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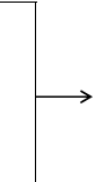
**9729/01**

**16 September 2024**

**1 hour**

Additional Materials: Multiple Choice Answer Sheet  
Data Booklet

Complete the information on the Answer Sheet as shown below.

1. Enter your **NAME** (as in NRIC). \_\_\_\_\_
2. Enter the **PAPER NUMBER**. \_\_\_\_\_
3. Enter your **CT GROUP**. \_\_\_\_\_
4. Enter your **NRIC NUMBER** or **FIN Number** 
5. Now **SHADE** the corresponding circles in the grid for **EACH DIGIT** or **LETTER**

[illegible]

NRIC / FIN										
(S)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(A)	(K)	(U)
(F)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(B)	(L)	(V)
(G)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(C)	(M)	(W)
(T)	(3)	(3)	(3)	(3)	(3)	(3)	(3)	(D)	(N)	(X)

The use of an approved scientific calculator is expected, where appropriate.

- 1 Heavy water is a form of water whose hydrogen atoms are all replaced by deuterium ( $^2\text{H}$ ), and is used in nuclear reactors.

What are the numbers of electrons and neutrons in  $\text{D}_3\text{O}^+$ ?

	electrons	neutrons
<b>A</b>	10	11
<b>B</b>	11	11
<b>C</b>	10	8
<b>D</b>	11	8

- 2 Which species has two unpaired electrons?

**A**  $\text{Li}^+$                       **B**  $\text{Ti}^+$                       **C**  $\text{Mg}$                       **D**  $\text{S}$

- 3 The Valence Shell Electron Pair Repulsion theory (VSEPR) is used to predict the bond angles of molecules.

Which bond angle is correctly predicted by VSEPR?

	number of bonded electron pairs around central atom	number of lone pairs around central atom	bond angle
<b>A</b>	2	1	$105^\circ$
<b>B</b>	2	2	$118^\circ$
<b>C</b>	3	1	$107^\circ$
<b>D</b>	3	2	$90^\circ$

- 4 *Use of the Data Booklet is relevant to this question.*

Some information about the carbonate ion,  $\text{CO}_3^{2-}$ , is given.

- all carbon-oxygen bonds are of the same length
- $\pi$  electrons are delocalised throughout the structure

What is the likely carbon-oxygen bond energy, in  $\text{kJ mol}^{-1}$ , in the carbonate ion?

**A** 360                                      **B** 485  
**C** 740                                      **D** 805

- 5 Which bonding type corresponds to its description of physical properties?

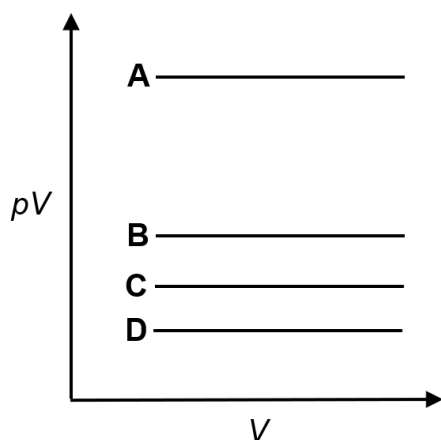
	bonding type	physical properties
1	giant covalent	high melting point, conducts electricity when in solution but not when solid
2	simple covalent	low melting point, does not conduct electricity in any state
3	metallic	variety of melting points, conducts electricity when solid and when molten
4	ionic	low melting point, conducts electricity in any state

- A** 1 and 2 only    **B** 3 and 4 only    **C** 2 and 3 only    **D** 1 and 4 only

- 6 The volumes and pressures of equal masses of four gases, nitrogen, methane, chlorine and helium, are separately investigated, at constant temperature.

The results are plotted on a graph of  $pV$  against  $V$ . All four gases behave as ideal gases under the conditions chosen.

Which plot shows the results for methane?



- 7 When a sample of a gas is compressed at constant temperature from 15 atm to 60 atm, its volume changes from 76 cm<sup>3</sup> to 20.5 cm<sup>3</sup>.

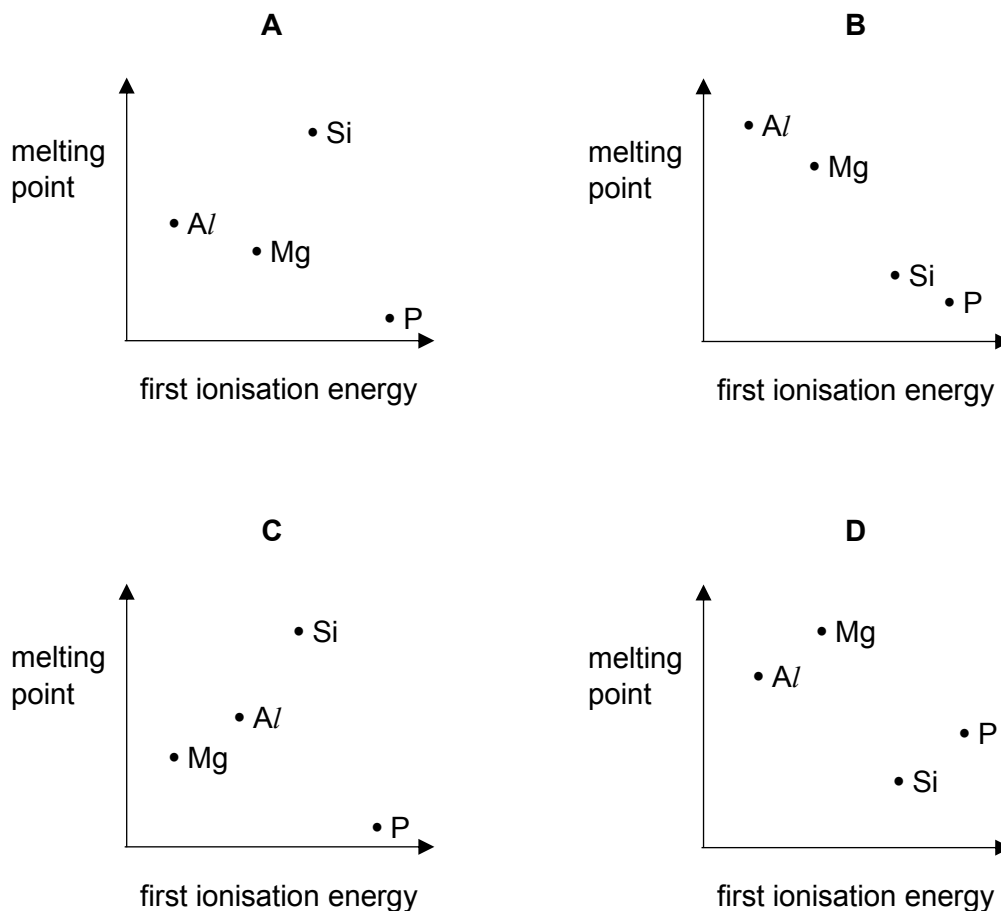
Which statements are possible explanations for this observation?

- 1 The gas behaves non-ideally.
- 2 Some of the gas dimerises.
- 3 There are significant intermolecular forces of attraction between the gas molecules.

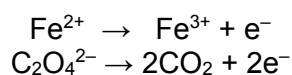
- A** 1 only    **B** 1 and 2 only    **C** 1 and 3 only    **D** 2 only

- 8 Use of the Data Booklet is relevant to this question.

Which diagram shows the correct trends when the melting points of the elements Mg, Al, Si and P are plotted against their first ionisation energies?



- 9 Consider the following half equations:



In an experiment, 20 cm<sup>3</sup> of an acidified solution of 0.020 mol dm<sup>-3</sup> of FeC<sub>2</sub>O<sub>4</sub> is oxidised by 15 cm<sup>3</sup> of 0.020 mol dm<sup>-3</sup> KMnO<sub>4</sub>.

What is the final oxidation state of manganese, given that both Fe<sup>2+</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup> can be oxidised by KMnO<sub>4</sub>?

- A** +1                      **B** +2                      **C** +3                      **D** +4

**10** Given 1.0 g samples of the same mixture of magnesium carbonate and barium carbonate, which method allows one to determine the mole fraction of magnesium carbonate in the mixture?

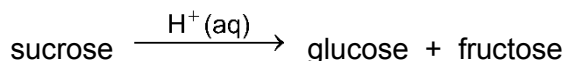
- 1 Add a known volume of  $0.1 \text{ mol dm}^{-3} \text{ HCl(aq)}$ , in excess, and back titrate the excess of acid.
- 2 Add an excess of  $\text{HCl(aq)}$  and measure, at known temperature and pressure, the volume of  $\text{CO}_2$  liberated.
- 3 Add an excess of  $\text{HCl(aq)}$  followed by an excess of  $\text{H}_2\text{SO}_4\text{(aq)}$ ; filter, dry and weigh the precipitate.

- |                       |                       |
|-----------------------|-----------------------|
| <b>A</b> 3 only       | <b>B</b> 1 and 2 only |
| <b>C</b> 2 and 3 only | <b>D</b> 1, 2 and 3   |

**11** Which enthalpy change is always exothermic?

- A** lattice energy
- B** bond breaking
- C** ionisation energy
- D** electron affinity

**12** The hydrolysis of sucrose in aqueous solution is catalysed by  $\text{H}^+\text{(aq)}$  ions, for example, from hydrochloric acid.

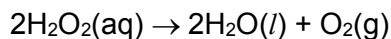


Which procedure can be used to determine the order of reaction with respect to  $\text{H}^+\text{(aq)}$  ions?

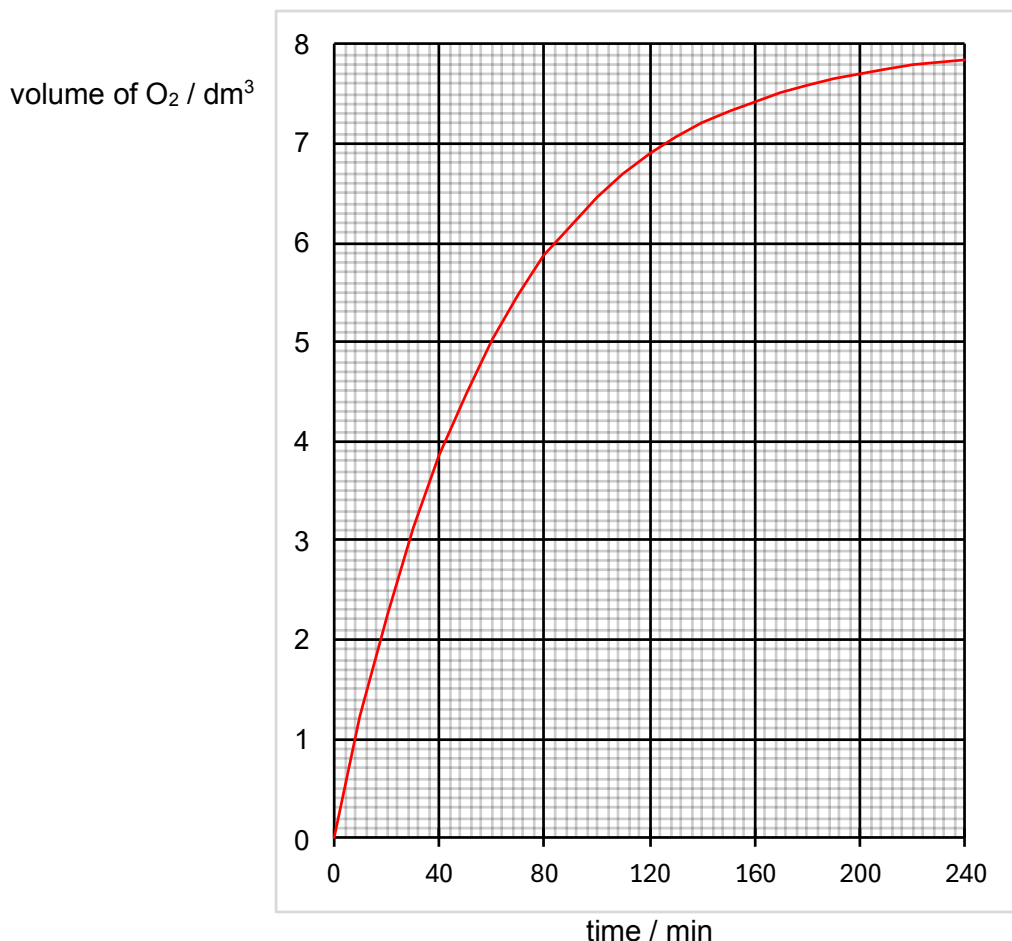
- A** Measure the change in pH during the reaction.
- B** Remove samples at various time intervals, quench using excess water, then titrate against a standard solution of sodium hydroxide.
- C** Add a suitable acid-base indicator and watch for the time when the colour changes.
- D** Measure the time taken for a fixed amount of sucrose to be consumed in the presence of different concentrations of hydrochloric acid each time.

**13** Use of the Data Booklet is relevant to this question.

Hydrogen peroxide solution decomposes. The equation for this reaction is shown.



A  $280\text{ cm}^3$  sample of  $2.38\text{ mol dm}^{-3}$  hydrogen peroxide solution is warmed. The volume of oxygen gas collected over time, measured at r.t.p., is recorded in the graph below.



