ANDERSON SERANGOON JUNIOR COLLEGE

2022 JC 2 PRELIMINARY EXAMINATION

NAME:_____ ( ) **CLASS:** 22 / ____

CHEMISTRY **9729/03**

Paper 3 Free Response Questions **16 September 2022**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number on all the work you hand in.
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.

For Examiner's Use				
Paper 3	A1	/ 18	Paper 1 (15%)	/ 30
	A2	/ 19	Paper 2 (30%)	/ 75
	A3	/ 23	Paper 3 (35%)	/ 80
	B4*	/ 20	Paper 4 (20%)	/ 55
	B5*	/ 20	Percentage	
	*Circle the question you have attempted		Grade	

This document consists of **32** printed pages.

Section A

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

1 NO_2 has been identified as a pollutant with strong evidence for public health concern. Exposure to NO_2 can irritate airways and aggravate respiratory diseases.

(a) **(i)** Draw a dot–and–cross diagram to show the bonding in a molecule of NO_2. [1]

(ii) The 2s and 2p orbitals of nitrogen atoms can hybridise in the same way as the 2s and 2p orbitals of carbon atoms.
State the shape with respect to the nitrogen atom in NO_2. Hence, suggest the hybridisation state of nitrogen in NO_2. [1]

Table 1.1 shows the bond lengths of two nitrogen–oxygen bonds.

Table 1.1

Bond	N–O	N=O
Bond length (pm)	136	115

The observed bond length of each nitrogen–oxygen bond in the NO_2 is 119 pm.

(iii) What do you understand by the term *bond length*? [1]

(iv) With reference to your answers to **(a)(i)** and **(a)(ii)**, explain the observed bond length in NO_2. [2]

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(b) At room temperature, reddish brown nitrogen dioxide, NO_2, dimerises into colourless nitrogen tetroxide, N_2O_4. The two gases are in dynamic equilibrium as shown.

$$\underset{\textit{reddish brown}}{2\,NO_2(g)} \rightleftharpoons \underset{\textit{colourless}}{N_2O_4(g)} \qquad \Delta H = -58.0\ kJ\ mol^{-1}$$

(i) Using your answer in **(a)(i),** explain why the dimerisation of NO_2 to form N_2O_4 is an exothermic process. [1]

The graph in Fig. 1.1 shows the pressure-temperature (*p*–T) relationship of two separate gaseous samples in an enclosed volume.

At 273 K, the first sample contains 1 mole of helium gas and the second sample contains 1 mole of gaseous N_2O_4. As temperature increases, it is observed that the second sample behaves differently from the helium gas in the first sample.

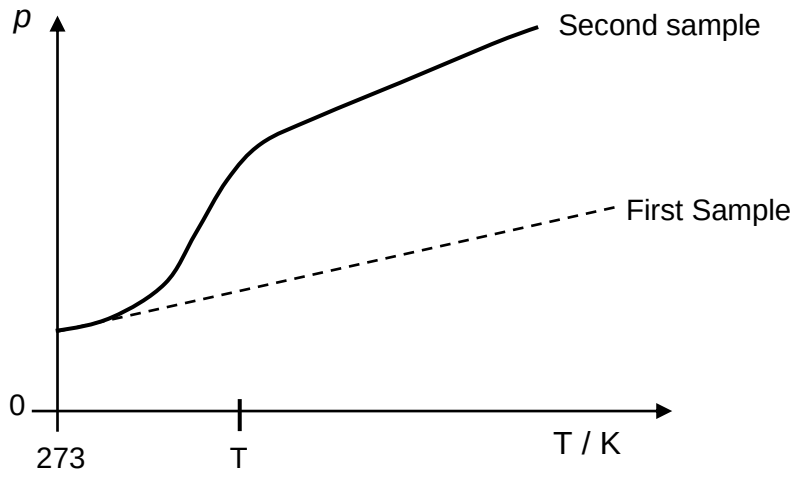

Fig. 1.1

(ii) Explain the shape of *p*–T graph for the second sample in Fig. 1.1.

- The steeper slope as temperature increases from 273 K to T K.
- The gentler slope as temperature increases after temperature T K. [3]

(iii) State the visible observation that would be made for the second sample as the temperature increases. [1]

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As NO_2 has detrimental impacts on human health, it is important to monitor the level of ambient NO_2 in the atmosphere. One method to detect and measure ambient NO_2 involves the use of open tube diffusion sampler to collect air samples and measure the concentration of NO_2 in the air.

