* 0000800000001 *

Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME	

CENTRE NUMBER						CANDIDATE NUMBER					

9291939002

CHEMISTRY **9701/44**

Paper 4 A Level Structured Questions **May/June 2025**

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. Any blank pages are indicated.

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1 **(a)** **(i)** Describe the trend in the thermal stabilities of the carbonates of the Group 2 elements.

Explain your answer.

....

....

....

....

.... [3]

(ii) Copper(II) carbonate decomposes on heating in a similar way to the carbonates of Group 2.

Write an equation for the decomposition of copper(II) carbonate.

.... [1]

(b) **(i)** Complete the electrons in boxes diagram in Fig. 1.1 to show the electronic configuration of a copper(II) ion.

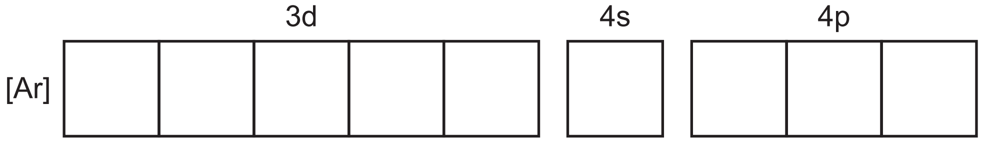


Fig. 1.1

[1]

(ii) There are five different 3d orbitals.

Sketch the shape of a 3d$_{z^2}$ orbital in Fig. 1.2.

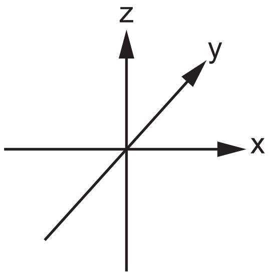


Fig. 1.2

[1]

(iii) Copper can form stable complexes in the +1 and +2 oxidation states.

Explain why transition elements have variable oxidation states.

....

.... [1]

(c) **(i)** 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, *en*, can act as a bidentate ligand.

Explain what is meant by a bidentate ligand.

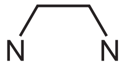
....

....

.... [2]

(ii) The complex $[Cu(H_2O)_2(en)_2]^{2+}$ exists as stereoisomers.

Complete the three-dimensional diagrams in Fig. 1.3 to show the **three** different stereoisomers of $[Cu(H_2O)_2(en)_2]^{2+}$.

The *en* ligand can be represented using  .

