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Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER

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* 3 8 7 8 8 2 4 8 1 4 *

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2024**

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.

DC (DE/CB) 326721/4

1 **(a)** Describe the trend in the solubility of the sulfates of magnesium, calcium and strontium.

Explain your answer.

.... > .... > ....
most soluble least soluble

....

....

....

....

....

.... [4]

(b) Define lattice energy, ΔH_{latt}.

....

.... [2]

(c) State and explain the main factors that affect the magnitude of lattice energies.

....

....

....

....

.... [2]

(d) Table 1.1 shows some energy changes.

Table 1.1

energy change	value / $kJ\,mol^{-1}$
standard enthalpy change of atomisation of potassium	+89
first ionisation energy of potassium	+419
second ionisation energy of potassium	+3070
standard enthalpy change of atomisation of sulfur	+279
S–S bond energy	+265
first ionisation energy of sulfur	+1000
second ionisation energy of sulfur	+2260
first electron affinity of sulfur	–200
second electron affinity of sulfur	+640
standard enthalpy change of formation of potassium sulfide, $K_2S(s)$	–381

(i) Born–Haber cycles can be used to determine the lattice energies of ionic compounds.

Complete the Born–Haber cycle in Fig. 1.1 for potassium sulfide, $K_2S(s)$.

Include state symbols for all of the species.

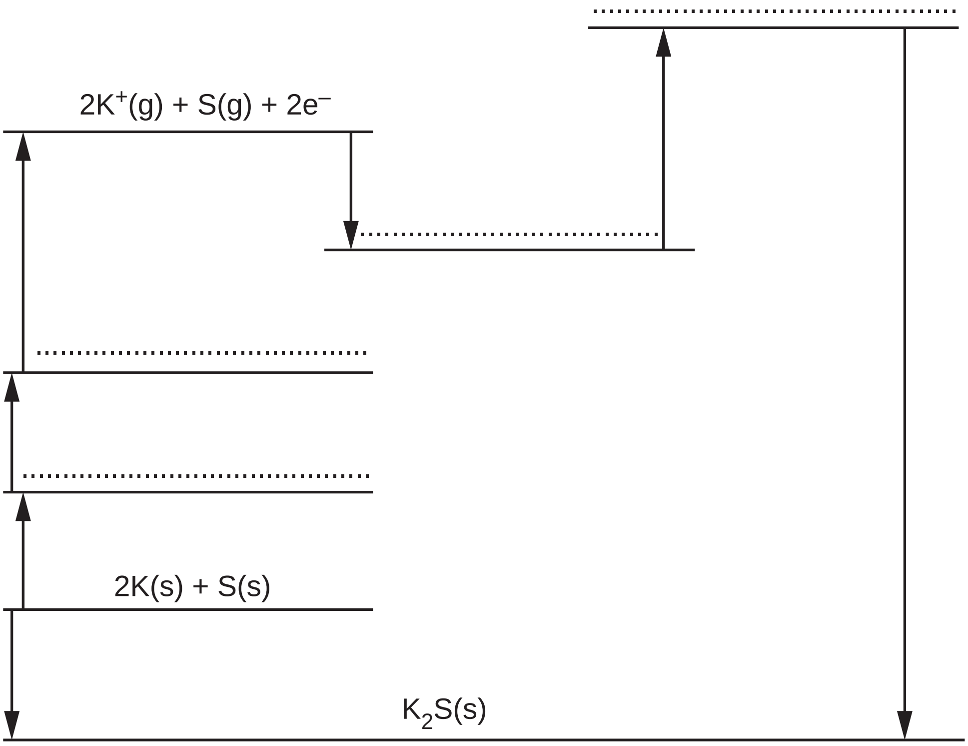

Fig. 1.1

[3]

(ii) Calculate the lattice energy, $\Delta H^{\ominus}_{latt}$, of $K_2S(s)$ using relevant data from Table 1.1.

Show your working.

$\Delta H^{\ominus}_{latt}$ of $K_2S(s)$ = ... $kJ\,mol^{-1}$ [2]

[Total: 13]

2 **(a)** **(i)** Lithium nitrate, $LiNO_3$, decomposes on heating in a similar way to Group 2 nitrates to give the metal oxide, a brown gas and oxygen.