The process of determination of NO_2 can take place in three main stages:

(c) Stage 1: Collection of gas sample using a diffusion tube

Fig. 1.2 shows a typical diffusion tube used for sample collection. It has a length (*L*) of 7.1 cm and cross-sectional area (*A*) of 0.91 cm^2.

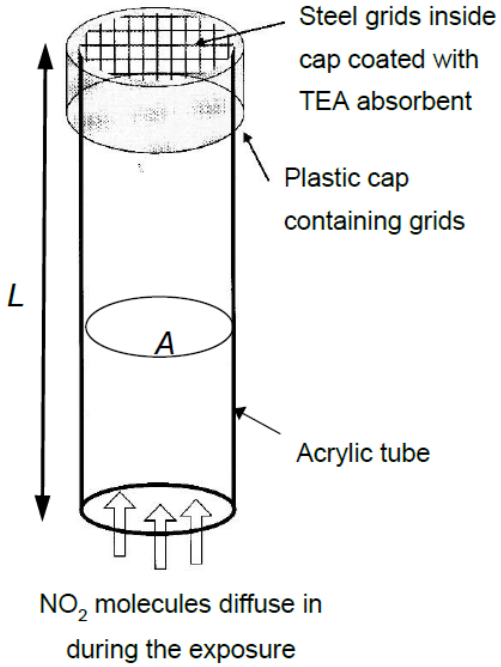

Fig. 1.2

The air sample to be analysed diffuses into the tube through an opening at the bottom. Triethanolamine (TEA), $(HOCH_2CH_2)_3N$, which is coated on the steel mesh grid, absorbs and converts NO_2 to produce nitrite NO_2^- in Stage 2.

Stage 2: Conversion of NO_2 to NO_2^-

The following mechanism, consisting of steps I to V, has been proposed for the conversion of NO_2 to NO_2^- by TEA.

I	$2\ NO_2$	$\rightleftharpoons$	N_2O_4
II	$N_2O_4 + (HOCH_2CH_2)_3N$ (TEA)	$\longrightarrow$	$(HOCH_2CH_2)_3NNO^+ + NO_3^-$
III	$(HOCH_2CH_2)_3NNO^+ + H_2O$	$\longrightarrow$	$(HOCH_2CH_2)_3NH^+ + HNO_2$ **A**
IV	$(HOCH_2CH_2)_3NH^+$ **A**	$\longrightarrow$	$(HOCH_2CH_2)_3N + H^+$ (TEA)
V	HNO_2	$\longrightarrow$	$H^+ + NO_2^-$

(i) Write an overall equation for the reaction between NO_2 and TEA. Hence, state the type of reaction that has taken place. [2]

(ii) The species in the reaction mechanism have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason for each case, the roles of TEA and species **A**. [2]

(iii) TEA dissociates in water forming its conjugate acid **F** as shown.

$(HOCH_2CH_2)_3N(aq) + H_2O(l) \rightleftharpoons (HOCH_2CH_2)_3NH^+(aq) + OH^-(aq)$ $pK_b = 6.23$

TEA **F**

Calculate the pH of an aqueous solution containing 6.00×10^{-2} mol dm^{-3} of species **F**. [2]

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(d) Stage 3: Analysis and determination of the concentration of NO_2

The NO_2^- produced is treated with suitable reagents to form a purple-coloured azo dye before it is placed in a colorimeter. The absorbance of light by the dye, measured at fixed wavelength, is proportional to the concentration of NO_2^-.

The average concentration of nitrogen dioxide in the air, $[NO_2]_{av}$, in μg m^{-3}, can be determined using the expression given below.

$$[NO_2]_{av} = \frac{Q\,L}{A\,D\,t}$$

where Q is the amount of NO_2^- (μg),

L is the length of the diffusion tube (m),

A is the cross-sectional area of the diffusion tube (m^2),

D is the diffusion coefficient for NO_2 in the air at room temperature = 1.56×10^{-5} m^2 s^{-1},

t is the duration of exposure (s).

The World Health Organisation (WHO) guideline states that ambient air quality is good when the concentration of NO_2 is below 25 μg m^{-3} (24-hour mean).

To monitor the quality of ambient air in a school compound, a diffusion tube with dimensions as shown in Fig. 1.2 was installed in the classroom for 10 days. The amount of NO_2^- was found to be 4.13×10^{-3} μg.

Hence, determine the average concentration of NO_2, in μg m^{-3}, in the ambient air of the school compound and use this to comment on the quality of air in terms of NO_2 level, during the 10-day monitoring.
($1\ \mu g = 10^{-6}$ g) [2]

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2 Iodine is found naturally in compounds in many different oxidation numbers and is essential in the synthesis of thyroid hormones in the human body.

