* 0000800000001 *

Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME	

CENTRE NUMBER		CANDIDATE NUMBER	

* 4 1 1 8 6 6 4 9 4 8 *

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **February/March 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 **28** pages. Any blank pages are indicated.

DC (PQ/SW) 342049/4

1 Silver, Ag, is a metal in the d-block of the Periodic Table.

(a) Silver can form compounds containing either Ag^+ or Ag^{2+} ions.

Explain why silver is a transition element.

....

.... [1]

(b) Table 1.1 gives data relevant to the Born–Haber cycle for silver(I) fluoride, AgF.

Table 1.1

standard energy change	value / $kJ\,mol^{-1}$
first ionisation energy of silver	+732
enthalpy change of atomisation of silver	+289
enthalpy change of atomisation of fluorine	+79
enthalpy change of formation of silver(I) fluoride	–203
lattice energy of silver(I) fluoride	–955

(i) Write equations for the standard enthalpy changes described.
Include state symbols.

- standard enthalpy change of atomisation of silver

....

- standard enthalpy change of formation of silver(I) fluoride

....

[2]

(ii) Define lattice energy.

....

....

.... [2]

(iii) Calculate the first electron affinity, EA_1, of fluorine, using data from Table 1.1.

It may be helpful to draw a labelled energy cycle as part of the working for your answer.

EA_1 = ... $kJ\,mol^{-1}$ [2]

(c) **(i)** Use the data in Table 1.2 to calculate the enthalpy change of solution, ΔH_{sol}, of AgF(s).

Table 1.2

energy change at 298 K	value / $kJ\,mol^{-1}$
lattice energy of AgF(s)	–955
enthalpy change of hydration of $Ag^+(g)$	–464
enthalpy change of hydration of $F^-(g)$	–506

ΔH_{sol} of AgF(s) = ... $kJ\,mol^{-1}$ [1]

(ii) Use your answer to **(c)(i)** to suggest whether AgF is soluble in water at 298 K. Explain your answer.

....

....

.... [1]

(d) Table 1.3 shows some data relevant to the silver(I) halides, AgCl to AgI.

Table 1.3

silver(I) halide	first electron affinity of halogen / kJ mol^{-1}	lattice energy / kJ mol^{-1}
AgCl	–349	–905
AgBr	–325	–890
AgI	–295	–876

(i) Explain the trend in the first electron affinities of the halogens, Cl to I.

....

....

....

.... [2]

(ii) Explain the trend in the lattice energies of the silver(I) halides, AgCl to AgI.

....

....

.... [1]

(e) An electrochemical cell is constructed using the electrodes shown in Table 1.4.

Table 1.4

electrode	half-equation	$E^{\ominus}$/V
1	$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	+0.222
2	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.342

(i) Calculate the standard cell potential, $E^{\ominus}_{cell}$.

Construct an equation for the overall cell reaction.

$E^{\ominus}_{cell}$ = ... V

equation ....

[2]

(ii) In a different experiment, electrode 1 is set up using a saturated solution of KC*l*.

Saturated KC*l*(aq) contains 36.0 g of KC*l* per 100 cm^3 of solution at 298 K.

The Nernst equation for electrode 1 is:

$$E = E^{\ominus} + \frac{0.059}{z} \log \frac{1}{[Cl^-(aq)]}$$

Calculate the electrode potential, *E*, of electrode 1 under these conditions.

E = ... V [3]

[Total: 17]

2 Propanone, CH_3COCH_3, is a common organic solvent and reagent.

(a) Propanone reacts with methanol, CH_3OH, under acidic conditions to form compound **A**, as shown by reaction 1.

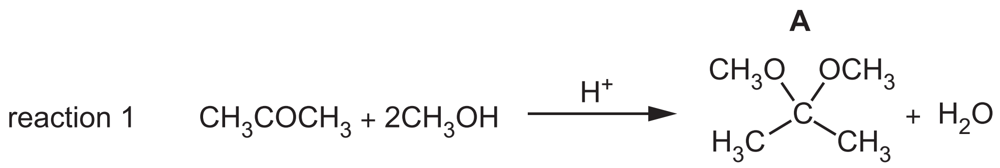


Fig. 2.1

The overall order of reaction 1 can be found by studying experimental data.

Table 2.1 shows how the initial rate of reaction changes as $[CH_3OH]$ and $[H^+]$ are varied. In each experiment, a large excess of CH_3COCH_3 is used.