Write an equation for the decomposition of $LiNO_3$.

.... [1]

(ii) The other Group 1 nitrates, MNO_3, decompose on heating to form the metal nitrite, MNO_2, and oxygen.

The thermal stability of these nitrates increases down the group.

Suggest why the thermal stability of MNO_3 increases down the group.

....

....

.... [2]

(b) Acidified manganate(VII) ions, MnO_4^-, can be used to analyse solutions containing nitrite ions, NO_2^-, by titration.

X is a solution of $NaNO_2$.

250.0 cm^3 of **X** is added to 50.0 cm^3 of 0.125 mol dm^{-3} acidified $MnO_4^-(aq)$. The $MnO_4^-(aq)$ ions are in excess; all the NO_2^- ions are oxidised in the reaction.

The unreacted $MnO_4^-(aq)$ required 22.50 cm^3 of 0.0400 mol dm^{-3} $Fe^{2+}(aq)$ to reach the end-point.

The relevant half-equations are shown.

$$NO_2^- + H_2O \rightleftharpoons NO_3^- + 2H^+ + 2e^-$$
$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$
$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

Calculate the concentration, in mol dm^{-3}, of $NaNO_2$ in **X**.

concentration of $NaNO_2$ in **X** = ... mol dm^{-3} [3]

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(c) Table 2.1 shows electrode potentials for some electrode reactions involving manganese compounds.

Table 2.1

electrode reaction	$E^{\ominus}$/V
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	–1.18
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$	+0.56
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$	+1.67
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$MnO_4^- + 2H_2O + 3e^- \rightleftharpoons MnO_2 + 4OH^-$	+0.59
$MnO_4^{2-} + 2H_2O + 2e^- \rightleftharpoons MnO_2 + 4OH^-$	+0.60
$MnO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons MnO_2 + 2H_2O$	+1.70

(i) Aqueous manganate(VI) ions, MnO_4^{2-}, are unstable in acidic conditions and undergo a disproportionation reaction.

The $E^{\ominus}_{cell}$ for this reaction is +1.14 V.

Construct an overall ionic equation for this disproportionation reaction.

.... [2]

(ii) Suggest and explain how the E_{cell} value of the disproportionation reaction changes with an increase in pH.

....

....

.... [1]

[Total: 9]

3 **(a)** Carbon disulfide, CS_2, is flammable and reacts readily with oxygen, as shown in reaction 1.

reaction 1 $CS_2(g) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$

Table 3.1 shows the standard enthalpy of formation, $\Delta H_f^{\ominus}$, and the standard entropy, $S^{\ominus}$, for some substances.

Table 3.1

	$CS_2(g)$	$O_2(g)$	$CO_2(g)$	$SO_2(g)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	116.7	0.0	–393.5	–296.8
$S^{\ominus}$ / J K^{-1} mol^{-1}	237.8	205.2	213.8	248.2

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) Carbon disulfide reacts with chlorine to form tetrachloromethane, as shown in reaction 2.

reaction 2 $CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$ $\Delta H^{\ominus} = -261.6$ kJ mol^{-1}

$\Delta S^{\ominus} = -365.5$ J K^{-1} mol^{-1}

Calculate the maximum temperature, in K, for reaction 2 to be feasible.

temperature = ... K [2]

[Total: 5]

4 **(a)** **(i)** Explain why transition elements have variable oxidation states.

....

.... [1]

(ii) Sketch the shape of a $3d_{z^2}$ orbital in Fig. 4.1.

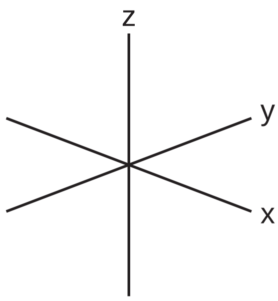

Fig. 4.1

[1]

(b) Samples of $[Cu(H_2O)_6]^{2+}(aq)$ are reacted separately with an excess of solution **A** and with an excess of solution **B**.

The reaction of $[Cu(H_2O)_6]^{2+}(aq)$ with solution **A** is a precipitation reaction.

The reaction of $[Cu(H_2O)_6]^{2+}(aq)$ with solution **B** is a ligand substitution reaction.

