



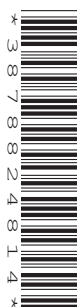
Cambridge International AS & A Level

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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.

Explain your answer.

..... > >

most soluble least soluble

.....

.....

.....

.....

.....

.....

[4

[2]

[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 ₂ S(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.

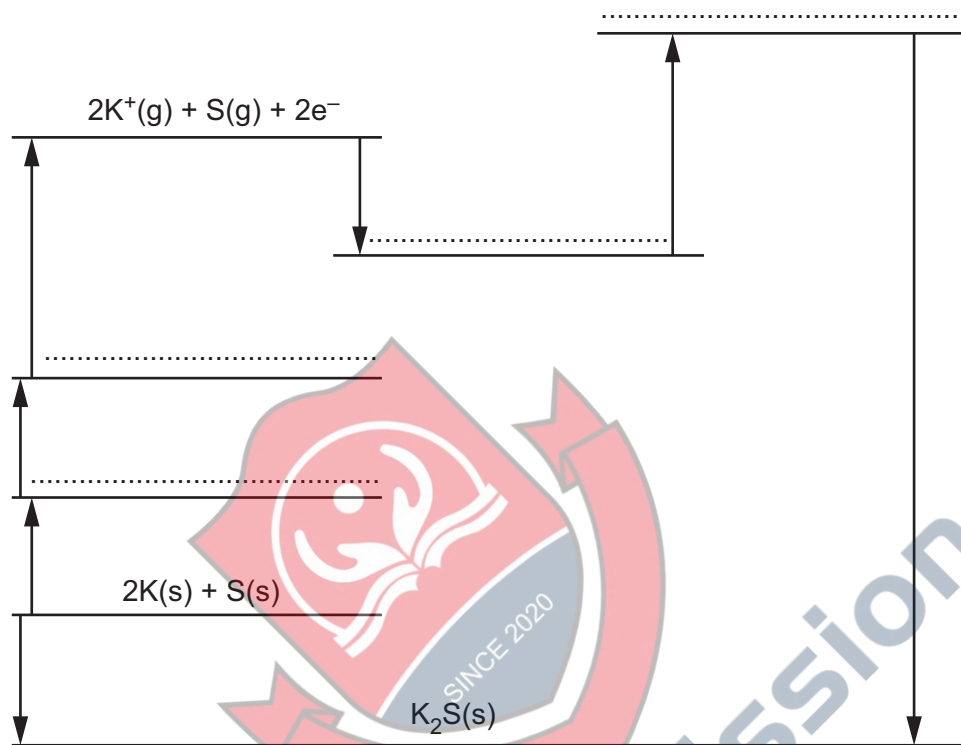


Fig. 1.1

[3]

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

Show your working.

$$\Delta H_{\text{latt}}^{\ominus} \text{ of } K_2S(s) = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

[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]

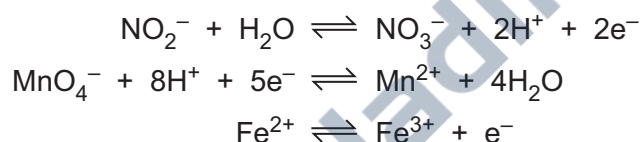
- (b) Acidified manganate(VII) ions, MnO_4^- , can be used to analyse solutions containing nitrite ions, NO_2^- , by titration.

X is a solution of NaNO_2 .

250.0 cm³ of **X** is added to 50.0 cm³ 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 cm³ of 0.0400 mol dm⁻³ Fe^{2+} (aq) to reach the end-point.

The relevant half-equations are shown.



Calculate the concentration, in mol dm⁻³, of NaNO_2 in **X**.

concentration of NaNO_2 in **X** = mol dm⁻³ [3]



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

Table 2.1

electrode reaction	$E^\ominus/V$
$\text{Mn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mn}$	-1.18
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$\text{MnO}_4^- + \text{e}^- \rightleftharpoons \text{MnO}_4^{2-}$	+0.56
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$	+1.67
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.52
$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 4\text{OH}^-$	+0.59
$\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{MnO}_2 + 4\text{OH}^-$	+0.60
$\text{MnO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$	+1.70

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

The $E^\ominus_{\text{cell}}$ 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.