Table 2.1

experiment	$[CH_3OH]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	relative initial rate of reaction
1	0.010	0.010	1.00
2	0.015	0.015	2.25
3	0.015	0.020	3.00

(i) Explain why a large excess of CH_3COCH_3 is used in each experiment.

....

....

.... [1]

(ii) Use the data in Table 2.1 to determine the order of reaction 1 with respect to CH_3OH and to H^+ ions. Explain your answers.

....

....

....

....

.... [2]

(iii) In a separate experiment, a large excess of CH_3OH and H^+ ions are added to a solution containing a known concentration of CH_3COCH_3.

Fig. 2.2 shows how $[CH_3COCH_3]$ varies over time.

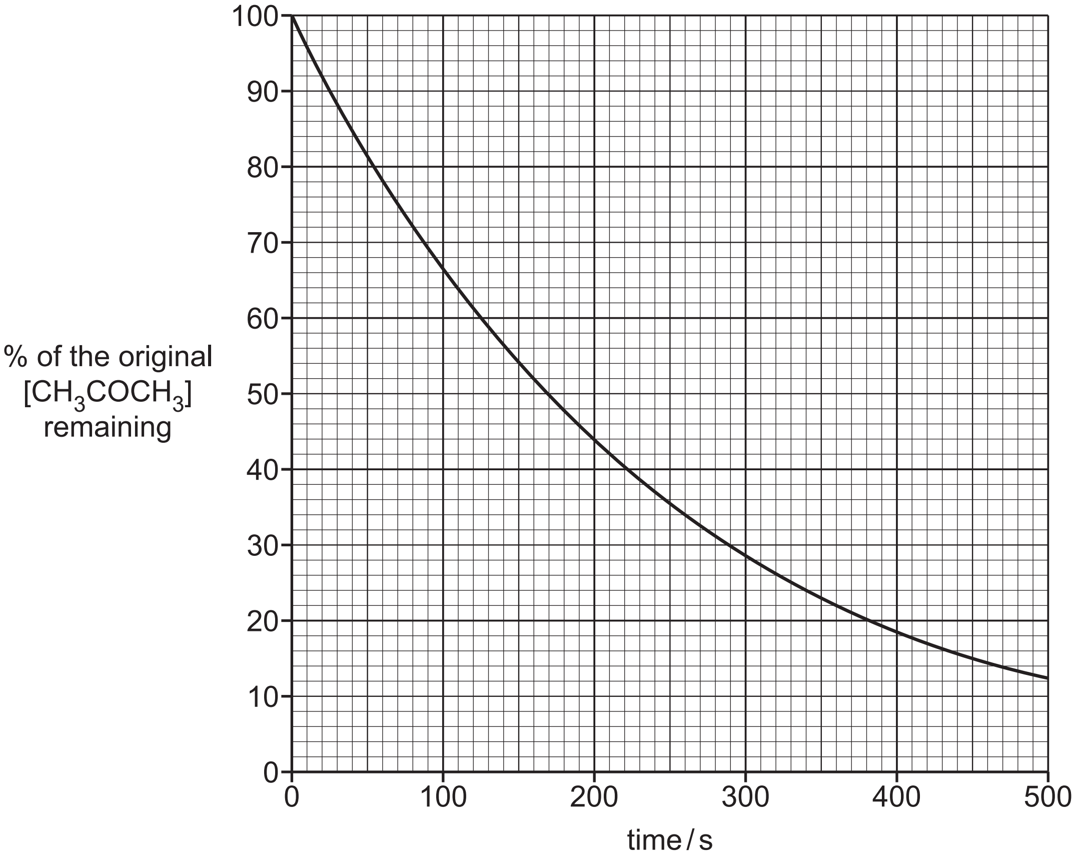


Fig. 2.2

Use Fig. 2.2 to show how, under these conditions, reaction 1 is first order with respect to CH_3COCH_3.

....

....

....

.... [1]

(b) Propanone also reacts with acidified cyanide ions to form the hydroxynitrile compound **B**, as shown by reaction 2.

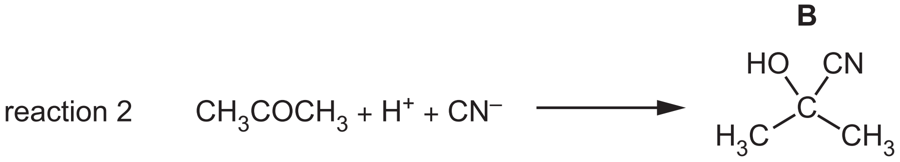


Fig. 2.3

The following rate equation is determined for reaction 2.

$$\text{rate} = k\,[CH_3COCH_3]\,[H^+]$$

Four possible mechanisms for reaction 2 are shown in Table 2.2.