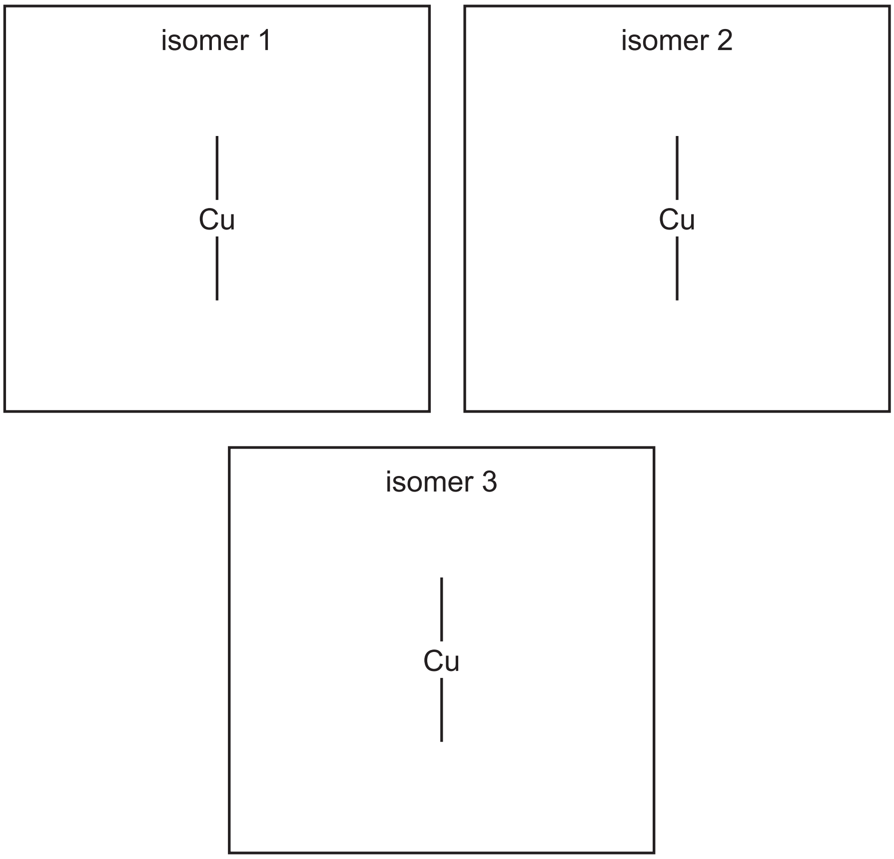


Fig. 1.3

[3]

(iii) State the different types of stereoisomerism shown by $[Cu(H_2O)_2(en)_2]^{2+}$.

.... [1]

(iv) Identify **one** isomer in **(c)(ii)** that is **polar**. Explain your answer.

isomer ....

....

.... [1]

(d) **(i)** The mineral ore cryolite, Na_3AlF_6, contains a single anion which is a complex ion.

Complete Table 1.1 to suggest the formula of the complex ion and to identify the ligand present in Na_3AlF_6.

Table 1.1

complex ion in Na_3AlF_6	
ligand in Na_3AlF_6	

[1]

(ii) When a solution of Al_2O_3 in molten cryolite is electrolysed, aluminium metal is formed at the cathode. The equation is shown.

$$Al^{3+} + 3e^- \rightarrow Al$$

Calculate the maximum mass of aluminium produced when a current of 1.5A is passed through this solution for 30 minutes.

Give your answer to **two** significant figures.

mass of aluminium = ... g [4]

[Total: 19]

2 **(a)** Anhydrous barium chloride can be obtained from the hydrated salt, as shown in reaction 1.

reaction 1 $BaCl_2•2H_2O(s) + 2SOCl_2(l) \rightarrow BaCl_2(s) + 2SO_2(g) + 4HCl(g)$

(i) Describe **one** observation when reaction 1 is carried out.

....

.... [1]

(ii) Define the term entropy, *S*.

....

.... [1]

(iii) The entropy change, $\Delta S^\ominus$, for reaction 1 at 25 °C is +768 J K^{-1} mol^{-1}.

Explain why $\Delta S^\ominus$ has a large positive value.

....

.... [1]

(iv) Table 2.1 shows the enthalpy changes of formation, $\Delta H_f^\ominus$, for the compounds in reaction 1.

Table 2.1

compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
$BaCl_2(s)$	–859
$BaCl_2•2H_2O(s)$	–1460
$SOCl_2(l)$	–246
$SO_2(g)$	–297
$HCl(g)$	–92

Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, in kJ mol^{-1}, for reaction 1 at 25 °C.

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

(b) When aqueous solutions of $BaCl_2$ and $Na_2Cr_2O_7$ are mixed, a yellow precipitate of $BaCrO_4(s)$ is produced and an acidic solution remains.

(i) Write the ionic equation for this reaction.

.... [1]

(ii) Explain why $BaCrO_4(s)$ is coloured.

....

....

....

....

....

.... [3]

(c) Barium sulfate is the least soluble of the Group 2 sulfates.

Explain the trend in the solubilities of the Group 2 sulfates.

....

....

....

....

....

.... [3]

[Total: 13]

3 **(a)** Nickel(II) iodate(V), $Ni(IO_3)_2$, is sparingly soluble in water. The concentration of its saturated solution is $2.30 \times 10^{-2}\,mol\,dm^{-3}$ at 298 K.

(i) Complete the expression for the solubility product, K_{sp}, of $Ni(IO_3)_2$. Include the units.

K_{sp} =

units = ...

[2]

(ii) Calculate the numerical value for K_{sp} of $Ni(IO_3)_2$ at 298 K.

K_{sp} = ... [1]

(b) An electrochemical cell is set up as shown in Fig. 3.1.