Which statements are correct?

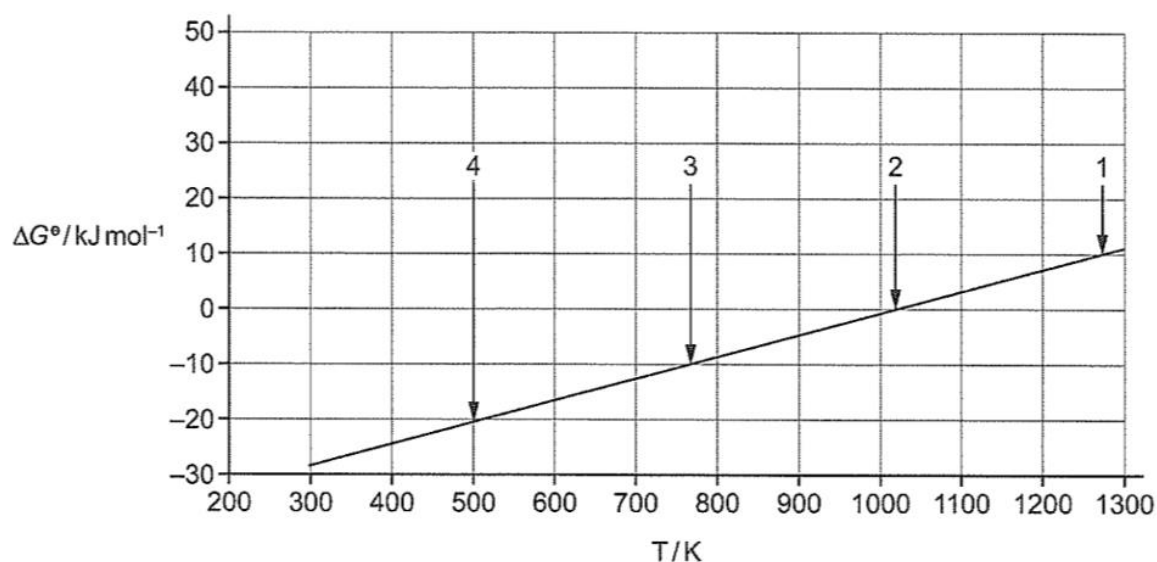
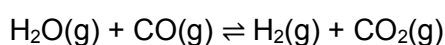
- 1 The total volume of oxygen gas collected at the end of the reaction is  $8.0\text{ dm}^3$ .
- 2 The rate constant for this reaction is  $0.017\text{ min}^{-1}$ .
- 3 The half-life for the reaction will be about 20 min if initial concentration is  $1.19\text{ mol dm}^{-3}$ .

**A** 1 only      **B** 1 and 2 only      **C** 2 and 3 only      **D** 1, 2 and 3

14 Which statement about the Haber process for the manufacture of ammonia is correct?

- A At higher temperatures, the yield goes up and the rate of production of ammonia is faster.
- B At higher pressure, the yield goes up and the rate of production of ammonia is faster.
- C In the presence of a catalyst, the yield goes down but the rate of production of ammonia is faster.
- D When more nitrogen is added, the yield goes down but the rate of production of ammonia is faster.

15 The graph shows how  $\Delta G^\circ$  changes with temperature for the reaction shown.



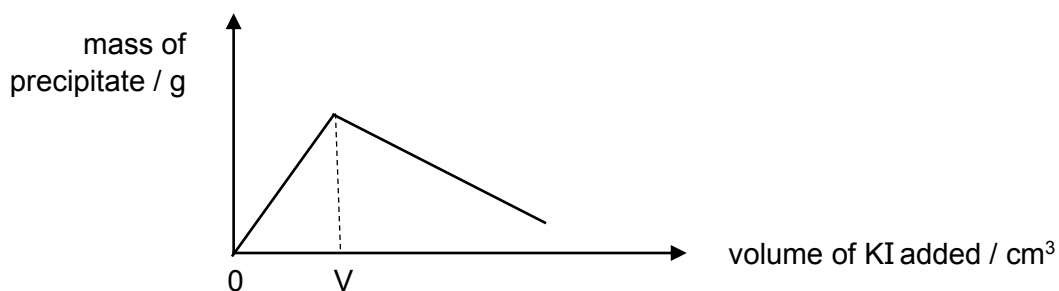
Equimolar amounts of  $\text{H}_2\text{O}$  and  $\text{CO}$  were introduced into a sealed container and allowed to reach equilibrium.

Which statement about this equilibrium is true?

- A The concentration of  $\text{CO}_2$  is greater than the concentration of  $\text{H}_2\text{O}$  at point 1.
- B The concentration of  $\text{CO}_2$  is greater than the concentration of  $\text{H}_2\text{O}$  at point 2.
- C The concentration of  $\text{H}_2$  is greater than the concentration of  $\text{CO}_2$  at point 3.
- D The concentration of  $\text{H}_2$  is greater than the concentration of  $\text{CO}$  at point 4.

- 16 When a solution of potassium iodide, KI, was added to a solution of lead(II) nitrate, a bright yellow precipitate,  $\text{PbI}_2$ , was formed.

A sketch of the mass of precipitate formed against the volume of the KI solution added is shown below.



Which statements can be used to explain the shape of the graph beyond  $V \text{ cm}^3$ ?

- 1 Lead(II) nitrate is the limiting reagent.
- 2 The position of equilibrium of  $\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{I}^{-}(\text{aq})$  shifts right.
- 3  $\text{PbI}_2$  reacts with excess KI to form a complex,  $\text{PbI}_4^{2-}$ .

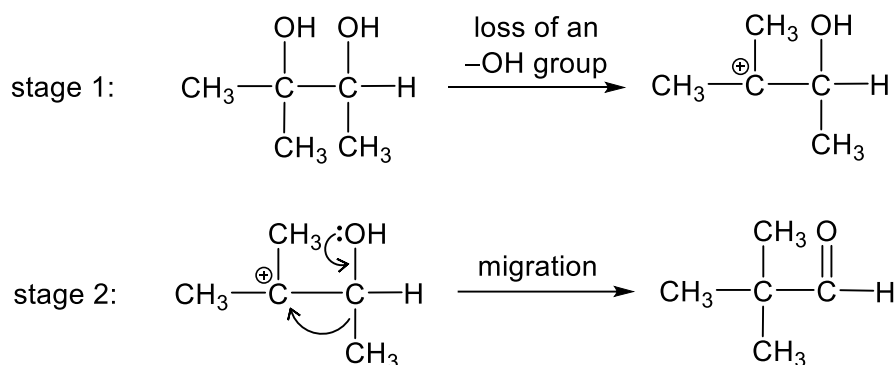
**A** 3 only      **B** 1 and 2 only      **C** 2 and 3 only      **D** 1, 2 and 3

- 17 How many constitutional isomers are possible for  $\text{C}_4\text{H}_{10}\text{O}$ ?

**A** 5      **B** 6      **C** 7      **D** 8

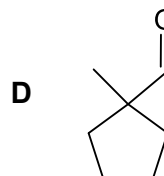
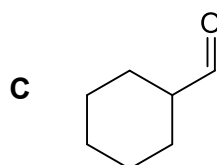
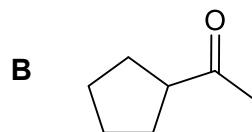
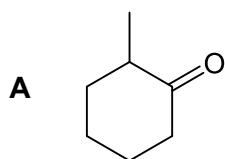
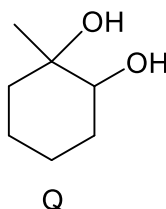
- 18 The pinacol rearrangement is a method for converting a 1,2-diol to an aldehyde or ketone. An example is shown below using 2-methylbutane-2,3-diol.





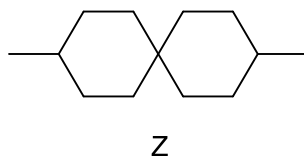
Stage 1 favours the production of a more stable carbocation. This is followed by the migration of an alkyl group in stage 2.

What is the major product when Q undergoes the pinacol rearrangement?



19 Which statement regarding the free radical substitution of methylcyclohexane is correct?

- A** Hydrogen gas is a product.
- B** Ignoring stereoisomers, there are seven possible monosubstituted products.
- C** Two of its monosubstituted products are chiral.
- D** Z can be formed as one of its termination products.

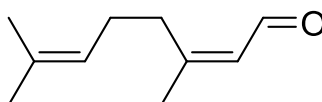


20 What is the intermediate that leads to the major product in the reaction between propene and aqueous bromine?

+

- A**  $\text{CH}_2(\text{Br})-\text{CHCH}_3$
- B**  $\overset{+}{\text{CH}}_2-\text{CH}(\text{Br})\text{CH}_3$
- C**  $\overset{+}{\text{CH}}_2-\text{CH}(\text{OH})\text{CH}_3$
- D**  $\text{CH}_2(\text{Br})-\underset{\text{O}^-}{\text{CH}}\text{CH}_3$

**21** Citral is present in the volatile oils of several plants.



citral

Which statements about citral are correct?

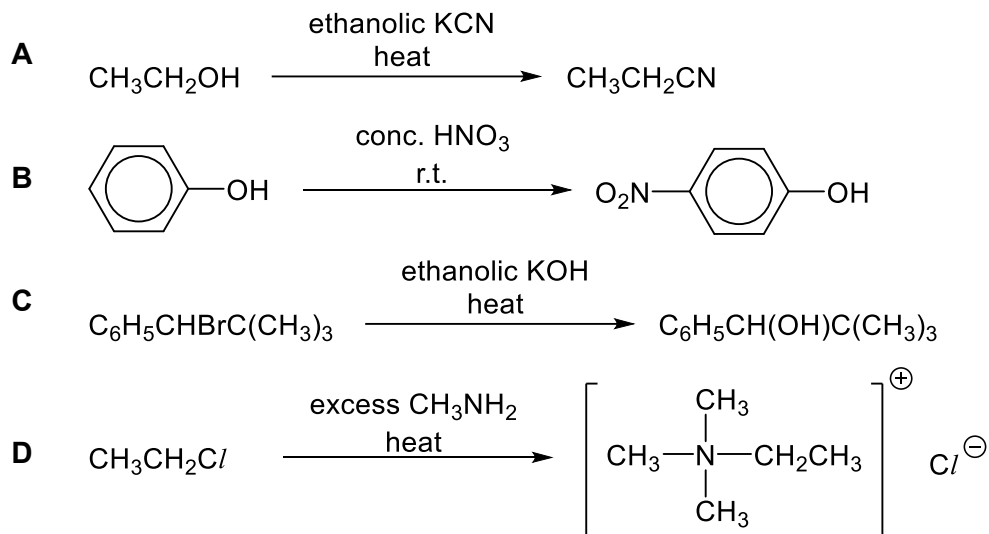
- 1 It gives a positive test with ammoniacal silver nitrate.
- 2 Carbon dioxide is produced when citral is heated with acidified potassium manganate(VII).
- 3 The number of  $\text{sp}^3$ -hybridised carbon atoms is equal to the number of  $\text{sp}^2$ -hybridised carbon atoms in the citral molecule.

- A** 1 only      **B** 3 only      **C** 2 and 3 only      **D** 1, 2 and 3

**22** Which statement about benzene reacting with concentrated  $\text{HNO}_3$  is correct?

- A** Electrons in the  $\pi$  electron cloud are donated to a nucleophile.
- B** Electrons in the carbon-carbon  $\sigma$  bond are donated to an electrophile.
- C** The hybridisation state of all the carbon atoms of benzene remains unchanged at every step of the reaction.
- D** Benzene undergoes a substitution reaction so that the delocalised  $\pi$  electron system remains undisrupted at the end of the reaction.

23 Which reaction will give the product indicated?



24 Which compound gives a yellow solid with warm alkaline aqueous iodine?

- A**  $\text{CH}_3\text{CHO}$   
**B**  $(\text{CH}_3)_3\text{COH}$   
**C**  $\text{CH}_3\text{CO}_2\text{CH}_3$   
**D**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

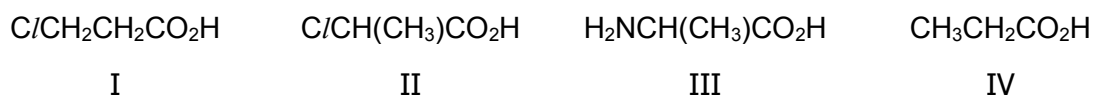
25 The following three compounds are present in a sample in the ratio  $\text{X} : \text{Y} : \text{Z} = 1 : 1 : 2$ .

- X**  $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CH}=\text{CHCO}_2\text{H}$   
**Y**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHCOCH}_3$   
**Z**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}=\text{CHCHO}$

How many hydrogen atoms would be incorporated on average per molecule when the sample is reacted with excess  $\text{LiAlH}_4$ ?

- A** 1.50                      **B** 2.50                      **C** 2.67                      **D** 5.50

26 Four compounds are shown below.



What is the correct order in terms of increasing acid strength of the carboxylic acid group?

- A**  $\text{III} < \text{IV} < \text{I} < \text{II}$                       **B**  $\text{IV} < \text{I} < \text{II} < \text{III}$   
**C**  $\text{III} < \text{IV} < \text{II} < \text{I}$                       **D**  $\text{IV} < \text{II} < \text{I} < \text{III}$

- 27 The same carboxylic acid is obtained either by the hydrolysis of a nitrile **P** or by the oxidation of an alcohol **Q**.