Table 2.2

proposed reaction mechanism		steps
1	fast	$CH_3COCH_3 + H^+ \rightarrow [CH_3C(OH)CH_3]^+$
	slow	$[CH_3C(OH)CH_3]^+ + CN^- \rightarrow CH_3C(OH)(CN)CH_3$
2	fast	$H^+ + CN^- \rightarrow HCN$
	slow	$CH_3COCH_3 + HCN \rightarrow CH_3C(OH)(CN)CH_3$
3	slow	$CH_3COCH_3 + CN^- \rightarrow CH_3C(O^-)(CN)CH_3$
	fast	$CH_3C(O^-)(CN)CH_3 + H^+ \rightarrow CH_3C(OH)(CN)CH_3$
4	slow	$CH_3COCH_3 + H^+ \rightarrow [CH_3C(OH)CH_3]^+$
	fast	$[CH_3C(OH)CH_3]^+ + CN^- \rightarrow CH_3C(OH)(CN)CH_3$

Suggest which of these mechanisms is consistent with the rate equation for reaction 2. Explain your answer.

proposed reaction mechanism ....

explanation ....

....

....

....

[3]

(c) Carboxylic acid **C**, $C_4H_8O_3$, forms when **B** is hydrolysed under hot acidic conditions.

(i) Draw the structure of **C**.

[1]

(ii) The pK_a of **C** is 3.95. Calculate the pH of a 0.500 mol dm^{-3} solution of **C**.

Show your working.

pH = ... [2]

(d) **C** can be used to form buffer solution **D**.

(i) Define a buffer solution.

....

....

.... [2]

(ii) Buffer solution **D** is made when 20.0 cm^3 of 1.00 mol dm^{-3} NaOH(aq) is added to 100 cm^3 of a 0.500 mol dm^{-3} solution of **C**.

The pK_a of **C** is 3.95.

Calculate the pH of buffer solution **D**.

Show your working.

pH = ... [3]

[Total: 15]

[Turn over

3 Fe^{2+} and Fe^{3+} ions are able to form a variety of complexes with different species.

(a) **(i)** Define complex.

....

....

.... [1]

(ii) Table 3.1 gives some details of different complexes of Fe^{2+} and of Fe^{3+}.

Complete Table 3.1.

Table 3.1

complex	ion	ligand	coordination number	formula and charge of complex
E	Fe^{2+}	NH_3	6	
F				$[FeCl_4]^{2-}$
G		en		$[Fe(en)_3]^{3+}$

[3]

(iii) Complete Fig. 3.1 to show the splitting of the d-orbitals in a tetrahedral complex.

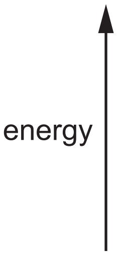


Fig. 3.1

[1]

(b) Table 3.2 gives details of some complexes of Fe^{3+}.

Table 3.2

complex	colour	value of K_{stab}
$[Fe(H_2O)_6]^{3+}$	violet	1
$[Fe(H_2O)_5SCN]^{2+}$	red	1.40×10^2
$[Fe(H_2O)_5F]^{2+}$	colourless	2.40×10^5

(i) Explain the reason for the difference in colour of the two complexes $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5SCN]^{2+}$.

....

....

....

.... [2]

(ii) Write an expression for K_{stab} of $[Fe(H_2O)_5SCN]^{2+}$.

K_{stab} =

[1]

(iii) Use information in Table 3.2 to calculate the value of the equilibrium constant, K_c, for the following reaction.

$$[Fe(H_2O)_5SCN]^{2+} + F^- \rightleftharpoons [Fe(H_2O)_5F]^{2+} + SCN^-$$

K_c = ... [1]

(iv) A few drops of KF(aq) are added to a solution of $[Fe(H_2O)_6]^{3+}$(aq), followed by a few drops of KSCN(aq).

Use information in Table 3.2 to describe any observations after each addition. Explain your answer.

....

....

....

.... [2]

(c) Hydrated compound **J**, $K_3Fe(C_2O_4)_3{\bullet}xH_2O$, contains the green complex ion $[Fe(C_2O_4)_3]^{3-}$.

The value of *x* can be determined by titration of a sample of **J** with acidified MnO_4^- ions.