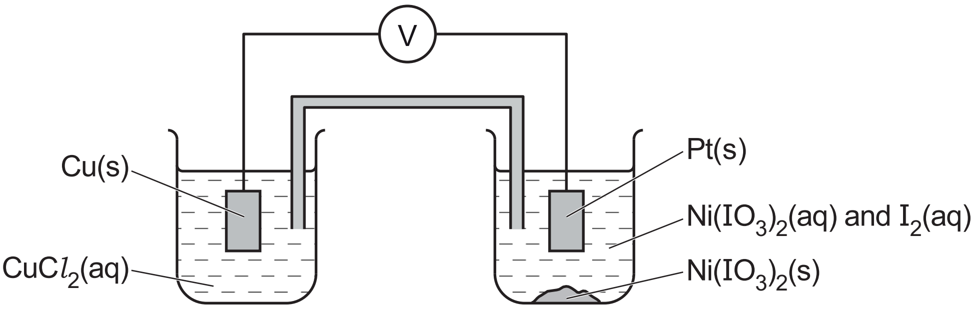


Fig. 3.1

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

$$IO_3^-(aq) + 6H^+(aq) + 5e^- \rightleftharpoons \tfrac{1}{2}I_2(aq) + 3H_2O(l) \qquad E^{\ominus} = +1.19\,V$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^{\ominus} = +0.34\,V$$

(i) Use this information to calculate the value of $E^{\ominus}_{cell}$. State which electrode is positive.

$E^{\ominus}_{cell}$ = ... positive electrode is ....

[1]

(ii) Suggest how the measured E_{cell} of this cell compares to the $E^{\ominus}_{cell}$ under standard conditions.

Explain your answer.

....

.... [1]

(iii) Complete Table 3.1 by placing **one** tick (✓) to indicate how the E_{cell} of this cell changes when a small amount of $NiSO_4(aq)$ is added to the beaker containing $Ni(IO_3)_2(aq)$ and $I_2(aq)$ in Fig. 3.1.

Explain your answer.

Table 3.1

change in E_{cell}		
less positive	no change	more positive

....

....

.... [2]

(c) In solution, iodic(V) acid, HIO_3, ionises as shown.

$$HIO_3(aq) \rightleftharpoons IO_3^-(aq) + H^+(aq)$$

The pH of a 1.0 mol dm^{-3} solution of HIO_3 is 0.47.

(i) Calculate $[H^+(aq)]$, in mol dm^{-3}, in a 1.0 mol dm^{-3} solution of HIO_3.

$[H^+(aq)]$ = ... mol dm^{-3} [1]

(ii) Use your answer from **(c)(i)** to calculate the equilibrium concentrations of $HIO_3(aq)$ and $IO_3^-(aq)$, in mol dm^{-3}, in a 1.0 mol dm^{-3} solution of HIO_3.

$[HIO_3(aq)]$ = ... mol dm^{-3}

$[IO_3^-(aq)]$ = ... mol dm^{-3}
[1]

(iii) Use your answers from **(c)(i)** and **(c)(ii)** to calculate the K_a, in mol dm^{-3}, of HIO_3.

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

(d) The *Dushman reaction* is the reaction between iodate(V) ions and iodide ions in acid solution.

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$$

The rate equation for this reaction is shown.

$$\text{rate} = k\,[IO_3^-][I^-]^2[H^+]^2$$

The rate of this reaction is investigated in a buffer solution.

The initial concentrations are shown.

$[IO_3^-] = 0.500\,\text{mol dm}^{-3}$ $[I^-] = 1.00 \times 10^{-3}\,\text{mol dm}^{-3}$ $[H^+] = 1.00 \times 10^{-2}\,\text{mol dm}^{-3}$

Under these conditions the initial rate of the reaction is $2.10 \times 10^{-2}\,\text{mol dm}^{-3}\,\text{s}^{-1}$.

(i) Define buffer solution.

....

....

.... [2]

(ii) Use the information to calculate the rate constant, *k*. State its units.

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

(iii) This reaction is repeated at the same temperature and with the same initial values of $[IO_3^-]$ and $[I^-]$. The $[H^+]$ is increased to $3.00 \times 10^{-2}\,\text{mol dm}^{-3}$.

Calculate the initial rate of this reaction.