What could be **P** and **Q**?

	<b>P</b>	<b>Q</b>
<b>A</b>	$\text{CH}_3\text{CH}_2\text{CN}$	$\text{CH}_3\text{CH}_2\text{OH}$
<b>B</b>	$\text{CH}_3\text{CH}_2\text{CN}$	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
<b>C</b>	$(\text{CH}_3)_2\text{CHCN}$	$(\text{CH}_3)_3\text{COH}$
<b>D</b>	$\text{C}_6\text{H}_5\text{CN}$	$\text{C}_6\text{H}_5\text{OH}$

- 28 Which statements are correct about the reaction between ethylamine and ethanoyl chloride?

- 1 During the reaction, a carbon-chlorine bond is broken and a carbon-nitrogen bond is formed.
- 2 The same reaction will take place if ethanoyl chloride is replaced by ethanoic acid.
- 3 The organic product formed, when dissolved in water will give a solution that has a pH greater than 7.

**A** 1 only      **B** 1 and 2 only      **C** 2 and 3 only      **D** 1, 2 and 3

- 29 Use of the Data Booklet is relevant to this question.

When the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half cell in standard conditions is joined to a standard hydrogen electrode, the  $E^\ominus_{\text{cell}} = +0.77\text{V}$ .

Which changes to the cell conditions would lead to a lower cell potential?

- 1 Adding water into the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half cell.
- 2 Increasing the pressure of  $\text{H}_2(\text{g})$ .
- 3 Adding an excess of  $\text{CN}^-(\text{aq})$  into the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half cell.

**A** 1 only      **B** 3 only      **C** 1 and 3 only      **D** 2 and 3 only

- 30 Transition metal ions can react in a number of different ways. Listed are four different reactions of transition metal ions with relevant observations.

Which observation does **not** involve ligand exchange?

- A When a purple solution of chromium(III) sulfate is warmed, a green solution containing  $[\text{Cr}(\text{H}_2\text{O})_5\text{SO}_4]^+$  is formed.
- B When an excess of aqueous ammonia is added to a solution of cobalt(II) chloride, a brown solution of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ions is made.
- C When an excess of aqueous sodium hydroxide is added to a solution of iron(III) chloride, a reddish-brown precipitate of  $\text{Fe}(\text{OH})_3$  is formed.
- D When concentrated hydrochloric acid is added to a blue-green solution of aqueous copper(II) chloride, a yellow solution of aqueous  $[\text{CuCl}_4]^{2-}$  is formed.



CANDIDATE  
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## CHEMISTRY

9729/02

Paper 2 Structured Questions

28 August 2024

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

### READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group**, **centre number** and **index number** on all the work you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE ON ANY BARCODES.

Answer all questions in the spaces provided in the Question Paper.

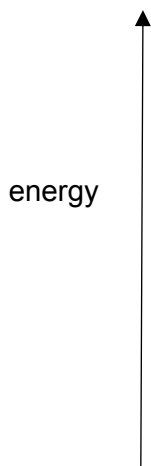
The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

No. of sheets of writing paper submitted (if any)	
For Examiner's Use	
1	/ 6
2	/ 13
3	/ 18
4	/ 15
5	/ 23
Deductions (s.f.)	
Deductions (units)	
Deductions (structures)	
Total	/ 75

Answer **all** questions in the space provided.

- 1 (a) Complete the energy level diagram in Fig. 1.1, showing the relative energy levels of orbitals in the 3<sup>rd</sup> principal quantum shell.



**Fig. 1.1**

[2]

- (b) (i) Explain what is meant by the term *first ionisation energy*.

.....  
 ..... [1]

- (ii) Use your knowledge of the variation in first ionisation energy of the Period 3 elements (Na to Ar) to predict and explain how the first ionisation energy varies in each pair of elements.

- arsenic and selenium

.....  
 .....  
 .....

- bromine and krypton

.....  
 .....  
 .....  
 .....

[3]

[Total: 6]

- 2 Polyfluoroalkyl substances (PFAS) is a group of compounds that have multiple fluorine atoms attached to an alkyl chain, giving these compounds waterproof properties, leading to widespread use in textiles, cosmetics, and food packaging.

Poly(tetrafluoroethene), PTFE, is an early and popular example of PFAS made by polymerising tetrafluoroethene,  $F_2C=CF_2$ .

- (a) (i) State the shape and bond angle around the carbon atom in  $F_2C=CF_2$ .

.....  
 ..... [2]

- (ii) Carbon atoms in  $F_2C=CF_2$  are  $sp^2$  hybridised.

Explain what is meant by  $sp^2$  hybridisation with reference to the carbon atom in  $F_2C=CF_2$ .

.....  
 .....  
 ..... [1]

- (iii) The shape of the carbon atom in  $F_2C=CF_2$  depends on the arrangement of the hybridised orbitals.

Apply the principles of the VSEPR theory to explain how the hybridised orbitals are arranged in the second shell of the  $sp^2$  carbon atom.

.....  
 ..... [1]

- (b) Explain why  $F_2C=CF_2$  is a gas at room temperature whereas PTFE is a solid.

.....  
 .....  
 .....  
 .....  
 ..... [2]

- (c) In recent years, scientific evidence indicates that PFAS pose health and environmental concerns. Due to its persistence in the environment, it has been dubbed “forever chemicals”.

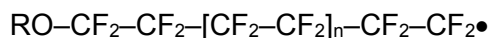
Suggest why PFAS would last in the environment “forever”.

.....  
 .....  
 ..... [1]



(d) The mechanism of polymerisation of PTFE consists of four separate stages **A** to **D**.

- A** homolytic fission of an organic peroxide,  $\text{RO-OR}$ , produces two  $\text{RO}\bullet$  radicals  
**B**  $\text{RO}\bullet$  reacts with one  $\text{F}_2\text{C}=\text{CF}_2$  molecule to produce a new radical  
**C** repeated steps involving production of a series of new radicals to produce



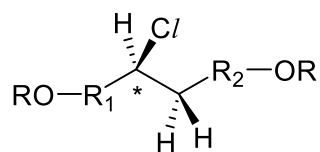
- D** two radicals combine to form  $\text{RO-CF}_2\text{-CF}_2\text{-[CF}_2\text{-CF}_2\text{]}_{(2n+2)}\text{-CF}_2\text{-CF}_2\text{-OR}$

- (i) This polymerisation can also be carried out using a non-symmetrical molecule such as  $\text{CH}_2=\text{CHCl}$  to give poly(chloroethene).

Write equations to show the formation of  $\text{RO-CHCl-CH}_2\bullet$  and  $\text{RO-CHCl-CH}_2\text{-CHCl-CH}_2\bullet$  in stages **B** and **C** of the polymerisation of  $\text{CH}_2=\text{CHCl}$ .

.....  
 ..... [2]

- (ii) Fig. 2.1 shows a section of poly(chloroethene), where  $\text{R}_1$  and  $\text{R}_2$  represent chlorinated alkyl chains.



**Fig. 2.1**

Explain why the carbon atom labelled with \* is chiral.

.....  
 .....  
 ..... [1]

(iii) Fig. 2.2 shows four repeating units within poly(chloroethene).

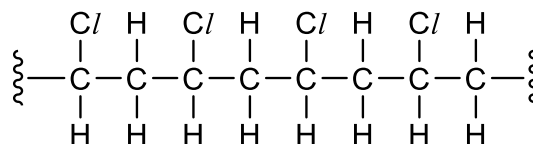


Fig. 2.2

The free radical polymerisation of poly(chloroethene) results in different stereochemical arrangements along the carbon chain.

The different arrangements can be classified into **three** types.

Types 1 and 2 result in polymers that have regular, crystal lattice structures with higher melting points.

Type 3 results in polymers that have poor packing and are unable to crystallise.

By considering Fig. 2.2 and your answers to (d)(i) and (d)(ii), complete Fig. 2.3 by showing the positions of hydrogen and chlorine atoms for the three types of arrangements.

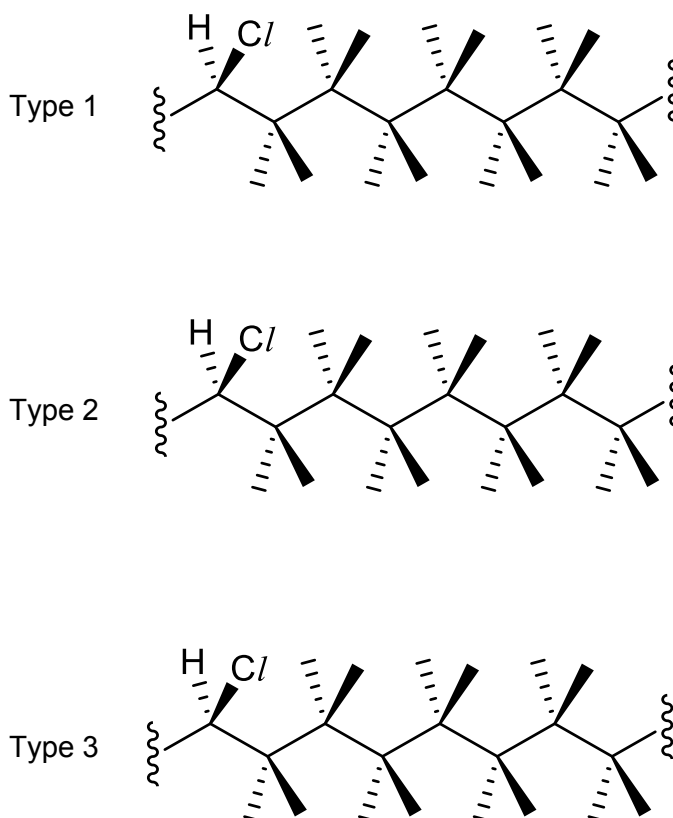


Fig. 2.3

[3]

[Total: 13]

- 3 (a) Explain, with the aid of a labelled Boltzmann distribution diagram, the effect on the rate of reaction by increasing temperature.

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.....[3]

- (b) Two different mechanisms for the nucleophilic substitution of halogenoalkanes are called  $S_N1$  and  $S_N2$ . 2-bromopropane, a secondary bromoalkane, can undergo both  $S_N1$  and  $S_N2$ .

- (i) Draw a mechanism for the reaction between 2-bromopropane and  $\text{OH}^-$  via  $S_N2$ . Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

[2]

- (ii) Using collision theory, explain how the rate of reaction varies as the concentration of 2-bromopropane increases.

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.....[2]

- (iii) An investigation of the kinetics of the nucleophilic substitution of 2-bromopropane with  $\text{OH}^-$  in a certain solvent is carried out. The overall rate equation of this nucleophilic substitution is found to be:

$$\text{rate} = y [\text{2-bromopropane}] + z [\text{2-bromopropane}][\text{OH}^-]$$

where  $y$  and  $z$  are rate constants.

Circle the part(s) of the rate equation which corresponds to  $\text{S}_{\text{N}}2$ . Explain your answer with reference to the mechanism you have drawn in **(b)(i)**.

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.....[2]

(iv) The results of two such experiments in (b)(iii) are recorded in Table 3.1.

**Table 3.1**

expt	[2-bromopropane] / mol dm <sup>-3</sup>	[OH <sup>-</sup> ] / mol dm <sup>-3</sup>	initial rate / mol dm <sup>-3</sup> s <sup>-1</sup>
1	0.10	0.10	$7.1 \times 10^{-7}$
2	0.10	0.20	$1.2 \times 10^{-6}$

Use the results to calculate the values of  $y$  and  $z$  for the rate equation shown in (b)(iii), stating their units.

$y = \dots\dots\dots$

units of  $y = \dots\dots\dots$

$z = \dots\dots\dots$

units of  $z = \dots\dots\dots$

[4]

(i) Complete Table 3.2 by stating the relevant observations for each test.

compound	observations on adding acidified silver nitrate	solubility of residue (if any)	
		in dilute aqueous ammonia	in concentrated aqueous ammonia
2-bromopropane	cream ppt	insoluble	
2-chloropropane		soluble	
iodobenzene			

(ii) With reference to the  $K_{sp}$  values in Table 3.3, explain why  $\text{AgCl}$  is soluble in dilute aqueous ammonia while  $\text{AgBr}$  is insoluble in dilute aqueous ammonia. You are not required to perform any calculations.

compound	value of $K_{sp}$
AgCl	$1.77 \times 10^{-10}$
AgBr	$5.35 \times 10^{-13}$

.....[3]

**[Turn Over**

4 Dicarboxylic acids are organic compounds that contain two carboxylic acid ( $-\text{CO}_2\text{H}$ ) functional groups. Industrially, they are important precursors in chemical synthesis of useful compounds.

(a) Maleic acid,  $\text{HO}_2\text{CCHCHCO}_2\text{H}$ , exhibits stereoisomerism. State the type of stereoisomerism present and explain how it arises.

.....  
 .....  
 .....  
 .....[2]

(b) Maleic acid ionises in two stages.



Maleic acid can be used to make a buffer that is used to determine the amount of trace metals in seawater. The pH of the buffer solution was adjusted to 6.50 with sodium hydroxide.