Suggest a possible identity for solution **A** and for solution **B**. Give relevant observations and the formula of the copper-containing product for each reaction.

solution **A** ....

observations ....

formula of the copper-containing product ....

solution **B** ....

observations ....

formula of the copper-containing product ....

[3]

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(c) Solutions containing the $[Ag(NH_3)_2]^+$ complex are colourless.

Explain why this complex is colourless.

....

....

....

.... [2]

(d) Two bidentate ligands are shown in Fig. 4.2.

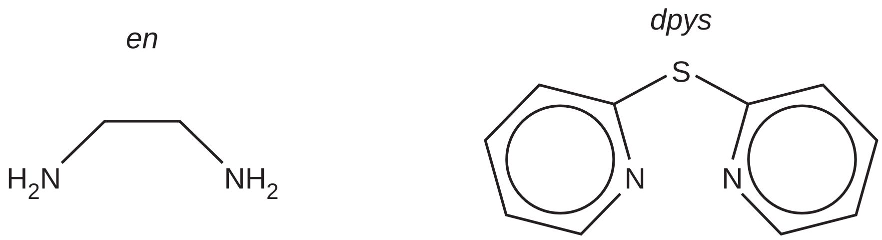


Fig. 4.2

Explain what is meant by a bidentate ligand.

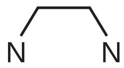
....

.... [2]

(e) Ruthenium(III) ions, Ru^{3+}, form an octahedral complex, $[Ru(\textit{dpys})_2Cl_2]^+$, with the ligands *dpys* and chloride ions.

This complex shows the same kind of stereoisomerism as $[Ru(NH_3)_4Cl_2]^+$ but also shows a different type of stereoisomerism.

(i) Complete the three-dimensional diagrams in Fig. 4.3 to show the **three** different stereoisomers of $[Ru(\textit{dpys})_2Cl_2]^+$.

The *dpys* ligand can be represented using .

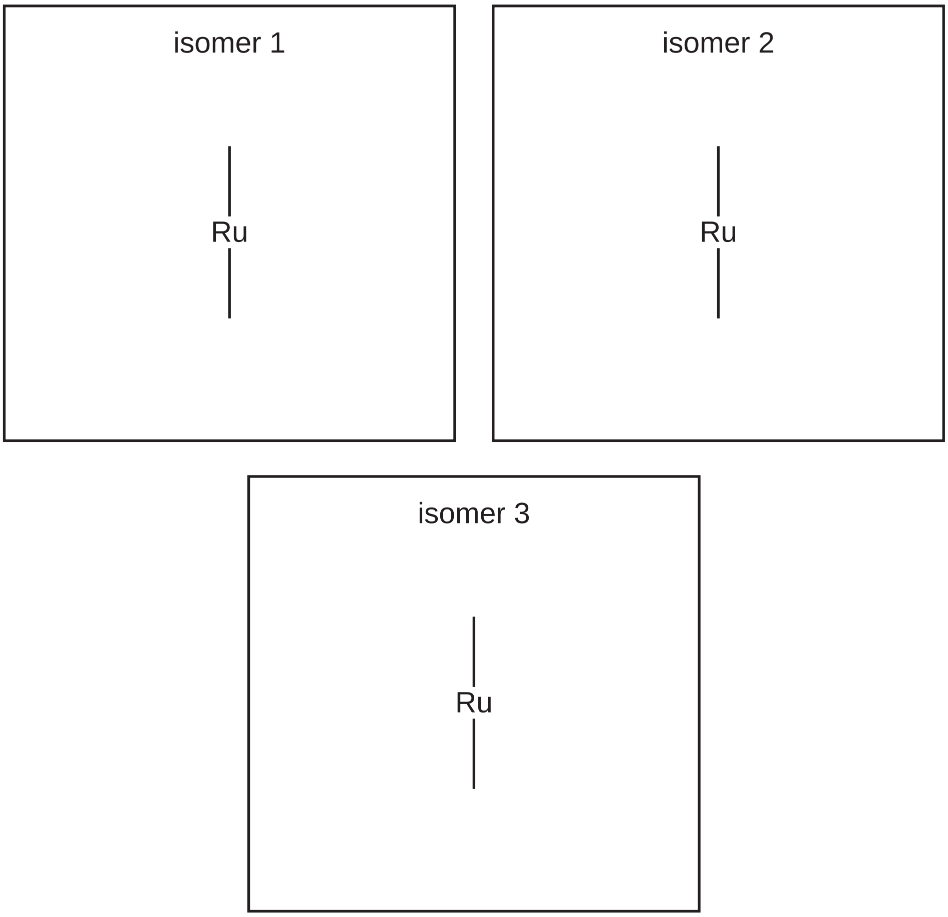


Fig. 4.3

[3]

(ii) State the different types of stereoisomerism shown by $[Ru(\textit{dpys})_2Cl_2]^+$.