(a) **(i)** Draw a fully labelled diagram to show how the standard electrode potential of the $I_2(aq)/I^-(aq)$ system can be measured.

You are to also include the labelling of

- the direction of electron flow
- the cathode and anode
- polarity of the electrodes [3]

(ii) Describe and explain the effect of the addition of a few drops of aqueous silver nitrate into the $I_2(aq)/I^-(aq)$ half-cell on the cell potential of the electrochemical cell described in **(a)(i)**. [2]

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(b) When sodium iodide is added to concentrated sulfuric acid, it is first converted to hydrogen iodide.
Hydrogen iodide, HI, formed undergoes further reaction with excess concentrated sulfuric acid present to form I_2, H_2O and H_2S as products. State the changes in oxidation number during the reaction of hydrogen iodide with concentrated sulfuric acid and use them to construct the balanced equation for the reaction. [2]

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(c) Molecular iodine is not very soluble in water but dissolves readily in aqueous solutions containing iodide ions. This is due to the formation of the complex triiodide ions, I_3^-, which exist in equilibrium with the iodine molecules, I_2 and iodide ions, I^-.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

Due to the difference in solubility of molecular iodine in water and organic solvent, iodine can be extracted from water when shaken with an organic solvent in a separating funnel as shown in Fig. 2.1.

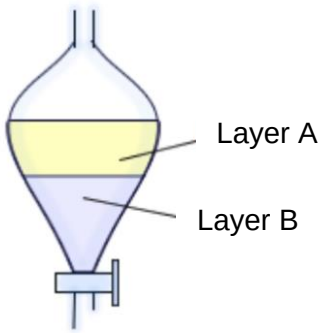

Fig. 2.1

An equilibrium is established when the mixture is left to stand.

$$I_2(aq) \rightleftharpoons I_2(\text{organic solvent})$$

The partition coefficient (K_{pc}) of iodine is the ratio of the concentrations of iodine in the two different immiscible solvents in contact with each other when equilibrium has been established at a particular temperature.

$$K_{pc} = \frac{[I_2 \text{ (organic solvent)}]}{[I_2(aq)]}$$

(i) An experiment was carried out to investigate the equilibriums represented above. 15 cm^3 of cyclohexane is added to a separating funnel with 50 cm^3 of an aqueous solution of I_2 in aqueous KI. The mixture is shaken and left to stand till no further change is observed.

A 25 cm^3 sample of the aqueous layer required 21.85 cm^3 of 0.010 mol dm^{-3} sodium thiosulfate solution for titration. You may assume that all the I_2 present in the aqueous layer exists as I_3^- and reacts with the thiosulfate as shown.

$$2S_2O_3^{2-} + I_3^- \rightarrow 3I^- + S_4O_6^{2-}$$

Given that the partition coefficient, K_{pc}, of I_2 between cyclohexane and water is 93.8, calculate the mass of I_2 extracted into the cyclohexane layer. [3]

(ii) Given the densities of water and cyclohexane is 1.00 g cm^{-3} and 0.779 g cm^{-3} respectively, state the colours in each of the layers, A and B, in the separating funnel after the equilibrium has been reached. [2]

(iii) Explain, in terms of the forces of attractions between the particles, why I_2 is more soluble in cyclohexane than in water. [1]

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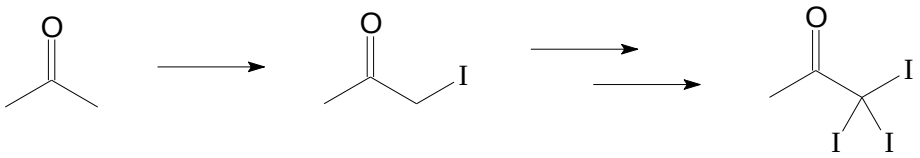
(d) Iodine is used in a chemical test to confirm the identity of an unknown organic compound such as propan-2-ol, through the formation of tri-iodomethane as a by-product.

$$CH_3CH(OH)CH_3 + 4I_2 + 6OH^- \rightarrow CH_3CO_2^- + CHI_3 + 5I^- + 5H_2O$$

The mechanism for the formation of tri-iodomethane and ethanoate ions from propan-2-ol takes place in four stages:

Stage 1: Alkaline aqueous I_2 oxidises propan-2-ol to propanone and itself is reduced to iodide ions.

Stage 2: The propanone formed reacts with I_2 in a series of substitution reaction to produce a tri–iodoketone as shown below.



tri-iodoketone

Stage 3: The hydroxide nucleophile reacts with the tri–iodoketone via a **two-step** nucleophilic acyl substitution mechanism.