(i) Explain why the predominant forms of maleic acid present in the above buffer are  $\text{HO}_2\text{CCHCHCO}_2^-$  and  $^-\text{O}_2\text{CCHCHCO}_2^-$ .

.....  
 .....[1]

(ii) Calculate the ratio of the concentrations of  $^-\text{O}_2\text{CCHCHCO}_2^-$  and  $\text{HO}_2\text{CCHCHCO}_2^-$  present in the above buffer solution.

[1]

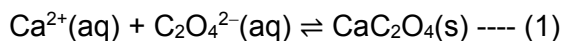
(iii) Write equations to show how the above buffer helps to maintain pH when a small amount of acid or base is added.

.....  
 .....[2]

- (iv) Deduce whether the above buffer is more effective in buffering against added acids or bases. Give your reasoning.

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 .....  
 .....[1]

- (c) Calcium ethanedioate,  $\text{CaC}_2\text{O}_4$ , is found in kidney stones. At sufficiently high concentrations, ethanedioate ions react with the calcium ions in the kidney to form solids via equilibrium 1 below.



- (i) The solubility of calcium ethanedioate is  $6.70 \times 10^{-3} \text{ g dm}^{-3}$  at  $25^\circ\text{C}$ . Calculate the value of its solubility product.

[2]

- (ii) The concentration of  $\text{Ca}^{2+}(\text{aq})$  in a sample of body fluids is  $2.20 \times 10^{-3} \text{ mol dm}^{-3}$ . Calculate the concentration of  $\text{C}_2\text{O}_4^{2-}(\text{aq})$  just before calcium ethanedioate begins to precipitate.

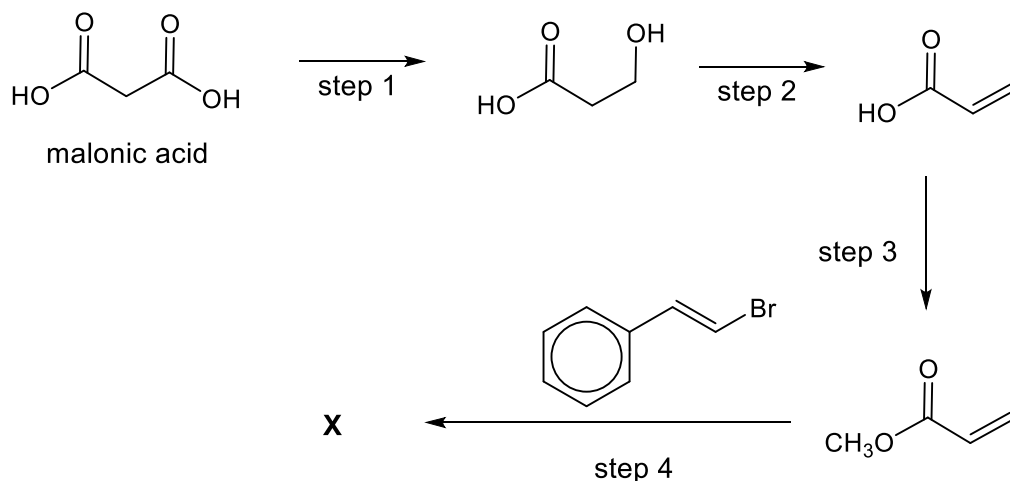
[1]

- (iii) By referring to equilibrium 1, suggest one way a person may try to reduce the formation of kidney stones. Explain your reasoning.

.....  
 .....  
 ..... [1]



(d) Malonic acid,  $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$ , is used as a precursor for the reaction scheme in Fig. 4.1.



**Fig. 4.1**

(i) Give the reagents and conditions for steps 1 to 3.

step 1: .....

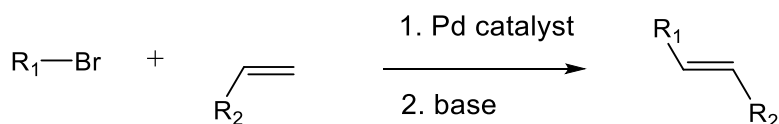
step 2: .....

step 3: .....

[3]

(ii) The Heck reaction is the palladium-catalysed C–C bond formation between halogen compounds and alkenes. This reaction produces a *trans* alkene as the major product.

An example of the Heck reaction is shown in Fig. 4.2.



**Fig. 4.2**

In step 4 of Fig. 4.1, palladium catalyst and base were also added. Suggest the structure of **X**.

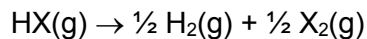
**X:** .....

[1]

[Total: 15]



- 5 (a) (i) The equation for the thermal decomposition of hydrogen halides is shown below.



Describe the thermal decomposition of HCl, HBr and HI, giving observations where relevant, and explain any variation in their thermal stabilities.

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.....[3]

- (ii) Using data from the *Data Booklet*, calculate the standard enthalpy change for the decomposition of 1 mole of HCl(g).

[2]

- (b) Dilute hydrochloric acid is frequently used in the chemistry laboratory. It is prepared via dilution of known volumes of concentrated HCl with suitable volumes of water, which allows for dilute solutions of different concentrations to be produced.

- (i) "37% w/w HCl" is a concentrated HCl reagent from manufacturers. This label indicates that 100 g of the reagent contains 37 g of HCl.

Calculate the concentration, in  $\text{mol dm}^{-3}$ , of HCl in this reagent, given that its density is  $1.2 \text{ g cm}^{-3}$ .

[2]

- (ii) Hence, calculate the volume,  $v \text{ cm}^3$ , of 37% w/w HCl which must be diluted with sufficient water to make  $250 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3}$  hydrochloric acid.  
If you were unable to obtain an answer in (b)(i), use the value of  $11.9 \text{ mol dm}^{-3}$ .

[1]

- (iii) Define the term *standard enthalpy change of formation* of a substance.

.....  
 .....[1]

- (iv) Using your answer in (a)(ii) and the information given in Table 5.1, calculate the standard enthalpy change for the following dilution, with the aid of an energy cycle.

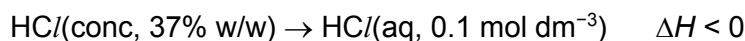


Table 5.1

standard enthalpy change of formation of $\text{HCl}(\text{aq, } 0.1 \text{ mol dm}^{-3})$	$-167.2 \text{ kJ mol}^{-1}$
standard enthalpy change for the reaction $\text{HCl}(\text{g}) \rightarrow \text{HCl}(\text{conc, 37\% w/w})$	$-62.6 \text{ kJ mol}^{-1}$

[3]

- (v) Two outlines for preparing 250 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> hydrochloric acid are presented below.

Outline A

1. Transfer  $v$  cm<sup>3</sup> of 37% w/w HCl into a 250 cm<sup>3</sup> volumetric flask. (volume  $v$  was calculated in (b)(ii))
2. Slowly add deionised water into the volumetric flask and top up to the mark.

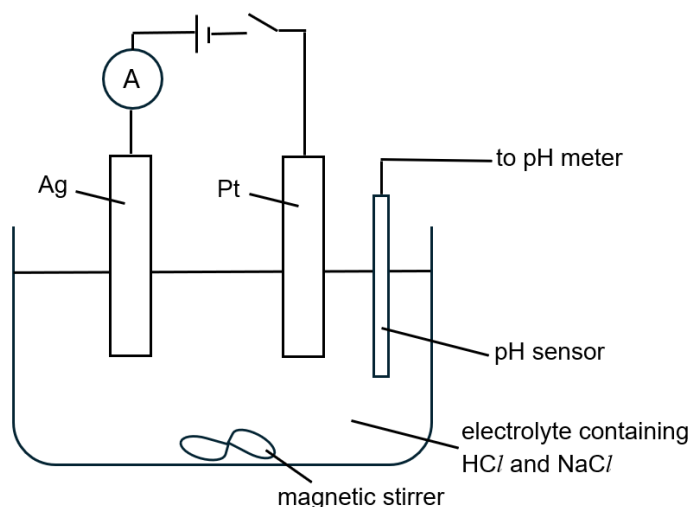
Outline B

1. Transfer 150 cm<sup>3</sup> of deionised water into a 250 cm<sup>3</sup> volumetric flask.
2. Slowly add  $v$  cm<sup>3</sup> of 37% w/w HCl into the volumetric flask.
3. Top up to the mark with deionised water.

Using the information provided about the dilution in (b)(iv), explain whether outline A or B is preferred.

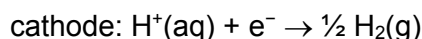
.....  
 .....[1]

- (c) The following experiment, based on an approach known as coulometric titration, aims to determine a value for Faraday's constant and Avogadro's constant. Fig. 5.1 shows the electrolytic setup for the experiment. The electrolyte contains a known amount of dilute hydrochloric acid, which will be neutralised as the electrolysis proceeds.

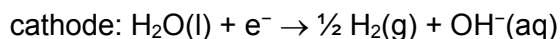


**Fig. 5.1**

When the switch is closed, the following reaction occurs at the inert Pt cathode before the known amount of dilute hydrochloric acid is completely used up, i.e. before the equivalence point is reached.

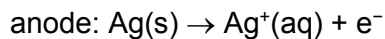


Once the equivalence point is reached, the following reaction occurs at the cathode.



Overall, for every electron passed during the electrolysis, one  $\text{H}^+(\text{aq})$  ion is consumed from the electrolyte (before the equivalence point) or one  $\text{OH}^-(\text{aq})$  ion is produced (after the equivalence point). The electrolyte pH thus increases in a similar way to a conventional titration.

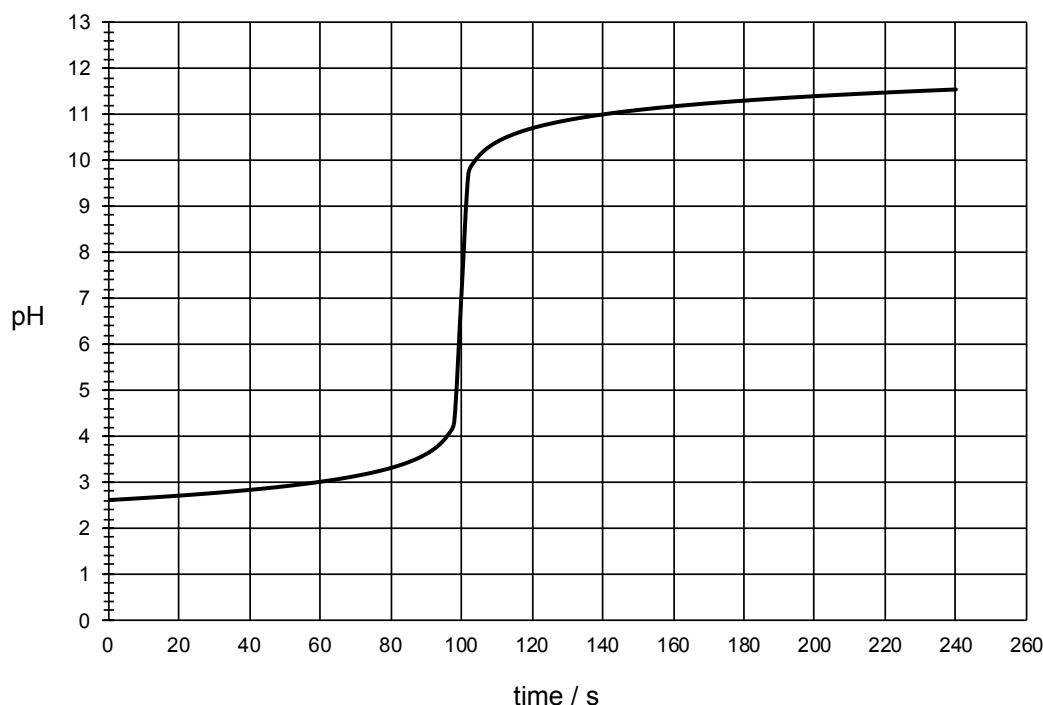
At the Ag anode, the following reaction occurs.



The procedure for the experiment is as follows:

1. Transfer  $2.50 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3} \text{ HCl(aq)}$  into a  $250 \text{ cm}^3$  beaker.
2. Add  $97.5 \text{ cm}^3$  of  $0.2 \text{ mol dm}^{-3} \text{ NaCl(aq)}$  into the beaker. ( $\text{NaCl(aq)}$  is added, instead of deionised water, to maintain sufficient electrical conductivity of the electrolyte.)
3. Construct the electrolytic setup in Fig. 5.1.
4. Close the switch and start a stopwatch at the same time. Record the pH of the electrolyte indicated by the pH meter and the current indicated by the ammeter at regular time intervals.
5. Open the switch at time  $t = 240 \text{ s}$ , which is beyond the equivalence point of the titration.

Student X carried out the experiment at a constant current of  $0.24 \text{ A}$ . Fig. 5.2 shows the variation of electrolyte pH with time obtained by student X.



**Fig. 5.2**

- (i) From Fig. 5.2, state the time taken to reach equivalence point,  $t_{\text{eq}}$ .

.....[1]

- (ii) Calculate the total quantity of charge that passed through the circuit up to time  $t_{\text{eq}}$ .

[1]

- (iii) Calculate the initial amount, in moles, of  $\text{HCl}$  in the electrolyte. Hence, calculate a value for Faraday's constant.