.... [1]

(iii) Deduce which stereoisomers in **(e)(i)** are **non-polar**. Explain your answer.

....

.... [1]

[Total: 14]

5 **(a)** Nitrosyl chloride, NOCl, can be formed by the reaction between nitrogen monoxide and chlorine, as shown.

$$2NO + Cl_2 \rightarrow 2NOCl$$

The initial rate of this reaction is investigated, starting with different concentrations of NO and Cl_2. The results obtained are shown in Table 5.1.

Table 5.1

experiment	[NO] / mol dm^{-3}	[Cl_2] / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
1	0.0250	0.0150	3.68×10^{-2}
2	0.0750	0.0150	3.32×10^{-1}
3	0.0500	0.0600	5.89×10^{-1}

(i) Use the data in Table 5.1 to deduce the rate equation for this reaction.

Explain your reasoning.

....

....

....

....

....

.... [3]

(ii) Use your rate equation from **(a)(i)** and the data from experiment 1 to calculate the rate constant, *k*, for this reaction. Include the units of *k*.

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

(b) NO_2Cl is another compound containing nitrogen, oxygen and chlorine.

In sunlight, NO_2Cl can undergo homolytic fission to release chlorine radicals which can catalyse the conversion of ozone, O_3, into oxygen.

Complete the mechanism for this process.

initiation (homolytic fission) NO_2Cl → .... + ...

propagation step 1 .... + O_3 → .... + ...

propagation step 2 .... + ... → .... + ...

[2]

(c) Ozone reacts with nitrogen dioxide, as shown.

$$O_3 + 2NO_2 \rightarrow N_2O_5 + O_2$$

The rate of reaction is first order with respect to O_3 and first order with respect to NO_2.

Suggest equations for a two-step mechanism for this reaction.

step 1 ....

step 2 ....

[2]

[Total: 9]

6 **(a)** Aqueous solutions of methanoic acid, HCOOH, and propanoic acid, CH_3CH_2COOH, are mixed together.

An equilibrium is set up between two conjugate acid–base pairs.

(i) Define conjugate acid–base pair.

....

.... [1]

(ii) The pK_a of HCOOH is 3.75 and of CH_3CH_2COOH is 4.87.

Complete the equation for the Brønsted–Lowry equilibrium between the stronger of these two acids and water.

.... + H_2O $\rightleftharpoons$ .... + ...
[1]

(b) **(i)** Write an expression for the acid dissociation constant, K_a, for butanoic acid, $CH_3CH_2CH_2COOH$.

K_a =

[1]

(ii) The pK_a of $CH_3CH_2CH_2COOH$ is 4.82.

A solution of $CH_3CH_2CH_2COOH(aq)$ has a pH of 3.25.

Calculate the concentration, in mol dm^{-3}, of $CH_3CH_2CH_2COOH$ in this solution.

concentration of $CH_3CH_2CH_2COOH$ = ... mol dm^{-3} [2]

(c) **(i)** Define buffer solution.

....

....

.... [2]

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(ii) A buffer solution containing a mixture of CH_3COOH and CH_3COONa is prepared as follows.

A solution of 600 cm^3 of CH_3COOH is mixed with 400 cm^3 of 0.125 mol dm^{-3} CH_3COONa.

The buffer solution has pH 5.70. The K_a of CH_3COOH is 1.78×10^{-5} mol dm^{-3}.

Calculate the initial concentration, in mol dm^{-3}, of CH_3COOH used.

concentration of CH_3COOH = ... mol dm^{-3} [3]

(d) A fuel cell is an electrochemical cell that can be used to generate electrical energy by using oxygen to oxidise a fuel.