- In the first step, the nucleophile attacks the carbonyl carbon to form an alkoxide intermediate.
- In the second step, the intermediate reforms the C=O bond and breaks a C-C bond to form ethanoic acid and CI_3^-.

Stage 4: Ethanoic acid and CI_3^- then react to form the organic products shown in the above balanced equation.

(i) State the oxidation number of the carbon atom which is directly bonded to the hydroxyl group in propan-2-ol. [1]

(ii) Construct a chemical equation for the reaction in Stage 1 between iodine and propan-2-ol. [1]

(iii) Suggest the nucleophilic acyl substitution mechanism in Stage 3.
Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(iv) State the type of reaction taking place in stage 4. [1]

(v) The tri-iodomethane chemical test can be used to test positively for CH_3COCH_3 but not CH_3COCl. Suggest why CH_3COCl does not have a positive tri-iodomethane test. [1]

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[Total: 19]

3 **(a)** Describe how the halogenoethanes, C_2H_5Cl, C_2H_5Br and C_2H_5I could be distinguished using aqueous sodium hydroxide with other suitable reagents. State the observations for each of the halogenoethanes. [2]

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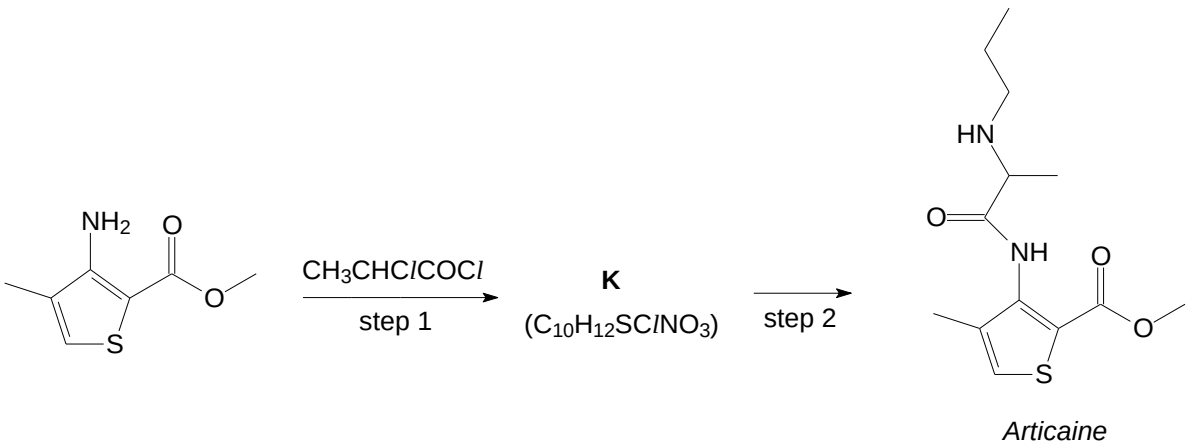
Organohalogeno-compounds is a versatile group of polar organic compounds where the reactivities of carbon-halogen bond can be exploited by changing the reaction conditions.

(b) The reaction scheme in Fig. 3.1 outlines the synthesis of *Articaine*, a local anaesthetic used in dentistry. Step 1 of the synthesis involves the use of a dichloro-compound, $CH_3CHClCOCl$.



Articaine

Fig. 3.1

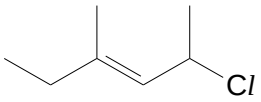
(i) Deduce the structure for the organic compound **K** and state the reagent required for step 2. [2]

(ii) Explain the difference in the reactivities of the two chlorine atoms in $CH_3CHClCOCl$. [1]

(iii) *Articaine* is a safer anaesthetic than other similar amide-containing local anaesthetic as its structure contains an additional ester group which is rapidly hydrolysed by enzymes in the blood and tissues.

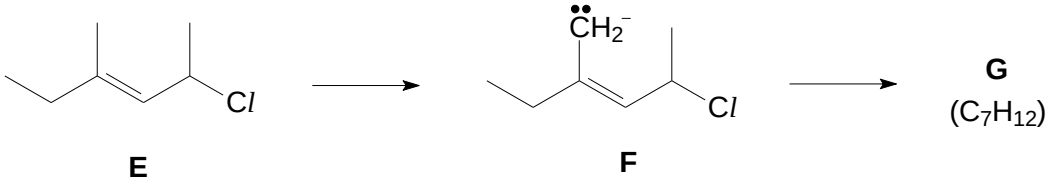
Suggest why an ester group is more rapidly hydrolysed than an amide group. [1]

(c) In the presence of different bases, compound **E** undergoes nucleophilic substitution reactions to form different products.



compound **E**

In the presence of a strong base, such as $NaNH_2$ in liquid ammonia, the nucleophilic substitution reaction occurs via a negatively-charged organic intermediate, **F**, to form a cyclic product **G**, C_7H_{12}.