[2]

- (iv) Use your answer in (c)(iii) to find a value for Avogadro's constant, given that the electronic charge is  $1.60 \times 10^{-19} \text{ C}$ .

[1]

- (v)  $\text{NaCl(aq)}$  was added in step 2 to maintain electrical conductivity. Another reason was to prevent silver ions produced at the anode from reaching the cathode, by precipitating them as silver chloride.

With reference to relevant  $E^\ominus$  values, explain why it is important that silver ions are prevented from reaching the cathode.

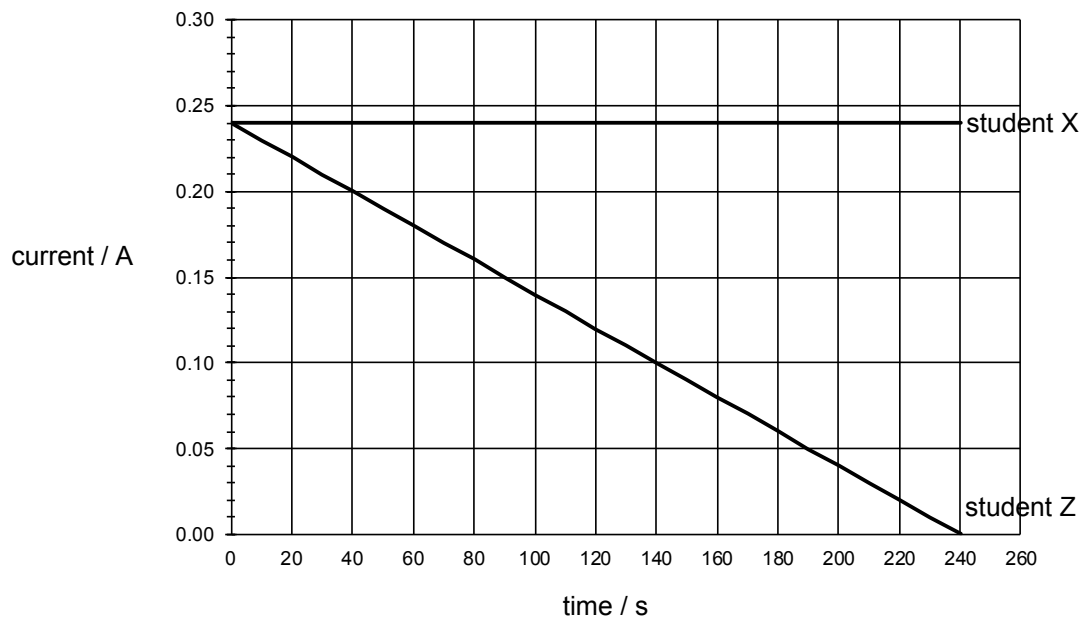
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 .....  
 .....  
 .....[2]

- (vi) Student Y also carried out the experiment, but he did not use a pH meter. Instead, he added a few drops of an acid-base indicator (working range = 10.2 to 12.0) into the electrolyte, and recorded the time  $t_{\text{eq}}$  when the indicator changed colour.

By referring to Fig. 5.2, suggest whether the value of  $t_{\text{eq}}$  obtained by student Y will be smaller or larger than expected (if different from expected). Give your reasoning.

.....  
 .....[1]

- (vii) Student Z also carried out student X's experiment over 240 s, but controlled the applied current such that it decreased linearly during this time period. Fig. 5.3 shows the variation of current with time in the experiments conducted by both students on the same axes.



**Fig. 5.3**

Use Fig. 5.3 to suggest the value of the ratio of total charge passed in student Z's experiment to the total charge passed in student X's experiment. Hence, use Fig. 5.2 to suggest the final pH obtained in **student Z's** experiment.

ratio: .....

final pH: .....

[2]

[Total: 23]







CANDIDATE  
NAME

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## CHEMISTRY

9729/03

Paper 3 Free Response

11 September 2024

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

### READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group**, **centre number** and **index number** on all the work you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE ON ANY BARCODES.

Answer all questions in the spaces provided in the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

### Section A

Answer **all** questions.

### Section B

Answer **one** question.

A Data Booklet is provided.

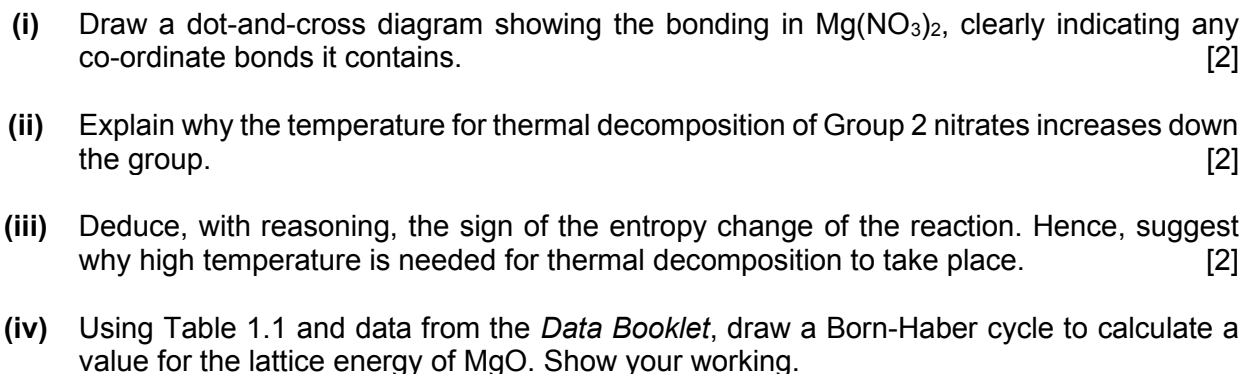
The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

No. of sheets of writing paper submitted (write 0 if none)	
For Examiner's Use	
1	/ 20
2	/ 19
3	/ 21
Circle your option below	
4 / 5	/ 20
Deductions (s.f.)	
Deductions (units)	
Deductions (structures)	
Total	/ 80

1 (a) Like Group 2 carbonates, Group 2 nitrates also undergo thermal decomposition according to the following equation:



	$\Delta H^\ominus / \text{kJ mol}^{-1}$
1 <sup>st</sup> electron affinity of oxygen	−142
2 <sup>nd</sup> electron affinity of oxygen	+844
standard enthalpy change of atomisation of Mg(s)	+148
standard enthalpy change of formation of MgO(s)	−602

This image shows a full page of white paper with horizontal dashed lines, typical of primary-ruled notebook paper. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.



- (b) Describe the reactions, if any, of the oxides  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{P}_4\text{O}_{10}$  with water. Write equations for any reaction and state the pH of the resultant mixtures. [3]

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- (c) In the presence of  $\text{AlCl}_3$ , methylbenzene can undergo electrophilic substitution with halogens like chlorine.

- (i) Explain why  $\text{AlCl}_3$  can act as a Lewis acid. [1]
- (ii) Draw the structures of the major organic products formed in the electrophilic substitution reaction between methylbenzene and chlorine. [1]
- (iii) Write a balanced equation for the reaction between methylbenzene and hot acidified potassium manganate(VII). Use [O] to represent the oxidising agent. [1]

If the halogen is changed to iodine, electrophilic substitution of methylbenzene occurs much less readily. To increase its reactivity, reagents like iodine monochloride,  $\text{ICl}$ , in the presence of  $\text{AlCl}_3$  are used instead.

- (iv) Explain why  $\text{ICl}$  is more reactive in the electrophilic substitution of methylbenzene compared to  $\text{I}_2$ . [1]
- (v) Draw the mechanism of the reaction between methylbenzene and  $\text{ICl}$ , showing the formation of the electrophile and any intermediates. Use curly arrows to indicate the movement of electron pairs, and show any relevant lone pairs. [3]

**[Turn Over**

- 2 (a) Describe and explain the difference in reactivity of alkenes and carbonyl compounds towards nucleophilic reagents. [2]

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- (b) In the pharmaceutical industry, understanding optical activity and addressing the effects of racemic mixtures is crucial in drug development.

(i) Explain why a racemic mixture is optically inactive. [2]

(ii) With reference to a reaction involving a suitable alkene **or** carbonyl compound of your choice, explain why a racemic mixture is obtained in the reaction.  
Give the organic compound and reagents used, and draw structures to illustrate the type of stereoisomerism present in the product mixture. [3]

(iii) Stereoisomers of a drug such as ibuprofen often have different pharmacological activities. Suggest a reason for why this is so. [1]

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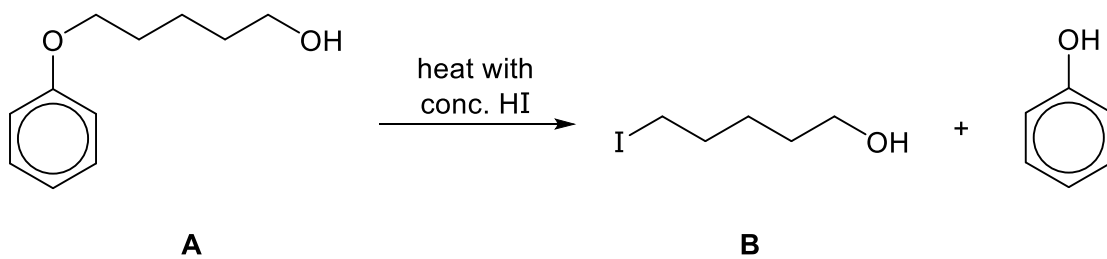
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(c) Fig. 2.1 shows the reaction of compound **A** with hot concentrated hydroiodic acid.

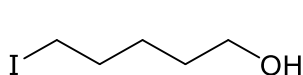


**Fig. 2.1**

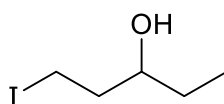
- (i) Suggest the *type of reaction* that occurs during this reaction. [1]
- (ii) Give the systematic name for **B**. [1]



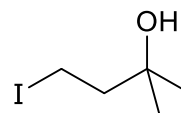
- (iii) **C** and **D** are constitutional isomers of **B**. The three compounds may be distinguished via a two-step procedure.



**B**



**C**

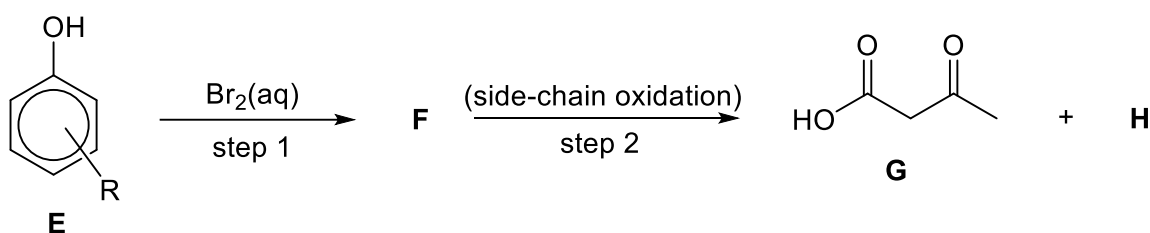


D

- I.** In step 1, the three compounds are heated separately with acidified potassium dichromate(VI). State what would be observed for each compound.
- II.** The organic products formed from positive tests in step 1 are isolated for a further test in step 2. Suggest a reagent, other than 2,4-dinitrophenylhydrazine, that can be used to distinguish these products, and state the observations for each compound. [3]
- (iv)** Phenol can be converted to phenyl ethanoate via a two-step process. State the reactant required for each step of this process. [2]

[illegible]

**(d)** Fig. 2.2 shows a synthetic scheme for the conversion of compound **E** to compounds **G** and **H**. In **E**, the R group could be at positions 2, 3 or 4 relative to the –OH group on the benzene ring.



**Fig. 2.2**

- (i) Draw the structure of the organic product formed when compound **G** is reacted with 2,4-dinitrophenylhydrazine. [1]
- (ii) In step 1 of Fig. 2.2, the relative molecular mass of **E** changes from 178.0 to 335.8 in **F**, the major product of the reaction.  
Deduce, with reasoning, the position of the R group relative to the –OH group in **E**. [1]
- (iii) Based on your answer to (d)(ii) and the following information, suggest the structures of **F** and **H**, both of which contain brominated benzene rings.
- **G** and **H** are the only carbon-containing products formed when **F** undergoes side-chain oxidation in step 2
  - one mole of **H** produces one mole of hydrogen gas on complete reaction with sodium metal
  - **F** gives orange precipitate with 2,4-dinitrophenylhydrazine [2]

[Total: 19]

3 (a) Explain why transition metal complexes are often coloured.

[3]

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(b) (i) State the electronic configuration of chromium.

[1]

(ii) Explain why chromium can exhibit a number of different oxidation states in its compounds.

[1]

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(c) A black oxide  $\text{CrO}$ , dissolves readily in dilute acid to form a sky blue solution **A**. When left in the air, the solution changes to a green solution **B**. When a small amount of sodium hydroxide is added to **B**, a grey green precipitate **C** is formed. Upon the addition of excess sodium hydroxide, a complex  $[\text{Cr}(\text{OH})_6]^{3-}$  is formed which reacts with  $\text{H}_2\text{O}_2$  to form a yellow solution,  $\text{CrO}_4^{2-}$ .