Methanoic acid, HCOOH, is being investigated as a fuel in fuel cells.

When the cell operates, HCOOH is oxidised to carbon dioxide.

The half-equation for the reaction at the cathode is: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$.

In this fuel cell, the overall cell reaction is the same as that for the complete combustion of HCOOH.

(i) Deduce the half-equation for the reaction at the anode.

.... [1]

(ii) Calculate the volume, in cm^3, of oxygen used when a current of 3.75 A is delivered by the cell for 40.0 minutes. Assume the cell operates at room conditions.

volume of oxygen = ... cm^3 [2]

[Total: 13]

7 Methyl red can be synthesised as shown in Fig. 7.1.

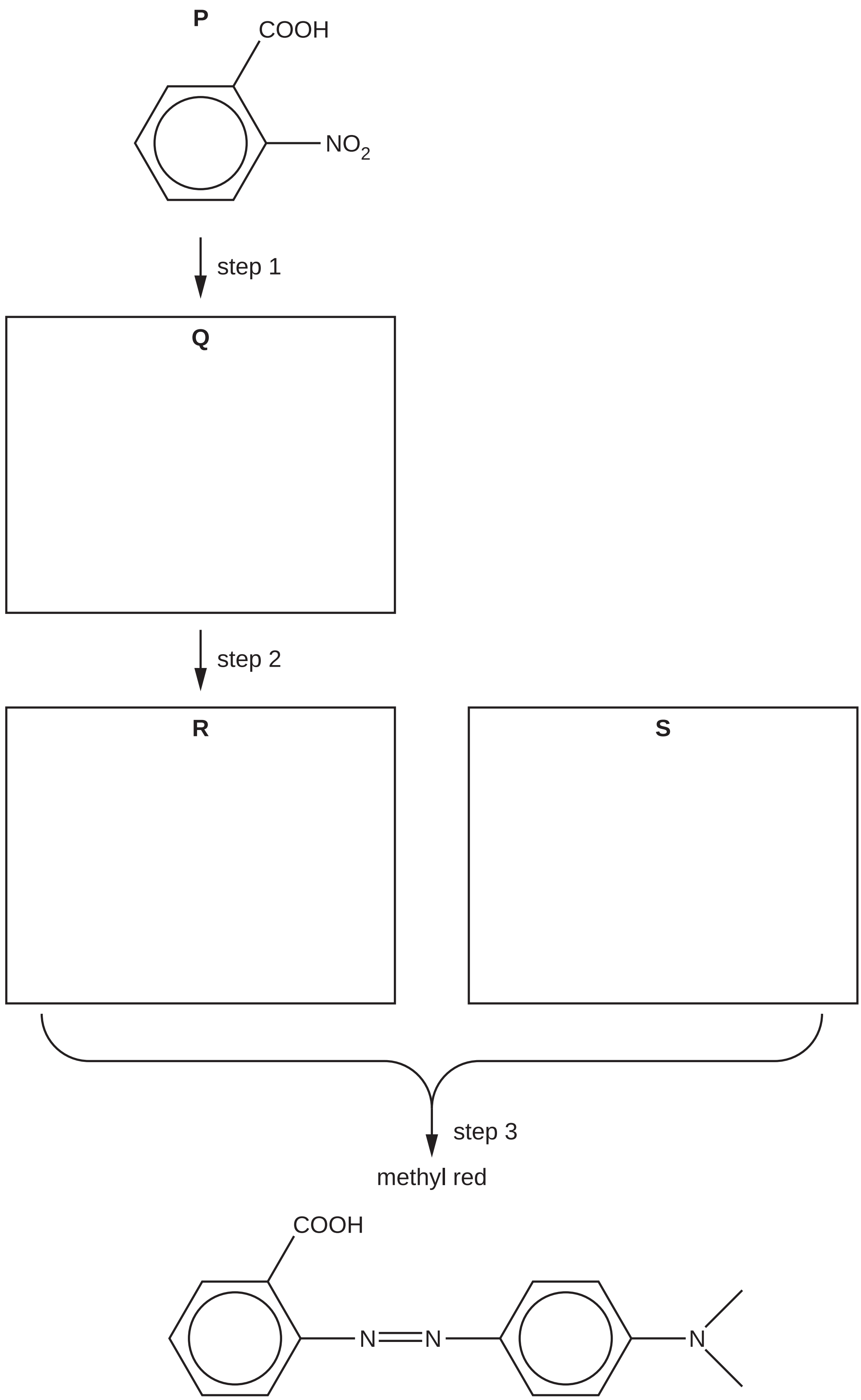

Fig. 7.1

(a) (i) Give the systematic name of **P**.

