NAME ______________________________ CLASS **23S**

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2024

CHEMISTRY **9729/03**

Higher 2 **12 September 2024**

Paper 3 Free Response **2 hour**

Candidates answer on the Question paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces at the top of this page.
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 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.
Write the Question number of the Question you have attempted, in the box provided below.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

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

For Examiner's Use	
1	
2	
3	
4 or 5	
Penalty (delete accordingly)	
Lack **3sf** in final answer	**–1 / NA**
Missing/wrong **units** in final ans	**–1 / NA**
Bond linkages	**–1 / NA**
Total	**80**

This document consists of **32** printed pages inclusive of 1 blank page.

Section A

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

For Examiner's Use

1 **(a)** One version of the Fischer-Tropsch process for manufacturing methane is the reaction of carbon monoxide with hydrogen.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \qquad \Delta H$$

A mixture of CO and H_2 in a 1:3 molar ratio was added into a sealed vessel and heated to 1200K. At equilibrium, 40% of the CO had reacted. The total pressure in the vessel was 12 atm at equilibrium.

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

(ii) Use your expression to calculate the value of K_p for the reaction at 1200K. Include its units. [3]

(iii) Given that the value of K_p decreases with increasing temperature, deduce the sign for the enthalpy change, ΔH of the forward reaction. Explain your reasoning. [1]

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(b) Describe and explain how the entropy of each of the following systems will change during the stated process.

- 1 mol of N_2(g) at 298K is added to 1 mol of CH_4(g) at 298K.
- 1 mol of Cl_2(g) at 298 K is heated to 373 K.

Assume the pressure of each gas remains at 1 atm throughout and no reaction occurs between N_2 and CH_4**.** [2]

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(c) **(i)** During the monobromination of pentane, three different bromoalkanes are formed as shown in Fig. 1.1.

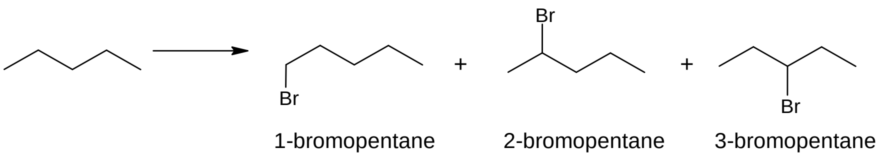

Fig. 1.1

Predict the expected theoretical ratio in which these three products would form if the monobromination of pentane occurs randomly.

Explain your answer. [2]

(ii) When the monobromination was practically carried out in an experiment, the percentage of 1-bromopentane was obtained in the lowest proportion.

Suggest an explanation for the difference between this experimental result and what you predicted in **(c)(i)**. [1]

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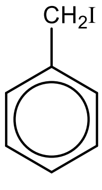
(d) The *Wurtz* reaction below shows two iodoalkanes react with Na in dry ether, to form a new carbon−carbon bond, resulting in the formation of a new alkane.

$$R{-}I + R'{-}I + 2Na \rightarrow R{-}R' + 2NaI$$

Reaction of a single iodoalkane, RI, with Na metal in dry ether via *Wurtz* reaction will give a good yield of symmetrical alkane product. Draw the organic product formed when (iodomethyl)benzene reacts with Na metal in dry ether.



(iodomethyl)benzene [1]

For Examiner's Use

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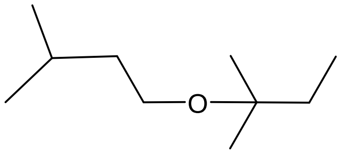
(e) Bromoalkanes and alkoxides react in the Williamson ether synthesis to form the ether functional group containing C-O-C, an example of which is shown below.

$$\underset{}{RBr} + \underset{\text{alkoxide}}{R'O^-} \rightarrow \underset{\text{ether}}{ROR'} + Br^-$$

It is known that S_N2 mechanism is usually undergone in Williamson ether synthesis.

Suggest the structures of the halogenoalkane and alkoxide ion RO^- you would use to synthesise the ether below, using the Williamson synthesis method.



[1]

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(f) **(i)** CH_3OCH_3, methoxymethane is the simplest ether which is used as aerosol propellants. Given that CH_3OCH_3, contains C-O-C bond, draw the 'dot-and-cross' diagram for CH_3OCH_3.