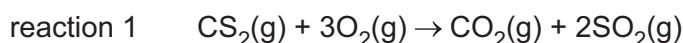


Table 3.1 shows the standard enthalpy of formation, $\Delta H_f^\ominus$, and the standard entropy, $S^\ominus$, for some substances.

Table 3.1

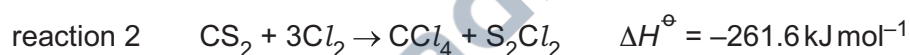
	$\text{CS}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{CO}_2(\text{g})$	$\text{SO}_2(\text{g})$
$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	116.7	0.0	-393.5	-296.8
$S^\ominus / \text{JK}^{-1} \text{mol}^{-1}$	237.8	205.2	213.8	248.2

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



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

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



$\Delta S^\ominus = -365.5 \text{ JK}^{-1} \text{mol}^{-1}$

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

temperature = $\dots\dots\dots$ 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.

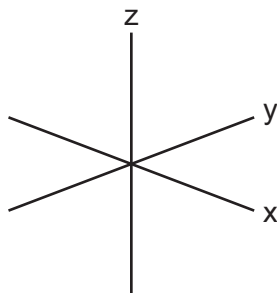


Fig. 4.1

[1]

- (b) Samples of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ are reacted separately with an excess of solution **A** and with an excess of solution **B**.

The reaction of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ with solution **A** is a precipitation reaction.

The reaction of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ 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]



- (c) Solutions containing the $[\text{Ag}(\text{NH}_3)_2]^+$ 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, $[\text{Ru}(\text{dpys})_2\text{Cl}_2]^+$, with the ligands *dpys* and chloride ions.

This complex shows the same kind of stereoisomerism as $[\text{Ru}(\text{NH}_3)_4\text{Cl}_2]^+$ 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 $[\text{Ru}(\text{dpys})_2\text{Cl}_2]^+$.

The *dpys* ligand can be represented using N  N.

