



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	/
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4 or 5	/
Penalty (delete accordingly)	
Lack 3sf in final answer	-1 / NA
Missing/wrong units in final ans	-1 / NA
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Total	80

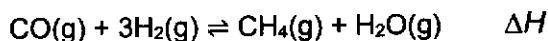
This document consists of **32** printed pages inclusive of 1 blank page.

Section A

Answer all the questions in this section.

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

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A mixture of CO and H₂ 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 .

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

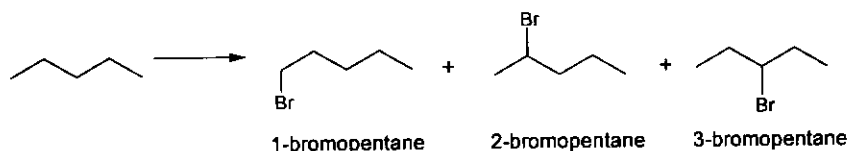


Fig. 1.1

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).

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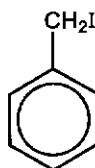
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- (d) The *Wurtz* reaction below shows two iodoalkanes react with Na in dry ether, to form a new carbon-carbon bond, resulting in the formation of a new alkane.



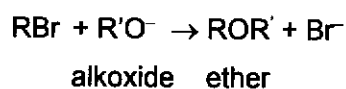
Reaction of a single iodoalkane, RI, with Na metal in dry ether via *Wurtz* reaction will give a good yield of symmetrical alkane product. Draw the organic product formed when (iodomethyl)benzene reacts with Na metal in dry ether.



(iodomethyl)benzene

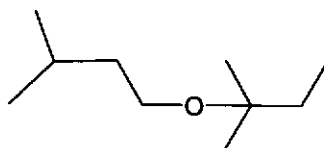
[1]

- (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.



It is known that $\text{S}_{\text{N}}2$ 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]

(f) (i) CH₃OCH₃, methoxymethane is the simplest ether which is used as aerosol propellants. Given that CH₃OCH₃, contains C-O-C bond, draw the 'dot-and-cross' diagram for CH₃OCH₃.

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 CH₃OCH₃ molecule. [3]

(ii) By considering the polarity of each of the bonds it contains, and the shape about the oxygen of the CH₃OCH₃ molecule, deduce the overall polarity of the CH₃OCH₃ 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 ₃ CH ₂ NH ₂	17
ethanol	46	CH ₃ CH ₂ OH	78
propane	44	CH ₃ CH ₂ CH ₃	-42

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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.

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

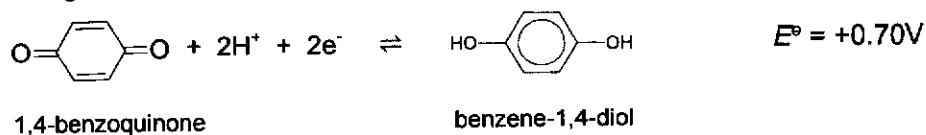


Fig. 2.1

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

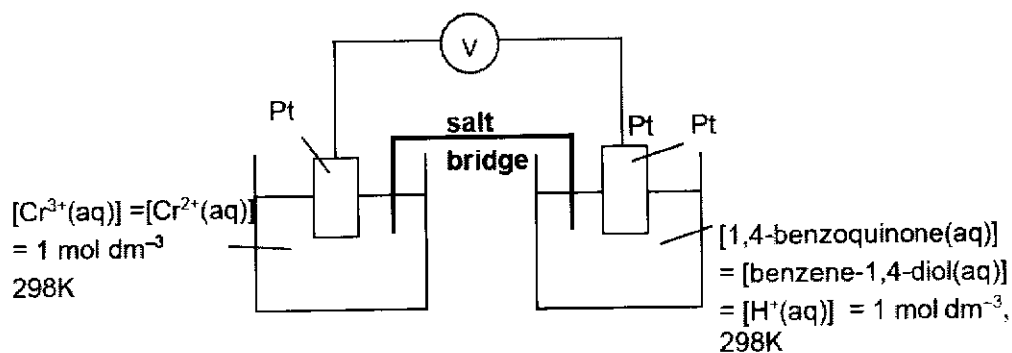


Fig. 2.2

- (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 ΔG^\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 $\text{Cr}^{3+}/\text{Cr}^{2+}$ electrode system.

- (i) Use the Nernst equation and the *Data Booklet* to calculate the electrode potential for the $\text{Cr}^{3+}/\text{Cr}^{2+}$ 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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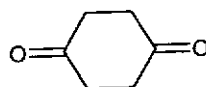
- (e) The aldol reaction is a useful method to make new carbon-carbon bonds in organic chemistry. It involves combining 2 molecules of the same aldehyde or ketone to form a product which contains both a carbonyl functional group (aldehyde or ketone) and alcohol functional group.

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	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{CHO} \\ \\ \text{H} \end{array} + \text{:OH}^- \rightleftharpoons \text{:CH}_2\text{CHO} + \text{H}_2\text{O}$ <p style="text-align: center;">B</p>
2	$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{C}-\text{CH}_3 \end{array} + \text{:CH}_2\text{CHO} \rightleftharpoons \begin{array}{c} \text{O}^- \\ \\ \text{H}-\text{C}-\text{CH}_2\text{CHO} \\ \\ \text{CH}_3 \end{array}$
3	$\begin{array}{c} \text{O}^- \\ \\ \text{H}-\text{C}-\text{CH}_2\text{CHO} \\ \\ \text{CH}_3 \end{array} + \text{H}-\text{OH} \rightleftharpoons \begin{array}{c} \text{OH} \\ \\ \text{H}-\text{C}-\text{CH}_2\text{CHO} \\ \\ \text{CH}_3 \end{array} + \text{:OH}^-$ <p style="text-align: center;">A</p>

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]

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- (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.

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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)

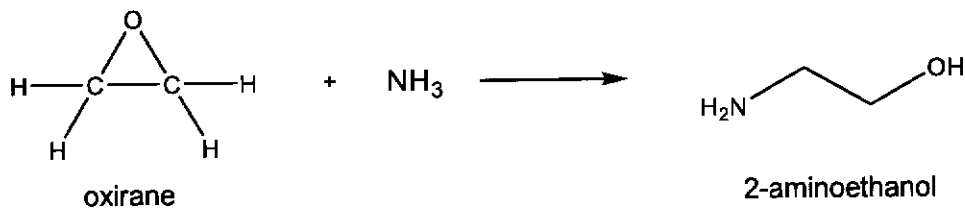
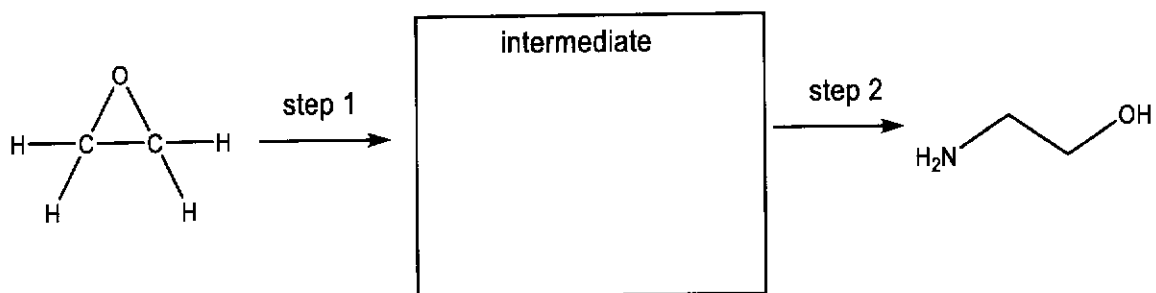


Fig. 3.1

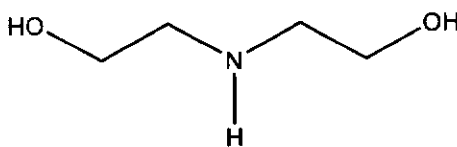
- (i) Complete the mechanism of step 1 on Fig. 3.2 by adding all relevant curly arrows, lone pairs of electrons, charges and partial charges; and draw the structure of the organic intermediate. [2]



NH_3

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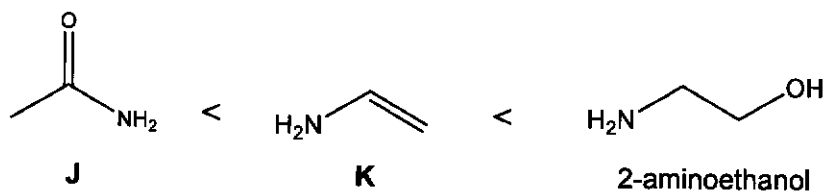
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- (b) By considering the structure of **each** compound **J**, **K** and 2-aminoethanol, explain the order of basicity of these 3 compounds, which are arranged in order of increasing basicity.

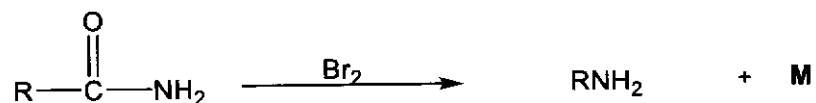
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[3]

- (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.