.... [1]

(ii) **P** can be synthesised as shown in Fig. 7.2.

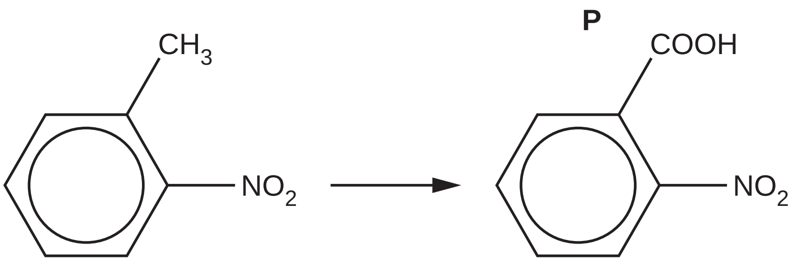

Fig. 7.2

Suggest reagents and conditions for this reaction.

.... [1]

(iii) A student attempts to synthesise **P** by an alternative route, as shown in Fig. 7.3.

Compound **T** is the major product in this reaction rather than **P**.

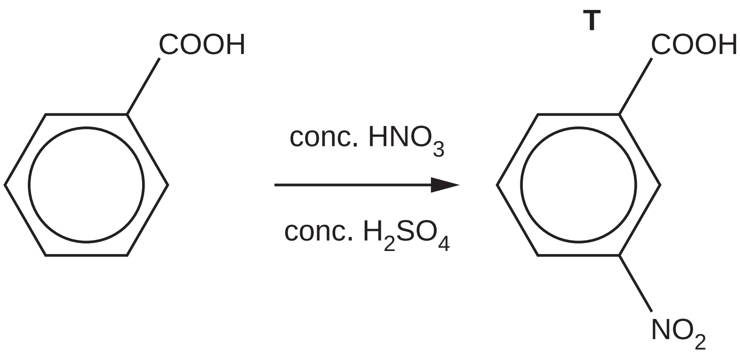

Fig. 7.3

Explain why **T** is the major product in this reaction.

....

.... [1]

(b) **S** reacts in a similar way to phenol in step 3.

(i) Draw the structures of **Q**, **R** and **S** in the boxes in Fig. 7.1. [3]

(ii) Suggest reagents and conditions for steps 1 and 2 in Fig. 7.1.

step 1 ....

step 2 ....

[3]

[Total: 9]

8 **(a)** State the relative basicities of phenylamine, $C_6H_5NH_2$, benzylamine, $C_6H_5CH_2NH_2$, and ammonia, NH_3, in aqueous solution. Explain your answer.

.... > .... > ....
most basic least basic

....

....

....

....

....
[3]

(b) An excess of Br_2(aq) is added to separate samples of $C_6H_5NH_2$ and benzene, C_6H_6.

(i) $C_6H_5NH_2$ reacts readily with Br_2(aq) to form organic product **M**.

State the expected observations for this reaction. Draw the structure of **M**.

observations ....

structure of **M**

[2]

(ii) C_6H_6 does **not** react with Br_2(aq).

Suggest why Br_2(aq) reacts with $C_6H_5NH_2$ but **not** with C_6H_6.

....

....

.... [2]

(c) Explain why benzamide, $C_6H_5CONH_2$, is a much weaker base than ammonia, NH_3.

....

.... [1]

(d) $C_6H_5CONH_2$ is formed by reacting benzoyl chloride, C_6H_5COCl, with NH_3.

Complete the mechanism in Fig. 8.1 for the reaction of C_6H_5COCl with NH_3.

Include all relevant lone pairs of electrons, curly arrows, charges and dipoles. Draw the structure of the organic intermediate.