MnO_4^- ions oxidise $C_2O_4^{2-}$ ions in acidic conditions.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(i) Write half equations for the oxidation of $C_2O_4^{2-}$ ions and for the reduction of MnO_4^- ions.

- oxidation of $C_2O_4^{2-}$

....

- reduction of MnO_4^-

....

[2]

(ii) A student prepares a solution containing 0.100 g of **J**.

The student titrates this solution with 0.0200 mol dm^{-3} acidified $KMnO_4(aq)$. The titre obtained is 12.20 cm^3.

Assume all of the $C_2O_4^{2-}$ ions are oxidised.

Calculate the value of *x* in $K_3Fe(C_2O_4)_3{\bullet}xH_2O$.

Give your answer to the nearest whole number. Show your working.

[M_r: $K_3Fe(C_2O_4)_3$, 437.1]

x = ... [4]

[Total: 17]

4 **(a)** State the difference in the basicities of ammonia, NH_3, propanamide, $CH_3CH_2CONH_2$, and propylamine, $CH_3CH_2CH_2NH_2$.

Explain your answer.

.... < .... < ....
weakest base   strongest base

....

....

....

....

....

.... [4]

(b) Fig. 4.1 shows two different ways to synthesise propylamine.

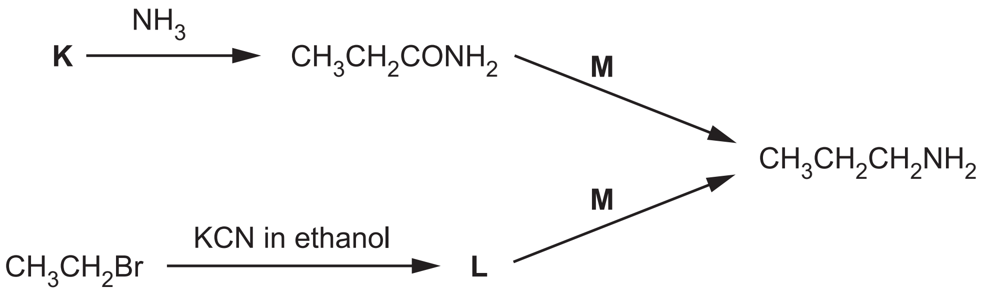


Fig. 4.1

Identify compounds **K** and **L** and reagent **M** from Fig. 4.1.

K ....

L ....

M .... [3]

(c) Compound **N** is shown in Fig. 4.2.

N

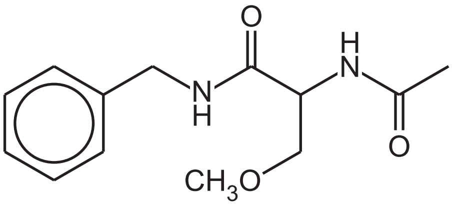


Fig. 4.2

Compound **N** is treated with an excess of concentrated HC*l*(aq).

N undergoes complete hydrolysis to form three organic products.

The products are isolated from the reaction mixture at pH 4.

Draw the structures of the three organic products at pH 4.

Assume that the CH_3O— group does **not** react.

[4]

(d) Compound **P** can be synthesised from 1-methyl-4-nitrobenzene by the route shown in Fig. 4.3.