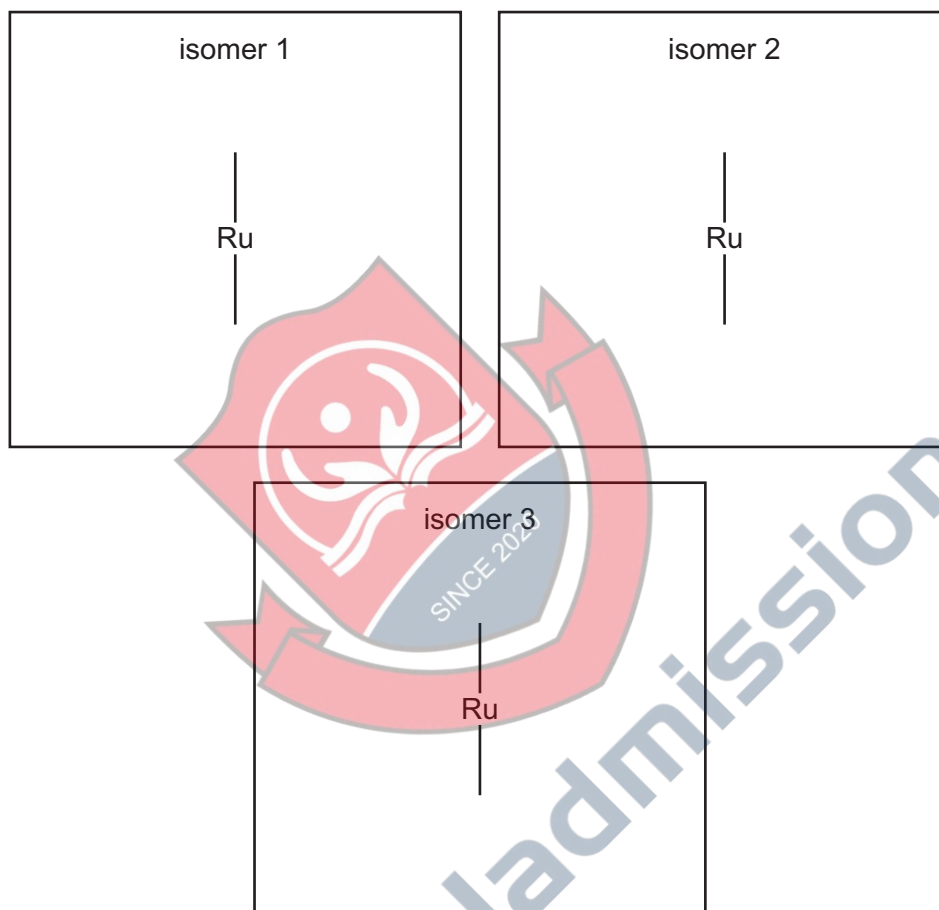


Fig. 4.3

- (ii) State the different types of stereoisomerism shown by $[\text{Ru}(\text{dpys})_2\text{Cl}_2]^+$.

[3]

..... [1]

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

.....

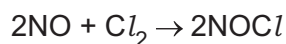
..... [1]

[Total: 14]





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



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	$[\text{NO}]/\text{mol dm}^{-3}$	$[\text{Cl}_2]/\text{mol dm}^{-3}$	initial rate/ $\text{mol dm}^{-3} \text{ min}^{-1}$
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.

.....

.....

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.....

..... [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 .

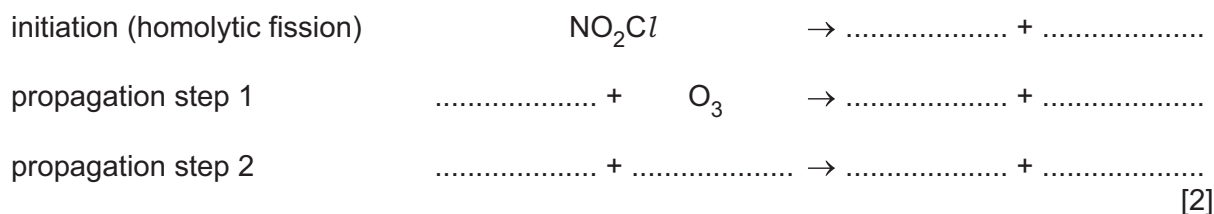
$k = \dots\dots\dots$ units $\dots\dots\dots$ [2]



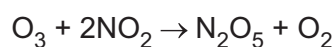
- (b) NO_2Cl is another compound containing nitrogen, oxygen and chlorine.

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.



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



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.



[Total: 9]





- 6 (a) Aqueous solutions of methanoic acid, HCOOH , and propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, are mixed together.

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

- (i) Define conjugate acid–base pair.

.....
 [1]

- (ii) The $\text{p}K_{\text{a}}$ of HCOOH is 3.75 and of $\text{CH}_3\text{CH}_2\text{COOH}$ is 4.87.

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

..... + $\text{H}_2\text{O} \rightleftharpoons$ + [1]

- (b) (i) Write an expression for the acid dissociation constant, K_{a} , for butanoic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$.

$K_{\text{a}} =$

[1]

- (ii) The $\text{p}K_{\text{a}}$ of $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ is 4.82.

A solution of $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}(\text{aq})$ has a pH of 3.25.

Calculate the concentration, in mol dm^{-3} , of $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ in this solution.

concentration of $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} =$ mol dm^{-3} [2]

- (c) (i) Define buffer solution.

.....

 [2]



- (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 $1.78 \times 10^{-5}\text{ mol dm}^{-3}$.

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: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$.