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

[Total: 15]

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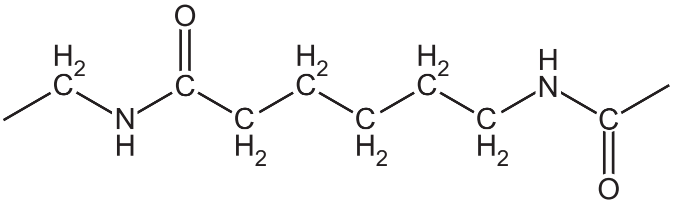
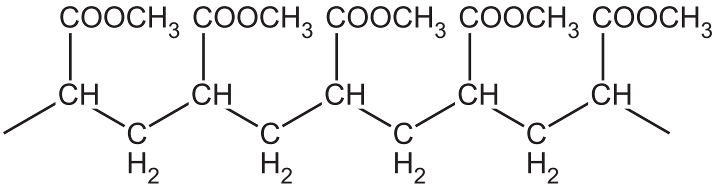
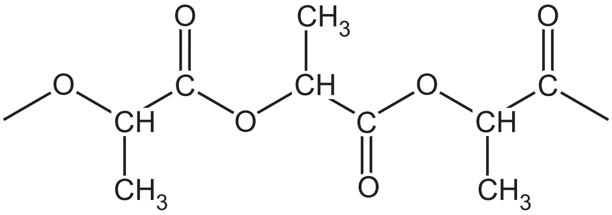
4 Table 4.1 shows the structures of sections of three polymers, **X**, **Y** and **Z**.

Each polymer is made from only **one** type of monomer.

Table 4.1

polymer	structure of section of polymer
X	
Y	
Z	

(a) Complete Table 4.2 to state the type of polymerisation and draw the structure of the monomer for each polymer, **X**, **Y** and **Z**.

Table 4.2

polymer	type of polymerisation	structure of monomer
X		
Y		
Z		

[4]

(b) Amino acids can act as monomers.

State what is meant by the isoelectric point of an amino acid.

....

.... [1]

(c) Electrophoresis can be used to separate and identify amino acids.

Table 4.3 shows information about the three amino acids glycine, lysine and glutamic acid.

Table 4.3

amino acid	structural formula of amino acid	isoelectric point
glycine (gly)	H_2NCH_2COOH	6.0
lysine (lys)	$H_2NCH(CH_2CH_2CH_2CH_2NH_2)COOH$	9.7
glutamic acid (glu)	$H_2NCH(CH_2CH_2COOH)COOH$	3.2

(i) A mixture containing these three amino acids is analysed in a buffer solution of pH 6.0.

Draw and label **three** spots on Fig. 4.1 to indicate the predicted position of each of these amino acids, gly, lys and glu, after electrophoresis.

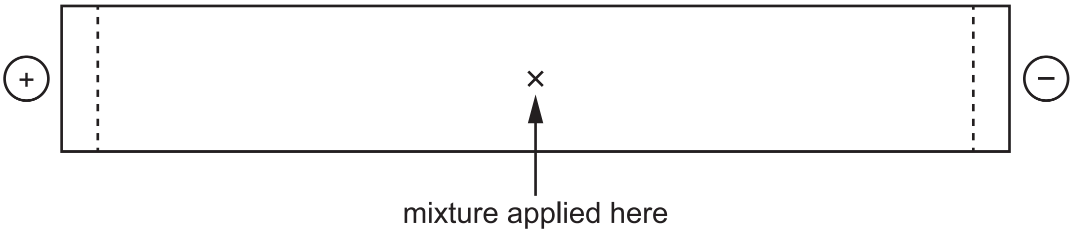


Fig. 4.1

[2]

(ii) Electrophoresis is repeated using a buffer solution of pH 11.

Predict how the position of glycine will change, if at all, after electrophoresis.

....