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 $1.00 \times 10^5 \text{ Pa}$). The addition of excess $\text{NaOH}(\text{aq})$ 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 $\text{NaOH}(\text{aq})$. [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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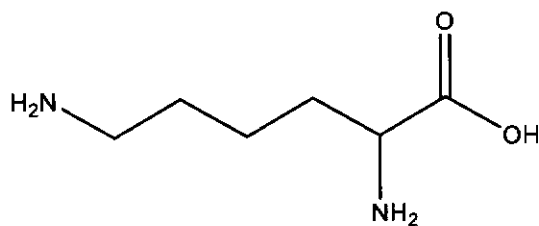
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- (d) Lysine is an essential α -amino acid that is a precursor to many proteins. Due to its importance in biological processes, a lack of lysine can lead to several illnesses including anaemia.



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. [2]
- pH 3.0
 - pH 9.7

Solution N, a 10 cm³ 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 cm³ of 0.200 mol dm⁻³ NaOH(aq) is added to 10 cm³ 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.

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

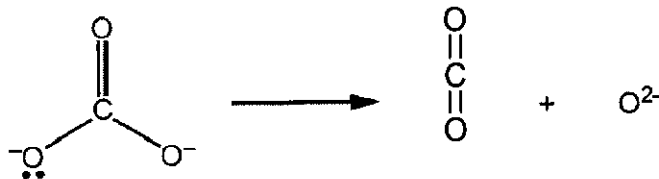


Fig. 4.1

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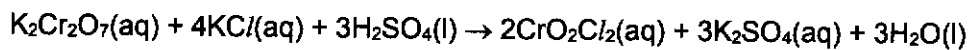
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- (b) Chromyl chloride, CrO_2Cl_2 , can be prepared by heating a mixture of potassium dichromate(VI) and potassium chloride with concentrated sulfuric acid.



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, $\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$	-2061
$\text{KCl}(\text{aq})$	-437
$\text{H}_2\text{SO}_4(\text{l})$	-814
$\text{CrO}_2\text{Cl}_2(\text{aq})$	-580
$\text{K}_2\text{SO}_4(\text{aq})$	-1438
$\text{H}_2\text{O}(\text{l})$	-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 HCl acid is shown below.
$$\text{Ca(s)} + 2\text{H}^+(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \quad \Delta H^\ominus = x \text{ kJ mol}^{-1}$$

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 CH₃CO₂H(aq) is less negative than x. [1]
Suggest an explanation for this.

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

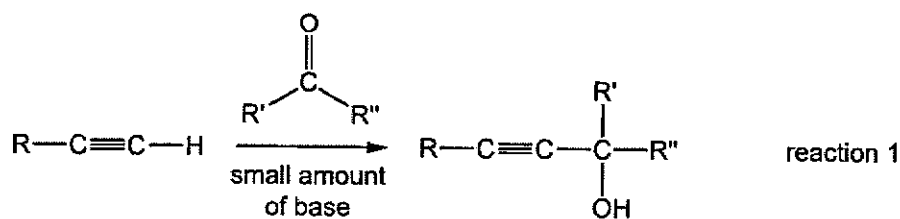


Fig. 4.2

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

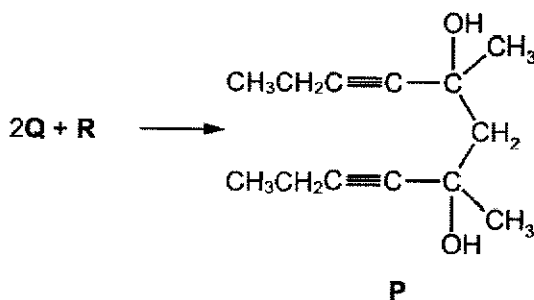


Fig. 4.3

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.

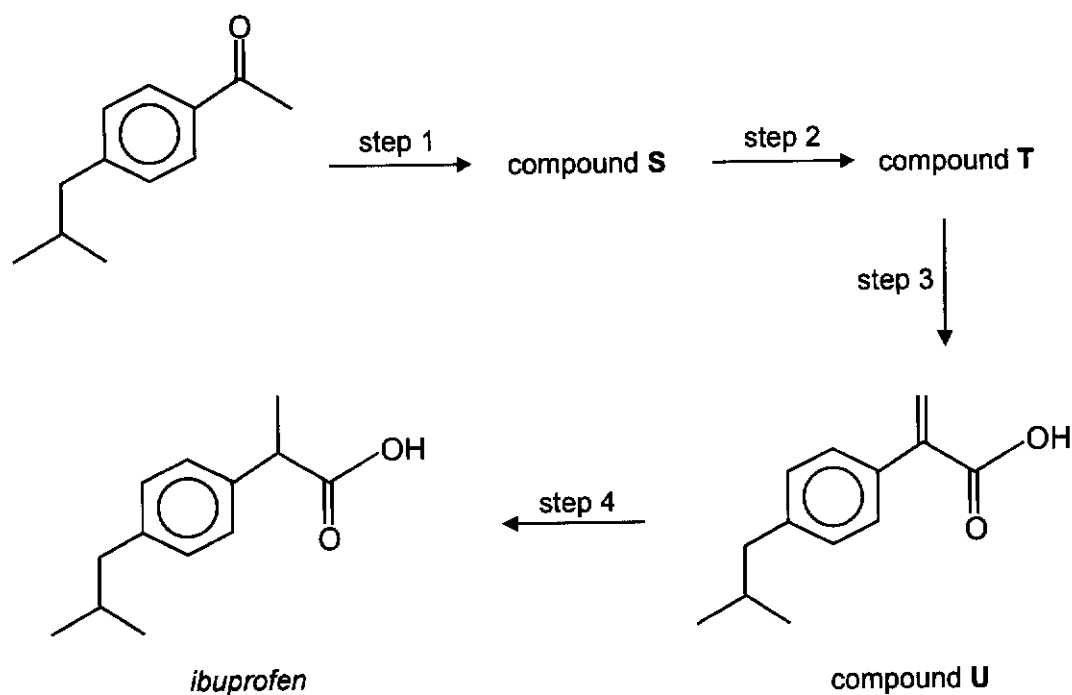


Fig. 4.4

- (i) Identify compounds S and T. [2]
- (ii) State the reagents and conditions for steps 1 to 4. [4]
- (iii) Compound U reacts with $\text{Br}_2(\text{aq})$ to give two isomers as shown in Fig. 4.5.

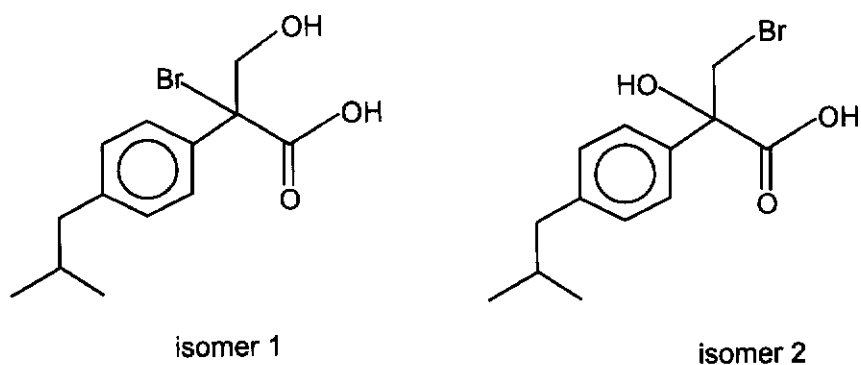


Fig. 4.5

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

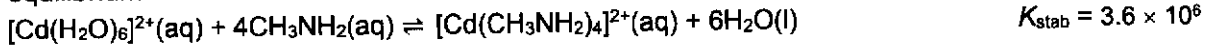
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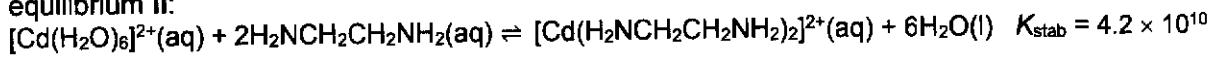
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5 (a) Cadmium ions form complexes with primary amines and with 1,2-diaminoethane.

equilibrium I:



equilibrium II:



- (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 $\text{CH}_3\text{NH}_2(\text{aq})$.

- (ii) A sample of ground water contains $1.00 \times 10^{-4} \text{ mol dm}^{-3}$ of $\text{Cd}^{2+}(\text{aq})$. Calculate the concentration of $\text{CH}_3\text{NH}_2(\text{aq})$ needed to reduce the concentration of $\text{Cd}^{2+}(\text{aq})$ 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 $[\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$ complex ion. [1]

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

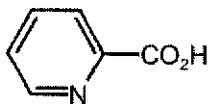


Fig. 5.1

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, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, in a 3 : 1 ratio to form a new neutral complex. [2]

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.

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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 $0.0250 \text{ mol dm}^{-3}$ 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.