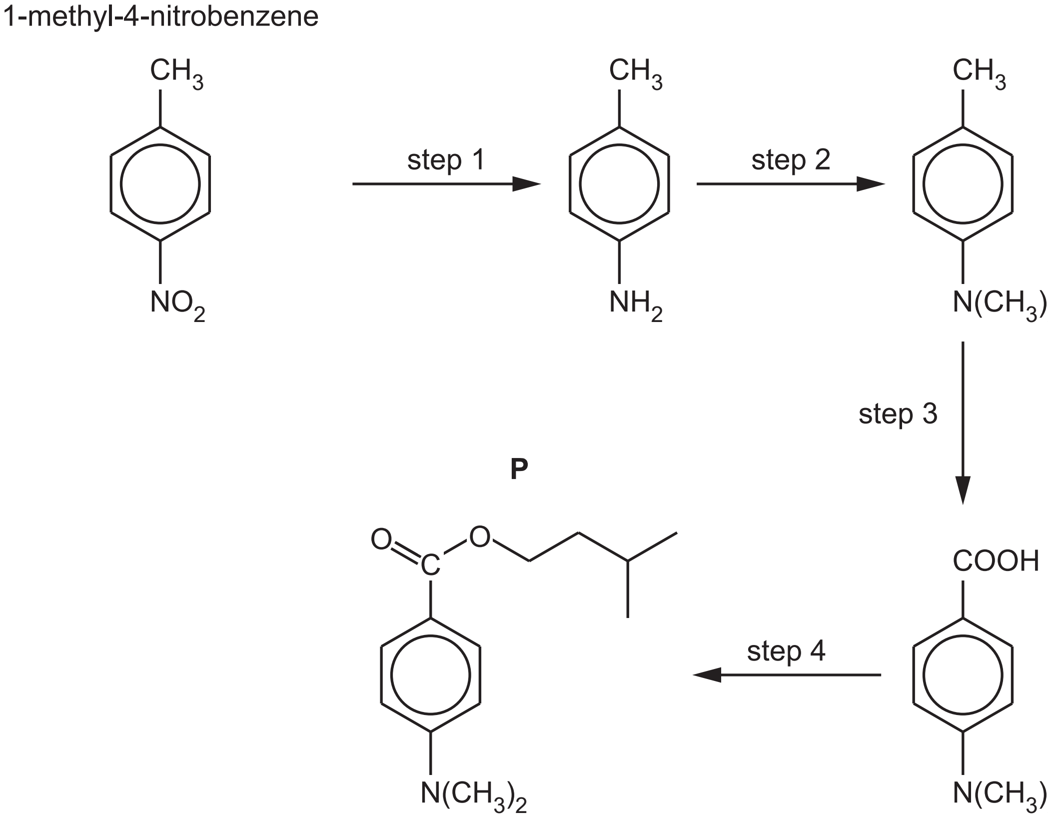


Fig. 4.3

(i) Step 1 is a reduction reaction.

Complete the equation for this reaction. Use [H] to represent an atom of hydrogen from the reducing agent.

$C_7H_7NO_2$ + ... [1]

(ii) Complete Table 4.1 to give details of each step of the synthesis shown in Fig. 4.3.

Table 4.1

step	reagents and conditions	type of reaction
1		reduction
2		
3		
4		condensation

[6]

[Total: 18]

5 Cumene is an aromatic hydrocarbon used in the synthesis of other useful chemicals.

cumene

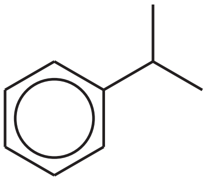


Fig. 5.1

(a) Complete Table 5.1 to show the number of sp^2 and sp^3 hybridised carbon atoms that are present in a molecule of cumene.

Table 5.1

type of hybridisation	sp^2	sp^3
number of carbon atoms		

[1]

(b) Cumene can be synthesised via a Friedel–Crafts alkylation reaction, as shown in Fig. 5.2.

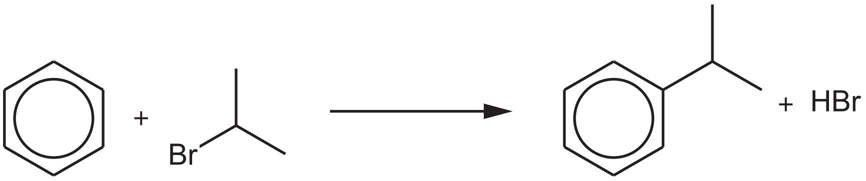


Fig. 5.2

(i) Name the mechanism involved in the Friedel–Crafts alkylation shown in Fig. 5.2.

.... [1]

(ii) The first step of the reaction forms the $(CH_3)_2CH^+$ cation.

Identify a suitable reagent for the formation of this cation from 2-bromopropane, $(CH_3)_2CHBr$.

.... [1]

(iii) Complete Fig. 5.3 to show the mechanism for the reaction of benzene with the $(CH_3)_2CH^+$ cation.

Include all relevant curly arrows and charges.