.... [1]

[Total: 8]

5 A group of drugs known as statins are used to lower cholesterol in blood. A commonly used statin is atorvastatin.

atorvastatin

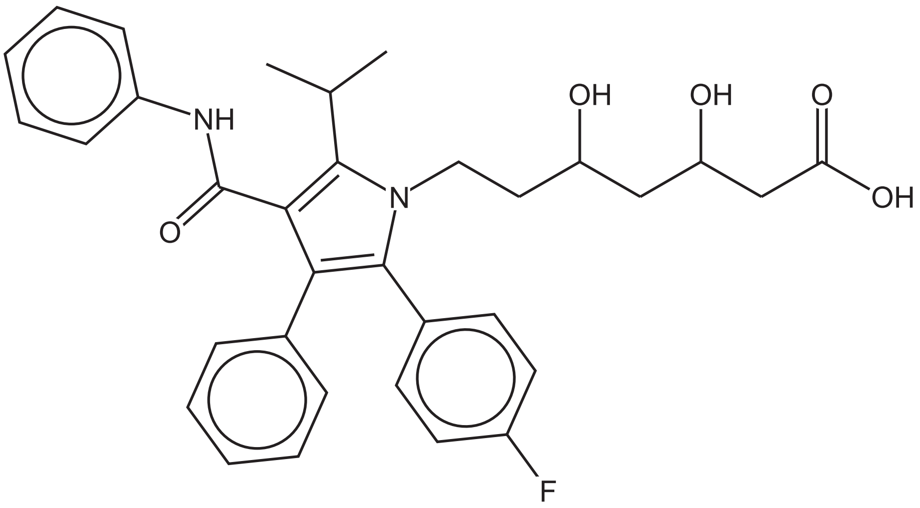


Fig. 5.1

(a) Statins can break down in the acid found in the stomach.

(i) Draw a line through the bond in the atorvastatin structure in Fig. 5.1 that could be broken under acid conditions. [1]

(ii) By referring to the structure, explain why atorvastatin dissolves in water.

....

.... [1]

(iii) Complete the molecular formula of atorvastatin.

$$\mathrm{C\ \ H_{35}N\ \ O\ \ F}$$

[1]

(iv) Atorvastatin contains chiral carbon atoms.

Circle **all** chiral carbon atoms in Fig. 5.1. [1]

(v) The synthetic preparation of atorvastatin requires the production of a single optical isomer.

Suggest why.

....

.... [1]

(b) **(i)** The proton (^1H) NMR spectrum of atorvastatin dissolved in $CDCl_3$ is recorded.

Use Table 5.1 to deduce the number of hydrogen atoms that could produce peaks in the region δ = 6.5–13.0 ppm.

.... [1]

(ii) The proton (^1H) NMR spectrum of atorvastatin dissolved in D_2O is recorded.

Predict the number of hydrogen atoms that would **not** show a peak in this spectrum.

Explain your answer.

....

....

.... [2]

Table 5.1

environment of proton	example	chemical shift range δ/ppm
alkane	$-C\mathbf{H}_3$, $-C\mathbf{H}_2-$, $>C\mathbf{H}-$	0.9–1.7
alkyl next to C=O	$C\mathbf{H}_3-C=O$, $-C\mathbf{H}_2-C=O$, $>C\mathbf{H}-C=O$	2.2–3.0
alkyl next to aromatic ring	$C\mathbf{H}_3-Ar$, $-C\mathbf{H}_2-Ar$, $>C\mathbf{H}-Ar$	2.3–3.0
alkyl next to electronegative atom	$C\mathbf{H}_3-O$, $-C\mathbf{H}_2-O$, $-C\mathbf{H}_2-Cl$	3.2–4.0
attached to alkene	$=C\mathbf{H}R$	4.5–6.0
attached to aromatic ring	$\mathbf{H}-Ar$	6.0–9.0
aldehyde	$\mathbf{H}COR$	9.3–10.5
alcohol	$RO\mathbf{H}$	0.5–6.0
phenol	$Ar-O\mathbf{H}$	4.5–7.0
carboxylic acid	$RCOO\mathbf{H}$	9.0–13.0
alkyl amine	$R-N\mathbf{H}-$	1.0–5.0
aryl amine	$Ar-N\mathbf{H}_2$	3.0–6.0
amide	$RCON\mathbf{H}R$	5.0–12.0

(c) Atorvastatin reacts with an excess of $LiAlH_4$.

Name all the functional groups in atorvastatin that react with $LiAlH_4$.

Name the new functional group that would be formed in each case.

names of functional groups in atorvastatin that react

....

names of the new functional groups formed

....

[2]

[Total: 10]

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6 **(a)** A list of tests for different organic groups is given in Table 6.1.

Complete Table 6.1 to identify an organic functional group, in aliphatic compounds, that produces a positive result in each test.