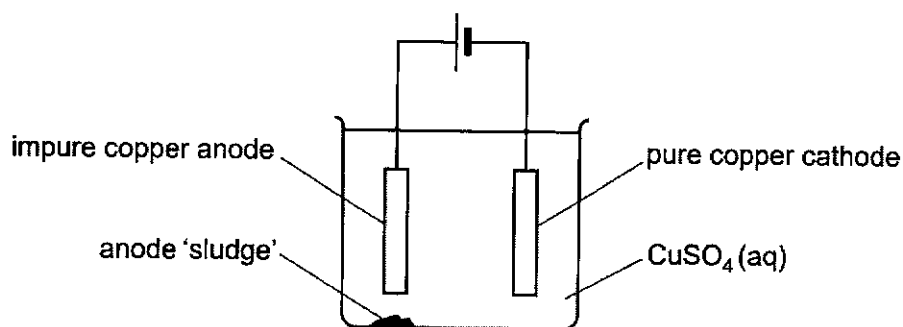


Fig. 5.2

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 relevant 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.

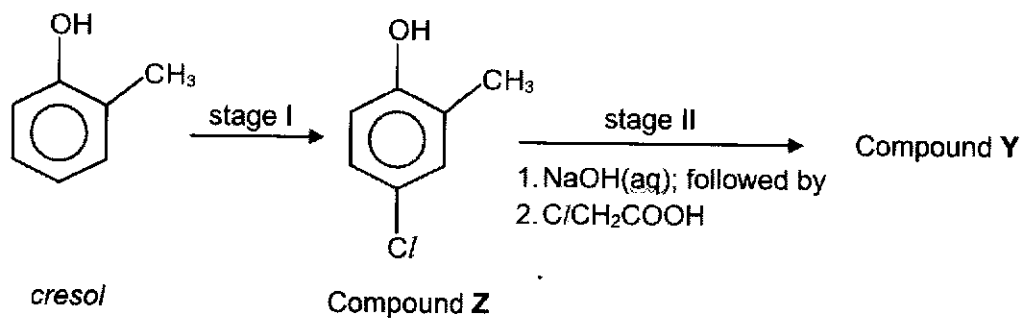


Fig. 5.3

- (i) Give the structure of compound Y. [1]
- (ii) Suggest why NaOH(aq) is added to compound Z in stage II before C/CH₂COOH is added. [1]

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JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2024

CHEMISTRY

9729/03

Higher 2

12 September 2024

Paper 3 Free Response Questions

2 hours

Candidates answer on the Question paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
 Write in dark blue or black pen on both sides of the paper.
 You may use a HB pencil for any diagrams, 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	
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

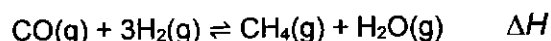
This document consists of **32** printed pages.

Section A

Answer all the questions in this section.

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

For
Examiner's
Use



A mixture of CO and H₂ in a 1:3 molar ratio was introduced 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 an expression for the equilibrium constant, K_p for this reaction.

$$K_p = \frac{p_{\text{H}_2\text{O}} \times p_{\text{CH}_4}}{p_{\text{CO}} \times (p_{\text{H}_2})^3}$$

[1]

Examiner's comments:

This was generally well answered. Common mistakes:

- Excluding partial pressure of water in the expression.
- Using []

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

	3H ₂ (g)	+ CO(g)	⇌	CH ₄ (g)	+H ₂ O (g)
Initial amount/mol	3x	x		–	–
Change/mol	–3(0.4) x	–0.4 x		+ (0.4) x	+ (0.4) x
Equilibrium amount/mol	1.8x	0.6 x		0.4 x	0.4x

$$\text{Total amount at equilibrium} = 1.8x + 0.6x + 0.8x = 3.2x$$

$$p_{\text{H}_2} = \frac{1.8x}{3.2x} \times 12 = \underline{6.75 \text{ atm}}$$

$$p_{\text{CO}} = \frac{0.6x}{3.2x} \times 12 = \underline{2.25 \text{ atm}}$$

$$p_{\text{CH}_4} = p_{\text{H}_2\text{O}} = \frac{0.4x}{3.2x} \times 12 = \underline{1.5 \text{ atm}}$$

$$K_p = \frac{(1.50)^2}{(6.75)^3 (2.25)} = \underline{0.00325 \text{ atm}^{-2}}$$

[3]

Examiner's comments:

This was generally well answered. Most students were able to get some marks. Answers in kPa are accepted but students are advised to leave their answers in units given in question and not to spend time converting the units.

- (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.

Since K_p decreases with increasing temperature, it implies that the position of equilibrium has shifted left to favour endothermic reaction or absorb some heat. Hence, the forward reaction is exothermic and the sign of ΔH of the forward reaction is negative.

[1]

Examiner's comments:

This was generally well answered. Some of the students failed to read the question carefully and just state that the forward reaction is exothermic without giving the sign.

- (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 .

- 1 mol of $N_2(g)$ at 298K is added to 1 mol of $CH_4(g)$ at 298K.
 $\Delta S^\ominus > 0$ as there is an increase in disorder of system since there is more ways of arranging the particles OR distributing the energy among the particles due to mixing.
- 1 mol of $Cl_2(g)$ at 298 K is heated to 373 K.
 $\Delta S^\ominus > 0$ as there is an increase in disorder of system since an increase in temperature increases the (average) kinetic energy of gas molecules causing a broadening of the Boltzmann energy distribution (emphasise in debrief), resulting in more ways of arranging the energy quanta among the particles in the hotter system.

[2]

Examiner's comments:

This was generally well answered. Most students missed out "mixing" to explain for the increase in disorderliness in the first part. Students are reminded to be carefully in their answers. The correct answer should be "Increase in entropy, S" or "change in entropy, ΔS^\ominus , is positive".

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

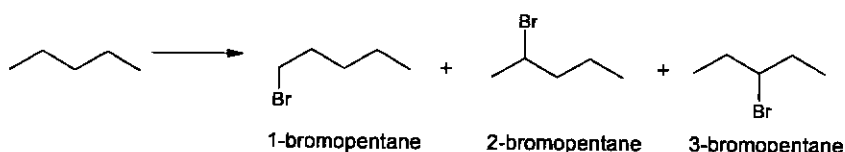


Fig. 1.1

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

Explain your answer.

[2]

1-bromopentane: 2-bromopentane: 3-bromopentane = 6:4:2 = 3:2:1

The substitution reaction is random.

There are 6 chemically equivalent H atoms that can be substituted to form 1-bromopentane, 4 chemically equivalent H atoms that can be substituted to form 2-bromopentane, 2 chemically equivalent H atoms that can be substituted to form 3-bromopentane.

[2]

Examiner's comments:

- This was generally well answered.

- (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).

The intermediate formed in free radical substitution to form 1-bromopentane is a primary radical which is most electron deficient and least stable, as it has least electron-donating alkyl groups bonded to it. Thus it is less favourably formed and is the minor product.

[1]

Examiner's comments:

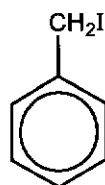
- This was generally not well answered.
- Common wrong responses were "the intermediate is a primary carbocation" or "less electron donating alkyl groups to disperse the charge".
- A significant number missed out "least stable" or "electron-donating".

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



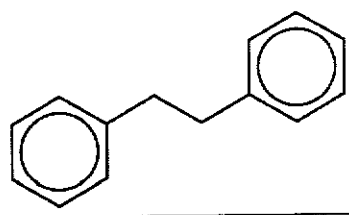
Reaction of a single iodoalkane with sodium metal in dry ether via *Wurtz* reaction will give a good yield of symmetrical alkane product.

Draw the organic product formed when (iodomethyl)benzene reacts with sodium metal in dry ether.



(iodomethyl)benzene

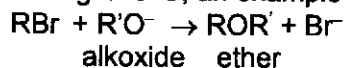
[1]



Examiner's comments:

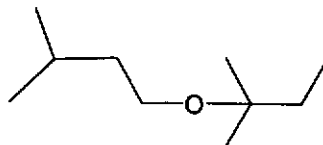
- This was generally well answered.

- (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.

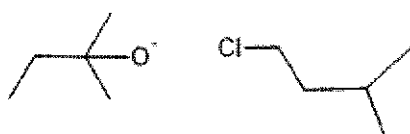


It is known that S_N2 mechanism is usually undergone in Williamson ether synthesis.

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



[1]



Should be primary halogenoalkane as S_N2 mechanism is undergone.

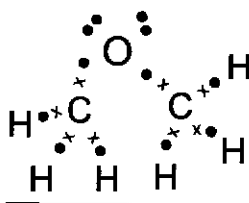
Examiner's comments:

- This part was generally well answered.
- Common wrong response was drawing a tertiary halogenoalkane.
- Students must learn to recognise that since the question is about S_N2, it should be a primary halogenoalkane.

- (f) (i) CH₃OCH₃, methoxymethane is the simplest ether which is used as aerosol propellants. Given that CH₃OCH₃ contains C-O-C bond, draw the 'dot-and-cross' diagram for CH₃OCH₃.

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 CH₃OCH₃ molecule.

[3]



Lone pair -lone pair repulsion > lone pair-bond pair repulsion > bond-pair-bond pair repulsion.

The O in CH₃OCH₃ has 2 bond pairs and 2 lone pairs of electrons. Shape is bent about O and C-O-C bond angle is 104.5 or 105°.

