_2 to represent **X**.





[4]

(d) $(C_2H_5)_2NH$ reacts with **Y** in reaction 2.

Explain why $(C_2H_5)_2NH$ can act as a nucleophile.

.....

..... [1]

(e) The purity of lidocaine can be checked using thin-layer chromatography.
Ethyl ethanoate is used as the solvent.

The R_f values of **X** and lidocaine are given in Table 6.1.

Table 6.1

compound	R_f
X	0.49
lidocaine	0.71

(i) Identify the substances used as the mobile and stationary phases in this thin-layer chromatography experiment.

mobile phase .....

stationary phase .....
[1]

(ii) Describe how an R_f value can be calculated.

.....

..... [1]

(iii) Suggest why the R_f value for **X** is less than that for lidocaine.

.....

..... [1]

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[Turn over

(f) The proton (^{1}H) NMR spectrum of lidocaine is shown in Fig. 6.2.

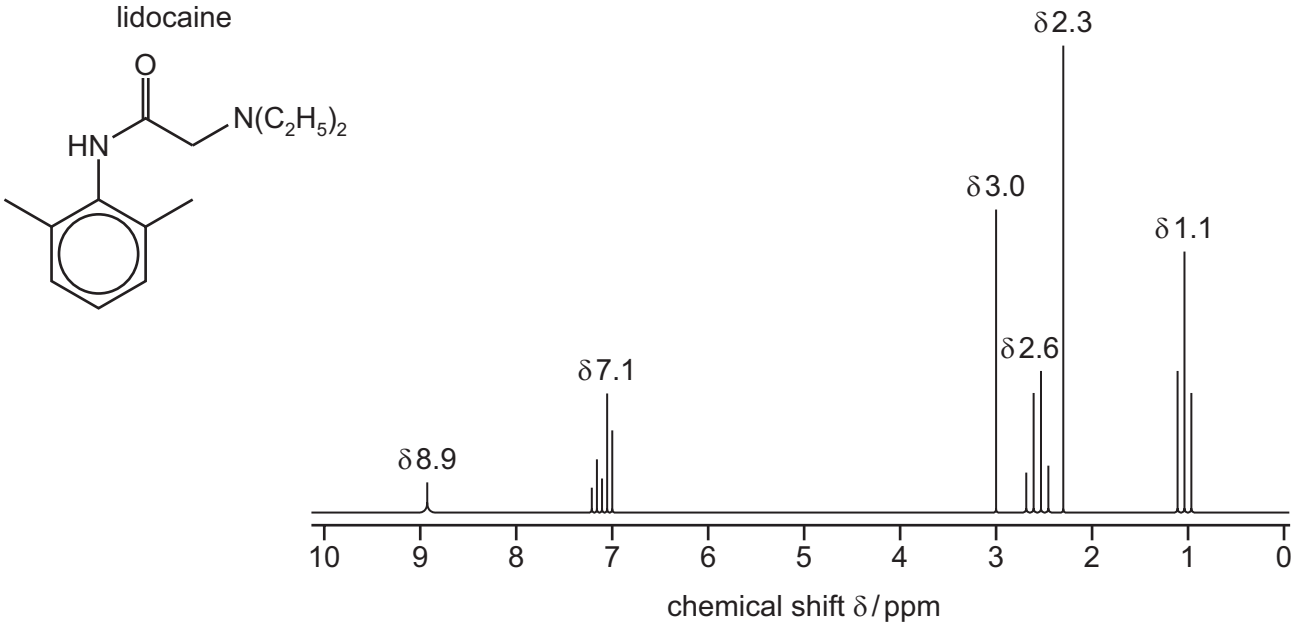

Fig. 6.2

Table 6.2

environment of proton	example	chemical 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**$_2$–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–N**H**$_2$	3.0–6.0
amide	RCON**H**R	5.0–12.0

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(i) Name the splitting patterns at δ2.6 and δ1.1.

δ2.6 ..... δ1.1 .....
[1]

(ii) The relative peak area of the peaks at δ3.0 and δ2.3 is 1 : 3 respectively.

Identify the protons in the ^{1}H NMR spectrum of lidocaine that are responsible for the peaks at the following chemical shift values.

δ7.1 .....

δ3.0 .....

δ2.3 .....
[2]

(iii) Predict the number of peaks in the **carbon-13** (^{13}C) NMR spectrum of lidocaine.

..... [1]

[Total: 14]

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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 144.4	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 –

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