Table 6.1

test					
sodium metal	$Na_2CO_3(aq)$	2,4-DNPH	$I_2(aq)$ + $OH^-(aq)$	warm with Fehling's reagent	$Br_2(aq)$

[4]

(b) Lavandulol is an aliphatic organic compound and the major component of lavender oil. Fig. 6.1 shows a reaction scheme involving lavandulol, **A**.

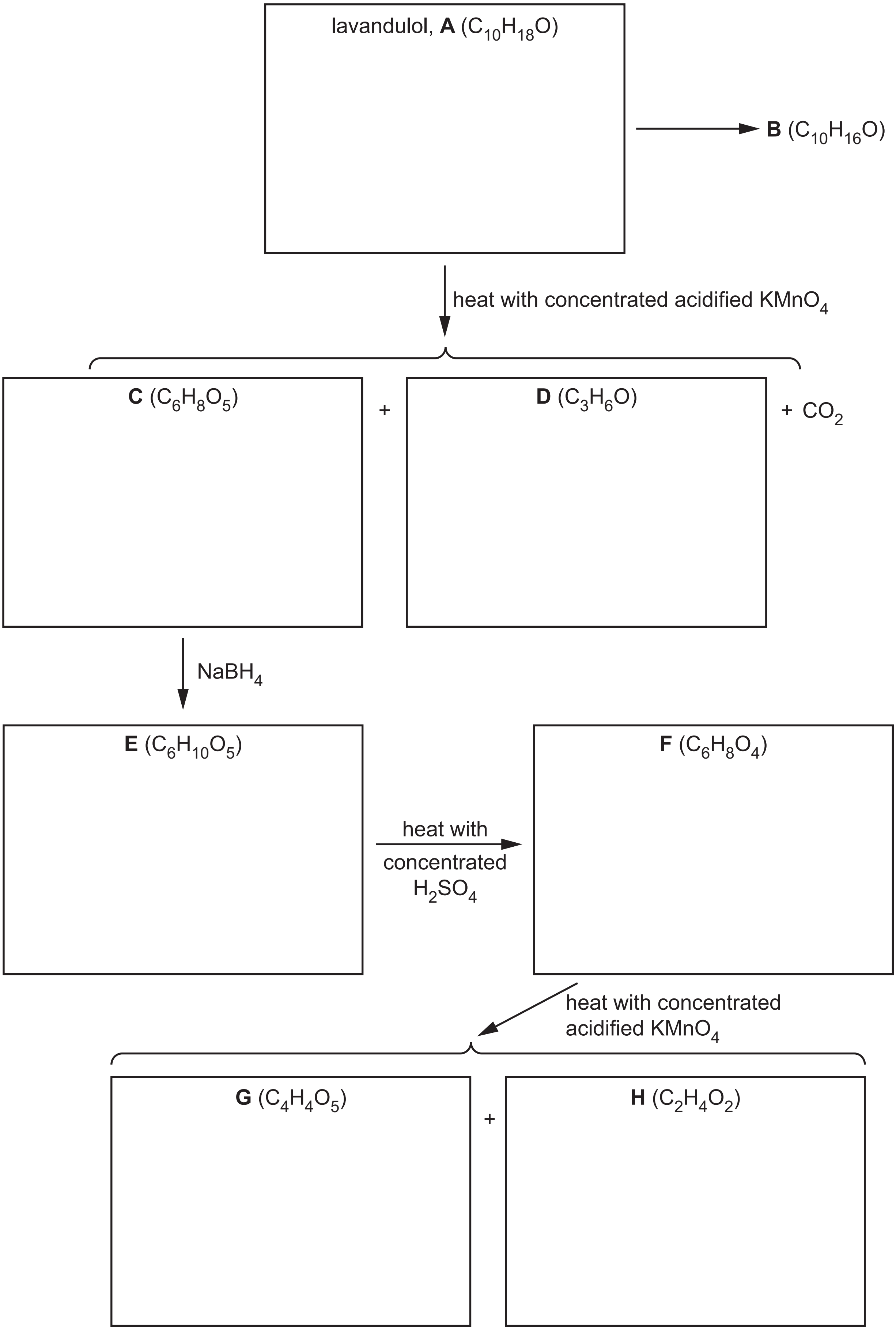


Fig. 6.1

Table 6.2 shows the results obtained when the tests in Table 6.1 are carried out on the eight organic compounds, **A–H**, in the reaction scheme in Fig. 6.1.

