BP~543

HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME
CT GROUP 21S
CENTRE NUMBER
INDEX NUMBER

CHEMISTRY **9729/01**

Paper 1 Multiple Choice **19 September 2022**

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

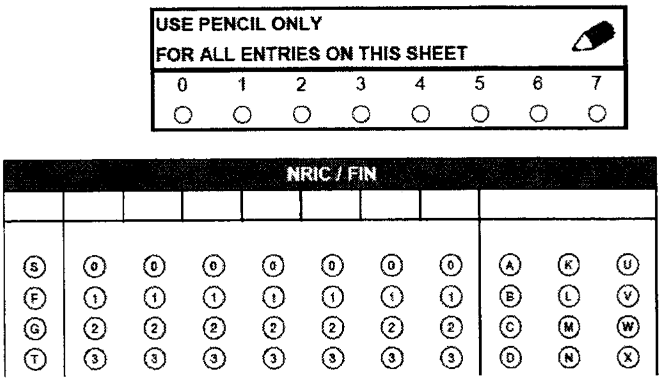
READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

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

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**



There are **thirty** questions on this paper. Answer **all** questions. For each question, there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

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

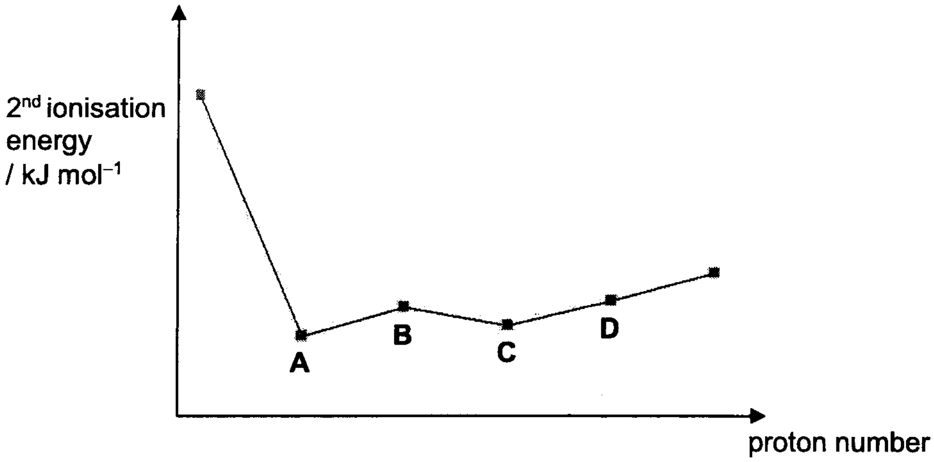
This document consists of **13** printed pages.

1 Which formula represents a particle with the composition of 1 proton, 2 neutrons and 3 electrons? (D represents deuterium, ^{2}H; and T represents tritium, ^{3}H)

A H^- **B** D^{2-} **C** T^{2-} **D** He^-

2 The variation in the second ionisation energy of six consecutive elements in the Periodic Table is shown in the graph.

Which element is a Group 13 element?



3 Which observation **cannot** be explained by intermolecular hydrogen bonding?

A Methanol dissolves readily in water.

B The boiling point of HBr is higher than that of HC*l*.

C The boiling point of 4-aminophenol is higher than that of 2-aminophenol.

D The relative molecular mass of ethanoic acid when dissolved in hexane is 120.

4 In which pairs of compounds does the first molecule have a smaller bond angle than that in the second molecule?

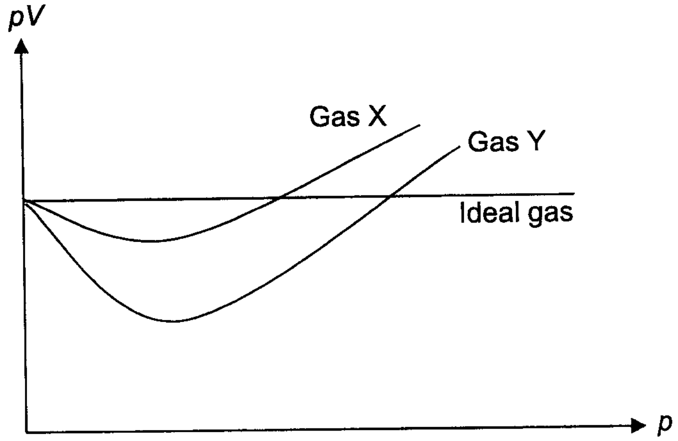
1 NF_3 CCl_4

2 H_2O XeF_4

3 SF_6 CS_2

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

5 The following graphs were obtained for three gases for the variation of pV with p, where p is the pressure and V is the volume of the gas.



Which row is correct if gas X is HCl at 300 K?

	gas Y	temperature / K
A	HCl	400
B	CH_4	400
C	O_2	300
D	HF	300

6 Methyl red ($C_{15}H_{15}N_3O_2$) is an organic compound used as an acid-base indicator. Why does methyl red, which is red in acidic solutions, turn yellow in alkaline solutions?

A It is oxidised by OH^- ions.

B It is reduced by OH^- ions.

C It forms a cation by gain of H^+ ions.

D It forms an anion by loss of H^+ ions.

7 Group 2 nitrates undergo thermal decomposition to give the metal oxide, nitrogen dioxide and oxygen.

0.118 g of a Group 2 nitrate was thermally decomposed and the residue was dissolved in 80.0 cm^3 of 0.0350 mol dm^{-3} $HCl(aq)$. The resultant solution required 21.60 cm^3 of 0.0780 mol dm^{-3} $NaOH(aq)$ for complete neutralisation.

What was the Group 2 metal in the nitrate?

A Mg **B** Ca **C** Sr **D** Ba

8 Astatine is below iodine in Group 17 of the Periodic Table.

Which properties are likely correct for astatine and its compounds?

1 Astatine is less volatile than iodine.

2 Silver astatide has less covalent character than silver iodide.

3 When a heated glass rod is inserted into a container of hydrogen astatide, it decomposes into its elements.

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

9 A 0.483 g sample of glycine (M_r = 75) was placed in a bomb calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.54 °C.

In a separate experiment using the same calorimeter, the combustion of 0.986 g of benzoic acid (M_r = 122) gave a temperature rise of 2.14 °C. The enthalpy change of combustion of benzoic acid is –3054 kJ mol^{-1}.

What is the enthalpy change of combustion, in kJ mol^{-1}, of glycine?

A –615 **B** –967 **C** –2423 **D** –3812

10 Group 2 hydroxides undergo thermal decomposition in a similar fashion to Group 2 carbonates.

Barium hydroxide undergoes decomposition as shown in the equation below:

$$Ba(OH)_2(s) \rightarrow BaO(s) + H_2O(g) \qquad \Delta H > 0$$

Which statements about this reaction are correct?

1 The Gibbs free energy change can be positive or negative depending on the temperature.

2 The decomposition is spontaneous only at high temperature.

3 The entropy change is negative.

4 Barium hydroxide decomposes at a lower temperature than magnesium hydroxide.

A 1 and 2 only

B 1 and 3 only

C 2 and 4 only

D 1, 2 and 4 only

11 The equation for the bromination of propanone is shown below.

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_3COCH_2Br + H^+ + Br^-$$

The rate of disappearance of the bromine colour was measured for several different concentrations of CH_3COCH_3, Br_2 and H^+ at a certain temperature.

$[CH_3COCH_3]$/ mol dm^{-3}	$[Br_2]$/ mol dm^{-3}	$[H^+]$/ mol dm^{-3}	rate of disappearance of Br_2 colour/ mol dm^{-3} s^{-1}
0.30	0.05	0.05	5.70×10^{-5}
0.30	0.10	0.05	5.70×10^{-5}
0.30	0.05	0.10	1.14×10^{-4}
0.40	0.05	0.20	3.04×10^{-4}

Which statement about the above reaction is correct?

A The rate equation for the reaction is rate = $k[CH_3COCH_3][Br_2]$.

B The rate constant for the reaction is 3.80×10^{-3} mol^{-1} dm^3 s^{-1}.

C The rate constant of the reaction doubles when $[CH_3COCH_3]$ is doubled.

D The time taken for the concentration of CH_3COCH_3 to decrease to half its initial value is the same for all experiments.

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

A At higher temperatures, the yield decreases but the rate of production of ammonia is faster.

B At lower temperatures, the value of K_p decreases.

C At higher pressures, the yield decreases but the rate of production of ammonia is faster.

D In the presence of a catalyst, the yield decreases but the rate of production of ammonia is faster.

13 0.50 moles of CH_3CO_2H and 0.50 moles of CH_3CH_2OH were mixed and an esterification reaction took place. The equilibrium constant for this reaction is 4.0.

What is the amount of CH_3CO_2H (in moles) in the mixture at equilibrium?

A 0.17 **B** 0.25 **C** 0.33 **D** 0.67

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

Water dissociates as shown.

$$H_2O \rightleftharpoons H^+ + OH^-$$

At 25 °C, the equilibrium value of $[H^+]$ is 10^{-7} mol dm^{-3}; $[H_2O] = 55.6$ mol dm^{-3}.

What is the order of increasing numerical value of pH, pK_a and pK_w for this equilibrium at this temperature?

	smallest		largest
A	pH	pK_a	pK_w
B	pH	pK_w	pK_a
C	pK_a	pK_w	pH
D	pK_w	pK_a	pH

15 Which combination of substances would result in a buffer solution?

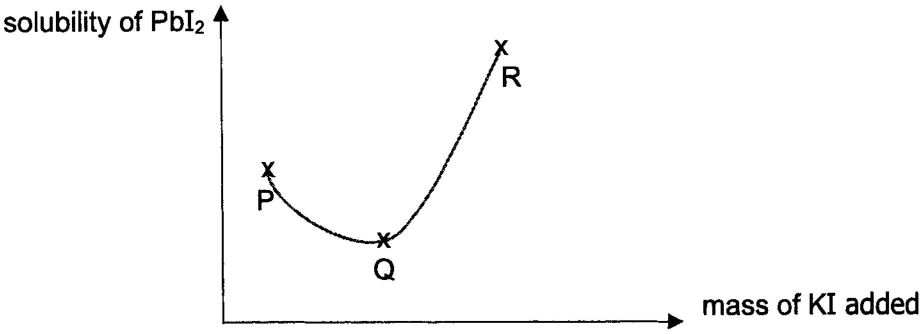
A 25.0 cm^3 of 0.100 mol dm^{-3} HC*l*(aq) and 20.0 cm^3 of 0.100 mol dm^{-3} NaC*l*(aq)

B 25.0 cm^3 of 0.100 mol dm^{-3} HC*l*(aq) and 25.0 cm^3 of 0.200 mol dm^{-3} NH_3(aq)

C 25.0 cm^3 of 0.100 mol dm^{-3} H_2CO_3(aq) and 50.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq)

D 20.0 cm^3 of 0.100 mol dm^{-3} CH_3CO_2H(aq) and 25.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq)

16 The following graph represents how the solubility of a sparingly soluble salt lead(II) iodide, PbI_2, changes upon addition of solid potassium iodide at a fixed temperature.



Which statement about the above graph is **not** correct?

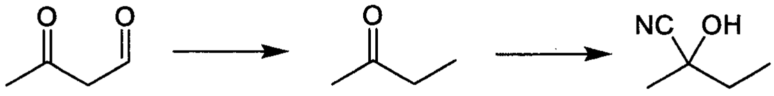
A The change in solubility along PQ is due to common ion effect.