Use VSEPR (valence shell electron pair repulsion) theory to describe and explain the shape about the oxygen and suggest the C-O-C bond angle of a CH_3OCH_3 molecule. [3]

(ii) By considering the polarity of each of the bonds it contains, and the shape about the oxygen of the CH_3OCH_3 molecule, deduce the overall polarity of the CH_3OCH_3 molecule. [1]

(iii) Boiling points of some compounds with similar M_r as methoxymethane such as propane, ethanol and ethylamine are given below in Table 1.1.

Suggest explanations for these differences.

Table 1.1

compound	M_r	formula	boiling point / °C
ethylamine	45	$CH_3CH_2NH_2$	17
ethanol	46	CH_3CH_2OH	78
propane	44	$CH_3CH_2CH_3$	-42

[3]

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2 **(a)** **(i)** Halogens can behave as Lewis acids or Lewis bases. The reaction of benzene and Cl_2 requires the use of $AlCl_3$, to generate the electrophile.

- Define what is meant by a Lewis acid.
- Using the reaction of Cl_2 with $AlCl_3$, state which species is behaving as Lewis acid and which is behaving as Lewis base. [2]

(ii) Benzene and phenol both undergo electrophilic substitution with halogens under different conditions.

Explain why the reaction of phenol with halogens occurs more readily and does not require the use of halogen carrier catalyst, $AlCl_3$, like benzene does. [1]

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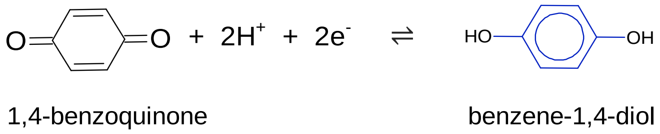
(b) The standard reduction potential for 1,4-benzoquinone /benzene-1,4-diol is shown in Fig. 2.1.



$E^\ominus = +0.70\text{V}$

Fig. 2.1

Fig. 2.2 below shows how the standard cell potential between the Cr^{3+}/Cr^{2+} half-cell and the 1,4-benzoquinone /benzene-1,4-diol half-cell is measured.

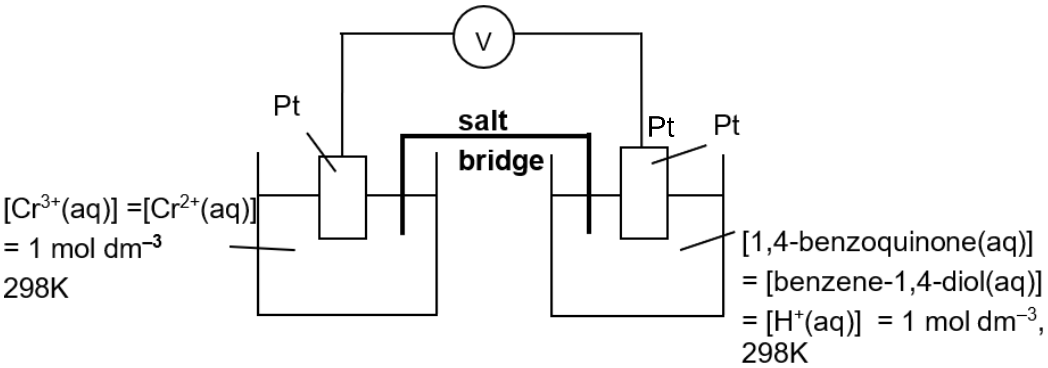


Fig. 2.2

(i) Using data from the *Data Booklet* and the above information, calculate $E^\ominus_{cell}$ for the cell in Fig. 2.2 and state which is the negative electrode. [2]

(ii) Construct the overall equation for the reaction that occurred in the cell. [1]

(iii) Calculate $\Delta G^\ominus$ for the reaction you wrote in **(b)(ii)**. [1]

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(c) State and explain what happens to the E_{cell} when pH of the 1,4-benzoquinone /benzene-1,4-diol half-cell decreased. [2]

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(d) Another experiment is set up using the same electrochemical cell. In this experiment, the Cr^{2+} concentration is changed to 0.15 mol dm^{-3}. All other concentrations remain at their standard values.

The Nernst equation is shown.

$$E = E^{\ominus} + \frac{0.059}{n}\log\frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

n = number of electrons transferred

$E^{\ominus}$ is the standard reduction potential for the Cr^{3+}/Cr^{2+} electrode system.