Table 6.2

letter of compound	test					
	sodium metal	Na_2CO_3(aq)	2,4-DNPH	I_2(aq) + OH^-(aq)	warm with Fehling's reagent	Br_2(aq)
A	✓	✗	✗	✗	✗	✓
B	✗	✗	✓	✗	✓	✓
C	✓	✓	✓	✓	✗	✗
D	✗	✗	✓	✓	✗	✗
E	✓	✓	✗	✓	✗	✗
F	✓	✓	✗	✗	✗	✓
G	✓	✓	✓	✗	✗	✗
H	✓	✓	✗	✗	✗	✗

(i) Deduce the functional group present in compound **A** using both the molecular formulae of **A** and **B** and the reaction of **B** with Fehling's reagent.

.... [1]

(ii) Name the type of reaction that occurs in each of the following conversions.

- **A** → **B** ....
- **C** → **E** ....
- **E** → **F** ....

[3]

(iii) Use the information in Table 6.2 and the molecular formulae to deduce structures for **G** and **H**. Draw your structures in Fig. 6.1. [2]

(iv) Use the information in Table 6.2, the molecular formulae and your answer to **(b)(iii)** to deduce structures for **A**, **C**, **D**, **E** and **F**. Draw your structures in Fig. 6.1. [5]

[Total: 15]

7 **(a)** State the relative acidities of benzoic acid, C_6H_5COOH, ethanol, CH_3CH_2OH, and phenol, C_6H_5OH, in aqueous solution. Explain your answer.

....

most acidic least acidic

....

....

....

....

....

.... [3]

(b) Draw the major products from the nitration of benzoic acid and phenol in the boxes in Fig. 7.1. The molecular formula for each major product is given in the boxes.

major product from benzoic acid, $C_7H_5NO_4$	major product from phenol, $C_6H_5NO_3$

[2]

Fig. 7.1

(c) Ethanol reacts with propanoyl chloride, C_2H_5COCl, to form ester **W**.

W

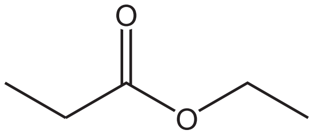


Fig. 7.2

(i) Give the systematic name for ester **W**.

.... [1]

(ii) Complete the mechanism in Fig. 7.3 for the reaction between C_2H_5COCl and ethanol.

R–OH represents ethanol.

Include all relevant lone pairs of electrons, curly arrows, charges and partial charges.

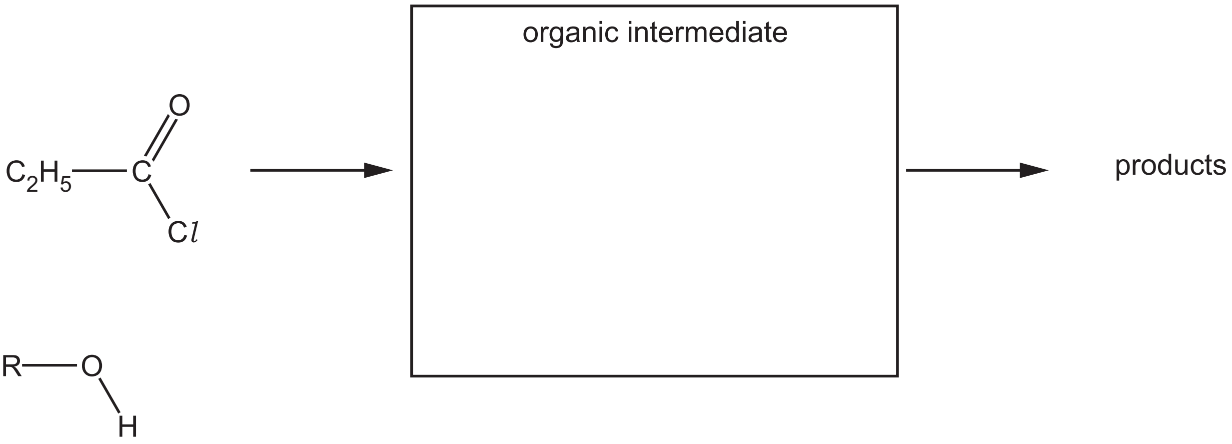


Fig. 7.3

[4]

(iii) Name the mechanism for the reaction shown in Fig. 7.3.