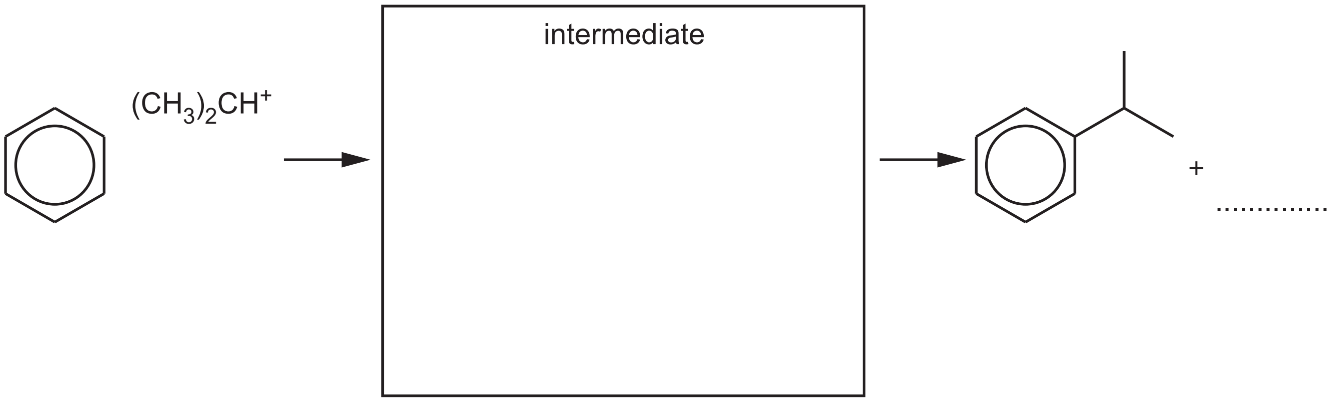


Fig. 5.3

[3]

(iv) The Friedel–Crafts alkylation of benzene by 1-bromopropane, $CH_3CH_2CH_2Br$, also produces cumene as the major product.

The $CH_3CH_2CH_2^+$ cation formed in the first step quickly rearranges to form the $(CH_3)_2CH^+$ cation.

Suggest why this is the case. Explain your answer.

....

....

.... [1]

(c) Cumene oxidises in air to form phenol, C_6H_5OH, and propanone, CH_3COCH_3.

reaction 1 $C_6H_5CH(CH_3)_2 + O_2 \rightarrow C_6H_5OH + CH_3COCH_3$ $\Delta H^{\ominus} = -371\,kJ\,mol^{-1}$

Table 5.2 gives some relevant standard entropies for reaction 1.

Table 5.2

compound	$C_6H_5CH(CH_3)_2$	O_2	C_6H_5OH	CH_3COCH_3
standard entropy, $S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	278	205	146	200

(i) Calculate the standard entropy change, $\Delta S^{\ominus}$, of reaction 1.

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

(ii) Show that reaction 1 is feasible at 25 °C.

[2]

(d) Fig. 5.4 shows two reactions of phenol.

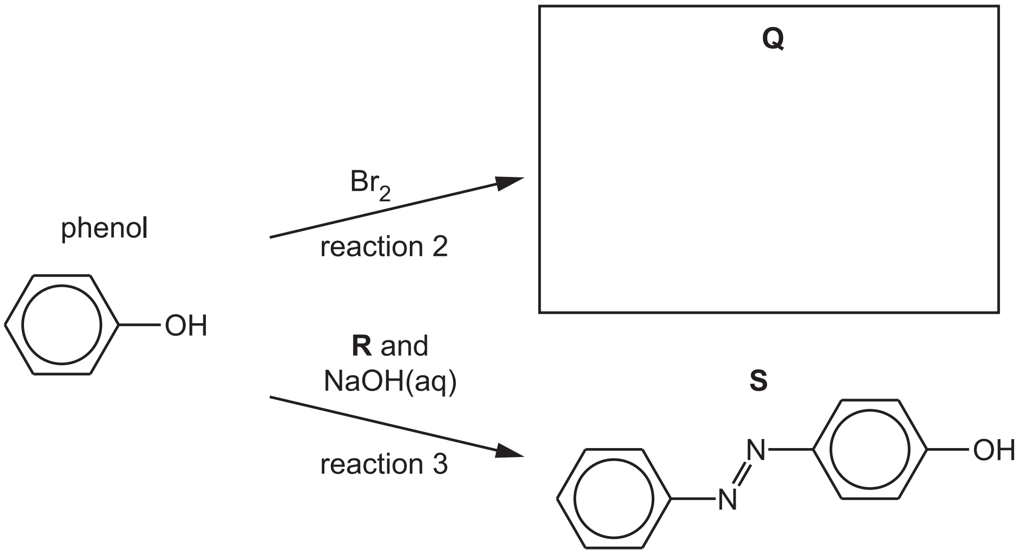


Fig. 5.4

(i) State the conditions for the bromination of phenol in reaction 2.

Explain why these conditions are different from those for the bromination of benzene.

conditions ....

explanation ....

....

....

....

....