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]



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

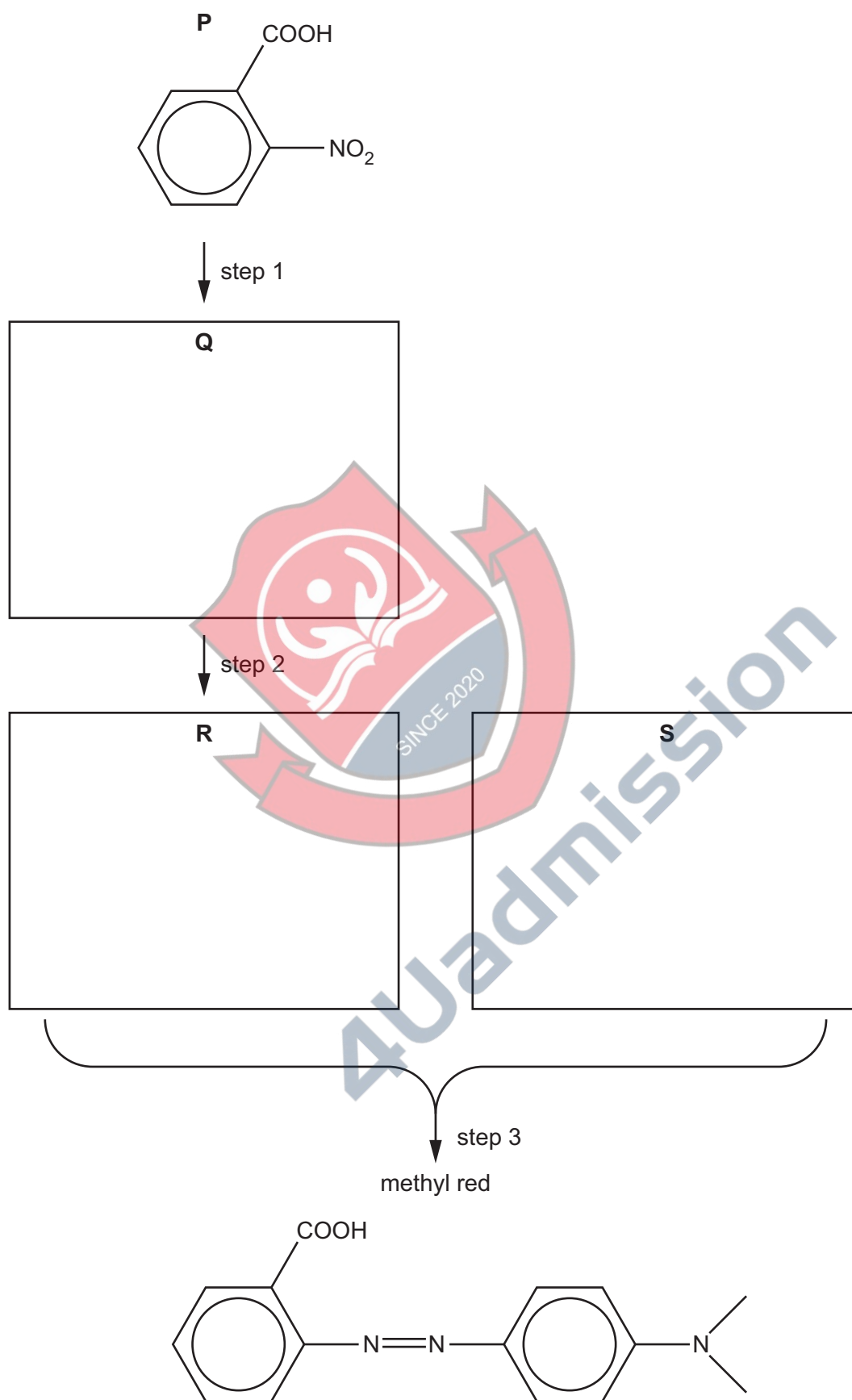


Fig. 7.1



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

..... [1]

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

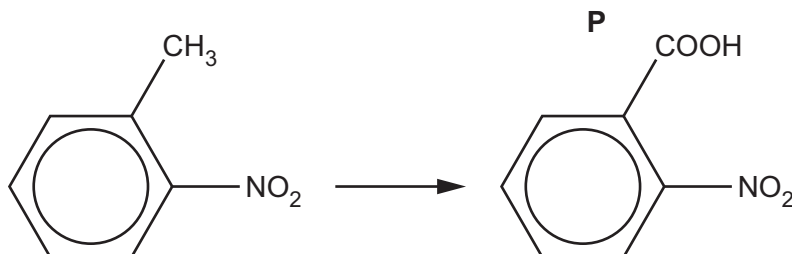


Fig. 7.2

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**.