Examiner's comments:

- Only a small proportion of students scored full marks for this part.
- Students should read the question carefully and note that they should use VSEPR theory to explain the shape. A significant number of students left out the explanation, and stated only shape and bond angle.

- (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]

- **C-O bonds are polar**
- Thus **dipole moments do not cancel out** or overall **molecule is polar or has net dipole moment**

Examiner's comments:

- This proved difficult for many students.
- A large number of students did not consider the polar C-O bonds caused by the difference in electronegativity, which results in dipole moments.
- For those who used drawings, they failed to indicate the dipole moment and partial charges on the C-O bonds, resulting in no marks being awarded.

- (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 ₃ CH ₂ NH ₂	17
Ethanol	46	CH ₃ CH ₂ OH	78
Propane	44	CH ₃ CH ₂ CH ₃	-42

[3]

Comparing boiling point propane < ethylamine < ethanol:

All have **simple molecular** or **simple covalent** structures.

Comparing why boiling point of propane < ethylamine:

Larger amount of energy is required to overcome the **stronger hydrogen bonding between C₂H₅NH₂ molecules** than that required for the weaker **instantaneous dipole-induced dipole attractions between propane molecules**

Comparing why boiling point of ethylamine < ethanol:

Since O is more electronegative than N, hence **O-H bond is more polar than N-H bond**, more energy is required to overcome the stronger hydrogen bonds between ethanol molecules than that between ethylamine molecules.

Examiner's comments:

This was generally well answered, with most candidates scoring 2 marks on average, but few candidates were able to gain full credit of 3 marks.

Common mistakes include:

- Did not state "simple molecular structure / simple covalent compounds / simple covalent molecules".
- Wrote that ethylamine or ethanol molecules have pd-pd between molecules rather than hydrogen bonds.
- Discussed polarity of C-O bond vs C-H bond, rather than O-H bond vs N-H bond.
- Did not mention energy required to overcome the IMFs.

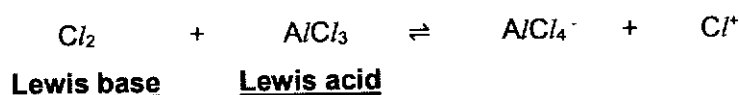
[Total:19]

- 2 (a) (i) Halogens can behave as Lewis acids or Lewis bases. The reaction of benzene and chlorine, Cl_2 requires the use of halogen carrier, $AlCl_3$, 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]

Lewis acid is an electron pair / lone pair acceptor.



Examiner's comments:

Performance for this part of the question was average.

Common mistakes for the definition include:

- did not state electron "pair" or lone "pair".
- wrongly stated "donor" rather than "acceptor".

- (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, like benzene does.

[1]

The lone pair of electrons on oxygen is delocalised into the pi-system of the benzene ring through p-p orbital overlap between O and pi electron cloud of the benzene ring) makes benzene ring more electron-rich, causing phenol to be more readily attacked by electrophiles.

Thus phenol do not require the need for a stronger electrophile created by reaction between Cl_2 with $AlCl_3$.

Examiner's comments:

This part of the question was not well done. Answers were often incomplete.

Please note that "increasing the -ve charge in benzene" is not accepted as benzene is a neutral molecule.

Correct phrases would be "increase the electron density in the benzene ring" or "making benzene more electron rich".

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

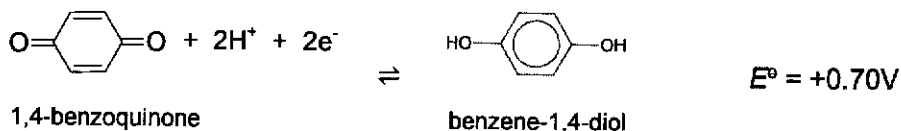


Fig. 2.1

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

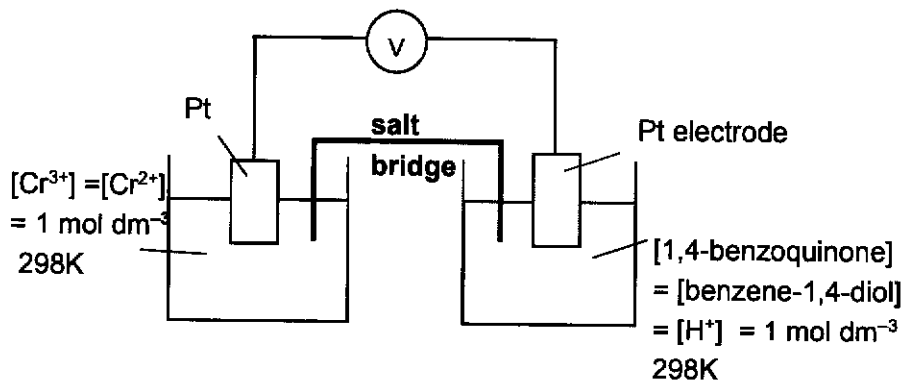
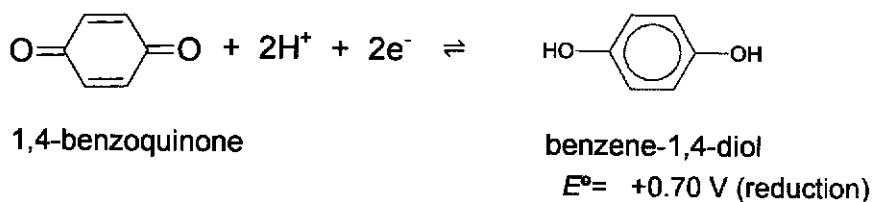


Fig. 2.2

- (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]



$$E^\ominus_{\text{cell}} = +0.70 - (-0.41) = \underline{+1.11 \text{ V}} > 0, \text{ energetically feasible.}$$

Negative electrode is the anode undergoing oxidation (producing electrons), is the $\text{Cr}^{3+}/\text{Cr}^{2+}$.

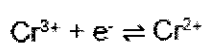
Examiner's comments:

Generally, well done.

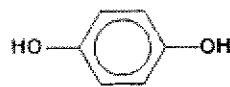
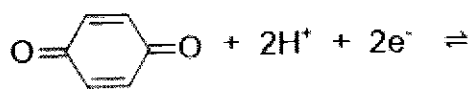
Most students were able to calculate E_{cell} correctly. However, many omitted the +ve sign and the units.

Quite a handful of students did not answer the second part of the question, which is to state which is the negative electrode

- (ii) Construct the overall equation for the reaction that has taken place in the cell. [1]



$$E^\ominus = -0.41 \text{ V (oxidation)}$$

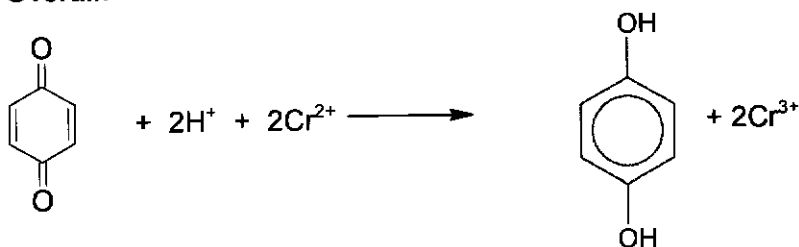


1,4-benzoquinone

benzene-1,4-diol

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

Overall:



Examiner's comments:

Performance for this part of the question was average.

Common mistakes include:

- species on the wrong side of the question. Eg. Cr^{3+} to Cr^{2+} .
- equations not balanced.
- using a reversible arrow instead of an irreversible arrow.

- (iii) Calculate ΔG° for the reaction you wrote in (b)(ii).

[1]

$$\Delta G^\circ = -nFE^\circ$$

$$n = 2$$

$$\Delta G^\circ = -2 \times 96500 \times (+1.11) = -214 \text{ kJ mol}^{-1}$$

Examiner's comments:

Simple question but many mistakes

Most common mistake in units in ΔG° . Wrong units, zero mark for this qn

Units for $\Delta G^\circ = -nFE^\circ$ is J mol^{-1} pls take note!

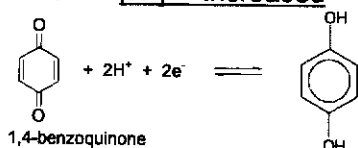
Another common mistake: missing out -ve sign. Pls memorise eqn!

When E° is positive, ΔG° is negative \Rightarrow Both mean reaction is energetically feasible.

- (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]

When $[\text{H}^+]$ increased this causes the position of equilibrium



1,4-benzoquinone

benzene-1,4-diol

to shift right, making $E(1,4\text{-benzoquinone/benzene-1,4-diol})$ or Ecathode more positive.

$\therefore E_{\text{cell}}$ becomes more positive.

Examiner's comments:

Major misconception

At least 20% mistakenly wrong $[\text{H}^+]$ drop when pH drop – wrong!

$$\text{pH} = -\log[\text{H}^+]$$

$[\text{H}^+]$ and pH are inversely related!

Another common mistake: Forgetting to write out the exact eqm that you are referring to. Pls write out the exact eqm in the A level exam (or you can make reference to eqm in Fig. 2.1 eg. in this question)

- (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.