B The change in solubility along QR is due to the formation of a complex between Pb^{2+} and I^-.

C At Q, the molar concentration of I^- ions is twice that of Pb^{2+} ions.

D K_{sp} remains constant along PR.

17 What types of reactions can be found in the following reaction scheme?



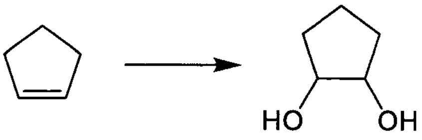
1 substitution

2 reduction

3 addition

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

18 What are the optimal reagents and conditions for the following reaction?



A steam, H_3PO_4 catalyst, high temperature and pressure

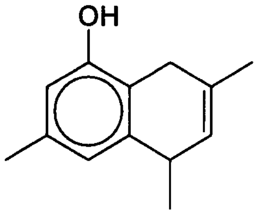
B $K_2Cr_2O_7$(aq), H_2SO_4(aq), 25°C

C $KMnO_4$(aq), H_2SO_4(aq), 25°C

D $KMnO_4$(aq), KOH(aq), 10°C

19 When mixed with aqueous Br_2, 1 mole of X reacts with 2 moles of Br_2.
What could X be?

A



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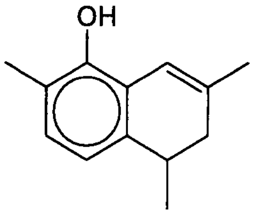

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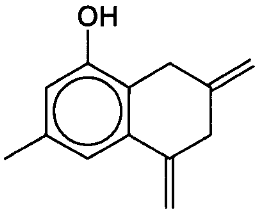

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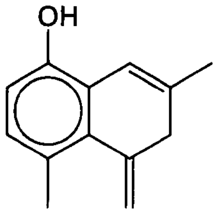
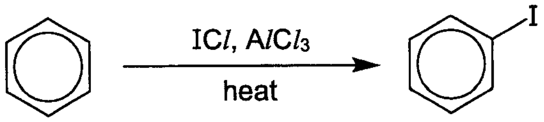


20 Which reaction has the correct reagents and conditions?

A



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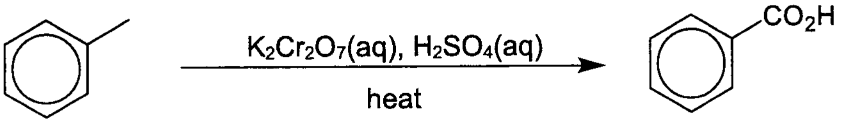
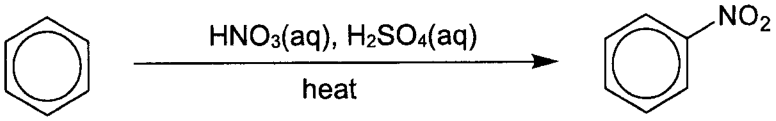
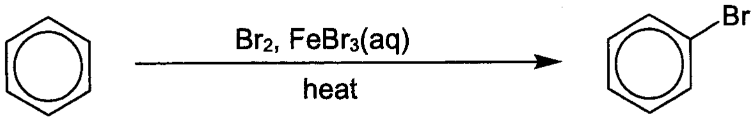


C

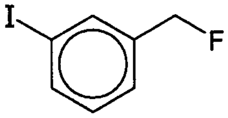


D

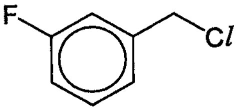


21 1 mole of each of the compounds below was heated with excess aqueous potassium hydroxide followed by acidification. Aqueous silver nitrate was then added to the mixture. Which compound will produce the least silver halide precipitate by mass?

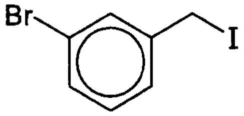
A



B



C



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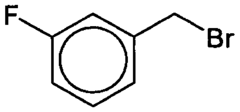
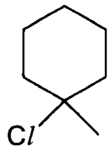
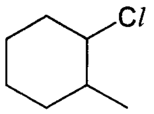
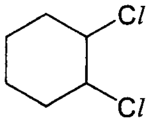


22 Which compounds exhibit stereoisomerism?

1 

2 

3 

A 1 only

B 2 only

C 2 and 3 only

D 1, 2 and 3

23 Which statement best explains the difference in reactivity of ethene and ethanal with lithium aluminium hydride?

A Ethanal has an electron deficient reaction centre.

B Ethene does not react as the electrons are delocalised.

C Ethanal adsorbs better onto the lithium aluminum hydride.

D Ethene cannot be reduced any further as it does not have any O atoms.

24 Which statement describes the conversion of a ketone to a cyanohydrin?

A The ketone acts as a nucleophile in the mechanism.

B The second step of the mechanism involves a reduction reaction.

C The hybridisation of the carbonyl carbon remains as sp^2 throughout the reaction.

D The reaction can proceed with KCN added to the ketone, followed by excess aqueous sulfuric acid at room temperature.

25 Which pair of compounds will result in an ester being formed immediately when mixed?

A ethanol and ethanoic acid

B ethanoic acid and ethanoyl chloride

C ethanol and ethanoyl chloride

D sodium phenoxide and ethanoic acid

26 Which reaction will **not** result in the formation of a compound with an amine functional group?

A heating propanamide with aqueous potassium hydroxide

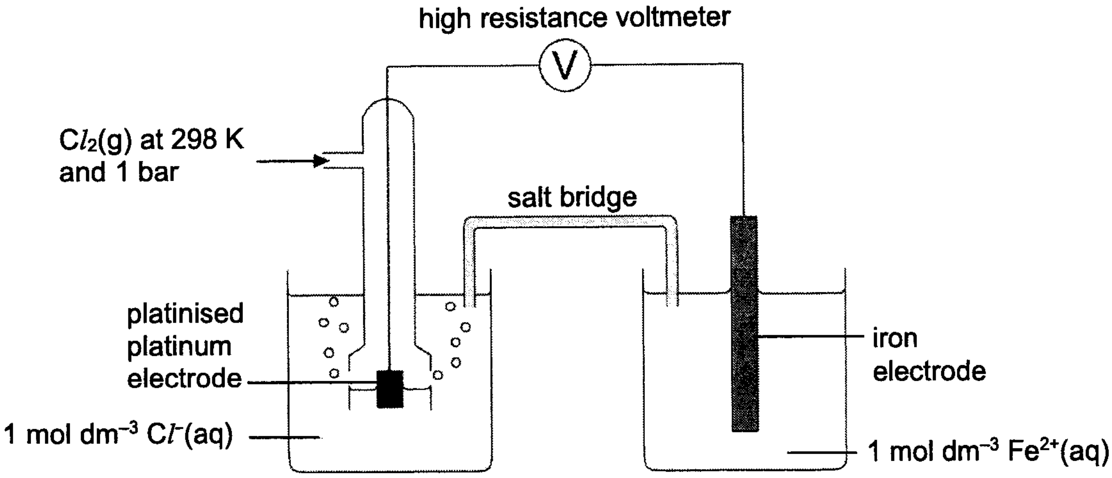
B reacting ethanamide with dry lithium aluminium hydride

C prolonged heating of a tripeptide in aqueous sodium hydroxide

D heating chloroethane with liquid ammonia under reflux

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

Which change to the half-cells will cause the high resistance voltmeter to show a less positive reading?



A using a bigger piece of iron electrode

B adding water to the half-cell on the right

C adding aqueous $AgNO_3$ to the half-cell on the left

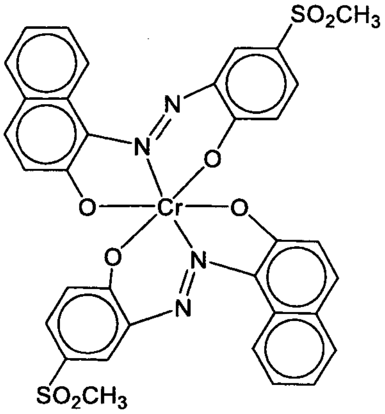
D decreasing the pressure of the chlorine gas

28 Four separate electrolysis experiments were performed as follows, under the same conditions of temperature and pressure.

In which experiment will a gas be produced at only one electrode?

	electrodes used	electrolyte used
A	carbon	dilute sodium chloride solution
B	carbon	concentrated sodium chloride solution
C	copper	copper(II) sulfate solution
D	carbon	copper(II) sulfate solution

29 The following chromium complex, C.I. Acid Violet 78, is used as a dye.



C.I. Acid Violet 78

What is the oxidation number of chromium in the complex above?

A 0

B +2

C +4

D +6

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

The colours of various vanadium-containing ions are given in the table below.

oxidation state	+5	+4	+3	+2
colour	yellow	blue	green	violet

When an excess of W was added to an aqueous solution of acidified ammonium vanadate(V), NH_4VO_3, a green solution was obtained at the end of the experiment.

What could be the identity of W?

1 zinc

2 sulfur dioxide

3 nitrogen dioxide

A 1, 2 and 3

B 1 and 2 only

C 1 and 3 only

D 2 only

BP~557

HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	21S
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/02

Paper 2 Structured Questions

29 August 2022

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** clearly in the spaces above.

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.

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.

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.

For Examiner's Use	
1	/ 11
2	/ 9
3	/ 13
4	/ 15
5	/ 27
Deductions	
Total	/ 75

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

1 Fossil fuels which are found in deposits have been formed from plants and animals that lived millions of years ago.

When fossil fuels are burned in internal combustion engines, CO_2 and H_2O are the main products, with NO and SO_2 also being formed.

(a) **(i)** What class of compound, present in fossil fuels, produces CO_2 and H_2O on combustion?

....[1]

(ii) NO and NO_2, collectively known as oxides of nitrogen, are pollutants that are also formed during combustion in motor vehicles. Write equations to show how each of these two gases are formed in vehicle engines.

....

....[1]

(iii) State one harmful effect of oxides of nitrogen on the environment.

....[1]

To meet emission standards in Singapore, sulfur emissions from cars have to be lower than 50 parts per million (ppm). This means that there should be less than 50 molecules of SO_2 for every 1×10^6 molecules of gas in the fuel exhaust for it to meet regulations.

(b) **(i)** A sample of fuel was combusted at 900 °C and 10.0 bar. At the end of the reaction, 63.2 dm^3 of gas was collected under the same conditions.

Determine the amount of gas, in moles, produced by combustion of the fuel sample.

[2]

(ii) Given that 0.0183 g of SO_2 was produced in **(b)(i)**, calculate the concentration of SO_2, in parts per million, and explain whether the fuel exhaust meets the sulfur emission standards.

[2]

(c) Describe the reactions, if any, of SO_3, Na_2O and Al_2O_3 with water. Include the approximate pH value of any resulting solutions, and write equations for any reactions that occur.

....

....

....

....

....

....

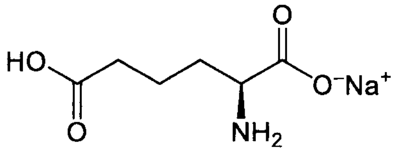
....

....

....[4]

[Total: 11]

2 Monosodium glutamate (MSG) is a natural flavour enhancer present in foods. Naturally occurring MSG can be extracted from seaweed and is commonly manufactured on a large scale by fermenting sugars.