E **F**

(i) Suggest the structure of the cyclic product **G**. [1]

(ii) The stability of alkyl carbocations can affect the rate of S_N1 reactions.

The allylic carbocation, where the positively charged carbon is adjacent to a C=C, is unusually stable. The stability of an allylic carbocation is due to resonance. An example of the two resonance forms of the allylic carbocation is shown in Fig. 3.2.

Fig. 3.2

Draw curly arrow on Fig. 3.2 to show how the resonance forms are converted into each other. [1]

When a single enantiomer of compound **E** reacts with another base, aqueous NaOH, the stereochemical outcome depends on whether the reaction goes via the S_N1 or S_N2 mechanism.

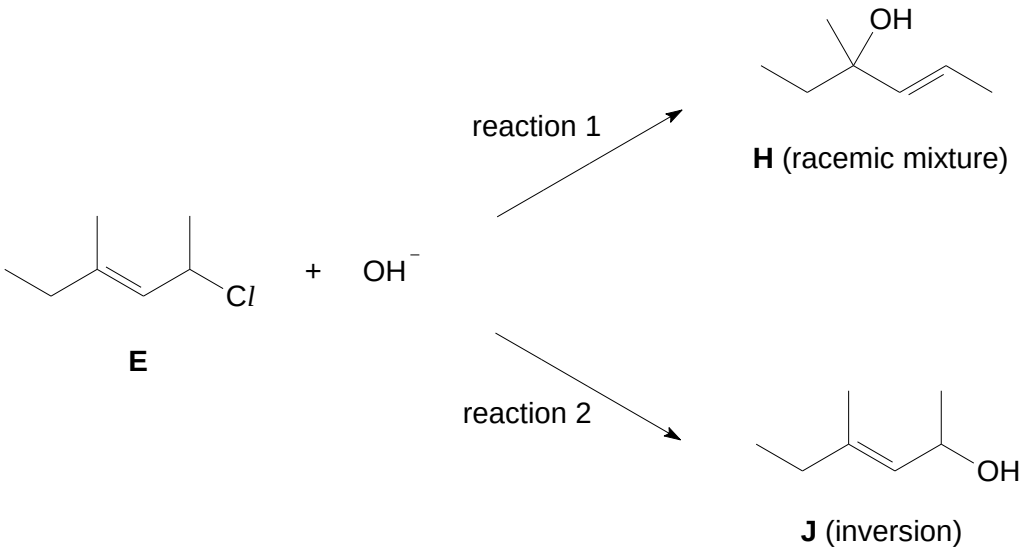


Fig. 3.3

(iii) Based on the information given in Fig. 3.3, state whether reaction 1 proceed via the S_N1 or the S_N2 mechanism.

[1]

(iv) With reference to information in **(c)(ii)** and your answers in **(c)(iii)**, suggest the mechanism for reaction 1.

Where appropriate, indicate curly arrows, lone pairs of electrons and dipoles in your mechanism. [3]

(v) Based on the mechanism for reaction 2 in Fig. 3.3, explain why **J** has an inversion of configuration. [1]

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(d) Organohalogen-compounds are important in the production of quaternary ammonium compounds, QACs. The general structure of a QAC is R_4N^+, where R can be the same or different alkyl or aryl group.

(i) A quaternary ammonium compound can be produced when excess C_2H_5Br is heated with NH_3 in ethanol. With reference to the mechanism of the reaction, explain why the QAC can be formed. [1]

An attempt to prepare QACs was made by reacting ethylamine with a 1:1 molar mixture of 1-chlorobutane and benzyl chloride, $C_6H_5CH_2Cl$.

(ii) Predict the number of different possible QACs that could be prepared. [1]

(iii) Draw the **skeletal** structure of the QAC which contains only one benzyl group. [2]

(e) Compound **L**, $C_7H_{12}Cl_2$ is a saturated cyclic compound. When **L** is heated with ethanolic KOH, compound **M**, C_7H_{10}, is formed as the only product. When treated with hot acidified $KMnO_4$, **M** forms an optically active compound **N**, $C_5H_8O_4$, as the only organic product. **N** does not react with 2,4-dinitrophenylhydrazine but liberates CO_2 from Na_2CO_3(aq).