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

n = number of electrons transferred

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

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

[1]

$$E = -0.41 + \frac{0.059}{1} \log \frac{[1]}{[0.15]} \text{ use of } n = 1$$

$$E = -0.41 + 0.05 = -0.36\text{V}$$

Application qn, badly done. 10% got this correct.

Read carefully n_e transferred = 1 in the $\text{Cr}^{3+} + e^- \rightleftharpoons \text{Cr}^{2+}$

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

[1]

$$E_{\text{cell}} = +0.70 - (-0.36) = \underline{+1.06 \text{ V} > 0}$$

Do not forget to write + sign for E_{cell} .

- (e) The aldol reaction is a useful method to make new carbon-carbon bonds in organic chemistry. It involves combining two 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 $\text{NaOH}(\text{aq})$ at room temperature. The three stages of the reaction are described in Table 2.1.

Stage	Equation
1	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{CHO} \\ \\ \text{H} \end{array} + \text{:OH}^- \rightleftharpoons \text{:CH}_2\text{CHO} + \text{H}_2\text{O}$ <p style="text-align: center;">B</p>
2	$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{C}-\text{CH}_3 \end{array} + \text{:CH}_2\text{CHO} \rightleftharpoons \begin{array}{c} \text{O}^- \\ \\ \text{H}-\text{C}-\text{CH}_2\text{CHO} \\ \\ \text{CH}_3 \end{array}$
3	$\begin{array}{c} \text{O}^- \\ \\ \text{H}-\text{C}-\text{CH}_2\text{CHO} \\ \\ \text{CH}_3 \end{array} + \text{H}-\text{OH} \rightleftharpoons \begin{array}{c} \text{OH} \\ \\ \text{H}-\text{C}-\text{CH}_2\text{CHO} \\ \\ \text{CH}_3 \end{array} + \text{:OH}^-$ <p style="text-align: center;">A</p>

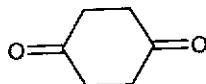
Table 2.1

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

[1]

Acid base

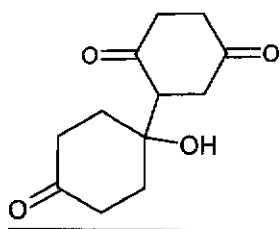
- (ii) 1,4-cyclohexanedione can be formed from 1,4-benzoquinone.



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]



Application qn, badly done. Pls revise aldol condensation mechanism in the carbonyl tutorial challenging question make sure you know it. Alpha C is C bonded to C=O directly and alpha H is acidic, lost H^+ to form nucleophile lone pair on alpha C, this nucleophile attack delta positive C.

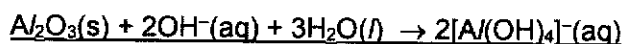
- (f) Aluminium objects have a thin insoluble oxide, Al_2O_3 , layer on their surfaces. This oxide can be removed by adding $NaOH(aq)$ to the aluminium object.

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

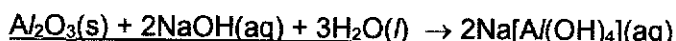
The hydration energy released upon forming ion-dipole interactions between the ions and water molecules is insufficient to compensate the energy required to overcome the strong ionic bonds between Al^{3+} and O^{2-} ions.

Hence, Al_2O_3 is insoluble in water.

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



or



- (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.

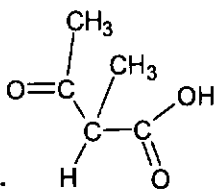
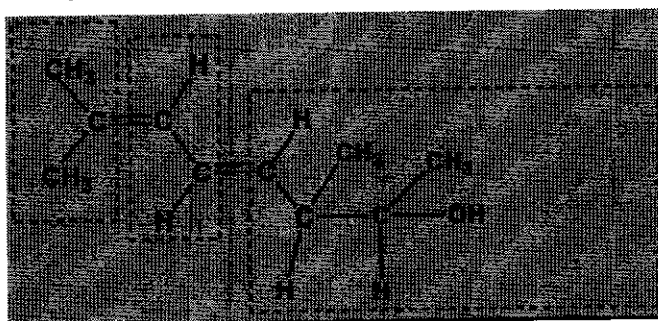
Suggest the structures of E, F and G. For each reaction, state the *type of reaction* and explain what the information tells you about the functional groups present in each compound.

[6]

Information	Type of reaction	Deduction (of functional group)
E rotates plane-polarised light.		<u>E contain a chiral carbon</u>

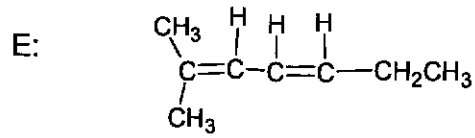
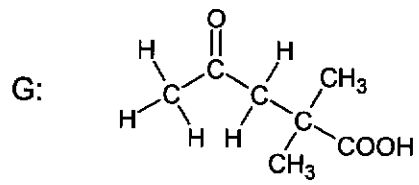
Ratio of C:H in E is not 1:1	-	No benzene in E
E reacts with aqueous Br ₂ .	<u>Electrophilic addition</u>	<u>Alkene</u> in E
E reacts with sodium, Na, to produce H ₂ (g).	E undergoes redox reject acid-metal	E contains <u>alcohol</u> Reject phenol/ carboxylic acid
E reacts with an excess hot concentrated KMnO ₄ to produce three different organic molecules, F, C ₃ H ₆ O, H, (CO ₂ H) ₂ , and G, C ₈ H ₁₀ O	<u>Oxidative cleavage/oxidation</u>	E contains <u>alkene or C=C</u>
G reacts with aqueous Na ₂ CO ₃ (aq) giving off effervescence of a colourless gas.	<u>Acid base reaction</u> Reject acid carbonate	G has <u>carboxylic acid</u> (✓)
F and G both react with 2,4-dinitrophenylhydrazine	<u>Condensation</u>	<u>F and G are ketone</u>
F and G react with aqueous alkaline iodine forming a yellow precipitate.	<u>Oxidation/ positive iodoform test</u>	G contains <u>-COCH₃</u>
E react with aqueous alkaline iodine forming a yellow precipitate.	<u>Oxidation/ positive iodoform test</u>	E contains <u>CH₃COCH₃</u>

Compound E:



F: CH₃COCH₃ G: _____

Alternative answers:



[Total:21]

- 3 2-aminoethanol molecules are a component in the formation of cellular membranes and are thus a molecular building block for life. Basic in nature, 2-aminoethanol is often used for alkalization of water in steam cycles of power plants.

(a) A synthesis of 2-aminoethanol is shown in Fig 3.1.

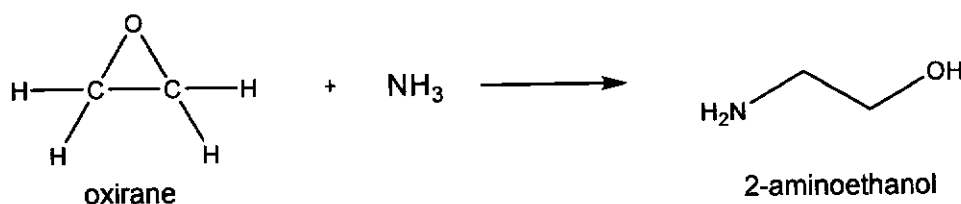


Fig. 3.1

- (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]

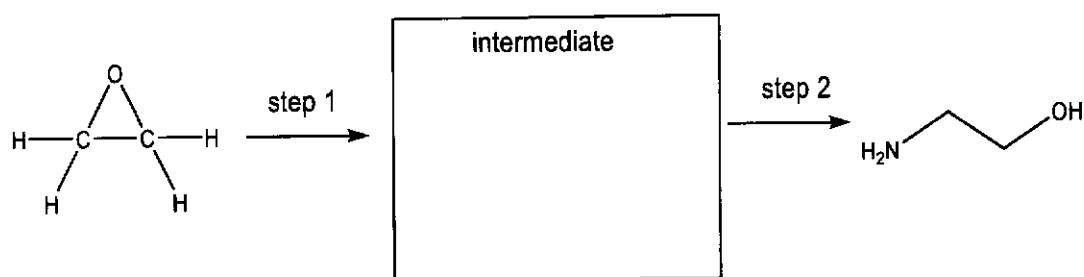
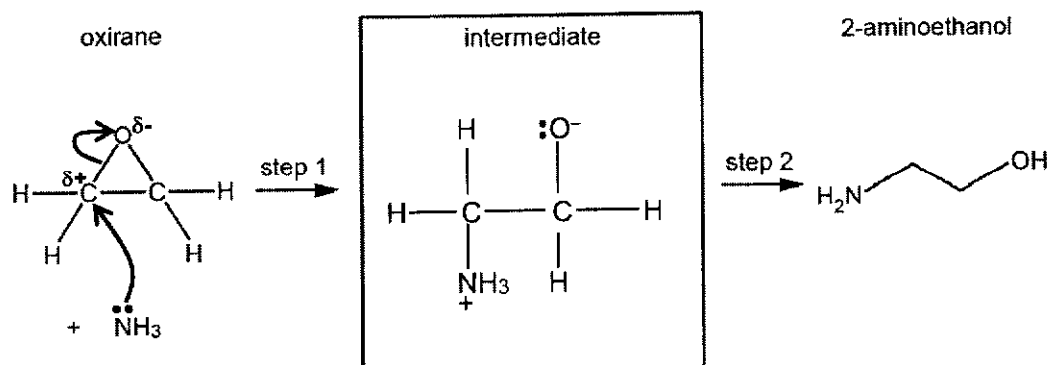
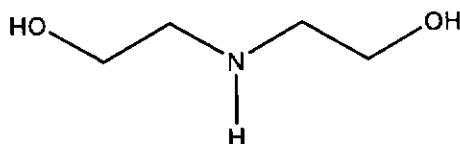


Fig. 3.2



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

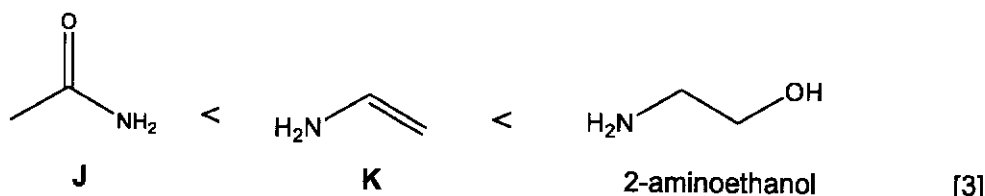


Suggest how the formation of the by-product can be minimised.