MSG

(a) **(i)** A chemist proposed to synthesise MSG using the following reaction scheme. Draw intermediates **A** and **B**, and state the reagents and conditions for step 1 and step 2.

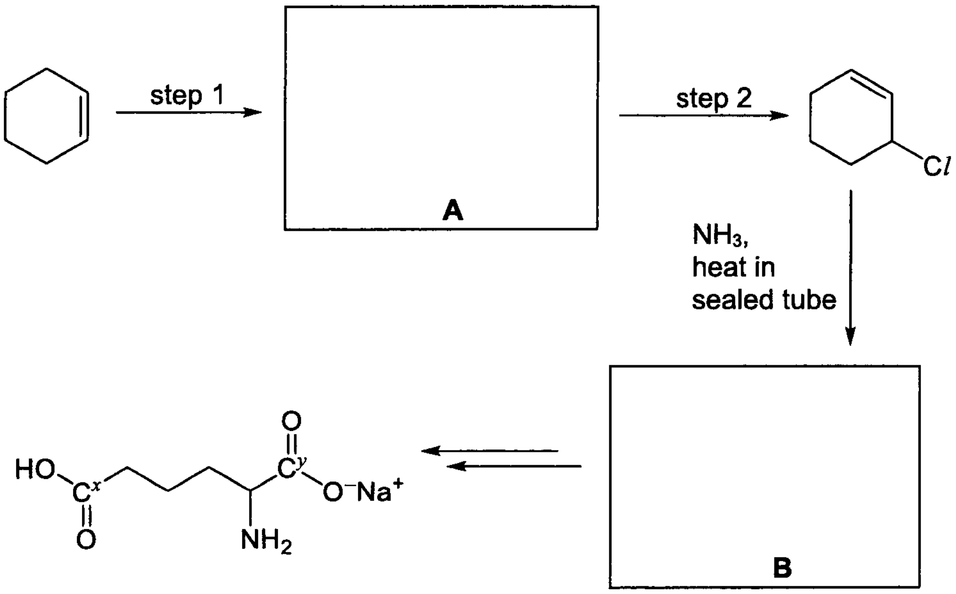


Fig. 2.1

step 1: ....

step 2: ....
[4]

(ii) In the final step of the reaction scheme, the $-C^yO_2H$ group is deprotonated instead of the $-C^xO_2H$ group. Explain why this is so.

....

....

....

....

....[2]

(iii) Food flavours enhanced by the MSG synthesised in the laboratory according to Fig. 2.1 might taste differently from flavours enhanced by naturally occurring MSG. Suggest why this is so.

....

....

....

....

....[1]

(b) High sodium content food is linked to increased risk of heart disease. Some health experts recommend using MSG instead of table salt ($NaCl$) to flavour food so as to reduce sodium intake. With the aid of suitable calculations, show that 1 g of MSG helps achieve lower sodium intake than 1 g of table salt.

[2]

[Total: 9]

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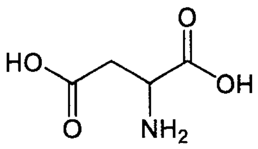
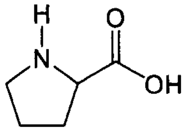
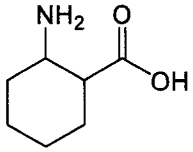
3 The structures of amino acids **A** to **D** are given below.



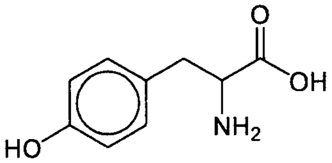
A



B



C



D

(a) Identify the amino acid that is **not** an α-amino acid.

.... [1]

(b) On complete hydrolysis, a tripeptide gave the other three amino acids not identified in **(a)** in equimolecular amounts.

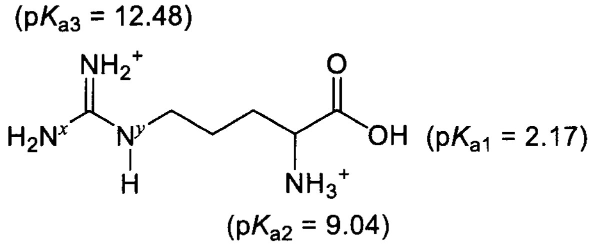
Draw the structural formula of one such tripeptide at pH 1 and pH 14.

At pH 1:

At pH 14:

[3]

(c) The pK_a values of the acidic groups in a fully protonated arginine are labelled below.



fully protonated arginine

(i) Given that N^x and N^y are both sp^2 hybridised, suggest why they are both very weak bases.

....

....

....[1]

When a 10.0 cm^3 sample of the fully protonated arginine is titrated against 0.100mol dm^{-3} NaOH, the following titration curve is obtained.

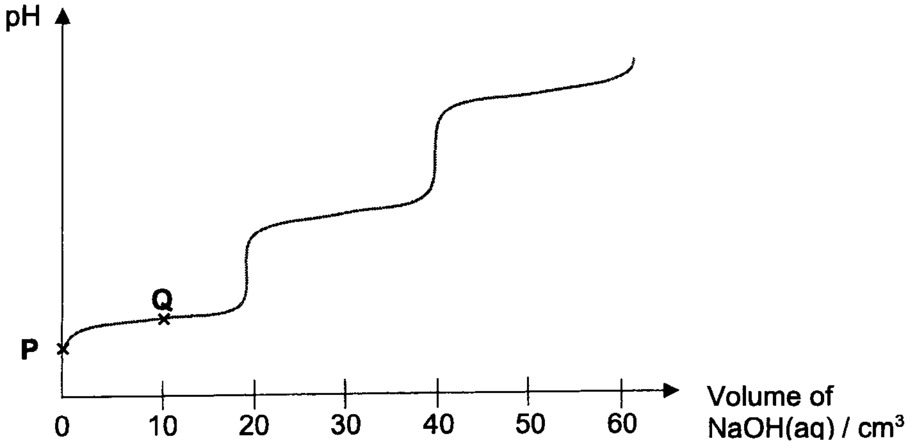


Fig. 3.1

(ii) Calculate the concentration of arginine in the 10.0 cm^3 sample.

[1]

(iii) Calculate the pH of the solution at point **P** (ignore the effects of the second and third acid dissociations on the pH).

[2]

(iv) Determine the pH at point **Q**.

[1]

(v) Explain, using an equation and the relevant ionic forms of arginine, why the pH changes only gradually around point **Q** as aqueous NaOH is added.

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....[3]

(vi) The isoelectric point is the pH at which the net electrical charge on an amino acid is zero.

On the titration curve in Fig. 3.1, label the isoelectric point of arginine clearly with an "X".

[1]

[Total: 13]

4 (a) A nickel(II) complex is prepared by adding excess aqueous ammonia to an aqueous solution of nickel(II) ions.

The water ligands are replaced by ammonia ligands in this reaction.

$$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

(i) What is meant by the term *ligand*?

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.... [1]

(ii) Explain why complexes of nickel(II) are coloured, and why the aqueous solution of nickel(II) changes colour when excess aqueous ammonia is added.

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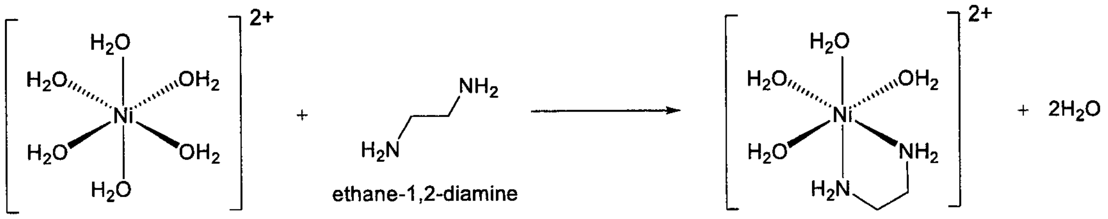
(b) Ethane-1,2-diamine, en, is a bidentate ligand, which can form 2 coordinate bonds to nickel(II) simultaneously.



When an excess of ethane-1,2-diamine is added to an aqueous solution of $[Ni(NH_3)_6]^{2+}$, the following equilibrium is established.

equation 4.1 $[Ni(NH_3)_6]^{2+}(aq) + 3en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) + 6NH_3(aq)$

Table 4.1 shows the standard enthalpy and entropy changes for equation 4.1 at 298 K.

Table 4.1

$\Delta H^\ominus_r$ / kJ mol^{-1}	−17.0
$\Delta S^\ominus_r$ / J K^{-1} mol^{-1}	+121

(i) Explain why equation 4.1 shows a large **and** positive value for $\Delta S^\ominus_r$.

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....[2]

(ii) Calculate $\Delta G^\ominus_r$ for equation 4.1.

[1]

(iii) State what the $\Delta G^\ominus_r$ value indicates about the position of equilibrium for equation 4.1. Hence, identify which ligand bonds preferentially with Ni^{2+}.

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....[2]

(iv) Bidentate ligands, like ethane-1,2-diamine, form coordinate bonds with metal centres very quickly compared to a similar reaction with ammonia ligands.

Suggest a reason for the rapid rate of reaction.

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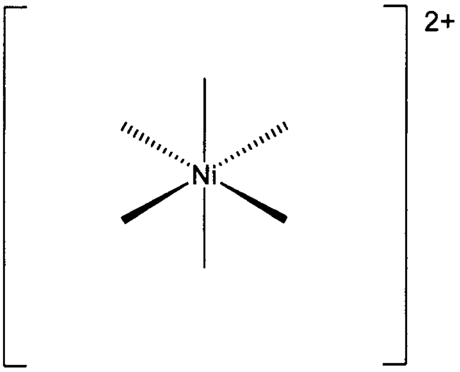
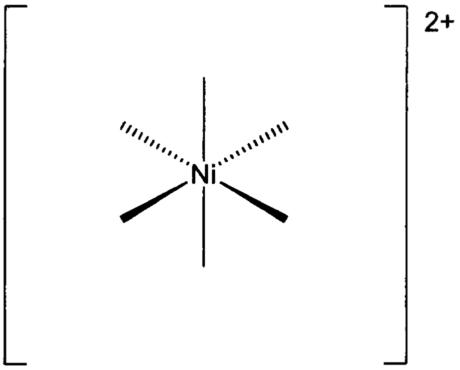
....[1]

(c) **(i)** The $[Ni(en)_3]^{2+}$ complex, formed in equation 4.1, is chiral.

Complete the drawings below to show the 3-dimensional structures of the two enantiomers of $[Ni(en)_3]^{2+}$.





[2]

(ii) Explain why $[Ni(en)_3]^{2+}$ is considered chiral.

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....[1]

(iii) Describe **one** similarity and **one** difference between the enantiomers of a $[Ni(en)_3]^{2+}$ containing compound in terms of their physical properties.

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....[2]

[Total: 15]

5 (a) Iron and its compounds are commonly used as homogeneous or heterogeneous catalysts to speed up reactions.

(i) Explain, with the aid of a Boltzmann distribution diagram, the effect on a rate constant of adding a catalyst.

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.... [3]

(ii) State the electronic configuration of an iron atom.

.... [1]

(iii) Complete Table 5.1 to show an example of a reaction where iron or its compound acts as a homogeneous catalyst or heterogeneous catalyst. State the identity of the catalyst used in each case, and briefly explain why it can act as this type of catalyst.

Table 5.1

	homogeneous catalysis	heterogeneous catalysis
balanced equation for catalysed reaction		
catalyst used		
reason why iron or its compound could act as this type of catalyst		

[4]

Two methods for the electrochemical synthesis of H_2O_2 are described in **(b)** and **(c)**.