(i) Give the formula of the unknown chromium-containing species present in **A**, **B**, and **C**. [3]

(ii) What type of reaction occurs when  $\text{CrO}_4^{2-}$  is formed from  $[\text{Cr}(\text{OH})_6]^{3-}$ ? [1]

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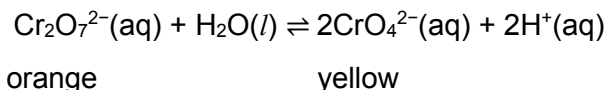
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(d) In an acidic medium, chromium(VI) exists as  $\text{Cr}_2\text{O}_7^{2-}$ .

(i) State one reason why aqueous  $\text{Cr}^{6+}$  ion does not exist. [1]

(ii) In aqueous solution,  $\text{Cr}_2\text{O}_7^{2-}$  exists in equilibrium with  $\text{CrO}_4^{2-}$  as shown below.



Describe the observation when an aqueous solution of  $\text{Cr}_2\text{O}_7^{2-}$  is diluted with water. Explain your reasoning. [2]

(iii) With the aid of  $E^\ominus$  values from the *Data Booklet*, explain why a reaction occurs when  $\text{SO}_2$  is bubbled into acidified  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ . Write an equation for this reaction. [2]

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(e) A hydrated salt **E** ( $M_r = 399.7$ ) contains 13.0 % of Cr, 27.0 % of  $H_2O$  and 60.0 % of Br by mass. An aqueous solution containing 0.400 g of **E** immediately gives 0.188 g of cream precipitate when treated with aqueous silver nitrate.

(i) Calculate the mole ratio of Cr:  $H_2O$ : Br in the hydrated salt **E**. [1]

(ii) Identify the cream precipitate and hence, determine the formula of the octahedral complex cation in the hydrated salt **E**. [3]

(iii) Given that the complex ion in **E** has a net dipole moment, draw the structure of this complex ion, showing clearly how the ligands are arranged around chromium. [1]

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- (f)** Fifty years ago, most sulfuric acid was manufactured by the “lead chamber process”.

The chamber used in the process must not be made of steel as iron rapidly dissolves in concentrated sulfuric acid, whereas lead is only superficially attacked. With the aid of  $E^\ominus$  values from the *Data Booklet*, explain why this is so. [2]

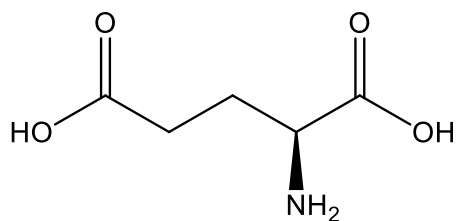
[illegible]

[Total: 21]

## Section B

Answer **one** question from this section.

- 4 (a) The structure of glutamic acid is shown below.



glutamic acid

There are three  $pK_a$  values associated with glutamic acid: 2.19, 4.25 and 9.67.

A  $10.0 \text{ cm}^3$  sample of the *fully protonated* form of glutamic acid is titrated against  $0.100 \text{ mol dm}^{-3} \text{ NaOH(aq)}$ . The titration curve is shown in Fig. 4.1.

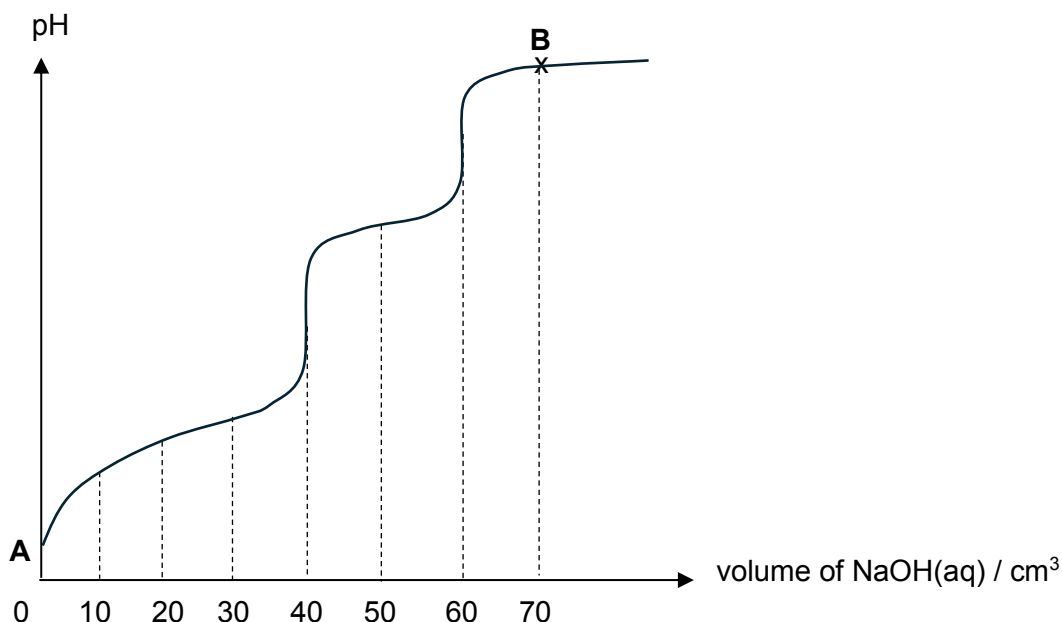


Fig. 4.1

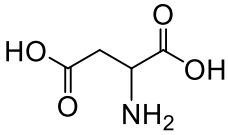
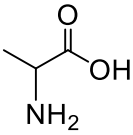
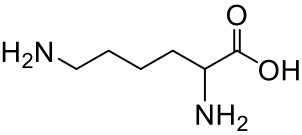
- (i) Define  $pK_a$ . [1]
- (ii) When  $60 \text{ cm}^3$  of NaOH is added, all three acidic groups are deprotonated. Calculate the concentration of glutamic acid in the given sample. [1]
- (iii) Calculate the pH of glutamic acid at point A. [2]
- (iv) Draw the zwitterion of glutamic acid. [1]
- (v) The isoelectric point (pI) is the pH where the amino acid exists primarily as the zwitterion. **On the titration curve in Fig. 4.1**, mark the point at which this occurs, with a cross. [1]
- (vi) Calculate the pH at point B. [2]





(b) Table 4.1 gives the structures and pI values of three different amino acids.

**Table 4.1**

amino acid			
	asp	ala	lys
pI	2.77	6.00	9.74

- (i) Draw the structure of the tripeptide asp-ala-lys. The left-most end of the peptide should be a free  $\text{-NH}_2$  group, while the right-most end is a free  $\text{-CO}_2\text{H}$  group. [2]

.....

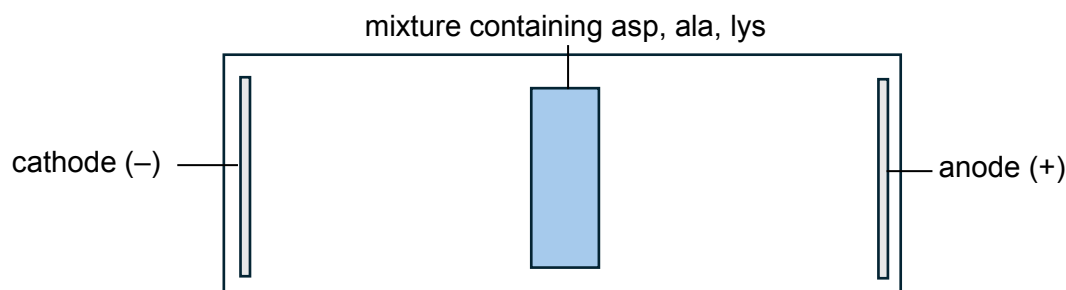
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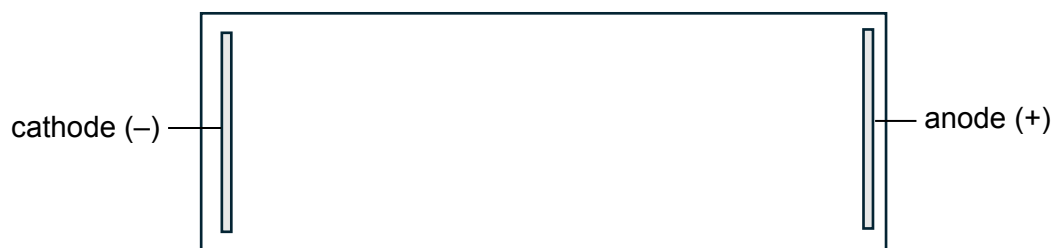
- (ii) A mixture of the three amino acids in Table 4.1 can be separated via a process known as electrophoresis.

The amino acid mixture is placed in the centre of a strip of filter paper soaked in a buffer solution of pH 6.00 as shown in Fig. 4.2. Two electrodes are then placed in contact with the edges of the filter paper.



**Fig. 4.2**

By considering the net charge on the predominant form of each amino acid at pH 6.00, label the positions of the three amino acids at the end of the experiment **on Fig. 4.3**. [2]

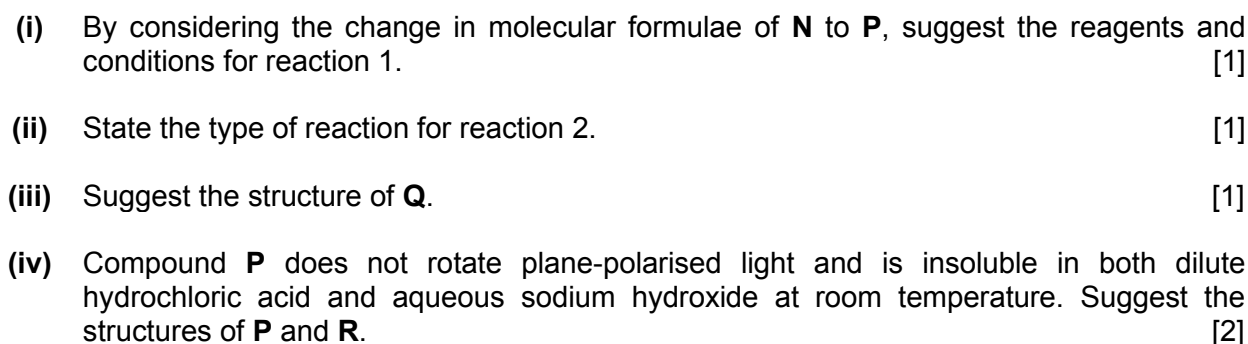


**Fig. 4.3**

- (c)** Describe and explain the relative basicities of ethylamine, diethylamine and triethylamine in the gaseous state. [3]

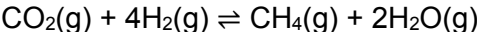
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[Total: 20]

[illegible]

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**5** The Sabatier reaction is the catalytic reduction of carbon dioxide to produce methane.



- (a) 1.00 mol of  $\text{CO}_2(\text{g})$  was reacted with 4.00 mol of  $\text{H}_2(\text{g})$  in a sealed vessel with a volume of  $6.87 \text{ dm}^3$ . The reaction mixture was allowed to reach *dynamic equilibrium* at a pressure of 30.0 bar and a temperature of  $500^\circ\text{C}$ .

- (i) Explain what is meant by the term *dynamic equilibrium*. [1]
- (ii) Using the ideal gas equation, calculate the total number of moles of gas present at equilibrium. [2]
- (iii) Hence, determine the partial pressures of each of the individual gases at equilibrium. [3]
- (iv) Write an expression for the equilibrium constant  $K_p$ , for the Sabatier reaction, including units. [2]
- (v) Calculate the value of  $K_p$  at 500 °C. [1]

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- This image shows a full page of white paper with horizontal dashed lines, typical of primary school handwriting practice paper. The lines are evenly spaced and run across the entire width of the page. There are no margins, text, or other markings present.

- (c) State an advantage of using the hydrogen-oxygen fuel cell to generate electricity as compared to coal-fired power plants. [1]

.....

.....

- (d) In recent years, there has been breakthroughs in producing methane-oxygen fuel cells that require lower operating temperatures, by changing the catalyst used at the anode. An example of a methane-oxygen fuel cell is shown in Fig. 5.1 below.

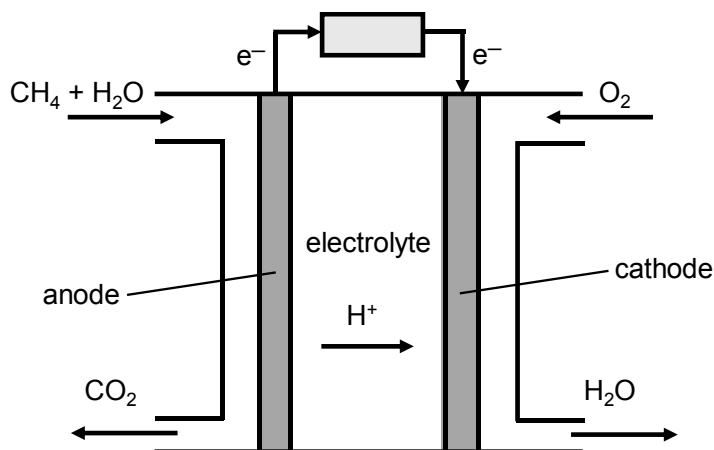
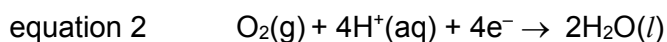
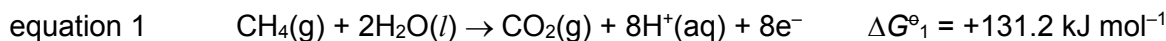
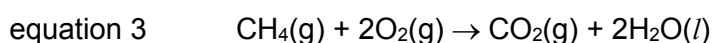


Fig. 5.1

The half-equations for the reactions at the anode and cathode are given by equations 1 and 2 respectively:



The overall equation of the reaction in the fuel cell is given by equation 3:



- (i) Use relevant data from the *Data Booklet* to calculate the standard Gibbs free energy change,  $\Delta G^\ominus_2$ , for the reaction in equation 2. [2]
- (ii) Hence, determine the standard Gibbs free energy change,  $\Delta G^\ominus_3$ , for the reaction in equation 3, and  $E^\ominus_{\text{cell}}$  for the methane-oxygen fuel cell.  $\Delta G^\ominus$  can be used in the same manner as  $\Delta H^\ominus$  in a Hess' law cycle but  $E^\ominus$  cannot. [2]

.....