Use an excess of ammonia or limiting amount of oxirane

[1]

- (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.



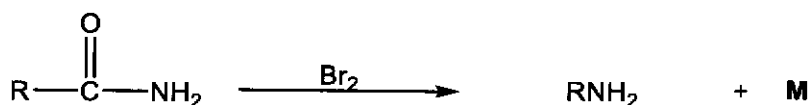
2-aminoethanol contains an electron-donating group, making the lone pair on N more available to accept a proton or donate to H⁺ acid, hence it is the most basic among the 3 compounds.

For amide J, the p-p orbital overlap results in delocalisation of lone pair of electrons on N atom into C=O and since C=O is a strong electron-withdrawing group, the lone pair of electrons on N atom is NOT available for protonation. Hence, J is neutral.

For K, the p-p orbital overlap results in delocalisation of lone pair of electrons on N atom into adjacent C=C and hence, making the lone pair of electrons on N atom less available to accept a proton.

- (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, Br₂, under suitable conditions, a gaseous primary amine and an unknown gas, M, are formed, as exemplified by the following equation.



When a primary amide, L, was reacted with Br₂ 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 cm³ (measured at 298 K and 1.00 × 10⁵ Pa). The addition of excess NaOH(aq) to the gaseous mixture caused its volume to decrease by 163 cm³.

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

Assuming that the gaseous mixture behaves like ideal gas (*i.e.* $pV = nRT$),

$$pV = \frac{nRT}{M_r}$$

$$\begin{aligned}
 \Rightarrow M_r \text{ of gaseous mixture} &= \frac{(0.586)(8.31)(298)}{(1.00 \times 10^5)(326 \times 10^{-6})} \\
 &= 44.5 \text{ (no unit)}
 \end{aligned}$$

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

CO₂

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

$$\text{Volume of CO}_2 = 163 \text{ cm}^3$$

$$\text{Volume of other gas} = 326 - 163 = 163 \text{ cm}^3$$

For gases measured at the same p and T , **volume ratio = mole ratio.**

$$\begin{array}{ccc} \text{volume of CO}_2 & : & \text{volume of other gas} \\ 163 & : & 163 \\ 1 & : & 1 \end{array}$$

$$\text{Average } M_r \text{ of mixture} = \sum (\text{relative abundance}) \times (M_r \text{ of individual gas})$$

$$44.5 = \left(\frac{1}{2} \times 44.0\right) + \frac{1}{2} \times M_r \text{ of other gas}$$

$$M_r \text{ of other gas} = \underline{45.0}$$

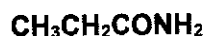
The other gas is needs to a primary amine, RNH_2

$$\text{Hence } 45 - (14+2) = 29;$$

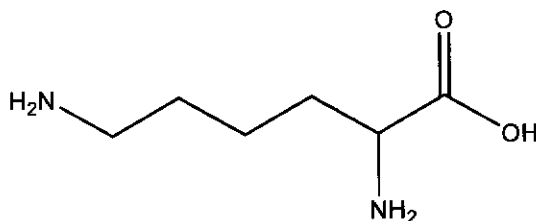
$$\text{Hence } R = \text{C}_2\text{H}_5$$

$$\text{gas} = \text{CH}_3\text{CH}_2\text{NH}_2$$

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



- (d) Lysine is an essential α -amino acid that is a precursor to many proteins. Due to its importance in several 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]

In the solid state, lysine exists in the **zwitterionic form**.

There exists **stronger electrostatic forces of attraction / ionic bonds between the positive $-\text{NH}_3^+$ and the negative $-\text{COO}^-$** , compared to ethanolamine, where there are **weaker hydrogen bonds between the 2-aminoethanol molecules**.

A larger amount of energy is required to overcome these forces of attraction between the zwitterions, hence the melting point of lysine is much higher than that of ethanolamine.

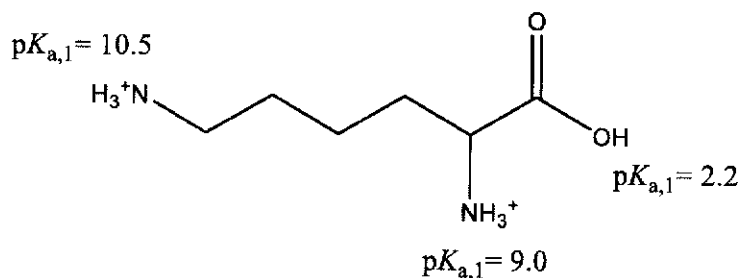
Examiner's Comments:

Many only scored one mark for this question as they did not identify the amino acid as zwitterions and also did not state that there is ionic bonds between the oppositely charged ions. Students should always state the attraction between the particles (ions, molecules etc) clearly. Many wrongly stated that the amino acids have hydrogen bonds between the molecules. Some did not even state the intermolecular forces of attractions for 2-aminoethanol when the questions clearly demand the explanation for physical states of both the compounds

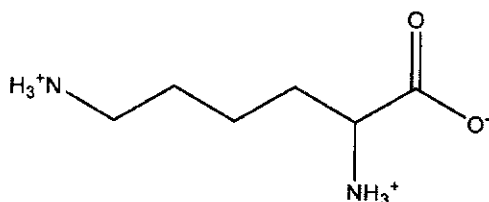
(ii) Make use of the above pK_a values to suggest the major species present in solutions of lysine at the following pH values.

- pH 3.0
- pH 9.7

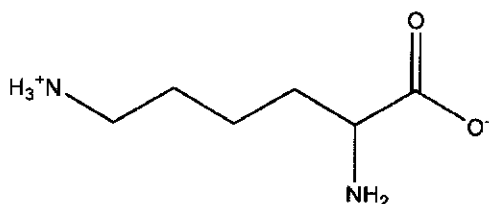
[2]



At pH 3.0



At pH 9.7

Examiner's Comments:

Very poorly done. This could be due to the wrong assigning of pK_a values to the groups in lysine. Students must revise this topic on how to assign the pK_a values for the protonated form of the amino acids. The details on how to do this is given below.

Determining the overall charge on an Amino Acid

Step 1: Draw the structure of amino acid at **low pH** (protonated form)

- 1) all $-COOH$ remains as $-COOH$
- 2) all $-NH_2$ are protonated to $-NH_3^+$

Step 2: **Assign pK_a values** to all acidic groups for **protonated form** of amino acid.

- 1) as $-COOH$ is **more acidic** than $-NH_3^+$, thus $pK_a(-COOH) < pK_a(-NH_3^+)$
- 2) α - $-COOH$ **more acidic** than side chain $-COOH$ group
- 3) α - $-NH_2$ **less basic** than side chain $-NH_2$ group

Step 3: Compare pH of the solution to the pK_a value of each acidic group to determine if the dominant form is the protonated or deprotonated form.