.... [1]

[Total: 11]

8 **(a)** **(i)** Define lattice energy, ΔH_{latt}.

....

.... [2]

(ii) Define enthalpy change of solution, ΔH_{sol}.

....

.... [1]

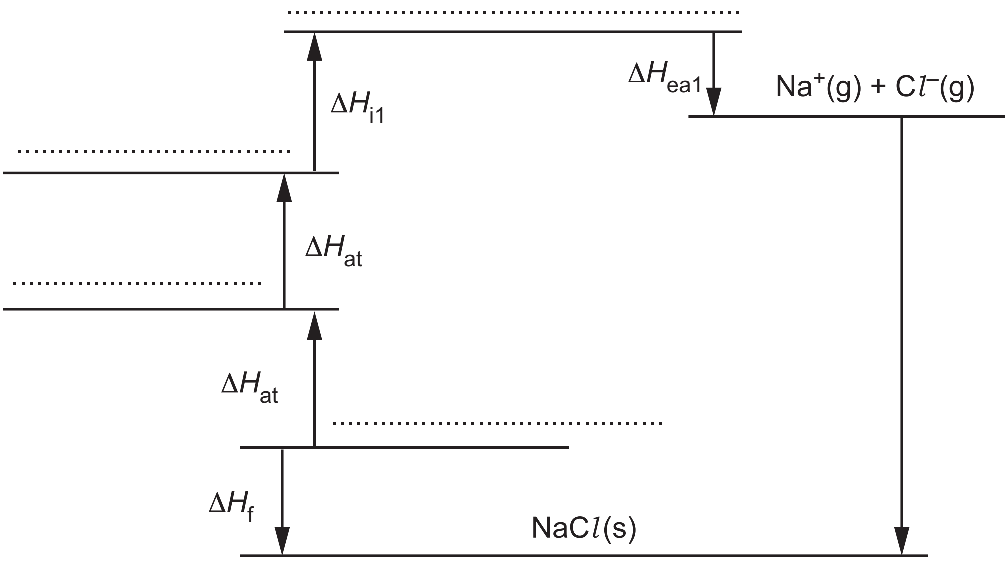
(b) The enthalpy change of hydration can be represented by ΔH_{hyd}.

Write the mathematical expression for the ΔH_{sol} of $\mathrm{NaC}l$ in terms of $\Delta H_{\text{latt}}(\mathrm{NaC}l)$, $\Delta H_{\text{hyd}}(\mathrm{Na}^+)$ and $\Delta H_{\text{hyd}}(\mathrm{C}l^-)$.

$\Delta H_{\text{sol}}(\mathrm{NaC}l)$ = ... [1]

(c) Complete the Born–Haber cycle in Fig. 8.1 for the ionic solid $\mathrm{NaC}l$.

Include state symbols of relevant species.



Key

ΔH_{i1}	first ionisation energy
ΔH_{ea1}	first electron affinity

Fig. 8.1

[3]

(d) Predict which of the ions, Cl^- or NO_3^-, has the more negative enthalpy change of hydration.

Explain your answer.

....

....

....

....

.... [2]

[Total: 9]

Important values, constants and standards

molar gas constant	$R = 8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$
Faraday constant	$F = 9.65 \times 10^4\,\mathrm{C\,mol^{-1}}$
Avogadro constant	$L = 6.02 \times 10^{23}\,\mathrm{mol^{-1}}$
electronic charge	$e = -1.60 \times 10^{-19}\,\mathrm{C}$
molar volume of gas	$V_m = 22.4\,\mathrm{dm^3\,mol^{-1}}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,\mathrm{dm^3\,mol^{-1}}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14}\,\mathrm{mol^2\,dm^{-6}}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,\mathrm{kJ\,kg^{-1}\,K^{-1}}$ ($4.18\,\mathrm{J\,g^{-1}\,K^{-1}}$)

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 144.2	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 –