(i) Use the Nernst equation and the *Data Booklet* to calculate the electrode potential for the Cr^{3+}/Cr^{2+} half cell in this experiment. [1]

(ii) Using your answer in **(d)(i)** and data given in **(b)**, calculate E_{cell} for this electrochemical cell. [1]

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For Examiner's Use

(e) The aldol reaction is a useful method to make new carbon–carbon bonds in organic chemistry. It involves combining 2 molecules of the same aldehyde or ketone to form a product which contains both a carbonyl functional group (aldehyde or ketone) and alcohol functional group.

The aldol **A** is made by reacting ethanal with a small amount of NaOH(aq) at room temperature. The 3 stages of the reaction are given in Table 2.1.

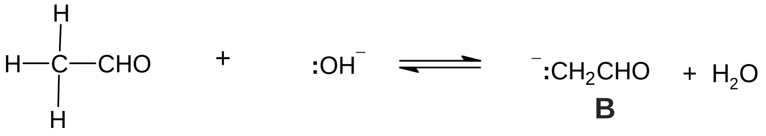
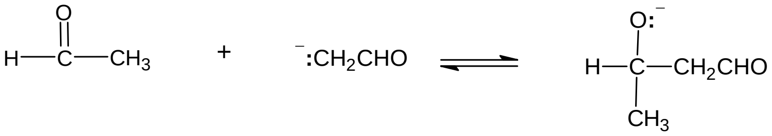
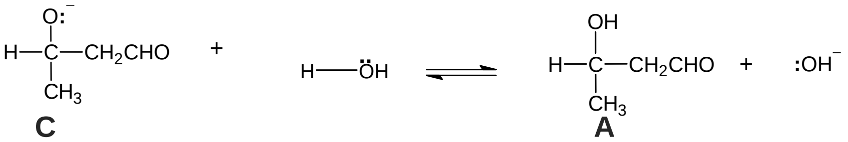
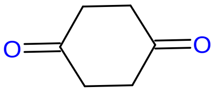
Stage	**Equation**
1	 $H{-}CH_2{-}CHO + :OH^- \rightleftharpoons {}^-:CH_2CHO + H_2O$ **B**
2	 $HC(=O)CH_3 + {}^-:CH_2CHO \rightleftharpoons H{-}C(O:^-)(CH_3){-}CH_2CHO$
3	 $H{-}C(O:^-)(CH_3){-}CH_2CHO + H{-}\ddot{O}H \rightleftharpoons H{-}C(OH)(CH_3){-}CH_2CHO + :OH^-$ **C** **A**

Table 2.1

(i) Suggest the type of reaction in stage 1. [1]

(ii) 1,4-cyclohexanedione can be formed from 1,4-benzoquinone.



1,4-cyclohexanedione

1,4-cyclohexanedione reacts with the presence of NaOH at room temperature via the 3 stages shown in Table 2.1. A product with 12 carbons, **D** was formed. Draw the structure of **D**. [1]

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(f) Aluminium objects have a thin insoluble oxide layer, Al_2O_3, on their surfaces. This oxide can be removed by adding NaOH(aq) to the aluminium object.

(i) Explain why Al_2O_3 is insoluble in water. [1]

(ii) Write an equation which describes the reaction occurring when NaOH(aq) is added to the aluminium oxide. [1]

(g) Compound **E**, $C_{10}H_{18}O$ is optically active and decolourises orange aqueous Br_2. **E** reacts with sodium, Na to form H_2 gas.

E reacts with an excess hot acidified concentrated $KMnO_4$ to produce three different organic molecules, **F**, C_3H_6O, **H**, $(CO_2H)_2$, and **G**, $C_5H_8O_3$. One of these organic molecules is further oxidised to CO_2.

F and **G** both react with 2,4-dinitrophenylhydrazine. **E**, **F** and **G** react with aqueous alkaline iodine forming a yellow precipitate. **G** reacts with aqueous Na_2CO_3(aq) giving off effervescence of a colourless gas.

Suggest the structures of **E**, **F** and **G**. For each reaction, state the *type of reaction* and explain what the information tells you about the functional groups present in each compound. [6]

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3 Epoxides such as oxirane are 3-membered ring cyclic ethers, which can undergo ring-opening reactions.

An example of an epoxide ring-opening reaction involves nucleophilic attack by NH_3 on oxirane in Fig. 3.1 as shown below.