(b) Fig. 5.1 shows a conventional fuel cell that produces H_2O_2 via a two-electron reduction of oxygen.

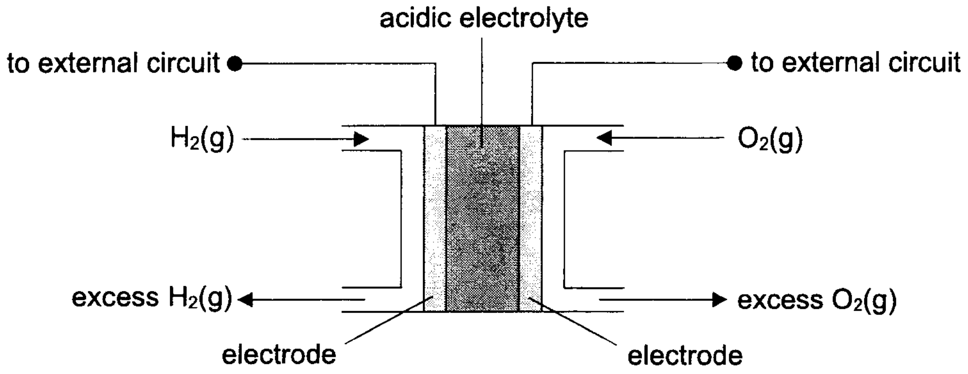

Fig. 5.1

The two half-equations involved in the electrode reactions are

half-equation 1 $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

half-equation 2 $O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$

A competing reaction can also occur at the cathode, where water is produced instead via a four-electron reduction of oxygen.

half-equation 3 $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Water may also be produced by the further reduction of H_2O_2 as shown.

half-equation 4 $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$

(i) Define the term *standard electrode potential.*

....

....

....[1]

(ii) **On Fig. 5.1**, label the polarity of each electrode and draw the direction of electron flow when the overall reaction as shown by half-equations 1 and 2 occurs. [2]

In this fuel cell, the cathode is coated with a catalyst. Depending on the transition metal catalyst used, **one** of the two mechanisms in Table 5.2 occurs.

In each mechanism, ∗ represents an unoccupied active site on the catalyst, while ∗OOH represents O–O–H adsorbed on the catalyst surface.

Table 5.2

mechanism 1	mechanism 2
$* + O_2(g) + H^+(aq) + e^- \rightarrow *OOH$ $*OOH + H^+(aq) + e^- \rightarrow H_2O(l) + O*$ $O* + H^+(aq) + e^- \rightarrow *OH$ $*OH + H^+(aq) + e^- \rightarrow H_2O(l) + *$	$* + O_2(g) + H^+(aq) + e^- \rightarrow *OOH$ $*OOH + H^+(aq) + e^- \rightarrow H_2O_2(aq) + *$

(iii) State which half-equation, 1 to 4, is represented by the two mechanisms in Table 5.2.

mechanism 1: ....

mechanism 2: .... [1]

(iv) The extent to which the O–O single bond is preserved in the mechanism determines whether H_2O_2 or H_2O is produced at the cathode. By considering the equations in Table 5.2 and the effect of adsorption, suggest why this is so.

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....[2]

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Question 5 continues on Page 17.

(c) Fig. 5.2 shows an electrolytic cell that produces H_2O_2 via a two-electron oxidation of water. Similar to the method described in **(b)**, a catalyst is coated on the electrode surface for the selective oxidation of water.

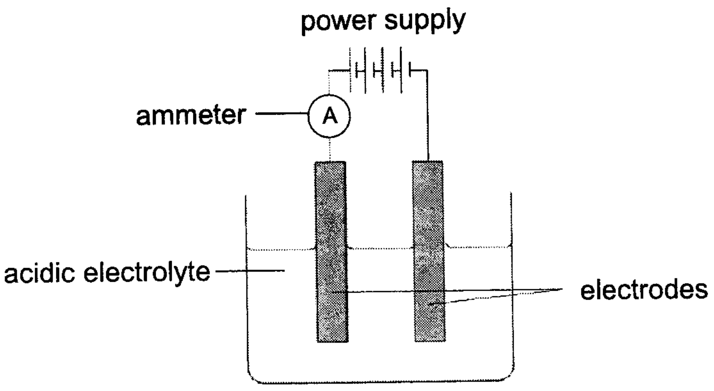

Fig. 5.2

The two half-equations which are involved in the electrode reactions are

half-equation 5 $2H^+(aq) + 2e^- \rightarrow H_2(g)$

half-equation 6 $2H_2O(l) \rightarrow H_2O_2(aq) + 2H^+(aq) + 2e^-$

(i) Write an equation, with state symbols, for a possible competing reaction at the anode. Use the *Data Booklet* to explain whether this reaction is more or less likely to occur than half-equation 6.

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....[3]

The amount of H_2O_2 produced in the electrolysis may be determined via a reaction with acidified cerium(IV) sulfate, $Ce(SO_4)_2$.

In this reaction, O_2 is produced and yellow $Ce^{4+}(aq)$ ions are reduced to colorless $Ce^{3+}(aq)$ ions. The concentration of $Ce^{4+}(aq)$ can be determined by measuring the absorbance of the solution at 316 nm.

(ii) Write an ionic equation for the reaction between H_2O_2 and $Ce(SO_4)_2$.

.... [1]

(iii) $\Delta G^{\ominus}$ for the overall reaction in **(c)(ii)** is -179.5 kJ mol^{-1}. Calculate the standard cell potential for this reaction, and hence the standard electrode potential for Ce^{4+}/Ce^{3+}.

[2]

The effectiveness of H_2O_2 production may be determined by calculating the Faradaic efficiency (FE) as shown

$$\text{FE} = \frac{n_{H_2O_2}\,\text{detected}}{\text{theoretical maximum } n_{H_2O_2}} \times 100\%$$

An experiment to determine the FE was conducted as follows.

1. A constant current of 1.00×10^{-4} A was passed through the electrolysis cell consisting of 100 cm^3 acidic electrolyte.
2. After an hour, the power supply was disconnected and the electrolyte was stirred.
3. 1.00×10^{-4} mol dm^{-3} acidified $Ce(SO_4)_2$ was prepared and its absorbance at 316 nm was found to be 0.567.
4. 100 cm^3 of the acidified $Ce(SO_4)_2$, which was in excess, was added to the 100 cm^3 electrolyte.
5. At the end of the reaction, the absorbance of the mixture in step 4 was measured again at 316 nm, and found to be 0.200.

(iv) Calculate the theoretical maximum amount, in moles, of H_2O_2 that can be produced in this electrolysis, based on half-equation 6.

[2]

(v) Given that the measured absorbance is directly proportional to the concentration of $Ce^{4+}(aq)$, calculate the final concentration of $Ce^{4+}(aq)$ in the 200 cm^3 reaction mixture in step 4.

[1]

(vi) Hence, calculate the amount, in moles, of $Ce^{4+}(aq)$ which reacted with the 100 cm^3 electrolyte in step 4.

[2]

(vii) Use your answers from **(c)(ii)**, **(c)(iv)** and **(c)(vi)** to calculate the actual amount, in moles, of H_2O_2 produced in this electrolysis and the FE.

[2]

[Total: 27]

HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	21S
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/03

Paper 3 Free Response

14 September 2022

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and CT group in the spaces at the top of this page.

Write in dark blue or black pen.

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

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

Answer **all** questions in the spaces provided on 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	**/ 16**
2	**/ 23**
3	**/ 21**
Circle your option below	
4 / 5	**/ 20**
Deductions	
Total	**/ 80**

This document consists of **30** printed pages.

Section A

Answer **all** the questions in this section.

1 (a) Shakudo is a Japanese alloy of copper and gold (typically 4–10% gold; the gold content is varied to control the colour of the alloy). Historically, Shakudo was used to construct or decorate Japanese sword fittings and small ornaments.

(i) A sample of Shakudo was analysed and found to contain two stable isotopes of copper.

Table 1.1

isotope	% abundance
^{63}Cu	74.1%
^{n}Cu	25.9%

Using information from Table 1.1 and the relative atomic mass, A_r, of copper from the Periodic Table, calculate the value of n. Give your answer to the nearest **integer**. [1]

(ii) Isotopes differ in their nucleon number.
What do you understand by the term *nucleon number*? [1]

(iii) Copper has electrons in the d orbitals. The d orbitals have two kinds of shapes.

Draw diagrams to illustrate the **two kinds** of shapes for the d orbitals. Include x, y and z axes and label the d orbitals that you have drawn. [2]

(b) A piece of Shakudo was suspected to contain small amounts of zinc.

In an electrolysis experiment, this piece of Shakudo was made the anode and a thin piece of pure copper was made the cathode. An aqueous solution of copper(II) sulfate was used as the electrolyte.

(i) Using the $E^\ominus$ data given below and relevant $E^\ominus$ data from the *Data Booklet*, explain what happens to the zinc and gold during the electrolysis.

$$Au^{3+} + 3e^- \rightleftharpoons Au \qquad E^\ominus = +1.52\ V$$

[2]

(ii) The electrolysis experiment was carried out for 12.0 minutes using a current of 1.10 A. The copper cathode increased in mass by 0.26 g.

What value of Avogadro constant, *L*, do **these figures** give? [2]

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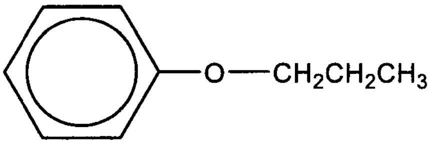
(c) Ethers have general formula R–O–R′, where R and R′ represent the alkyl or aryl groups. Propoxybenzene is an example of an ether.

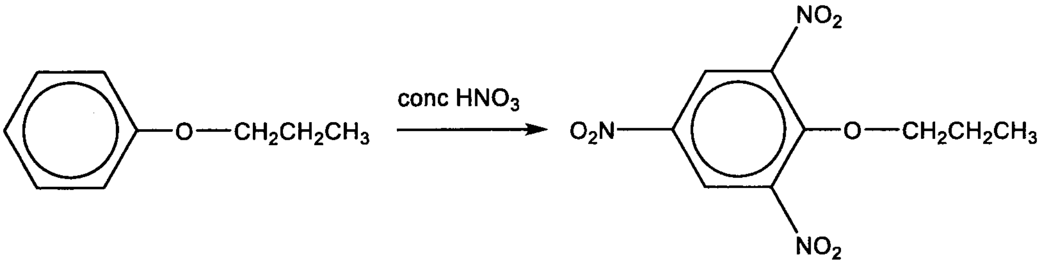


propoxybenzene

(i) The $-CH_2CH_2CH_3$ chain behaves like an alkane.

Explain why alkanes are unreactive. [1]

(ii) Propoxybenzene reacts similarly to phenol, such as in the nitration reaction shown below.



The nitration of benzene differs from that of propoxybenzene in two ways.

Describe and explain these two differences in terms of the reaction conditions and organic products. [2]

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(d) Epoxyethane is a cyclic ether and the simplest epoxide: a three-membered ring consisting of one oxygen atom and two carbon atoms.

A reaction scheme involving epoxyethane is shown in Fig. 1.1.