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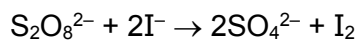
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- (e) The Sabatier reaction and the methane-oxygen fuel cell both require the use of transition metals as heterogeneous catalysts.

Transition metal compounds can also act as homogeneous catalysts. For instance, the catalytic role of  $\text{Fe}^{2+}$  in the reaction between  $\text{I}^-$  and  $\text{S}_2\text{O}_8^{2-}$  is well-known.



Using relevant data from the *Data Booklet*, suggest a transition metal cation, other than  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ , that can catalyse this reaction. Include relevant chemical equations and calculations to support your answer. [3]

[illegible]

[Total: 20]

**Additional answer space**

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

[illegible]





CANDIDATE  
NAME

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GROUP

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INDEX  
NUMBER

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## CHEMISTRY

9729/04

Paper 4 Practical

20 August 2024

2 hours 30 minutes

Candidates answer on the Question Paper.

### READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group**, **centre number** and **index number** on all the work you hand in.

Give details of the practical shift and laboratory where appropriate, in the boxes provided.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE ON ANY BARCODES.

Answer all questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 15 and 16.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
4	
Total	

Answer **all** questions in the spaces provided.

## 1 Qualitative Analysis of FA 1

**FA 1** is an aqueous solution containing two cations & one anion.

**FA 2** is hydrogen peroxide.

You will perform tests to identify the cations and anion in **FA 1**.

Unless otherwise stated, the volumes given are approximate and should be estimated rather than measured.

At each stage of any test, you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released, they should be identified by a test, **described in the appropriate place in your observations**.

You should indicate clearly at what stage in a test a change occurs.

**No additional tests for ions present should be attempted.**

(a) (i) Carry out the following tests. Carefully record your observations in Table 1.1.

**Table 1.1**

**Note: Observations to test 1 have been recorded for you.**

test		observations
1	To 1 cm depth of <b>FA 1</b> in a test-tube, add one spatula full of solid sodium carbonate.	Effervescence of colourless and odourless gas that gives white ppt in limewater.  White ppt observed after effervescence ceased.
2	Place 1 cm depth of <b>FA 1</b> in a <b>boiling tube</b> using a dropping pipette.  Measure 6 cm <sup>3</sup> of aqueous sodium hydroxide with a measuring cylinder.  Transfer 1 cm <sup>3</sup> of aqueous sodium hydroxide to <b>FA 1</b> in the boiling tube using a dropping pipette. Mix the contents of the tube thoroughly.  Repeat this with another 1 cm <sup>3</sup> of aqueous sodium hydroxide.  Repeat until the measuring cylinder is empty.	

	Filter the mixture into a clean test-tube using a filter funnel. While waiting, proceed to test 3.	
	Transfer 1 cm depth of the filtrate to a test-tube and add dilute sulfuric acid ( <b>FA 4</b> ) dropwise until no further changes are seen.	
	<p>If the earlier filtration is not completed, <b>carefully</b> decant the remaining liquid into the sink. <b>Wash</b> the residue by adding deionised water to the filter funnel until it is around half full.</p> <p>Wait for around one minute before <b>carefully</b> decanting the remaining liquid into the sink. Retain the residue for use in (<b>b</b>).</p>	
3	<p>To 1 cm depth of <b>FA 1</b> in a test-tube, add aqueous ammonia, dropwise with shaking.</p> <p>Continue adding aqueous ammonia until no further changes are seen.</p> <p>Leave the test-tube to stand.</p>	
4	<p>To 1 cm depth of <b>FA 1</b> in a test-tube, add 1 cm depth of aqueous <math>\text{Ba}(\text{NO}_3)_2</math>.</p> <p>Add dilute <math>\text{HNO}_3</math> to the above.</p>	

[6]

- (ii) Identify the two cations and one anion in **FA 1**. For each ion, complete Table 1.2 by stating evidence from tests 2 to 4.

Table 1.2

cation	evidence

anion	evidence

[3]

- (iii) Based on the given observations in test 1, describe the types of reaction that occurred and identify any new substances formed.

.....

.....

.....

.....[2]

- (b) (i) Carry out the following tests on the residue from **test 2** in **1(a)**.

test	observations
Place the filter funnel with the <b>washed</b> residue from <b>(a)</b> over a clean test-tube.  Carefully add dilute $\text{HNO}_3$ to the filter funnel until it is around half full. Collect around 1 cm depth of the filtrate.	
To the 1 cm depth of the filtrate in the test-tube, add 1 cm depth of <b>FA 2</b> .  Then, add aqueous sodium hydroxide <b>drop by drop carefully</b> , with shaking, until no further changes are seen.	

[3]

- (ii) By considering your observations in **1(b)(i)**, explain how the addition of aqueous sodium hydroxide affects the reaction involving **FA 2**.

.....

.....

.....

.....[1]

[Total: 15]

## 2 To study the kinetics of the reaction between potassium manganate(VII) and ethanedioic acid in the presence of FA 1

You are provided with the following.

**FA 3** is 0.100 mol dm<sup>-3</sup> potassium iodide.

**FA 4** is 1.00 mol dm<sup>-3</sup> sulfuric acid.

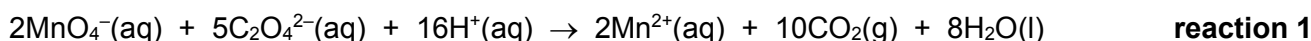
**FA 5** is 0.0050 mol dm<sup>-3</sup> sodium thiosulfate.

**FA 6** is 0.0200 mol dm<sup>-3</sup> potassium manganate(VII).

**FA 7** is 0.200 mol dm<sup>-3</sup> ethanedioic acid.

**Solution I** is starch indicator.

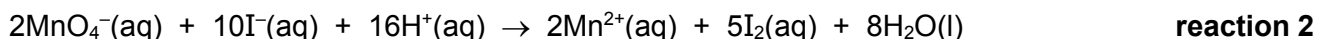
Manganate(VII) ions react with ethanedioate ions in acidic solution as follows.



### Part I

You will prepare a reaction mixture containing potassium manganate(VII), ethanedioic acid, sulfuric acid and **FA 1**.

At suitable time intervals, you will withdraw aliquots of the reaction mixture and add them to potassium iodide solution (in excess). The  $\text{MnO}_4^-$  ions (remaining in each aliquot at that time) react with iodide ions as follows.



You will then titrate the iodine produced against sodium thiosulfate solution, and the reaction is as follows.



You will analyse the results using a graph of volume of sodium thiosulfate against time.

- (a) *You are advised to study this entire series of steps before starting your experiment. You are also advised to manage your time effectively so that you can complete all the titrations and the question parts in the next few pages.*

### Measuring and filling of FA 3 and FA 5

- 1 Use a measuring cylinder to add about 10 cm<sup>3</sup> of **FA 3** into each of the five labelled boiling tubes.
- 2 Fill a burette with **FA 5**.

### Preparation of reaction mixture and withdrawing aliquots

- 3 Use separate measuring cylinders to add the following into the conical flask labelled 'reaction mixture'.
  - 48.0 cm<sup>3</sup> of deionised water
  - 50.0 cm<sup>3</sup> of **FA 7**
  - 5.0 cm<sup>3</sup> of **FA 4**
  - 2.0 cm<sup>3</sup> of **FA 1**



- 4 Use another measuring cylinder to measure  $20.0 \text{ cm}^3$  of **FA 6**. Add this **FA 6** into the mixture prepared in step 3, immediately starting the stopwatch when the two liquids contact. Swirl the reaction mixture thoroughly.
- 5 At approximately 1 minute, withdraw a  $10.0 \text{ cm}^3$  aliquot of the reaction mixture to a  $10 \text{ cm}^3$  measuring cylinder, using a dropping pipette. Immediately add this aliquot into boiling tube 1 (containing **FA 3**) and shake the sample carefully to prevent spillage. Record the transfer time in minutes and seconds, to the nearest second, when the aliquot is added.
- 6 At approximately 2 minutes, repeat step 5 but add the aliquot into boiling tube 2.
- 7 Choose three other time intervals at about 2-minute intervals. You should **not** exceed a maximum reaction time of 10 minutes. At each of your chosen times, repeat step 5 but add each aliquot into the corresponding boiling tube.

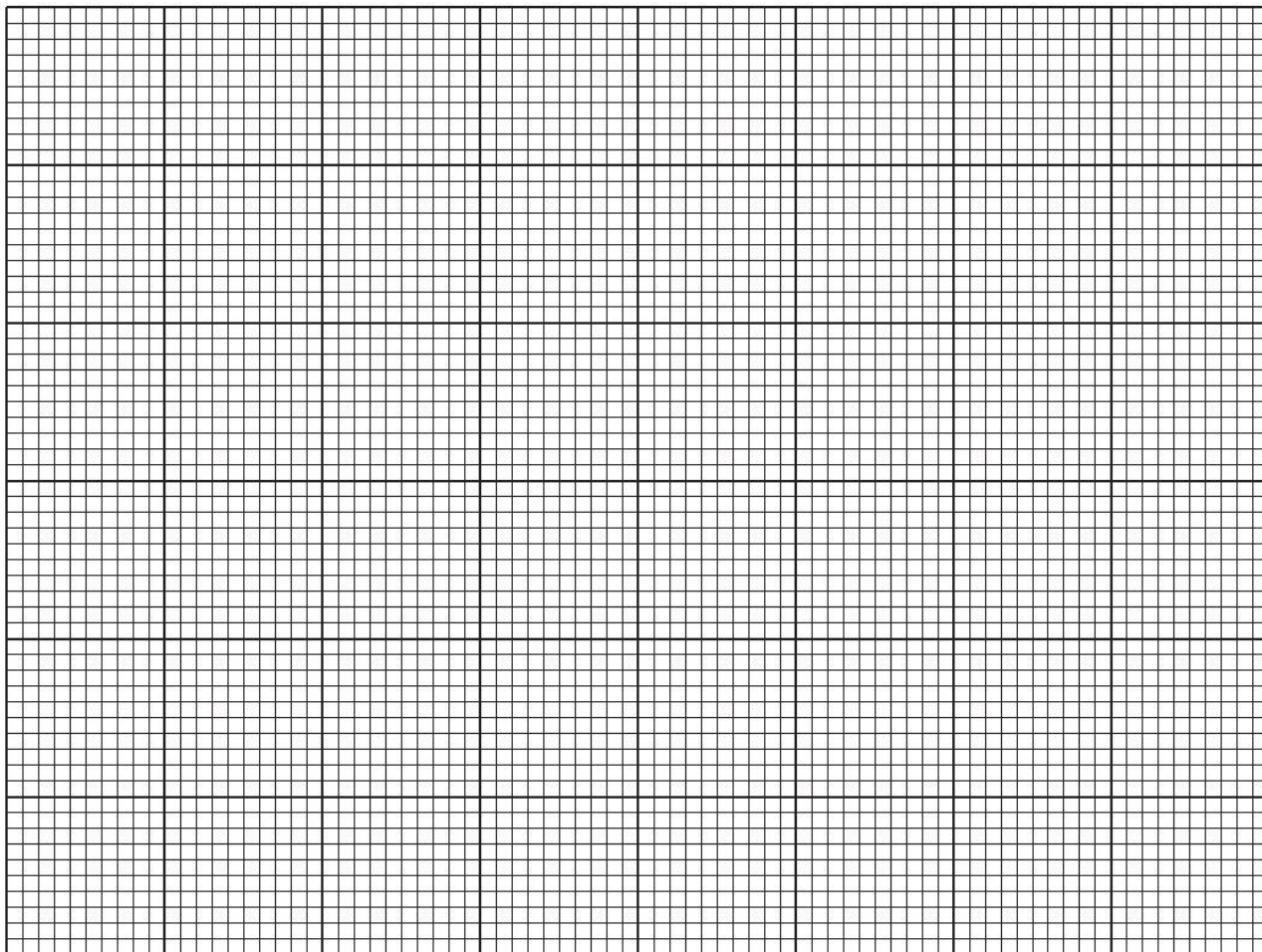
#### Titration of withdrawn samples

- 8 Add all of the contents of boiling tube 1 into a clean conical flask. Rinse this boiling tube with deionised water, and add the washings into the same conical flask.
- 9 Titrate the iodine in this solution with **FA 5** until the solution is pale yellow. Add  $1 \text{ cm}^3$  of **Solution I** into this solution and continue titrating until the point when the solution just turns colourless. The end-point of this titration is expected to be less than  $20 \text{ cm}^3$  of **FA 5**. Record your titration results.
- 10 After your titration, wash this conical flask thoroughly with water.
- 11 Repeat steps 8 to 10 for each of the other boiling tubes. *Note that each titration can only be performed once, and you are only given one conical flask for the titrations.*

Record all your experimental results below. In addition, you are to convert the transfer times to decimal values,  $t$ , in minutes, recorded to one decimal place. For example, a transfer time of 1 min 28 s becomes  $1 \text{ min} + 28/60 \text{ min} = 1.5 \text{ min}$ .