(a)

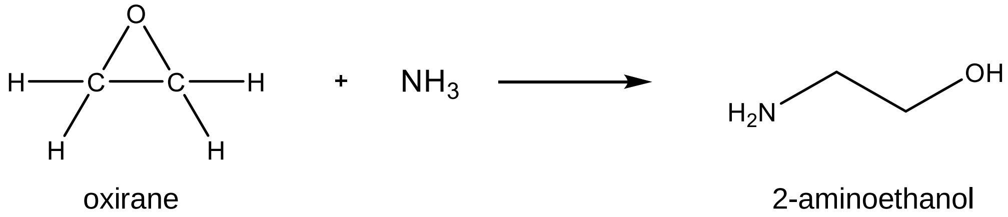


Fig. 3.1

(i) Complete the mechanism of step 1 on Fig. 3.2 by adding all relevant curly arrows, lone pairs of electrons, charges and partial charges; and draw the structure of the organic intermediate. [2]

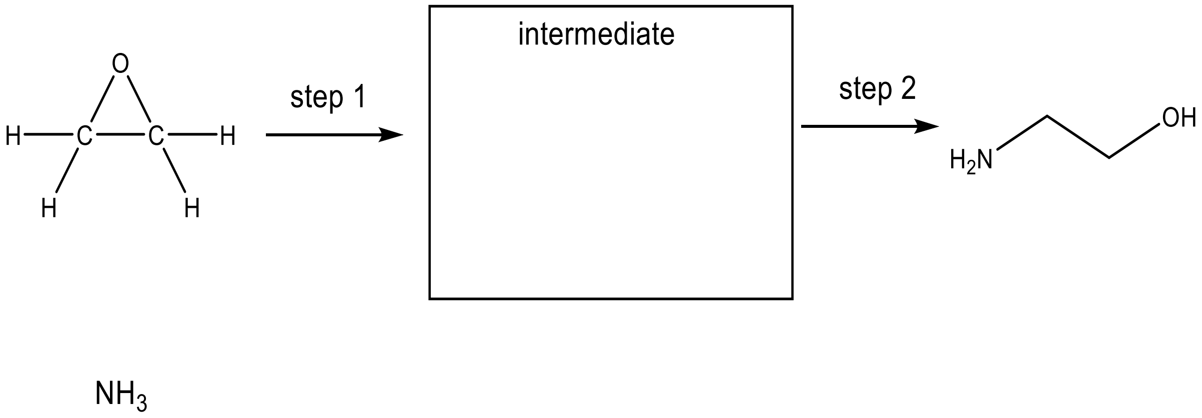
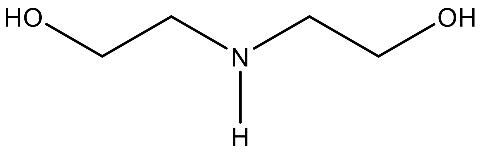


Fig. 3.2

(ii) A small amount of by-product, shown below, is produced during the reaction shown in Fig. 3.1.



Suggest how the formation of the by-product can be minimised. [1]

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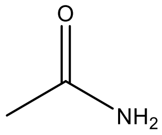
(b) By considering the structure of **each** compound **J**, **K** and 2-aminoethanol, explain the order of basicity of these 3 compounds, which are arranged in order of increasing basicity.



J

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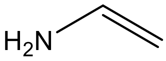

K

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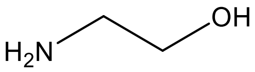

2-aminoethanol

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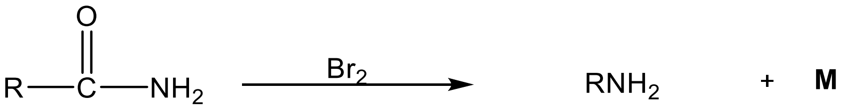
For Examiner's Use

(c) A method to synthesise amines directly from primary amides is the Hofmann rearrangement reaction, which was discovered by August Hofmann in 1881.

When a primary amide is treated with bromine, Br_2, under suitable conditions, a gaseous primary amine and an unknown gas, **M**, are formed, as exemplified by the following equation.



$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2} RNH_2 + \mathbf{M}$$

When a primary amide, **L**, was reacted with Br_2 under suitable conditions, 0.586g of a mixture of two gases: a gaseous primary amine and gas **M** were produced.