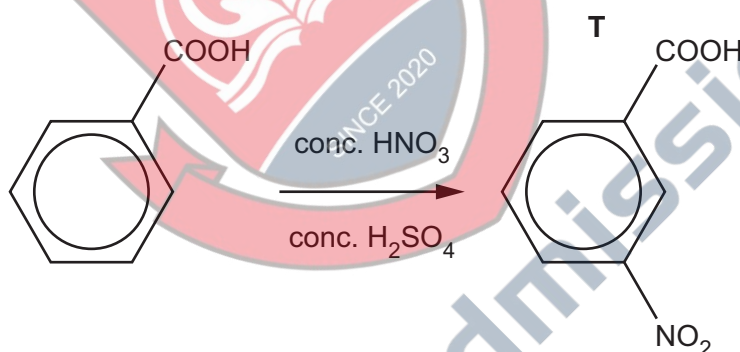


Fig. 7.3

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, $\text{C}_6\text{H}_5\text{NH}_2$, benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, and ammonia, NH_3 , in aqueous solution. Explain your answer.

..... > >
 most basic least basic

.....

.....

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.....

.....

[3]

- (b) An excess of $\text{Br}_2(\text{aq})$ is added to separate samples of $\text{C}_6\text{H}_5\text{NH}_2$ and benzene, C_6H_6 .

- (i) $\text{C}_6\text{H}_5\text{NH}_2$ reacts readily with $\text{Br}_2(\text{aq})$ 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 $\text{Br}_2(\text{aq})$.

Suggest why $\text{Br}_2(\text{aq})$ reacts with $\text{C}_6\text{H}_5\text{NH}_2$ but **not** with C_6H_6 .

.....

.....

.....

[2]

- (c) Explain why benzamide, $\text{C}_6\text{H}_5\text{CONH}_2$, is a much weaker base than ammonia, NH_3 .

.....

.....

[1]



(d) $\text{C}_6\text{H}_5\text{CONH}_2$ is formed by reacting benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$, with NH_3 .

Complete the mechanism in Fig. 8.1 for the reaction of $\text{C}_6\text{H}_5\text{COCl}$ with NH_3 .