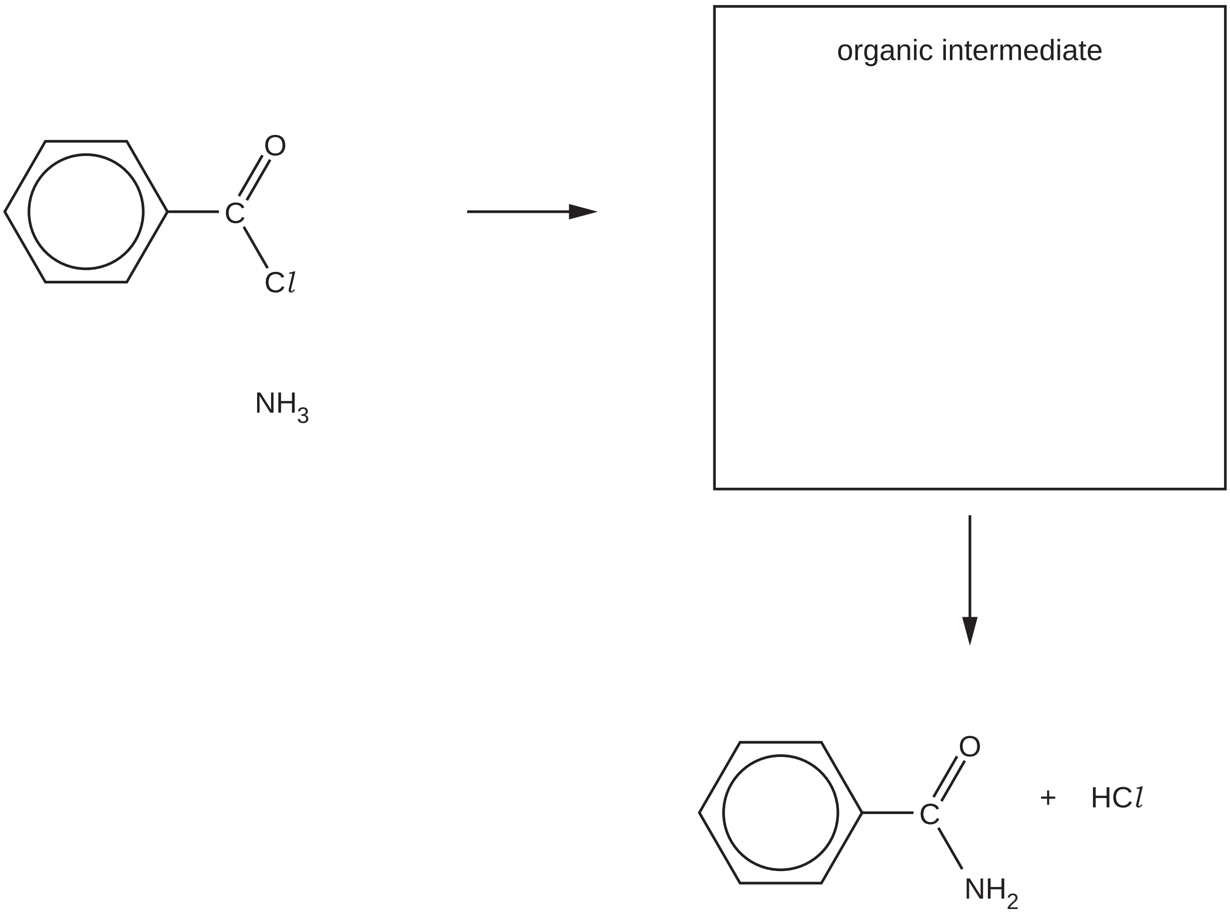

Fig. 8.1

[4]

(e) Phenylalanine, $C_6H_5CH_2CH(NH_2)COOH$, is an amino acid with an isoelectric point of 5.5.

(i) State what is meant by isoelectric point.

....

.... [1]

(ii) Draw the structure of $C_6H_5CH_2CH(NH_2)COOH$ at pH 10.

[1]

(f) $C_6H_5CH_2CH(NH_2)COOH$ and alanine, $CH_3CH(NH_2)COOH$, react to form a dipeptide containing both amino acid residues.

Draw the structure of this dipeptide.

The peptide functional group formed should be displayed.

[2]

[Total: 16]

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9 **(a)** Explain why trichloroethanoic acid, CCl_3COOH, is more acidic than ethanoic acid, CH_3COOH.