The gas mixture occupies a volume of 326 cm^3 (measured at 298 K and 1.00×10^5 Pa). The addition of excess NaOH(aq) to the gaseous mixture caused its volume to decrease by 163 cm^3.

(i) Prove that the average M_r for the gaseous mixture is 44.5. [1]

(ii) Suggest the identity of the gas that reacted with NaOH (aq). [1]

(iii) Hence calculate the M_r of the other gas in the gaseous mixture and suggest its identity. [2]

(iv) Suggest the structure formula for primary amide **L**. [1]

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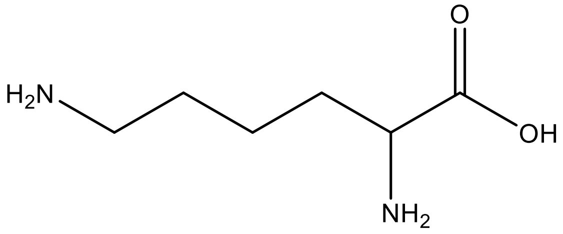
(d) Lysine is an essential α-amino acid that is a precursor to many proteins. Due to its importance in biological processes, a lack of lysine can lead to several illnesses including anaemia.



Lysine

There are three pK_a values associated with lysine: 2.2, 9.0 and 10.5.

(i) At room temperature, lysine exists as a white crystalline solid while 2-aminoethanol is a liquid. Explain the above. [2]

(ii) Make use of the above pK_a values to suggest the major species present in solutions of lysine at the following pH values.

- pH 3.0
- pH 9.7 [2]

Solution **N**, a 10 cm^3 sample containing 0.200 mol dm^{-3} of a **fully protonated** lysine, was titrated against 0.200 mol dm^{-3} NaOH (aq).

(iii) What is the initial pH of solution **N**? (ignore the effect of pK_2 and pK_3 on the pH). [2]

(iv) Sketch the pH-volume added curve you would expect to obtain when 40 cm^3 of 0.200 mol dm^{-3} NaOH(aq) is added to 10 cm^3 sample of solution **N**. Mark clearly the initial pH and the point(s) of maximum buffering capacity. [3]

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Section B

Answer **one** question from this section.

4 **(a)** Group 2 carbonates decompose when heated to form the metal oxide and carbon dioxide.

(i) Suggest a mechanism for the decomposition of the carbonate ion by adding two curly arrows on Fig. 4.1.

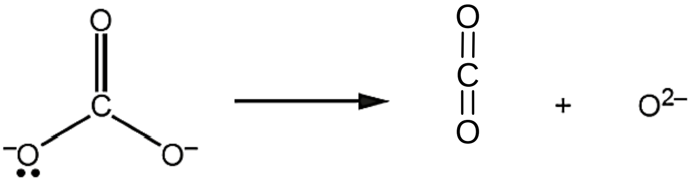

Fig. 4.1 [1]

Nickel carbonate, $NiCO_3$, and lithium carbonate, Li_2CO_3, decompose on heating in a similar manner to the Group 2 carbonates.

(ii) Suggest why $NiCO_3$ decomposes more readily than $CaCO_3$. [2]

(iii) Suggest why the Group 1 carbonates, other than Li_2CO_3, do not decompose when heated. [1]

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(b) Chromyl chloride, CrO_2Cl_2, can be prepared by heating a mixture of potassium dichromate(VI) and potassium chloride with concentrated sulfuric acid.

$$K_2Cr_2O_7(aq) + 4KCl(aq) + 3H_2SO_4(l) \rightarrow 2CrO_2Cl_2(aq) + 3K_2SO_4(aq) + 3H_2O(l)$$

Use the data in Table 4.1 to calculate the enthalpy change of the reaction, ΔH_r.

Table 4.1

compound	enthalpy change of formation, $\Delta H^\ominus_f$ / kJ mol^{-1}
$K_2Cr_2O_7(aq)$	–2061
$KCl(aq)$	–437
$H_2SO_4(l)$	–814
$CrO_2Cl_2(aq)$	–580
$K_2SO_4(aq)$	–1438
$H_2O(l)$	–286

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(c) **(i)** Define what is meant by the standard enthalpy change of atomisation of calcium. [1]

(ii) The ionic equation for the reaction of calcium with HC*l* acid is shown below.

$$Ca(s) + 2H^{+}(aq) \rightarrow Ca^{2+}(aq) + H_2(g) \qquad \Delta H^{\ominus} = \mathbf{x}\ kJ\ mol^{-1}$$

By constructing an energy cycle using the data in Table 4.2, and data from the *Data Booklet*, calculate a value for **x**.