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

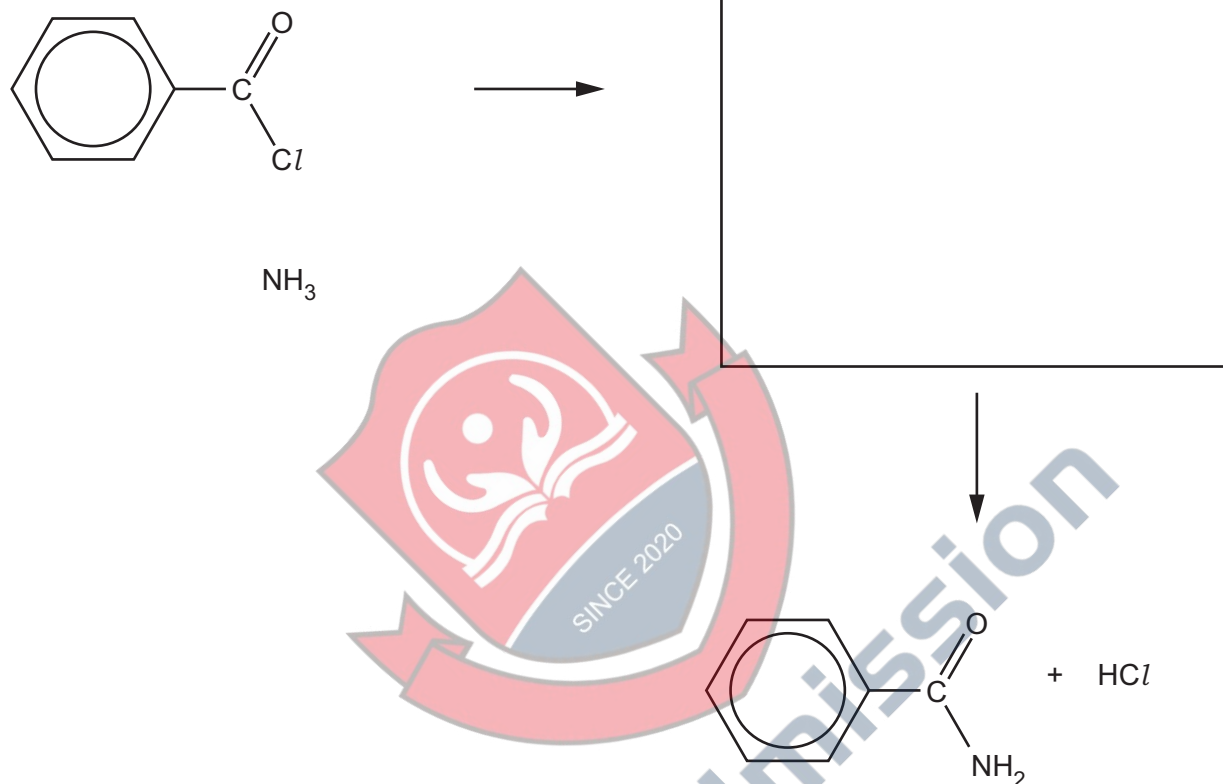


Fig. 8.1

[4]



(e) Phenylalanine, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$, 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 $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ at pH 10.

[1]

(f) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ and alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$, 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]



- 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, $(\text{COCl})_2$, can be prepared by reacting ethanedioic acid, $(\text{COOH})_2$, with an excess of SOCl_2 .

Write an equation for this reaction.

..... [1]

- (ii) Samples of $(\text{COCl})_2$ are reacted separately with an excess of warm acidified $\text{KMnO}_4(\text{aq})$ and with $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.

The carbon-containing product from the reaction with $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ has the molecular formula $\text{C}_4\text{H}_6\text{N}_2\text{O}_2$.

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

with warm acidified $\text{KMnO}_4(\text{aq})$	with $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$

Fig. 9.1

[2]

- (iii) A polyester can be synthesised from the reaction of $(\text{COCl})_2$ with ethane-1,2-diol, $\text{HOCH}_2\text{CH}_2\text{OH}$.

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

[2]



- (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 (1H) NMR spectrum of **H** in $CDCl_3$ is shown in Fig. 9.2.