[4]

(ii) Draw the structure of organic compound **Q** in Fig. 5.4. [1]

(iii) Identify organic reagent **R**.

[1]

(iv) Name the functional group that is formed in reaction 3.

.... [1]

(v) The reaction of phenol with HNO_3 produces a mixture of isomers with molecular formula $C_6H_5NO_3$.

Identify the **two** isomers that are produced in the largest quantities.

Explain your answer.

isomer 1	isomer 2

explanation ....

....

.... [2]

[Total: 19]

Question 6 starts on the next page.

6 **(a)** Maleic anhydride is an unsaturated cyclic compound used in the formation of several polymers.

Maleic anhydride can be used to form maleic acid and tartaric acid.

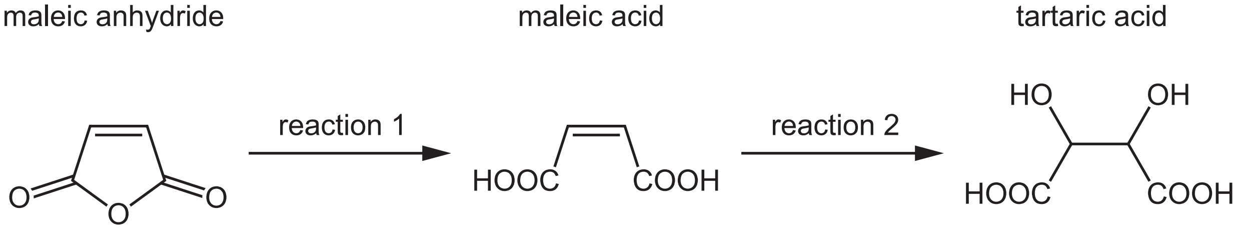


Fig. 6.1

(i) Maleic acid reacts with ethane-1,2-diol to form a condensation polymer.

Draw a section of this polymer, showing only **one** repeat unit.

The new functional group formed should be shown fully displayed.

[2]

(ii) Identify a suitable reagent and the conditions for reaction 2.

.... [1]

(b) Compound **U** can be formed from tartaric acid in two steps, as shown in Fig. 6.2.

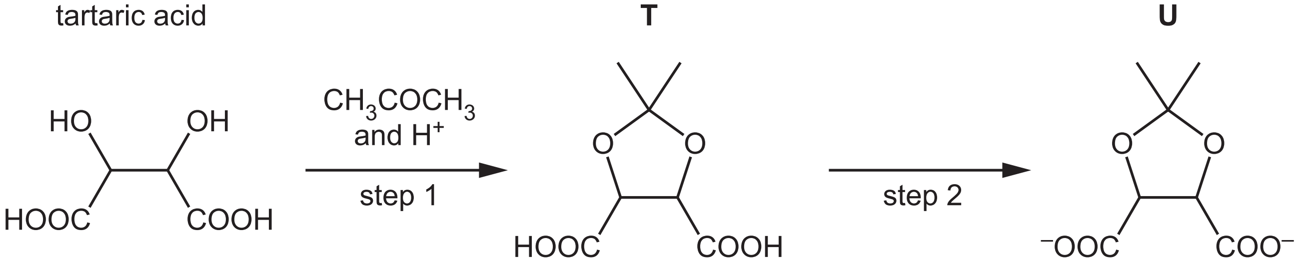


Fig. 6.2

(i) Suggest the type of reaction that occurs in step 1.

.... [1]

(ii) **U** can act as a bidentate ligand.

Explain what is meant by a bidentate ligand.

....

.... [2]

(iii) Complete the three-dimensional diagrams in Fig. 6.3 to show both stereoisomers of $[Cu(\mathbf{U})_3]^{4-}$.

Use  to represent ligand **U**.