Suggest the structural formula of **L**, **M** and **N**. Explain your reasoning. [6]

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Section B

Answer **one** question from this section

4 **(a)** When potassium dichromate(VI), $K_2Cr_2O_7$, is dissolved in 6 mol dm^{-3} of hydrobromic acid, HBr, and cooled, orange crystals of a potassium salt **A** are precipitated.

A has a formula mass of 219.0 and the following composition by mass: K, 17.9%; Cr, 23.7%; Br, 36.5% O, 21.9% and the oxidation state of the chromium in salt **A** is the same as that of $K_2Cr_2O_7$.

When aqueous silver nitrate was added to a solution of **A**, an acidic solution is produced and a cream–coloured precipitate **B** is formed. An initial yellow solution **C** is also observed which rapidly turns to an orange solution, **D**.

On addition of sulfur dioxide to solution **D**, a green solution **E** is obtained.

(i) Show that the formula of **A** is $KCrBrO_3$ and hence write a balanced equation showing its formation from potassium dichromate(VI), $K_2Cr_2O_7$. [2]

(ii) Identify species **B**, **C**, **D** and **E**.

Hence, state the type of reaction for the formation of solution **E** from solution **D**, giving a balanced equation for the reaction. [4]

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(b) Cis–trans isomers of transition metal complexes differ from each other in the arrangement of the ligands around the central metal ion or atom.

Cis isomers have two of the same ligands 90° apart from one another in relation to the centra metal ion or atom, whereas trans isomers have two of the same ligands 180° apart.

Propose the structures of the cis and trans isomers of tetraaquadichlorochromium(III) ion, $[Cr(H_2O)_4Cl_2]^+$. Label your structures clearly. [2]

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(c) Compound **K** can be synthesised using the following reaction scheme shown in Fig. 4.1.

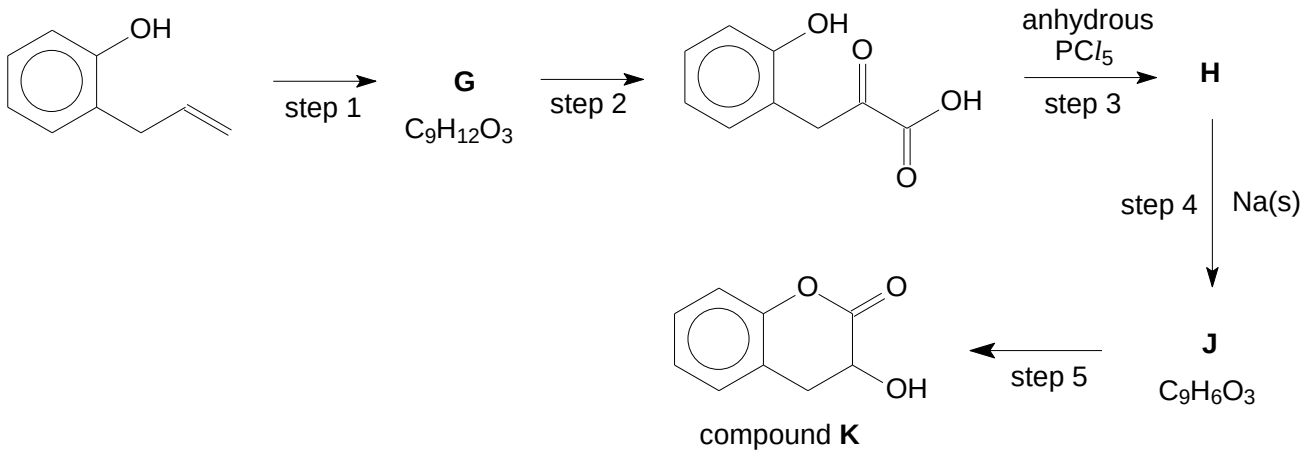

Fig. 4.1

(i) Suggest structures for the compounds **G**, **H** and **J**. [3]

(ii) Suggest reagents and conditions for each of the steps 1, 2 and 5. [3]

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(d) Magnesium chloride gives a weakly acidic solution when dissolved. It can be titrated with a strong base to give a rapid pH change upon complete reaction at the equivalence volume.

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$$

In an experiment, 50.0 cm^3 of aqueous magnesium chloride was titrated with 1.00 mol dm^{-3} sodium hydroxide. The pH of the solution changed as shown in Fig 4.2.