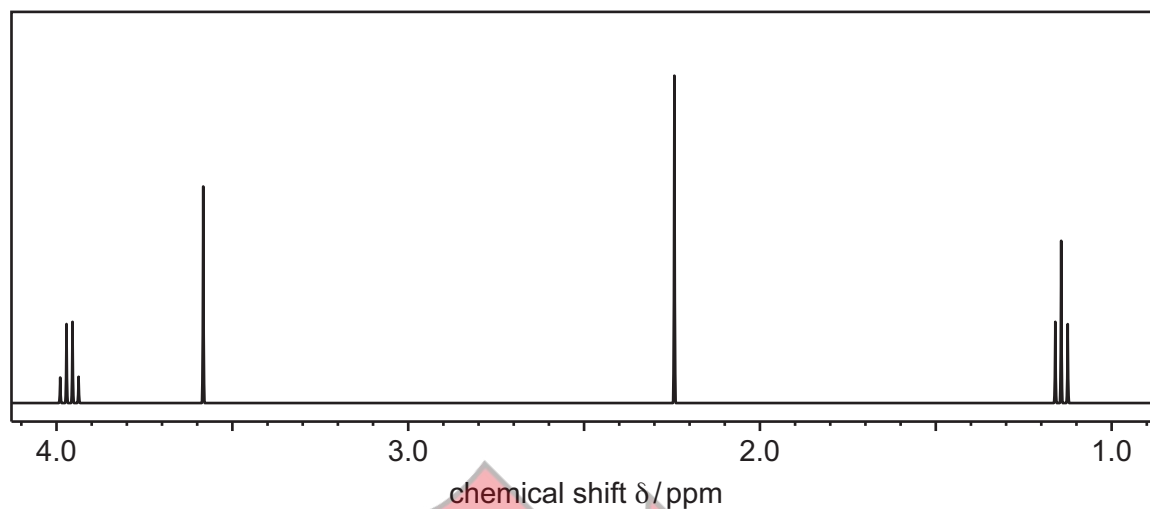


Fig. 9.2

Table 9.1

environment of proton	example	chemical shift range δ /ppm
alkane	$-CH_3$, $-CH_2-$, $>CH-$	0.9–1.7
alkyl next to $C=O$	$CH_3-C=O$, $-CH_2-C=O$, $>CH-C=O$	2.2–3.0
alkyl next to aromatic ring	CH_3-Ar , $-CH_2-Ar$, $>CH-Ar$	2.3–3.0
alkyl next to electronegative atom	CH_3-O , $-CH_2-O$, $-CH_2-Cl$	3.2–4.0
attached to alkene	$=CHR$	4.5–6.0
attached to aromatic ring	$H-Ar$	6.0–9.0
aldehyde	$HCOR$	9.3–10.5
alcohol	ROH	0.5–6.0
phenol	$Ar-OH$	4.5–7.0
carboxylic acid	$RCOOH$	9.0–13.0
alkyl amine	$R-NH-$	1.0–5.0
aryl amine	$Ar-NH_2$	3.0–6.0
amide	$RCONHR$	5.0–12.0



(i) Identify yellow precipitate J.

..... [1]

(ii) Complete Table 9.2 for the proton (^1H) NMR spectrum of H, $\text{C}_6\text{H}_{10}\text{O}_3$.

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, $\text{C}_6\text{H}_{10}\text{O}_3$.

[1]

[Total: 12]





4Uadmission

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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 J g ⁻¹ K ⁻¹)



4Uadmission





The Periodic Table of Elements

Group																		
1	2	Key										13	14	15	16	17	18	
		atomic number atomic symbol name relative atomic mass										1 H hydrogen 1.0						
3	4	3	4	5	6	7	8	9	10	11	12							
Li lithium 6.9	Be beryllium 9.0																	
11	12																	
Na sodium 23.0	Mg magnesium 24.3																	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
K potassium 39.1	Ca calcium 40.1	Sc scandium 45.0	Ti titanium 47.9	V vanadium 50.9	Cr chromium 52.0	Mn manganese 54.9	Fe iron 55.8	Co cobalt 58.9	Ni nickel 58.7	Cu copper 63.5	Zn zinc 65.4	Ga gallium 69.7	Ge germanium 72.6	As arsenic 74.9	Se selenium 79.0	Br bromine 79.9	Kr krypton 83.8	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
Rb rubidium 85.5	Sr strontium 87.6	Y yttrium 88.9	Zr zirconium 91.2	Nb niobium 92.9	Mo molybdenum 95.9	Tc technetium —	Ru ruthenium 101.1	Rh rhodium 102.9	Pd palladium 106.4	Ag silver 107.9	Cd cadmium 112.4	In indium 114.8	Sn tin 118.7	Sb antimony 121.8	Te tellurium 127.6	I iodine 126.9	Xe xenon 131.3	
55	56	57–71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
Cs caesium 132.9	Ba barium 137.3	lanthanoids	Hf hafnium 178.5	Ta tantalum 180.9	W tungsten 183.8	Re rhenium 186.2	Os osmium 190.2	Ir iridium 192.2	Pt platinum 195.1	Au gold 197.0	Hg mercury 200.6	Tl thallium 204.4	Pb lead 207.2	Bi bismuth 209.0	Po polonium —	At astatine —	Rn radon —	
87	88	89–103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	
Fr francium —	Ra radium —	actinoids	Rf rutherfordium —	Db dubnium —	Sg seaborgium —	Bh bohrium —	Hs hassium —	Mt meitnerium —	Ds darmstadtium —	Rg roentgenium —	Cn copernicium —	Nh nihonium —	Fl flerovium —	Mc moscovium —	Lv livermorium —	Ts tennessine —	Og oganesson —	

lanthanoids

actinoids

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
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 —