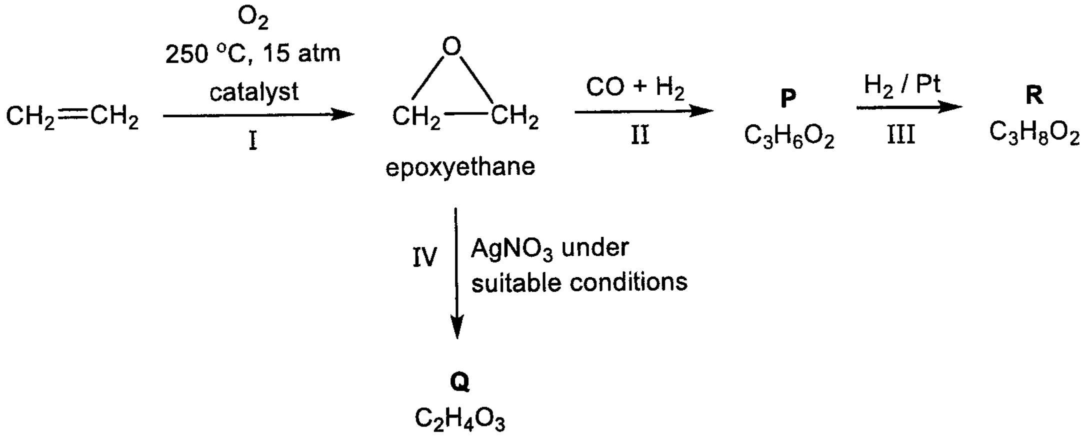

Fig. 1.1

Compounds **P** and **Q** give effervescence with sodium metal.

Both compounds do not exhibit enantiomerism.

P also gives a brick-red precipitate when warmed with Fehling's solution.

Q also gives effervescence with aqueous sodium carbonate.

Suggest the structures for **P**, **Q** and **R**. [3]

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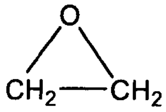
(e) Detergents can be made from epoxyethane.



epoxyethane

The initiation step involves homolytic fission of a C–O bond in epoxyethane, giving rise to a 'double-ended' free radical.

A chain reaction then occurs.

The reaction eventually produces a molecule that contains the following structure.

$$—CH_2CH_2–O–CH_2CH_2–O–CH_2CH_2–O–CH_2CH_2–O–CH_2CH_2–O–CH_2CH_2–O—$$

Suggest equations for the **initiation step** and the **first propagation step**.
Include curly half-arrows for the initiation step. [2]

[Total: 16]

2 **(a)** When solid sodium chloride reacts with concentrated sulfuric acid, white fumes of hydrogen chloride are observed as given in the equation:

$$NaCl(s) + H_2SO_4(l) \rightarrow HCl(g) + NaHSO_4(s)$$

However, when solid sodium iodide is used, very little white fumes are observed. Instead, dense purple iodine vapour and a pungent gas are formed.

(i) Solid sodium iodide is reacted with 0.00300 mol of concentrated sulfuric acid to give iodine as the only iodine-containing product. The iodine produced is dissolved in 100 cm^3 hexane.

25.0 cm^3 of this solution required 12.0 cm^3 of 0.500 mol dm^{-3} sodium thiosulfate for complete reaction.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Calculate the oxidation state of the sulfur-containing product in the reaction of sodium iodide with concentrated sulfuric acid. [3]

(ii) Use the *Data Booklet* to describe the relative reactivity of chloride and iodide as reducing agents. Hence, explain why different sulfur-containing products are formed when sodium chloride and sodium iodide react with concentrated sulfuric acid. [2]

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(b) **P** and **Q** are chlorides of Period 3 elements.

P is a solid with a high melting point. It conducts electricity when molten. **P** reacts with water to form a solution of pH 6.5.

Q is a colourless liquid at room temperature. The percentage by mass of chlorine in **Q** is 83.5%. It reacts with water to form white fumes and a solution with a low pH.

(i) Explain, in terms of the type of bonding present, the physical state of **P** and of **Q**. [2]

(ii) Identify **P** and **Q**. [2]

(iii) Explain the reactions of **P** and **Q** with water with the aid of relevant equations. [3]

(c) At high temperature, gaseous PCl_5 dissociates according to the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(i) Write the expression for the equilibrium constant, K_p, for the reaction. [1]

(ii) Gaseous PCl_5 is added to an evacuated vessel and allowed to reach equilibrium.

The initial pressure is 70% of the equilibrium total pressure, and the equilibrium partial pressure of PCl_5 is 84 kPa. Calculate the value of K_p and state its units. [3]

(iii) The volume of the vessel is reduced at time t_1.

In Fig. 2.1, sketch how the partial pressure of PCl_5 changes from t_1, until equilibrium is re-established at time t_2. Explain your answer. [2]

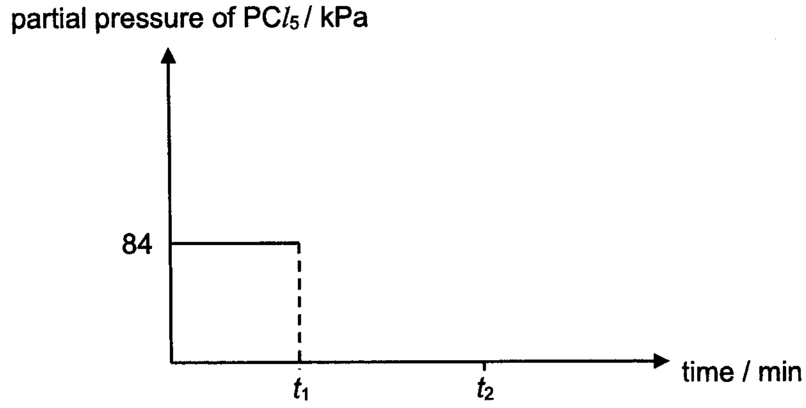

Fig. 2.1

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(d) Compound **X** ($C_9H_{11}O_3N$) gives a yellow precipitate when warmed with alkaline aqueous iodine.

When PCl_5 is added to **X**, white fumes and compound **Y** ($C_9H_{10}ClO_2N$) are formed. **Y** is heated with tin and concentrated hydrochloric acid, followed by aqueous NaOH, to give compound **Z** ($C_9H_{11}N$).

Deduce possible structures for **X**, **Y** and **Z**, and explain the chemistry of the reactions described above. [5]

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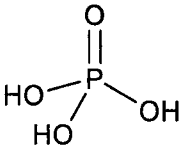
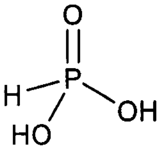
[Total: 23]

3 Phosphorus and nickel are two of the most abundant elements in the earth's crust.

(a) Phosphoric acid and phosphorus acid are two common oxo-acids of phosphorus. Phosphoric acid is a triprotic acid whereas phosphorus acid is a diprotic acid.



phosphoric acid
(H_3PO_4)



phosphorus acid
(H_3PO_3)

The phosphorus centres in these oxo-acids are sp^3 hybridised.

(i) Both nitrogen and phosphorus are in Group 15 of the Periodic Table. Explain why similar oxo-acids of nitrogen do not exist. [1]

(ii) State the number of σ bonds and π bonds in a molecule of H_3PO_3. [1]

(iii) Describe, in terms of orbital overlap, how the P–H bond in H_3PO_3 arises. Include a labelled diagram in your answer. [2]

(iv) The pK_{a1} of H_3PO_4 and H_3PO_3 are 2.1 and 1.3 respectively.

By using this information and the structures of their conjugate bases, suggest whether the –OH groups in H_3PO_4 and H_3PO_3 are electron-donating or electron-withdrawing. Explain your reasoning. [2]

(b) Nickel(II) phosphate, $Ni_3(PO_4)_2$, has potential catalytic property and has been studied extensively in recent years.

Use the data in Table 3.1, together with data from the *Data Booklet*, to calculate the standard enthalpy change of formation of $PO_4^{3-}(g)$, $\Delta H^\ominus_f$ $PO_4^{3-}(g)$.

$$P(s) + 2O_2(g) + 3e^- \rightarrow PO_4^{3-}(g) \qquad \Delta H^\ominus_f\ PO_4^{3-}(g)$$

Show your working. [4]

Table 3.1

	value/ kJ mol^{-1}
standard enthalpy change of solution of $Ni_3(PO_4)_2(s)$	+179
standard enthalpy change of atomisation of Ni(s)	+431
standard enthalpy change of formation of $PO_4^{3-}(aq)$	–1277
standard enthalpy change of formation of $Ni^{2+}(aq)$	–54
lattice energy of $Ni_3(PO_4)_2(s)$	–12300

(c) The Mond process was developed by Ludwig Mond in 1890 to extract and purify nickel. A key step involved reacting nickel ore with carbon monoxide.

$$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$$

(i) State **two** physical properties of nickel, apart from the colour of the metal, in which it differs from calcium. Explain the reasons for those differences. [2]

(ii) Explain why carbon monoxide, CO, is poisonous. [2]

(d) A phosphorus-containing ligand is called phosphine and it binds to a transition metal as an electrically neutral ligand (represented as 'L' in this question part).

Fig. 3.1 shows a catalytic cycle for the synthesis of adiponitrile, an important precursor to Nylon 66.

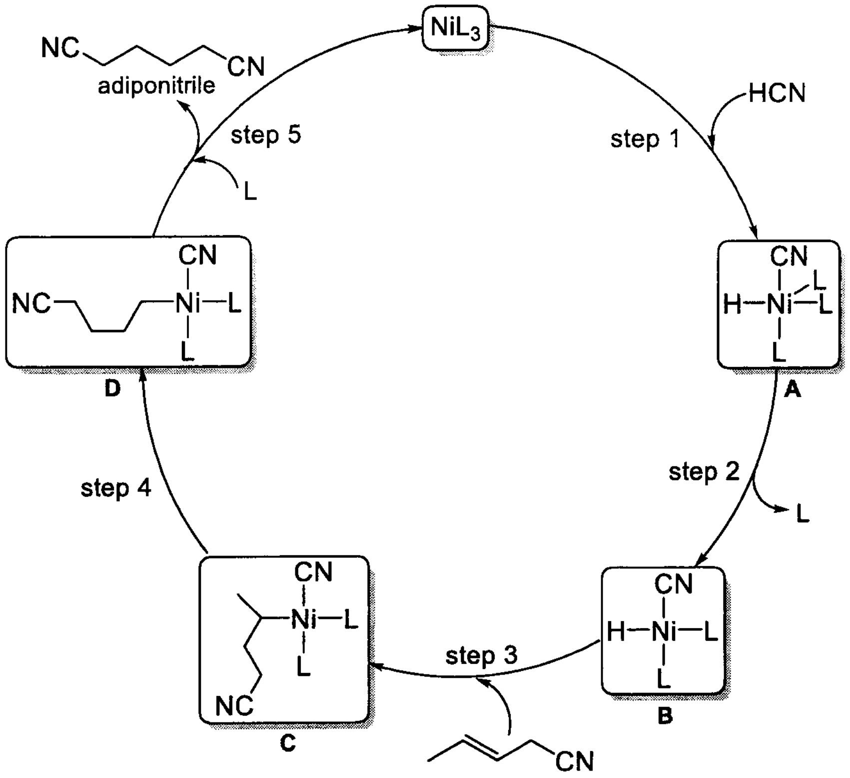


Fig. 3.1

The five steps in the above catalytic cycle can be written as five separate equations. For example, step 1 can be written as NiL_3 + HCN → **A**.