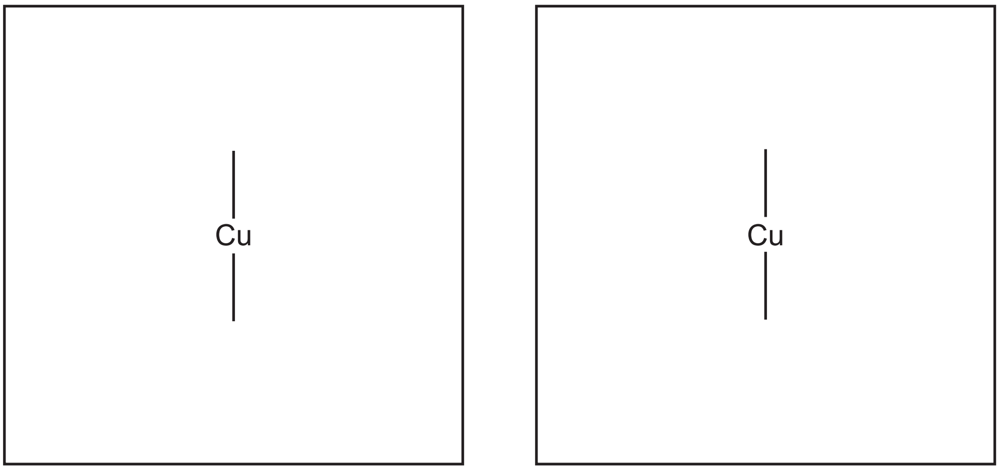


Fig. 6.3

[2]

(c) A student analyses an aromatic compound, **X**, $C_8H_8O_3$, using NMR spectroscopy.

Fig. 6.4 shows the carbon-13 NMR spectrum of a sample of **X** dissolved in D_2O.

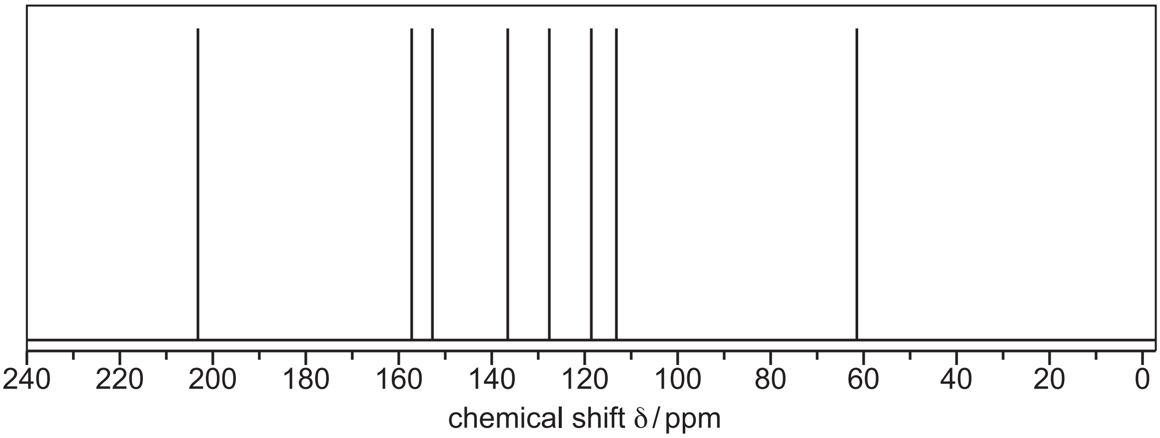


Fig. 6.4

Separate samples of **X** were analysed using proton (^1H) NMR spectroscopy.

Table 6.1 gives information obtained from this analysis.

Table 6.1

solvent	number of signals in proton (^1H) NMR spectrum
$CDCl_3$	6
D_2O	4

(i) Identify the number of different carbon environments present in **X**.

.... [1]

(ii) Explain why **X** is dissolved in D_2O before obtaining its proton (^1H) NMR spectrum.

....

.... [1]

(iii) Aromatic compound **X** gives a yellow precipitate when it reacts with alkaline I_2(aq).

Use the information in **(c)** to suggest a structure for **X**.

Explain your reasoning.

X, $C_8H_8O_3$

....

....

....

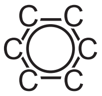
....

....

....

[4]

Table 6.2

environment of carbon atom	example	carbon-13 NMR chemical shift range δ / ppm
alkyl	$\mathbf{C}H_3$–, $\mathbf{C}H_2$–, –**C**H<, >**C**<	0–50
next to alkene/arene	–**C**–C=C, –**C**–Ar	25–50
next to carbonyl/carboxyl	**C**–COR, **C**–O_2R	30–65
next to halogen	**C**–X	30–60
next to oxygen	**C**–O	50–70
alkene or arene	>**C**=**C**<, 	110–160
carboxyl	R–**C**OOH, R–**C**OOR	160–185
carbonyl	R–**C**HO, R–**C**O–R	190–220
nitrile	R–**C**≡N	100–125

[Total: 14]

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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

Group

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
				Key			1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0			atomic number atomic symbol name relative atomic mass								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 A*l* aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 C*l* 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 T*l* 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 F*l* 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 –