Table 4.2

standard enthalpy change of atomisation of Ca(s)	+178 kJ mol^{-1}
standard enthalpy change of hydration of Ca^{2+}(g)	–1576 kJ mol^{-1}
standard enthalpy change of hydration of H^{+}(g)	–1090 kJ mol^{-1}

[3]

(iii) The standard enthalpy change for the reaction between Ca(s) and CH_3CO_2H(aq) is less negative than **x**.

Suggest an explanation for this. [1]

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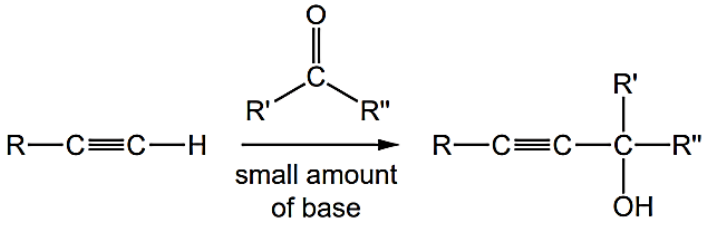
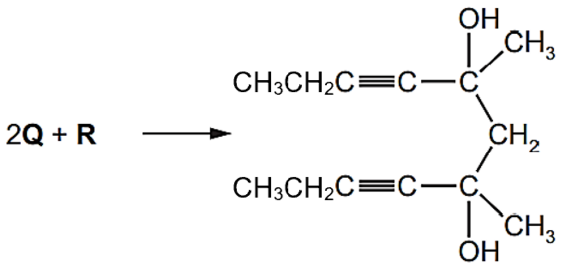
(d) Alkynes, compounds containing a C≡C, can react with carbonyl compounds under basic conditions as shown in reaction 1 in Fig.4.2.



reaction 1

Fig. 4.2

An alkyne, **Q**, and a carbonyl compound, **R**, react together to form compound **P** as shown in Fig. 4.3.



P

Fig. 4.3

Use reaction 1 to suggest the structures of alkyne **Q** and carbonyl compound **R**. [1]

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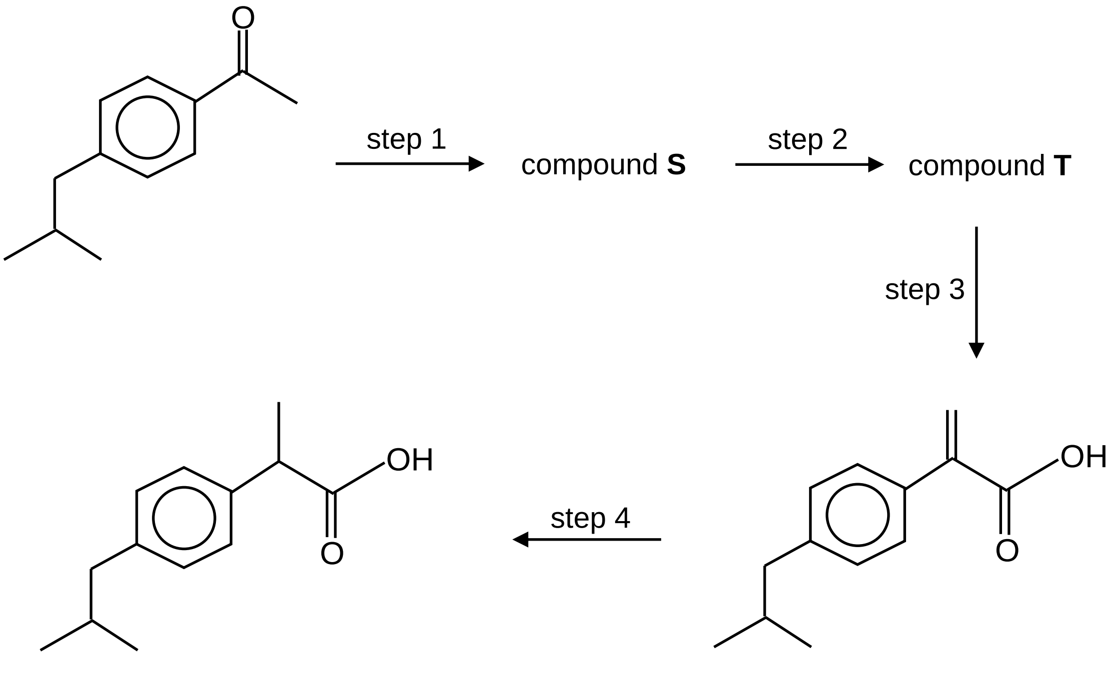
(e) The anti-inflammatory drug ibuprofen can be synthesised in the reaction scheme as shown in Fig. 4.4.