(i) Write an equation for the overall process. [1]

(ii) Besides the electrically neutral ligand L, the other two ligands bonded to Ni in **A** are hydride and cyanide.

Step 1 is termed '*oxidative addition*'. By considering the change in oxidation state of the Ni centre, explain the terms in italics. [2]

(iii) Intermediate **C** can undergo a similar reaction as that in step 5 to give NiL_3 and **E**. Suggest the structure of **E**. [1]

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(e) The rate equation for the overall reaction in Fig. 3.1 is as follows.

$$\text{rate} = k[\text{HCN}][\text{alkene}][\text{L}]^m$$

To study the order of reaction with respect to L, a large excess of HCN and alkene are used, and the rate law is simplified to the following

$$\text{rate} = k'[\text{L}]^m$$

where $k' = k[\text{HCN}][\text{alkene}]$

Taking common logarithm on both sides,

$$\lg(\text{rate}) = \lg k' + m\lg[\text{L}]$$

Fig. 3.2 summarises the results of the kinetics study.

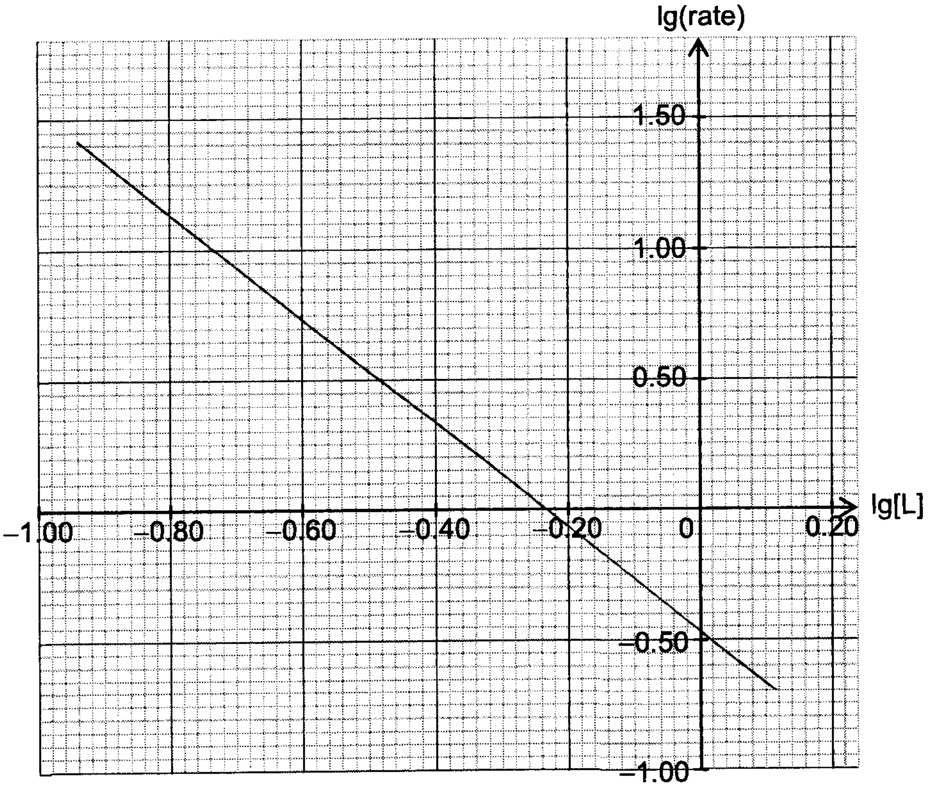

Fig. 3.2

(i) Explain why the rate law can be simplified to rate = $k'[\text{L}]^m$ in the kinetics study. [1]

(ii) Use Fig. 3.2 to determine the order of reaction with respect to L. [1]

(iii) Based on your answer in **(e)(ii)**, suggest by what factor the rate will change when [L] doubles. [1]

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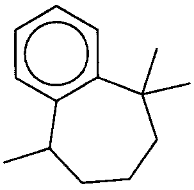
[Total: 21]

Section B

Answer **one** question from this section.

4 Users of essential oils believe that rubbing these oils onto the skin or vapourising and inhaling them are beneficial to health. A common molecule found in essential oils is ar-himachalene, which has a fused six and seven membered ring system.



ar-himachalene

(a) Human skin is waterproof and the skin glands produce protective oily secretions.

By referring to the structure and bonding of ar-himachalene, explain why it is easily absorbed onto the skin **and** is easily vapourised. [2]

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(b) Ar-himachalene can be synthesised from methylbenzene and compound **P** using the reaction scheme in Fig. 4.1.

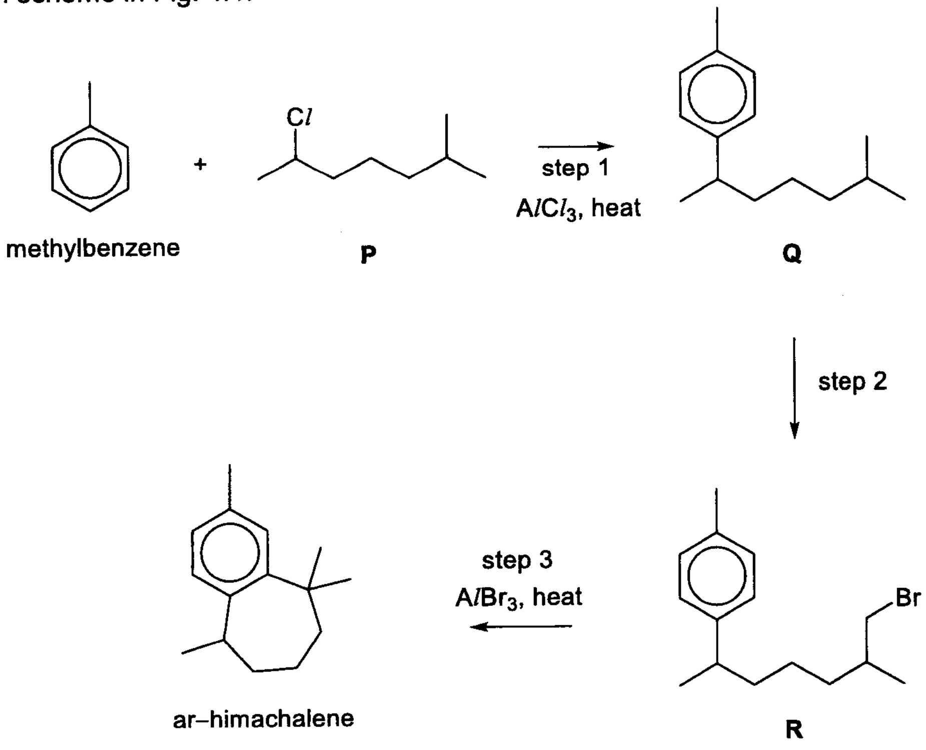

Fig. 4.1

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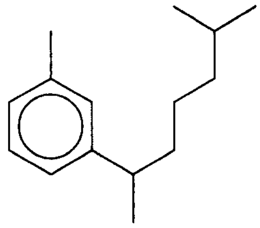
(i) State the name of compound **P**. [1]

(ii) In steps 1 and 3, $AlCl_3$ and $AlBr_3$ are used as Lewis acid catalysts.

Explain why $AlCl_3$ and $AlBr_3$ are able to function as Lewis acid catalysts. [1]

(iii) In step 1, compound **Q'** was formed as a minor product.



Q'

State the isomeric relationship between compounds **Q** and **Q'**, and explain why **Q'** was the minor product. [2]

(iv) State the reagents and conditions for step 2. [1]

(v) In step 2, bromination occurs on the terminal carbon of **Q** to produce **R** as the major product.

Explain why bromination is likely to take place at this position. [1]

(c) Step 3 of Fig. 4.1 produces carbocation **I** as shown in Fig. 4.2. Carbocation **I** undergoes a rearrangement reaction to form carbocation **II**.

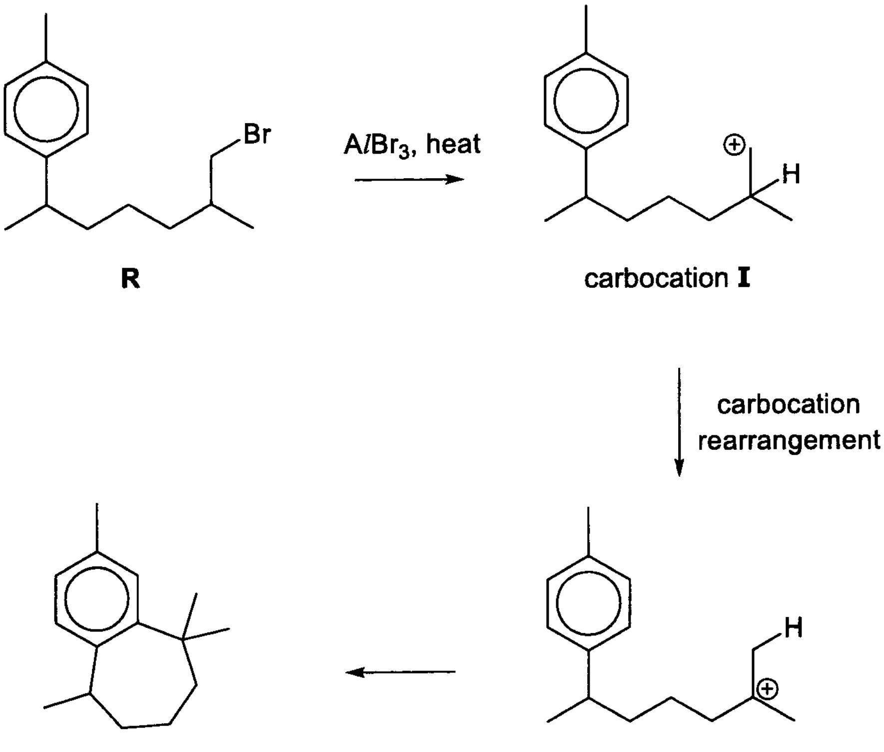


Fig. 4.2

In this rearrangement reaction, a hydrogen atom from the tertiary carbon atom is transferred to the terminal carbon atom. This is known as a *hydride shift*.

(i) Draw curly arrow(s) on Fig. 4.2 to suggest a mechanism for this *hydride shift*. [1]

(ii) By comparing the structures of carbocations **I** and **II**, explain why there is a tendency for this carbocation rearrangement to occur. [2]

(iii) Carbocation **II** undergoes an intramolecular reaction to form ar-himachalene.

State the type of reaction that occurs and describe this mechanism by using curly arrows to show the movement of electron pairs. [3]

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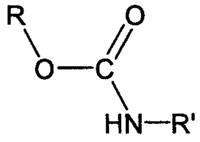
(d) Carbamates are organic compounds with the –OCO–NH– functional group as shown below. They are commonly used as insecticides.



carbamate

When the carbamate above was heated with dilute acid, ROH, R'–NH_3^+ and carbon dioxide gas were produced.

(i) State the type of reaction that occurred and write a balanced ionic equation for the reaction. You may use R and R' in your equation. [2]

(ii) The carbamate functional group resembles two other functional groups. By considering the similarities, or otherwise, suggest why the carbamate functional group is able to undergo the reaction in **(d)(i)**. [1]

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(e) Compound **S** ($C_{10}H_8N_2O_2$) has the following properties.

property 1	Like ar-himachalene, it contains a fused six and seven membered ring system.
property 2	It contains the carbamate functional group and liberates NH_3 when heated with NaOH(aq).
property 3	It exhibits optical activity.