....

....

.... [1]

(b) Acyl chlorides are formed by reacting carboxylic acids with thionyl chloride, $SOCl_2$.

(i) Ethanedioyl chloride, $(COCl)_2$, can be prepared by reacting ethanedioic acid, $(COOH)_2$, with an excess of $SOCl_2$.

Write an equation for this reaction.

.... [1]

(ii) Samples of $(COCl)_2$ are reacted separately with an excess of warm acidified $KMnO_4$(aq) and with $H_2NCH_2CH_2NH_2$.

The carbon-containing product from the reaction with $H_2NCH_2CH_2NH_2$ has the molecular formula $C_4H_6N_2O_2$.

Complete the boxes in Fig. 9.1 to suggest the structure of the carbon-containing product in each reaction.

with warm acidified $KMnO_4$(aq)	with $H_2NCH_2CH_2NH_2$

Fig. 9.1

[2]

(iii) A polyester can be synthesised from the reaction of $(COCl)_2$ with ethane-1,2-diol, $HOCH_2CH_2OH$.

Draw **two** repeat units of the polymer formed. Any functional groups should be displayed.

[2]

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(c) Compound **H**, $C_6H_{10}O_3$, reacts with alkaline I_2(aq) to form yellow precipitate **J** but does **not** react with Na_2CO_3(aq).

The proton (^{1}H) NMR spectrum of **H** in $CDCl_3$ is shown in Fig. 9.2.

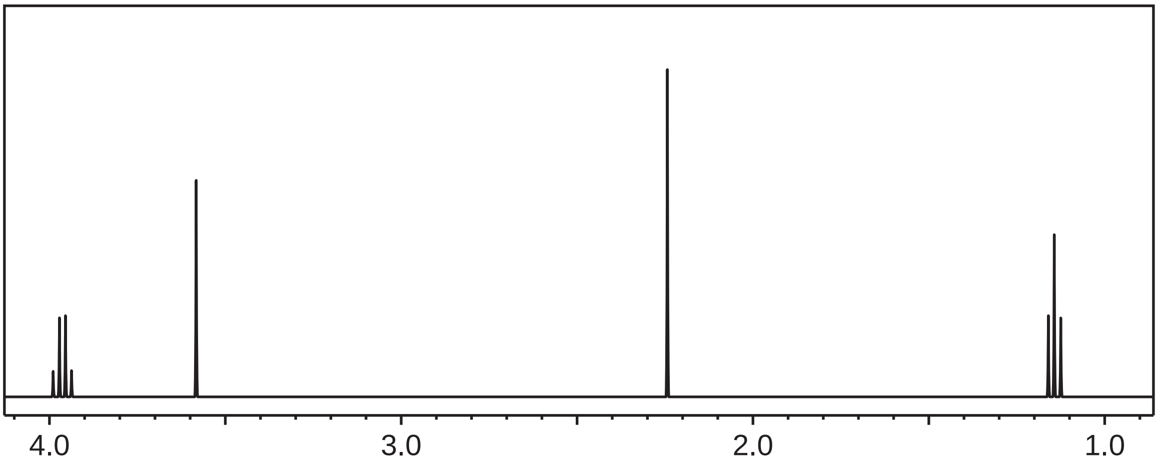

Fig. 9.2

Table 9.1

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**$_2$–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

(i) Identify yellow precipitate **J**.

.... [1]

(ii) Complete Table 9.2 for the proton (^1H) NMR spectrum of **H**, $C_6H_{10}O_3$.

Table 9.2

chemical shift δ / ppm	splitting pattern	number of ^1H atoms responsible for the peak	number of protons on adjacent carbon atoms
1.15			
2.25			
3.60			
3.95			

[4]

(iii) Suggest a structure for **H**, $C_6H_{10}O_3$.

[1]

[Total: 12]

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Important values, constants and standards

molar gas constant	$R = 8.31\,J\,K^{-1}\,mol^{-1}$
Faraday constant	$F = 9.65 \times 10^{4}\,C\,mol^{-1}$
Avogadro constant	$L = 6.022 \times 10^{23}\,mol^{-1}$
electronic charge	$e = -1.60 \times 10^{-19}\,C$
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	$K_w = 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$ (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 144.2	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 –