ibuprofen

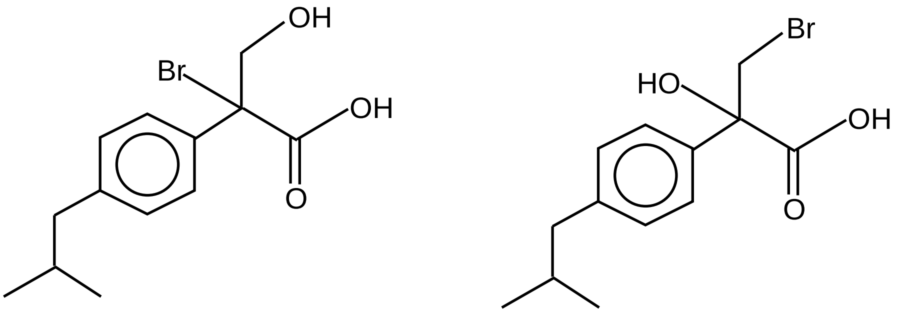
compound **U**

Fig. 4.4

(i) Identify compounds **S** and **T**. [2]

(ii) State the reagents and conditions for steps 1 to 4. [4]

(iii) Compound **U** reacts with $Br_2(aq)$ to give two isomers as shown in Fig. 4.5.



isomer 1

isomer 2

Fig. 4.5

State which isomer is formed at higher proportion. Explain your answer. [2]

[Total: 20]

5 **(a)** Cadmium ions form complexes with primary amines and with 1,2-diaminoethane.

equilibrium **I**:
$[Cd(H_2O)_6]^{2+}(aq) + 4CH_3NH_2(aq) \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}(aq) + 6H_2O(l)$ $K_{stab} = 3.6 \times 10^6$

equilibrium **II**:
$[Cd(H_2O)_6]^{2+}(aq) + 2H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Cd(H_2NCH_2CH_2NH_2)_2]^{2+}(aq) + 6H_2O(l)$ $K_{stab} = 4.2 \times 10^{10}$

(i) Write an expression for the stability constant, K_{stab}, for equilibrium **I**, and state its units. [1]

Cadmium ions are toxic and need to be removed from some water supplies. This is often done by adding a complexing agent such as $CH_3NH_2(aq)$.

(ii) A sample of ground water contains 1.00×10^{-4} mol dm^{-3} of $Cd^{2+}(aq)$. Calculate the concentration of $CH_3NH_2(aq)$ needed to reduce the concentration of $Cd^{2+}(aq)$ in the sample of ground water to $\frac{1}{1000}$ of its original concentration. [2]

(iii) 1,2-diaminoethane is a bidentate ligand. State the coordination number and the geometry of $[Cd(H_2NCH_2CH_2NH_2)_2]^{2+}$complex ion. [1]

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(b) The structure of picolinic acid is shown in Fig. 5.1 below.

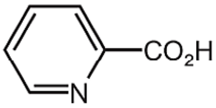

Fig. 5.1

When picolinic acid is placed in basic solution, a bidentate ligand, **V**, is formed.

(i) Draw the structure of **V** and on this structure, draw the lone pairs of electrons on the atoms that could form coordinate bonds to a transition metal ion. [1]

(ii) **V** reacts with aqueous chromium(III) ions, $[Cr(H_2O)_6]^{3+}$, in a 3 : 1 ratio to form a new neutral complex.

State the type of reaction that has occurred.

Draw a diagram of the structure of the new complex formed, showing the **3-dimensional** arrangement around the Cr(III) ion. [2]

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(c) A 0.155 g of impure sample of ammonium vanadate(V), NH_4VO_3, is dissolved in an excess of dilute acid.

In this solution all vanadium is present as VO_2^+ ions. An excess of zinc powder is added to the solution and all the VO_2^+ ions are reduced to V^{2+} ions. The mixture is filtered to remove any remaining zinc powder.