[3]


- (b) On the grid below, plot a graph of volume of **FA 5** on the y-axis, against ***t*** on the x-axis. Label the axes clearly. Draw a smooth curve taking into account all of the plotted points (but ignoring any anomalous points).



[3]

- (c) It has been claimed that the order of reaction with respect to  $\text{MnO}_4^-$  is one.

State whether you agree or disagree with this claim. Use the evidence from your graph above to support your answer.

.....  
 .....  
 .....  
 .....[2]

(d) In the following questions, you will use your graph in (b) to determine the rate of change of the concentration of  $\text{MnO}_4^-$  ions in the reaction mixture at  $t = 5$  min.

(i) Draw a tangent to your curve at  $t = 5$  min. [1]

(ii) Determine the gradient of your tangent, showing clearly how you obtained your answer.

gradient of tangent = .....  $\text{cm}^3 \text{ min}^{-1}$  [1]

(iii) Calculate the rate of change in amount of  $\text{S}_2\text{O}_3^{2-}$  ions needed for complete reaction at this time.

rate of change in amount of  $\text{S}_2\text{O}_3^{2-}$  ions = .....  $\text{mol min}^{-1}$  [1]

(iv) Calculate the rate of change in amount of  $\text{MnO}_4^-$  ions remaining in  $10 \text{ cm}^3$  of the reaction mixture at this time.

rate of change in amount of  $\text{MnO}_4^-$  ions in  $10 \text{ cm}^3$  = .....  $\text{mol min}^{-1}$  [1]

(v) Hence, calculate the rate of change of the concentration of  $\text{MnO}_4^-$  ions in the reaction mixture at this time.

rate of change of the concentration of  $\text{MnO}_4^-$  ions = .....  $\text{mol dm}^{-3} \text{ min}^{-1}$  [1]

## Part II

- (e) A similar experiment was performed by a student but without adding **FA 1**. Also, a total of  $50.0 \text{ cm}^3$  of deionised water was added instead so that the reaction mixture has the same volume as in Part I. The results obtained are shown in Fig. 2.1.

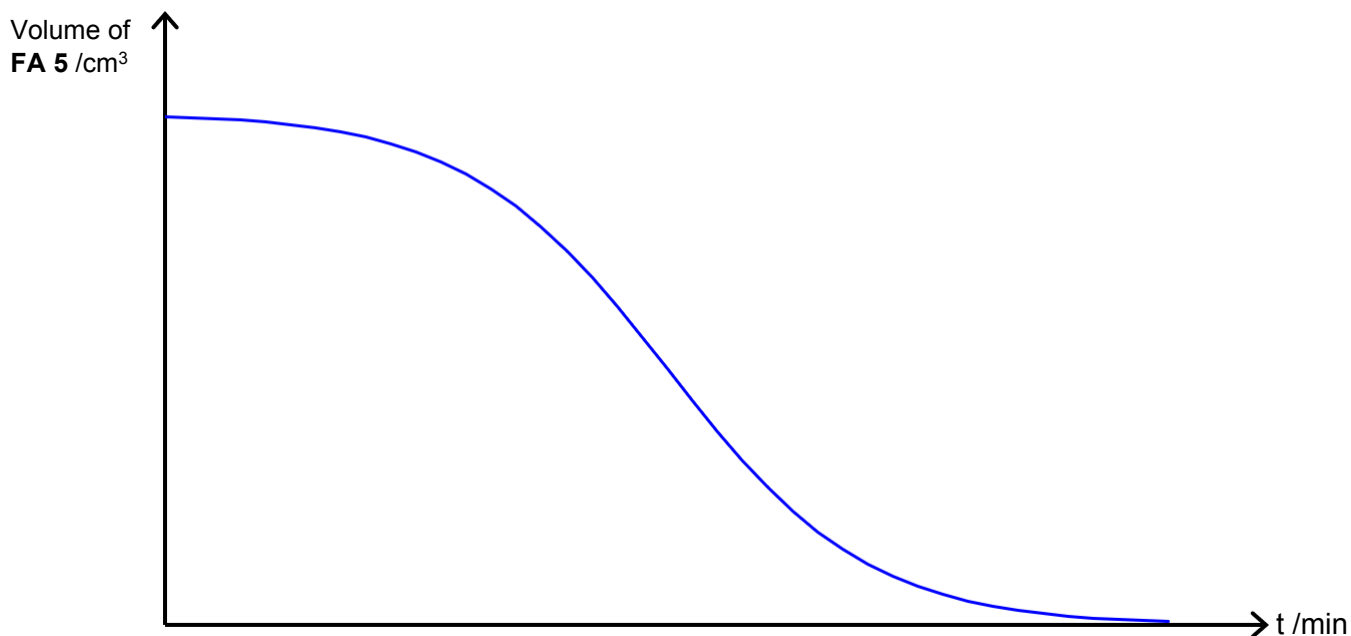


Fig. 2.1

- (i) Describe the shape of this line, linking to how the rate changes during the reaction.

.....  
 .....  
 .....  
 .....[2]

- (ii) Explain why the graph in Fig. 2.1 has a different shape from the one you plotted in **2(b)**.

.....  
 .....  
 .....  
 .....[2]

[Total: 17]

### 3 Determination of percentage purity by mass of a sodium carbonate, $\text{Na}_2\text{CO}_3$ , sample.

**FA 4** is  $1.00 \text{ mol dm}^{-3}$  sulfuric acid.

**FA 8** contains a sodium carbonate solution of unknown concentration.

**Solution II** is methyl orange indicator.

In this question, you will perform a titration to determine the concentration of a sodium carbonate solution.

**(a) (i) Titration of FA 8 against FA 4.**

1. Fill the burette with **FA 4**.
2. Use the pipette to transfer  $25.0 \text{ cm}^3$  of **FA 8** into a  $250 \text{ cm}^3$  conical flask.
3. Add a few drops of **Solution II** into the same conical flask.
4. Titrate the mixture in the conical flask until the end-point is reached.
5. Record your titration results, to an appropriate level of precision, in the space provided below.
6. Repeat steps 2 to 5 until consistent results are obtained.

**Titration Results**

final burette reading / $\text{cm}^3$			
initial burette reading / $\text{cm}^3$			
volume of <b>FA 4</b> added / $\text{cm}^3$			


[3]

- (ii)** From your titrations, obtain a suitable volume of **FA 4** to be used in your calculations. Show clearly how you obtained this value.


volume of **FA 4** = ..... [3]

- (b) (i)** Write the balanced equation for the reaction between sodium carbonate and sulfuric acid.

..... [1]

- (ii) **FA 8** was initially prepared by dissolving 90.0 g of an impure sample of sodium carbonate in 1.00 dm<sup>3</sup> of water. Calculate the percentage purity by mass of the original sample.  
[A<sub>r</sub>: H, 1.0; C, 12.0; O, 16.0; Na, 23.0]


[4]

[Total: 11]

#### 4 Planning: Determining the enthalpy change of combustion of ethanol

The combustion of ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , is an exothermic process. The heat evolved during combustion can be used to heat up a fixed amount of water in a copper can. By measuring the temperature rise of the water, the enthalpy change of combustion of ethanol,  $\Delta H_c$ , can be determined.

However, the heat absorbed by the copper can must be taken into account in order to obtain a more accurate result.

The heat capacity of a copper can,  $C$ , is defined as the amount of heat needed to raise the temperature of the copper can by 1 K. Its units is given as  $\text{J K}^{-1}$ .

The value of  $C$  can be determined experimentally by mixing a known volume of hot water into a known volume of cold water in a copper can. The difference between heat lost by the hot water and heat gained by the cold water is the heat absorbed by the copper can.

Use the following information for your calculations:

- specific heat capacity of water =  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$
- density of water =  $1.00 \text{ g cm}^{-3}$

- (a) A student performed an experiment to determine the heat capacity of the copper can,  $C$ . The student poured  $75 \text{ cm}^3$  of hot water into the copper can which already contained  $75 \text{ cm}^3$  of cold water. The final temperature of the water in the copper can was measured. The results are shown in Table 4.1.

**Table 4.1**

Temperature of cold water and copper can before mixing / $^{\circ}\text{C}$	8.9
Temperature of hot water before mixing / $^{\circ}\text{C}$	60.4
Final temperature of water and copper can after mixing / $^{\circ}\text{C}$	25.6

Determine the value of  $C$  in  $\text{J K}^{-1}$ .

.....

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.....

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.....

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.....

.....

..... [3]

- (b)** Plan an experiment to collect sufficient data to enable you to determine the enthalpy change of combustion of ethanol,  $\Delta H_c$ , using a copper can calorimeter.

In your plan, the temperature rise of the water in the copper can,  $\Delta T$ , should be chosen to be at least 10 °C. You may assume that sufficient ethanol is provided to achieve the required temperature rise of water.

You may assume you are provided with:

- 200 cm<sup>3</sup> copper can
- spirit burner with wick and ethanol
- the equipment normally found in a school or college laboratory.

Your plan should include details of:

- a labelled diagram of the apparatus you would use, including how you would minimise heat lost to the surroundings
- the quantities you would use
- the procedure you would follow
- the measurements you would take.

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.....

.....

.....

.....

.....

..... [6]

(c) Describe how you would use the results obtained in (a) and (b) to determine  $\Delta H_c$ .

State an assumption that you have made in your calculations.

[ $M_r$  of ethanol = 46.0]

.....

.....

.....

.....

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.....

.....

..... [3]

[Total: 12]

**Qualitative Analysis Notes**

[ppt. = precipitate]

**(a) Reactions of aqueous cations**

<b>cation</b>	<b>reaction with</b>	
	NaOH(aq)	NH <sub>3</sub> (aq)
aluminium, Al <sup>3+</sup> (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH <sub>4</sub> <sup>+</sup> (aq)	ammonia produced on heating	–
barium, Ba <sup>2+</sup> (aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca <sup>2+</sup> (aq)	white ppt. with high [Ca <sup>2+</sup> (aq)]	no ppt.
chromium(III), Cr <sup>3+</sup> (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu <sup>2+</sup> (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe <sup>2+</sup> (aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe <sup>3+</sup> (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg <sup>2+</sup> (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn <sup>2+</sup> (aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn <sup>2+</sup> (aq)	white ppt. soluble in excess	white ppt. soluble in excess

**(b) Reactions of anions**

<i>anion</i>	<i>reaction</i>
carbonate, $\text{CO}_3^{2-}$	$\text{CO}_2$ liberated by dilute acids
chloride, $\text{Cl}^-(\text{aq})$	gives white ppt. with $\text{Ag}^+(\text{aq})$ (soluble in $\text{NH}_3(\text{aq})$ )
bromide, $\text{Br}^-(\text{aq})$	gives pale cream ppt. with $\text{Ag}^+(\text{aq})$ (partially soluble in $\text{NH}_3(\text{aq})$ )
iodide, $\text{I}^-(\text{aq})$	gives yellow ppt. with $\text{Ag}^+(\text{aq})$ (insoluble in $\text{NH}_3(\text{aq})$ )
nitrate, $\text{NO}_3^-(\text{aq})$	$\text{NH}_3$ liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil
nitrite, $\text{NO}_2^-(\text{aq})$	$\text{NH}_3$ liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil; $\text{NO}$ liberated by dilute acids (colourless $\text{NO} \rightarrow$ (pale) brown $\text{NO}_2$ in air)
sulfate, $\text{SO}_4^{2-}(\text{aq})$	gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (insoluble in excess dilute strong acids)
sulfite, $\text{SO}_3^{2-}(\text{aq})$	$\text{SO}_2$ liberated with dilute acids; gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (soluble in dilute strong acids)

**(c) Test for gases**

<i>gas</i>	<i>test and test result</i>
ammonia, $\text{NH}_3$	turns damp red litmus paper blue
carbon dioxide, $\text{CO}_2$	gives a white ppt. with limewater (ppt. dissolves with excess $\text{CO}_2$ )
chlorine, $\text{Cl}_2$	bleaches damp litmus paper
hydrogen, $\text{H}_2$	"pops" with a lighted splint
oxygen, $\text{O}_2$	relights a glowing splint
sulfur dioxide, $\text{SO}_2$	turns aqueous acidified potassium manganate(VII) from purple to colourless

**(d) Colour of halogens**

<i>halogen</i>	<i>colour of element</i>	<i>colour in aqueous solution</i>	<i>colour in hexane</i>
chlorine, $\text{Cl}_2$	greenish yellow gas	pale yellow	pale yellow
bromine, $\text{Br}_2$	reddish brown gas / liquid	orange	orange-red
iodine, $\text{I}_2$	black solid / purple gas	brown	purple