When **S** was heated with acidified $KMnO_4$(aq), the purple $KMnO_4$ was decolourised and effervescence occurred. Compound **T** ($C_8H_6O_4$) was obtained.

(i) By considering the molecular formula of **S** and property 2, suggest which other nitrogen-containing functional group is present in **S**. [1]

(ii) Suggest the structures of **S** and **T**. [2]

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[Total: 20]

5 **(a)** **(i)** Propene undergoes an electrophilic addition reaction with aqueous bromine. Suggest a mechanism for this reaction and use it to predict the major product formed. [2]

(ii) Propene can be synthesised from butanone in three steps as shown in Fig. 5.1.

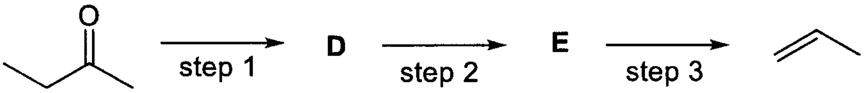

Fig. 5.1

Suggest reagents and conditions for each of the steps 1, 2 and 3. Draw the structures of the intermediate compounds **D** and **E**. [3]

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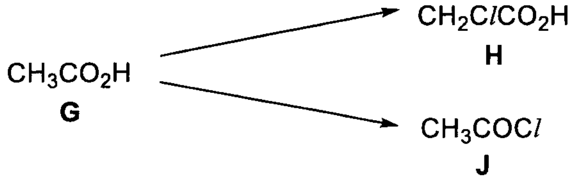
(b) Two chlorine-containing compounds can be made from ethanoic acid by the following routes.



(i) Warming **G** with $SOCl_2$ produces **J**.
Draw a dot-and-cross diagram to show the bonding present within a $SOCl_2$ molecule.
Predict its shape and bond angle. [2]

(ii) When separate portions of water are added to compounds **G**, **H** and **J**, solutions with pH values of 0.5, 2.5 and 3.0 are formed (not necessarily in the order of **G**, **H** and **J**). When aqueous silver nitrate is added to these three solutions, two solutions show no reaction, but the third solution produces a thick white precipitate.

Suggest, with explanations, which pH value is associated with each of **G**, **H** and **J**. Explain the formation of white precipitate in terms of relative reactivity of the organic functional groups present. [5]

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(c) The concentration of Cl^- ion in a water sample can be determined by titrating the sample with a solution of $AgNO_3(aq)$ of known concentration.

A student carried out this experiment by titrating 25.0 cm^3 of a water sample containing unknown concentration of Cl^- ion against a solution of 0.0500 mol dm^{-3} $AgNO_3(aq)$. The concentration of Ag^+ ion in the water sample is monitored and recorded as the titration progresses.

A sketch of the titration curve obtained is shown in Fig. 5.2. The concentration of Ag^+ ion is expressed in terms of pAg, where $pAg = -\log_{10}[Ag^+]$.

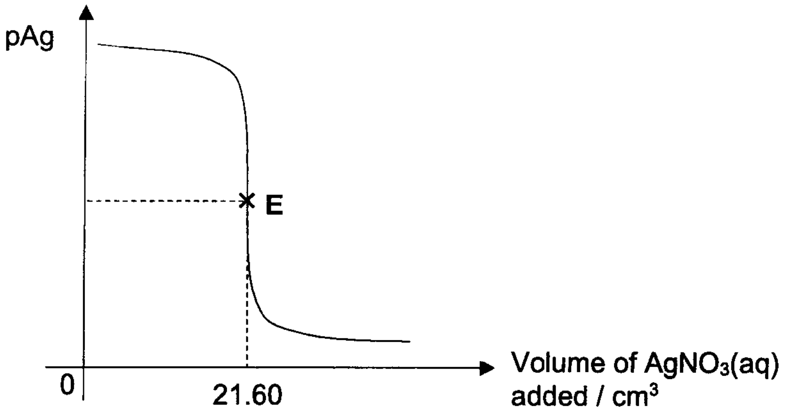

Fig. 5.2

The solubility product, K_{sp}, for $AgCl$ is 1.80×10^{-10} mol^2 dm^{-6}.

(i) Calculate the concentration of Cl^- ions in mol dm^{-3} in the water sample, assuming that all Cl^- ions in the water sample have reacted with $AgNO_3(aq)$ at point **E**. [1]

(ii) Show that a precipitate will be observed when 0.100 cm^3 of $AgNO_3(aq)$ is added to the water sample during the titration. Show your working clearly. [2]

(iii) Given that the pAg at point **E** is 4.87, calculate the concentration of Cl^- ions in mol dm^{-3} at this point. [1]

(iv) Explain why the gradient of the curve is gentle at first and becomes steeper when passing through point **E**. [2]

(v) Predict and explain how your answer in **(c)(i)** will be affected if the water sample is contaminated with a small amount of $NH_3(aq)$. [2]

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[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.

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HWA CHONG INSTITUTION
C2 Preliminary Examination
Higher 2

NAME		**CT GROUP**	**21S**

CHEMISTRY

9729/04

Paper 4 Practical

25 August 2022

2 hours 30 minutes

Candidates answer on the Question Paper

READ THESE INSTRUCTIONS FIRST

Write your name and class 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 an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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 16 and 17.

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	
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This document consists of **17** printed pages.

1 **Determination of the basicity of an acid and the strength of a base**

FA 1 is 1.50 mol dm^{-3} sodium hydroxide, NaOH.
FA 2 is 0.75 mol dm^{-3} acid **A**, which is either monobasic (monoprotic) or dibasic (diprotic).
FA 3 is 1.50 mol dm^{-3} base **B**, which is monoacidic (monoprotic) and is either a strong base or a weak base.

You will perform experiments to determine whether acid **A** is monobasic or dibasic. You will then calculate the enthalpy change of neutralisation, ΔH_{neut}, between NaOH and acid **A**.

You will also design one more experiment to determine whether base **B** is a strong base or a weak base.

(a) (i) **Experiment 1**

1. Place one polystyrene cup inside a second polystyrene cup. Place these in a glass beaker to prevent them from tipping over.
2. Use a measuring cylinder to transfer 40.0 cm^3 of **FA 1** into the first polystyrene cup. Stir the **FA 1** in the polystyrene cup with the thermometer with **0.2 °C divisions**. Read and record the initial temperature of **FA 1** in Table 1.1.
3. Use another measuring cylinder to measure 20.0 cm^3 of **FA 2**. Add **FA 2** to **FA 1** in the polystyrene cup. Stir the mixture using the same thermometer and record the maximum temperature reached.
4. Wash and dry the thermometer and the polystyrene cup.

Experiment 2

Repeat experiment 1 using 20.0 cm^3 of **FA 1** and 40.0 cm^3 of **FA 2**.

Use your results to determine the maximum change in temperature, ΔT, for each experiment and complete Table 1.1. You may assume that the initial temperature of **FA 2** is the same as that of **FA 1**.

Table 1.1

experiment	Volume of **FA 1** /cm^3	Volume of **FA 2** /cm^3	Initial temperature of **FA 1** /°C	Maximum temperature /°C	Maximum change in temperature, ΔT /°C
1	40.0	20.0			
2	20.0	40.0			

[2]

(ii) Use your ΔT results of experiments 1 and 2 to deduce whether acid **A** is monobasic or dibasic. Explain your deduction.

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.... [2]

(iii) Hence, calculate the enthalpy change of neutralisation, ΔH_{neut}, between NaOH and acid **A**.

Assume that the specific heat capacity of the reaction mixture is 4.18 J g^{-1} K^{-1}, and that the density of the reaction mixture is 1.00 g cm^{-3}.

ΔH_{neut} = ... [2]

(iv) A student repeated **experiment 2** but using solutions of double the concentrations (3.00 mol dm^{-3} NaOH and 1.50 mol dm^{-3} acid **A**).

Suggest the effect this would have on the value of ΔT for experiment 2. Hence, deduce and explain the effect this would have on the value for ΔH_{neut}.

....

....

.... [2]

(b) **(i)** **Experiment 3**

FA 3 contains a monoacidic base, base **B**, that has the same concentration as the NaOH in **FA 1**.

Design one more experiment, the results of which, when compared against **your experiment 2**, will allow you to deduce whether base **B** is a strong or weak base.

Fill Table 1.2 with your chosen volumes of **FA 3** and **FA 2**.
Carry out this experiment.
Complete Table 1.2.

Table 1.2

experiment	Volume of **FA 3** /cm^3	Volume of **FA 2** /cm^3	Initial temperature of **FA 3** /°C	Maximum temperature /°C	Maximum change in temperature, ΔT /°C
3					

[1]

(ii) Use your ΔT results of experiment 3 and **experiment 2** to deduce whether base **B** is a strong base or a weak base. Explain your deduction.

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.... [1]

[Total: 10]

2 Investigation of the kinetics of the catalysed decomposition of hydrogen peroxide

Hydrogen peroxide decomposes very slowly to form water and oxygen as shown in equation **1**.

equation **1** $2H_2O_2 \rightarrow 2H_2O + O_2$

Many transition element ions are able to catalyse the decomposition of hydrogen peroxide. Iron(III) nitrate, $Fe(NO_3)_3$, is an effective catalyst for this reaction.

FA 4 is iron(III) nitrate, $Fe(NO_3)_3$.
FA 5 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.
FA 6 is aqueous hydrogen peroxide, H_2O_2.
FA 7 is 0.2 mol dm^{-3} sulfuric acid, H_2SO_4. (**FA 7** is also used in **Question 3**.)

You will add a measured volume of **FA 4** to a measured volume of **FA 6** and, at timed intervals, you will transfer aliquots (portions) of the reaction mixture.

It is necessary that you titrate each aliquot against **FA 5 before** transferring the next aliquot.

Acidified $KMnO_4$ and H_2O_2 react as shown in equation **2**.

equation **2** $2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$

(a) (i) Preparation and titration of the reaction mixture

Notes: You will perform each titration **once** only. Great care must be taken that you do not overshoot the end-point.

Once you have started the stopwatch, it must continue running for the duration of the experiment. You must **not** stop it until you have finished this experiment.

You should transfer your first aliquot within the first three minutes of starting the reaction.

The titre volume for your first titration is expected to be greater than 30 cm^3.

You should **not** exceed a maximum reaction time of 25 minutes for this experiment.

In an appropriate format in the space provided on the next page, prepare a table in which to record for each aliquot

- the time of transfer, t, in minutes and seconds,
- the decimal time, t_d, in minutes, to 0.1 min, for example, if t = 4 min 33 s then t_d = 4 min + 33/60 min = 4.6 min,
- the burette readings and the volume of **FA 5** added.

1. Fill a burette with **FA 5**.
2. Using a measuring cylinder, add 100.0 cm^3 of **FA 6** to the conical flask labelled **reaction mixture**.