When the resulting solution is titrated, 21.10 cm^3 of 0.0250 mol dm^{-3} acidified MnO_4^- oxidises all V^{2+} ions back to VO_2^+ ions.

(i) Construct an ionic equation for the reaction between V^{2+} and acidified MnO_4^-. [1]

(ii) Calculate the percentage by mass of NH_4VO_3 in the 0.155 g impure sample of NH_4VO_3. [2]

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(d) When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with minor nickel and silver impurities.

In order to purify it, this alloy was made the anode of an electrolytic cell similar to the one shown in Fig. 5.2.

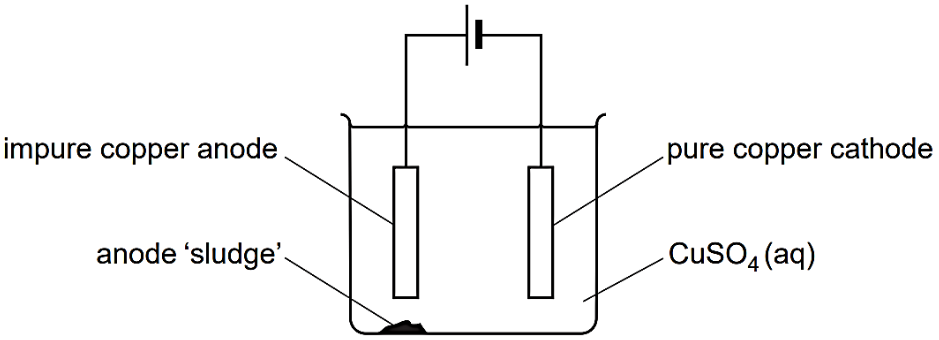

Fig. 5.2

At the impure copper anode, Cu is oxidised to Cu^{2+} which goes into the solution. At the pure copper cathode, Cu^{2+} is reduced to Cu which deposits on the cathode.

(i) Explain, with reference to relevent $E^\ominus$ values from the *Data Booklet*, what happens to the nickel and silver impurities during this purification procedure. [2]

(ii) Calculate the expected increase in mass of the cathode when a current of 15.0 A was passed through the cell for 5.0 hours. [2]

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(e) When yellow-brown anhydrous $CuCl_2$ is dissolved in water, it gives a blue solution.

(i) When the blue solution is boiled with copper metal and aqueous hydrochloric acid, a colourless solution **W**, which contains complex ion of copper and chlorine, is formed.

After filtering off the excess copper metal and diluting the colourless solution with water, a white solid **X**, containing copper and chlorine only, is formed. The oxidation number of copper in **W** and **X** are the same.

Identify the complex ion in **W** and the solid compound **X**. [2]

(ii) When concentrated hydrochloric acid is added to the blue solution, the colour changes to yellow-green. When water is added to the resulting yellow-green solution, the colour changes back to blue.

Suggest an explanation of these observations with an aid of a balanced equation. [2]

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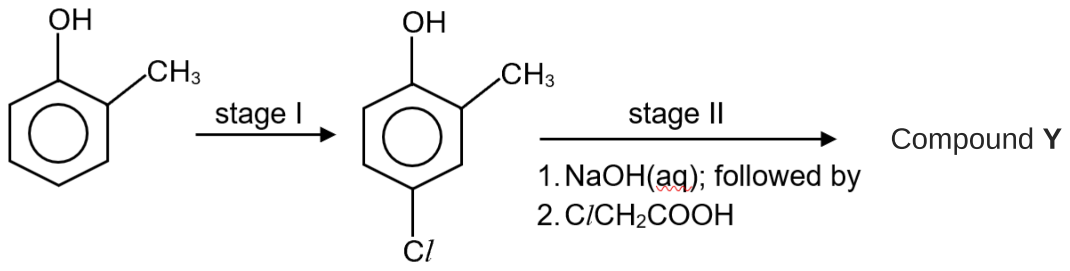
(f) Cresols are precursors or synthetic intermediate to other compounds and materials, including plastics, pesticides, pharmaceuticals, and dyes.

An organic compound **Y**, a selective herbicide, can be synthesised from cresol by the following route in Fig. 5.3.



cresol Compound **Z**

Fig. 5.3

(i) Give the structure of compound **Y**. [1]

(ii) Suggest why NaOH(aq) is added to compound **Z** in stage II before $ClCH_2COOH$ is added. [1]

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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.