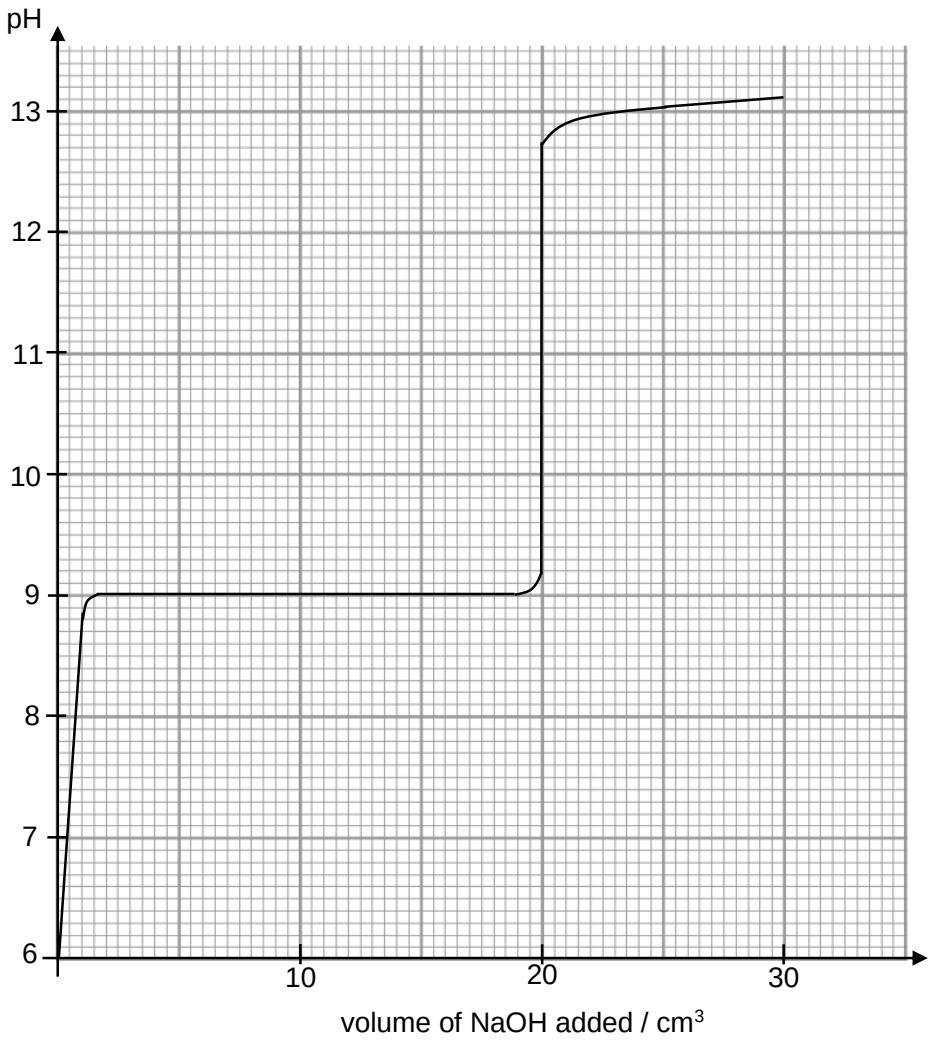

Fig. 4.2

(i) Explain, with the aid of equations, why aqueous $MgCl_2$ has an initial pH of about 6. [2]

(ii) Determine the concentration of aqueous $MgCl_2$ used in the above titration. [1]

(iii) Write an expression for the solubility product, K_{sp}, of magnesium hydroxide. [1]

(iv) When 10 cm^3 of NaOH was added, the concentration of Mg^{2+}(aq) is found to be half of the value in **(d)(ii)**.

Use information from Fig. 4.2 to calculate the K_{sp} value for $Mg(OH)_2$. [2]

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5 **(a)** Describe the reaction, if any, of the chlorides of sodium and silicon with water, stating the approximate pH of any solution formed. Include equations where appropriate. [3]

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(b) Ethylenediamine, $H_2NCH_2CH_2NH_2$, can act as a ligand for transition metal ions.

(i) A student proposed to synthesise ethylenediamine from cyanogen, $(CN)_2$. Deduce the number of σ bonds and π bonds in one molecule of cyanogen. [1]

(ii) The proposed synthesis in **(b)(i)** did not yield the desired product.
Instead, ethylenediamine can be synthesised from ethene in two steps. Suggest reagents and conditions for each step. Draw the structure of the intermediate compound. [3]

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(c) Nickel(II) chloride reacts with ethylenediamine (en) to form an octahedral complex with the formula, $[Ni(en)_3]^{2+}$.

(i) Each molecule of ethylenediamine can form two coordinate bonds to a transition metal ion.