- 1) If $pH < pK_a$, protonated form remains (H^+ is added)
- 2) If $pH > pK_a$, deprotonation takes place (H^+ is removed)

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? [2]

Ignore the effect of pK_{a2} and pK_{a3}

Use $pK_{a,1}$ to find pH

$$[H^+] = \sqrt{c \times K_{a,1}}$$

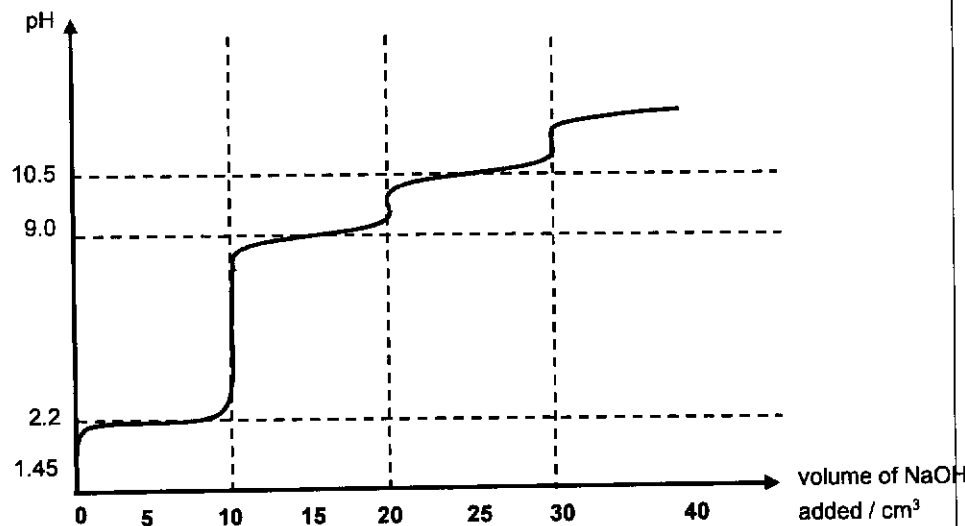
$$= \sqrt{0.200 \times 10^{-2.2}} = \underline{0.0355\text{ mol dm}^{-3}}$$

$$pH = -\lg(0.0355) = \underline{1.45}$$

Examiner's Comments:

Students clearly did not take into account of the statement on ignoring pK_2 and pK_3 and calculated the pH when $3H^+$ is liberated which is wrong.

(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]



Examiner's Comments:

Generally was poorly done. Since there are 3 pK_a values, there should be 3 equivalence points (3 vertical segments in the graph) and 3 buffers shown by the max buffering capacity values at 2.2, 9.0 and 10.5 at 5 cm^3 , 15 cm^3 and 25 cm^3 respectively. Many did not state the volumes and only state the pH values of the buffers and so lost 1 mk for that. Must also calculate the volume of NaOH needed at the respective equivalence pts (10 cm^3 , 20 cm^3 and 30 cm^3) and shown clearly on the graph.

[Total: 20]

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

For
Examiner's
Use

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

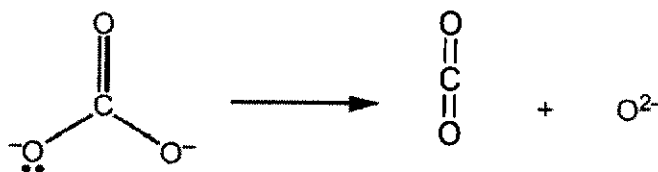


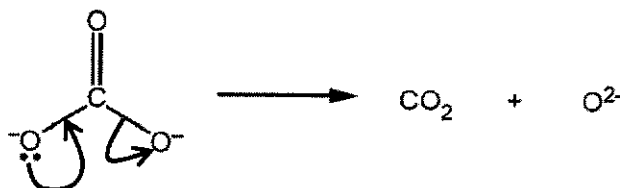
Fig. 4.1

[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]

(i)



- (ii) Ni^{2+} has a **higher charge density** than Ca^{2+} since the **radius/size of Ni^{2+} is smaller**.

Hence Ni^{2+} has a **greater ability to polarise the large CO_3^{2-} anion** (or **greater polarising power**) than Ca^{2+} and the **C—O bond in CO_3^{2-} is weakened to a larger extent** for NiCO_3 .

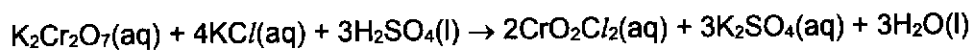
Since it is **easier to break the C—O bond** in NiCO_3 , NiCO_3 is thermally less stable and it decomposes more readily than CaCO_3 .

- (iii) **Other Group 1 cations have low/lower charge density due to their large/larger radius/size** and hence they cannot polarise the large CO_3^{2-} anion (or they have low polarising power).
∴ other Group 1 carbonates do not decompose when heated.

Examiner's Comments:

- (i) Many didn't get the credit due to the first curly arrow. The first curly arrow should point from the lone pair (given) to the bond. Many pointed the arrow to the carbon instead.
- (ii) This part was generally quite well done. Some discussed charge density and polarising power of Ni vs Ca instead of Ni^{2+} vs Ca^{2+} . Some compared ionic bond strength.
- (iii) Many did not discuss the radii of M^+ as compared to Li^+ .

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

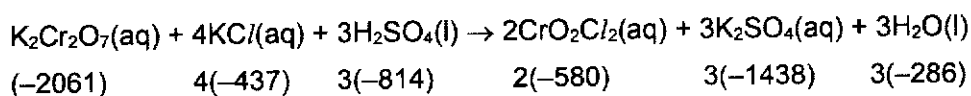


Use the data in Table 4.1 to calculate the enthalpy change of the reaction, ΔH_r .

Table 4.1

compound	enthalpy change of formation, $\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$	-2061
$\text{KCl}(\text{aq})$	-437
$\text{H}_2\text{SO}_4(\text{l})$	-814
$\text{CrO}_2\text{Cl}_2(\text{aq})$	-580
$\text{K}_2\text{SO}_4(\text{aq})$	-1438
$\text{H}_2\text{O}(\text{l})$	-286

[2]



$$\begin{aligned} \Delta H_r^\ominus &= \sum m\Delta H_f^\ominus (\text{products}) - \sum n\Delta H_f^\ominus (\text{reactants}) \\ &= 2(-580) + 3(-1438) + 3(-286) - (-2061) - 4(-437) - 3(-814) \\ &= \underline{-81.0} \text{ (or } \underline{81}) \text{ kJ mol}^{-1} \end{aligned}$$

Examiner's Comments:

This was quite well done. Those who solved by energy cycle were less successful in getting the correct answer. Some used the wrong formula and ended with a +ve sign in their answer.

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

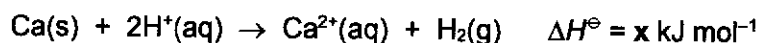
It is the **heat energy absorbed when 1 mole of calcium gaseous atoms, $\text{Ca}(\text{g})$, is formed from its element at standard state, $\text{Ca}(\text{s})$, at 298 K and 1 bar.** [1]

Examiner's Comments:

This was not well done.

Many did not state "1 mole", the standard conditions "298 K & 1 bar" or make reference to Ca. It is inappropriate to state "solid Ca atoms" even though the chemical symbol ($\text{Ca}(\text{s})$) may seem to imply this as Ca element in its standard state is a metal with strong electrostatic attractions between the metal cations and the delocalised valence electrons.

- (ii) The ionic equation for the reaction of calcium with hydrochloric acid is shown below.



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

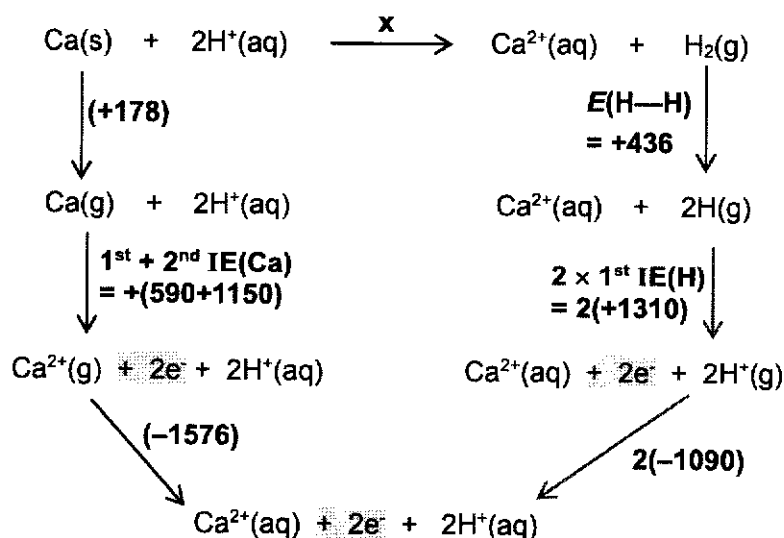
standard enthalpy change of atomisation of Ca(s)	+178 kJ mol ⁻¹
standard enthalpy change of hydration of Ca ²⁺ (g)	-1576 kJ mol ⁻¹
standard enthalpy change of hydration of H ⁺ (g)	-1090 kJ mol ⁻¹

[3]

- (iii) The standard enthalpy change for the reaction between Ca(s) and CH₃COOH(aq) is less negative than x .

Suggest an explanation for this.

(i)



By Hess' Law,

$$\begin{aligned}
 x &= +(+178) + (590+1150) + (-1576) - 2(-1090) - 2(+1310) - (+436) \\
 &= \underline{-534}
 \end{aligned}$$

Examiner's Comments:

This was generally not well done.

Some students did not close their energy cycles and hence were not successful in getting the correct final answer.

BOD was given to those who left out '2e⁻' in their IE eqn.

- (ii) HCl is a strong acid which ionises/dissociates completely in water while CH_3COOH is a weak acid which ionises/dissociates partially in water. Some heat energy is absorbed to fully/completely ionise/dissociate the CH_3COOH .

Hence ΔH^\ominus is less exothermic than x.

Examiner's Comments:

This was generally not well done.

Common mistakes are "heat was lost to the surroundings" and "the bond energy was an average value".