   Do **not** use the H_2O_2 bench reagent for this step.
3. Using a measuring cylinder, add 2.0 cm^3 of **FA 4** to the same conical flask. Start the stopwatch and swirl the mixture thoroughly to mix its contents.
4. Using a measuring cylinder, add 50.0 cm^3 of **FA 7** to a second conical flask.
5. Before 3 minutes, withdraw a 10.0 cm^3 aliquot (portion) of the reaction mixture to a 10 cm^3 measuring cylinder, using a dropping pipette.
6. **Immediately** transfer this aliquot into the second conical flask from step 4 and vigorously swirl the mixture. Read and record the time of transfer in minutes and seconds, to the nearest second, when the aliquot is added.
7. **Immediately** titrate the H_2O_2 in the second conical flask with **FA 5**. The end-point is reached when a permanent **pale** pink colour is obtained. Record your titration results.
8. Wash out the second conical flask with water.
9. Repeat steps **4** to **8** until a total of **five** aliquots have been titrated and their results recorded.

   You should **not** exceed a maximum reaction time of 25 minutes for this experiment.

Results

[5]

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(a) **(ii)** Plot a graph of the volume of **FA 5** added, on the y-axis, against decimal time, t_d, on the x-axis on the grid in Fig. 2.1.

Draw the most appropriate best-fit curve taking into account all of your plotted points.

Extrapolate (extend) this curve to the y-axis and read the value of V_0, the volume of **FA 5** required at t_d = 0.0 min.

Fig 2.1

V_0 = ... cm^3 [4]

(b) The **initial rate** of change of the concentration of hydrogen peroxide, $[H_2O_2]$, can be determined from the gradient of the tangent to the graph in Fig. 2.1 at time t_d = 0.0 min.

(i) Draw a tangent to your graph in Fig. 2.1 at time t_d = 0.0 min.
Determine the gradient of this line, showing clearly how you did this.

gradient = ... cm^3 min^{-1} [2]

(ii) Use your gradient to determine the rate of change of the amount of MnO_4^- ions required in mol min^{-1}.

rate of change of the amount of MnO_4^- ions required = ... mol min^{-1} [1]

(iii) Determine the amount of H_2O_2 decomposed per minute and hence deduce the rate of change of $[H_2O_2]$ at t_d = 0.0 min, in mol dm^{-3} min^{-1}.

amount of H_2O_2 decomposed = ... mol min^{-1}

rate of change of $[H_2O_2]$ at t_d = 0.0 min = ... mol dm^{-3} min^{-1} [3]

(iv) It has been claimed that the decomposition of hydrogen peroxide is first order with respect to $[H_2O_2]$.

State whether you agree or disagree with this claim. Use evidence from your graph in Fig. 2.1 to support your answer.

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.... [2]

(c) Steps **1** to **4** represent a possible mechanism for the catalysed decomposition of H_2O_2. In this mechanism, the O_2H ligand on one of the complex ions represents the H–O–O⁻ ion and the O represents an oxygen atom.

step **1** $[Fe(H_2O)_6]^{3+}(aq) + H_2O_2(aq) \rightleftharpoons [Fe(H_2O)_5(O_2H)]^{2+}(aq) + H_3O^+(aq)$

step **2** $[Fe(H_2O)_5(O_2H)]^{2+}(aq) \rightarrow OH^-(aq) + [Fe(H_2O)_5O]^{3+}(aq)$

step **3** $[Fe(H_2O)_5O]^{3+}(aq) + H_2O_2(aq) \rightarrow [Fe(H_2O)_6]^{3+}(aq) + O_2(g)$

step **4** $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$

(i) Perform the test described in Table 2.1 and record your observations in the table. Test and identify any gases produced.

Table 2.1

test	observations
Put about 2 cm depth of H_2O_2 from the bench reagent bottle into a test-tube. Add about 2 cm depth of **FA 4** to the same test-tube and shake the mixture thoroughly. Observe the mixture until no further changes are seen.	

[2]

(ii) Identify from the mechanism in **(c)**, the complex ions that are responsible for the colour changes you observed in Table 2.1.

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.... [2]

(iii) Explain fully how you can tell that the $[Fe(H_2O)_6]^{3+}$ ions are acting as a catalyst in this reaction, using evidence from your observations in Table 2.1 and from the mechanism.

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.... [3]

[Total: 24]

3 Qualitative Analysis

FA 8 is a solid oxide of an unknown metal **Z**. This oxide has an M_r **not** exceeding 140.

[A_r of A*l*: 27.0; Ba: 137.3; Ca: 40.1; Cr: 52.0; Cu: 63.5; Fe: 55.8; Mg: 24.3; Mn: 54.9; O: 16.0; Zn: 65.4]

FA 9 is solid potassium ethanedioate, $K_2C_2O_4$.

(a) Perform the tests described in Table 3.1, and record your observations in the table. Test and identify any gases produced.

Table 3.1

test	observations
Add all of the solid **FA 9** into a boiling tube. Add 15 cm³ of **FA 7** into this boiling tube. Gently warm the boiling tube and stir the mixture using the thermometer with **1 °C divisions**, until the temperature of the mixture reaches about 60 °C. Turn off the Bunsen flame.	
Use a spatula to add **FA 8** to the mixture, until no further change is seen. When you think that the reaction is complete, stop adding **FA 8**. Filter the mixture into another boiling tube.	
To 1 cm depth of the filtrate in a test tube, add aqueous sodium hydroxide dropwise, until in excess.	

[4]

(b) Explain how you have decided to stop adding **FA 8** at the point you have chosen.

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.... [1]

(c) What is the chemical role of **FA 8** in the reaction between **FA 8** and **FA 9**? Support your answer using your observations from Table 3.1.

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.... [1]

(d) **(i)** Identify the cation in the filtrate, using your observations from Table 3.1.

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.... [1]

(ii) Hence, suggest the formula of the oxide of **Z** in **FA 8** and explain your reasoning by referring to your answer in **(c)** and the information provided on page 10.

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.... [2]

[Total: 9]

4 Planning

When some aqueous ethanoic acid is added to cyclohexane, the ethanoic acid distributes itself in the two immiscible solvents until an equilibrium is set up:

$$CH_3CO_2H\text{(in water)} \rightleftharpoons CH_3CO_2H\text{(in cyclohexane)}$$

The equilibrium constant for this system is called the *partition coefficient*, K, which is a constant at a given temperature.

$$K = \frac{\text{[ethanoic acid] in cyclohexane}}{\text{[ethanoic acid] in water}}$$

To determine the value of K, it is necessary to determine the amount and then the concentration of ethanoic acid in each solvent layer at equilibrium. One way of doing this is described below.

Known volumes of aqueous ethanoic acid and cyclohexane are placed in a separating funnel, shown in Fig. 4.1, and mixed well.

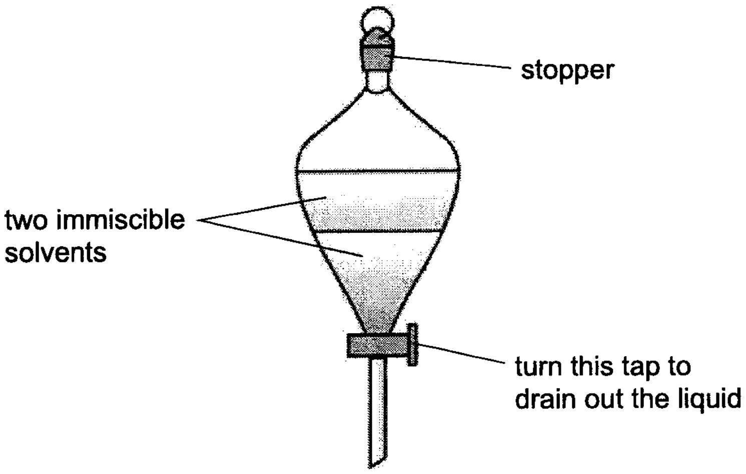

Fig. 4.1

Sufficient time must be provided to allow the following to occur.

- Distribution of the ethanoic acid molecules from the water solvent into the cyclohexane solvent until equilibrium is reached.
- Separation of the mixture into two immiscible aqueous and cyclohexane layers. (The density of cyclohexane is 0.78 g cm^{-3}. You may assume that the density of the aqueous layer is the same as that of water, 1.00 g cm^{-3}.)

Most of the aqueous layer is then taken out, from which a 10.0 cm^3 aliquot is withdrawn for titration.

The experiment is repeated using different volumes of aqueous ethanoic acid, and adding water such that the total volume of the aqueous and cyclohexane layers is kept constant.

Each titration only needs to be done once.

(a) Using the information given, write a plan to collect sufficient data to plot a graph of the equilibrium concentration of ethanoic acid in cyclohexane against that in water, at room temperature.

You are provided with:

- 0.250 mol dm^{-3} aqueous ethanoic acid,
- cyclohexane,
- deionised water,
- 0.100 mol dm^{-3} aqueous sodium hydroxide,
- a separating funnel with capacity 250 cm^3,
- other apparatus normally found in a school laboratory.

Your plan should include:

- essential details for the preparation of each equilibrium mixture,
- essential details for the titration of each aqueous aliquot against the sodium hydroxide using thymol blue indicator.

Thymol blue indicator has two pH working ranges as follows.

pH working range	colour in acidic region	colour in basic region
1.2 – 2.8	red	yellow
8.0 – 9.6	yellow	blue

Your first equilibrium mixture should be prepared using 50 cm^3 of aqueous ethanoic acid and 50 cm^3 of cyclohexane. You may draw a table to show the volumes of aqueous ethanoic acid, deionised water and cyclohexane used to prepare each equilibrium mixture.

You may assume that temperature stays constant throughout your experiment.

[5]

(b) Outline how you would calculate the concentration (in mol dm^{-3}) of ethanoic acid in each solvent, for **equilibrium mixture 1**, assuming that the titre volume is *V* cm^3.

[4]

(c) **(i)** Sketch on Fig. 4.2, a graph to show the relationship between the equilibrium concentrations of ethanoic acid in the two solvents.

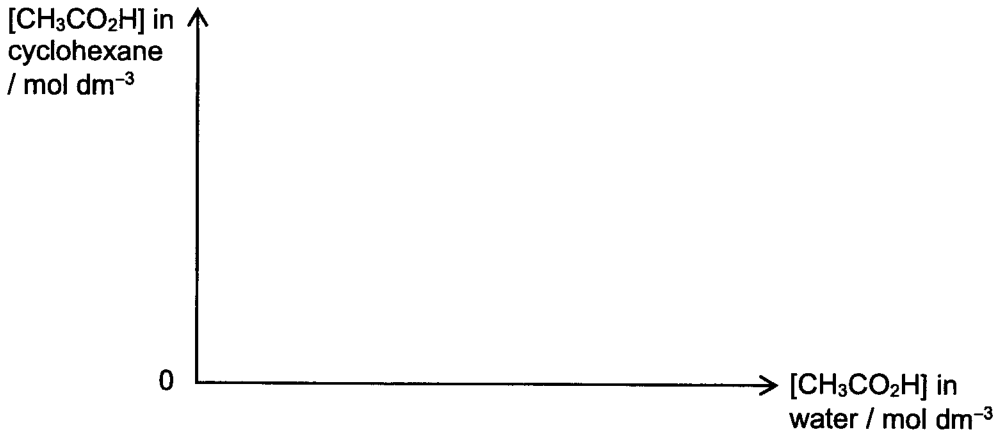

Fig. 4.2

[1]

(ii) How would you use this graph to determine a value for the partition coefficient, *K*, of ethanoic acid in cyclohexane and water?

.... [1]

(d) An important assumption made in this experiment is that the solute *remains in the same molecular form* in the two solvents. Suggest how this assumption might **not** be true in this experiment.

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.... [1]

[Total: 12]

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(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^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(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^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

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(b) Reactions of aqueous anions

anion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Test for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

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