Draw the structure of ethylenediamine and on this structure circle the two atoms that could form these coordinate bonds. [1]

(ii) Complete the diagram in Fig. 5.1 to suggest the structure of the complex formed, showing the 3-dimensional arrangement around the Ni(II) ion. Indicate the overall charge on this complex. [1]

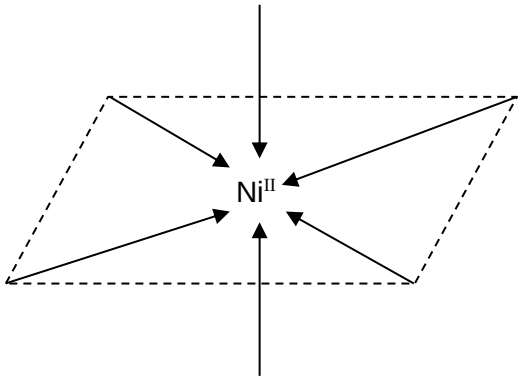

Fig. 5.1

(iii) The $[Ni(en)_3]^{2+}$ complex that you have drawn in **(c)(ii)** can exist as a pair of stereoisomers with different effects on plane-polarised light.

State the type of isomerism present and draw the structure of its stereoisomer. [2]

The colour of a given transition metal ion in a complex depends on its oxidation state, shape and the ligands that it is bonded to. Cu(I) compounds are usually white or colourless while Cu(II) compounds are usually coloured.

(iv) Copper(I) chloride, CuC*l*, is insoluble in water but dissolves in concentrated aqueous sodium chloride to give a colourless solution. The complex anion **Q** in the colourless solution has a linear shape and contains copper and chlorine only.

CuC*l* reacts with an aqueous solution of ethylenediamine (en = $H_2NCH_2CH_2NH_2$) to form a blue solution, **R** and a pink-coloured solid, **S**. The complex in solution **R** contains only the ethylenediamine ligand and has a square planar shape.

With aqueous silver nitrate, the blue solution **R** gives a white precipitate, **T**, which is soluble in dilute aqueous ammonia.

Identify species **Q**, **R**, **S** and **T** and write equations for all reactions. [5]

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(d) **(i)** Define what is meant by the term enthalpy change of solution. [1]

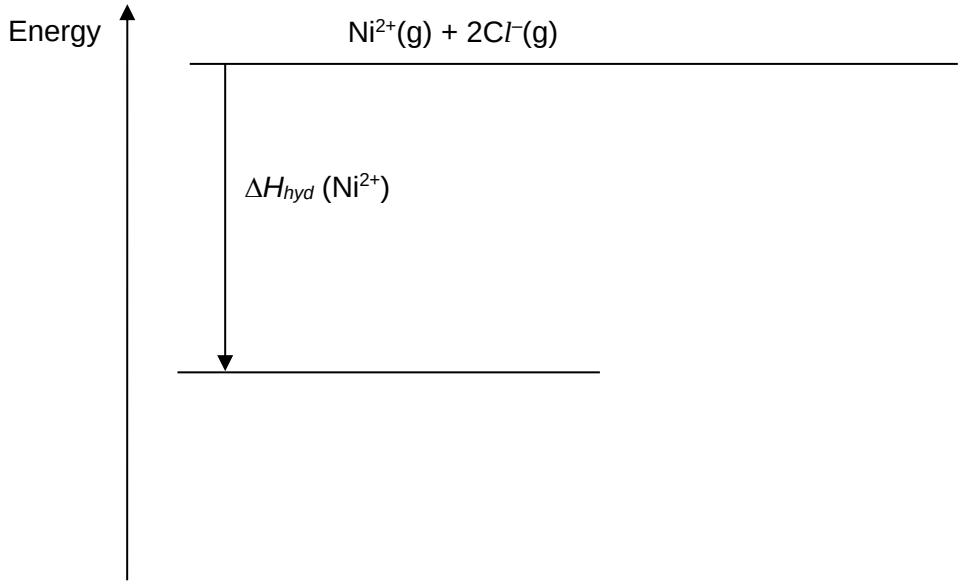
(ii) Use the following data to determine the enthalpy change of solution, ΔH_{soln} of nickel(II) chloride.

	kJ mol^{-1}
Enthalpy change of hydration of Cl^-	–381
Enthalpy change of hydration of Ni^{2+}	–2096
Lattice energy of nickel(II) chloride	–2753

[1]

(iii) On the energy level diagram below, draw arrows to show the enthalpy change of solution, ΔH_{soln} of nickel(II) chloride and each of the enthalpy changes you have used in the calculation above.

Label each level with the appropriate formulae.



[2]

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[Total: 20]

Additional answer space

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