- (d) Alkynes, compounds containing a $\text{C}\equiv\text{C}$, can react with carbonyl compounds under basic conditions as shown in reaction 1 in Fig.4.2.

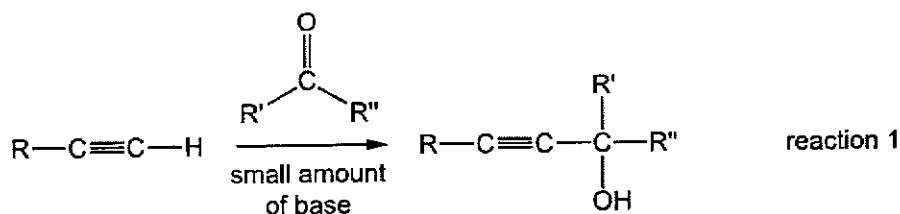


Fig. 4.2

An alkyne, **Q**, and a carbonyl compound, **R**, react together to form compound **P** as shown in Fig. 4.1.

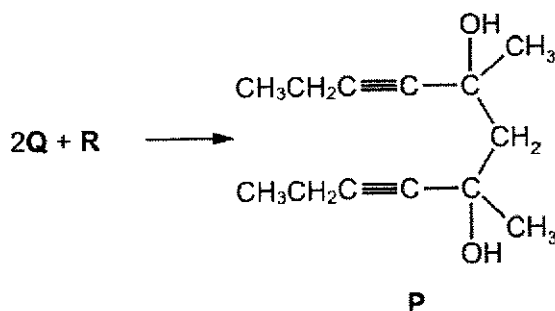


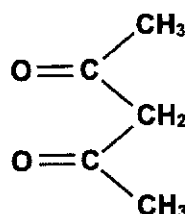
Fig. 4.3

Use reaction 1 to suggest the structures of **Q** and **R**.

[1]

Q: $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$

R:



Examiner's Comments:

A significant number of students did not attempt this question.

Some students have difficulty deducing the structure of **R**.

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

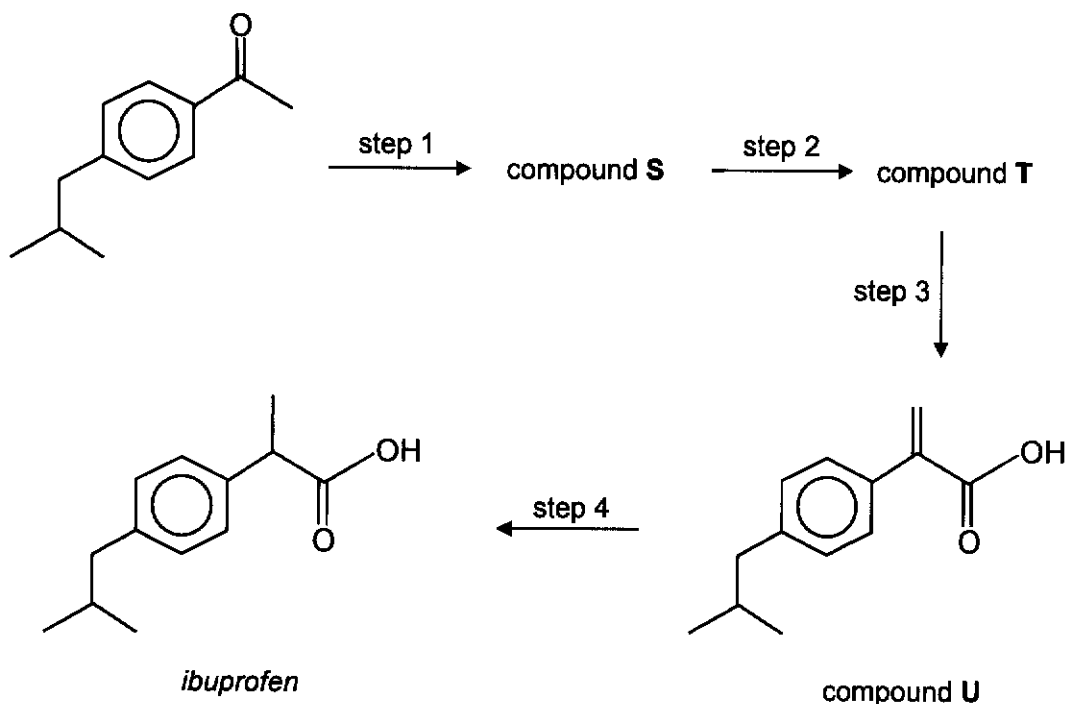
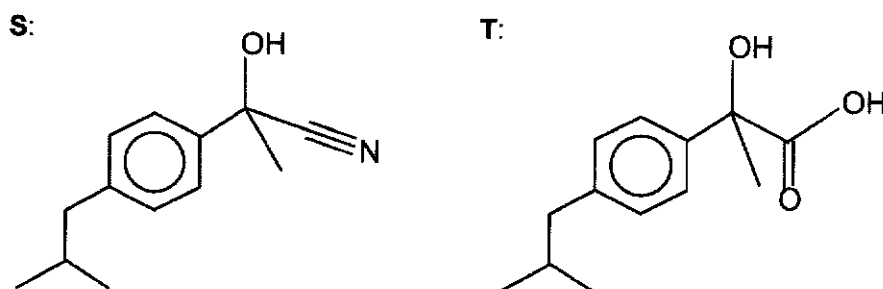


Fig. 4.4

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



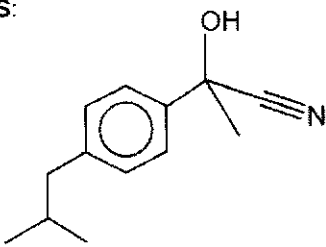
- (ii) State the reagents and conditions for steps 1 to 4. [4]

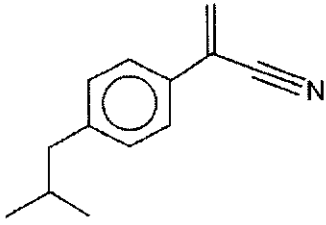
step 1: HCN, trace amount of NaCN (or NaOH), cold

step 2: H₂SO₄(aq) (or HCl(aq)), heat

step 3: excess concentrated H₂SO₄, heat
OR Al₂O₃, heat (or high temperature)

step 4: H₂, Ni, heat OR H₂, Pt, r.t (emphasise Pt no heat).

(i) OR S:  [1]

T:  [1]

(ii) step 1: HCN, trace amount of NaCN (or NaOH), cold [1] reject 'heat'
 step 2: excess concentrated H₂SO₄, heat [1] reject 'H₂SO₄(aq)'
 OR Al₂O₃, heat (or high temperature)
 step 3: H₂SO₄(aq) (or HCl(aq)), heat [1] must state "aq"
 step 4: H₂, Ni, heat OR H₂, Pt, r.t [1]

Examiner's Comments:

A significant number of students did not complete this part question.

- (i) Many students could get the structures of S and T. Some left out the methyl group.
- (ii) Many students could get step 1 and 4 correct. Step 2 and 3 proved to be challenging for students esp the elimination step.

(iii) Compound U reacts with $\text{Br}_2(\text{aq})$ to give two isomers as shown in Fig 4.5.

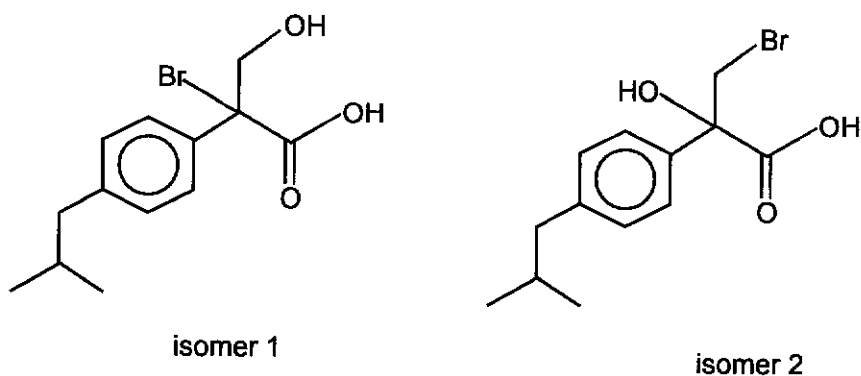
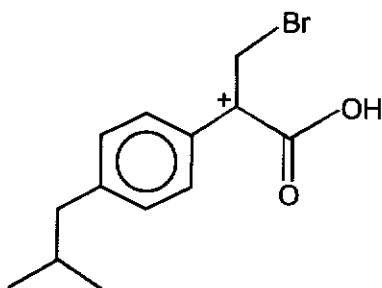


Fig. 4.5

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

(iii) Isomer 2.



The tertiary carbocation to form isomer 2 is more stable due to resonance effect as the positive charge on benzylic C can be delocalised into the benzene ring or the adjacent C=O through p-p orbital overlap, thereby dispersing the charge.

Examiner's Comments:

A significant number of students did not complete this part question.

This part proved to be challenging for students as nearly all students could not explain their answer.

The common mistake was to state that the reaction intermediate has "three/more electron-donating alkyl groups bonded to C^+ ".

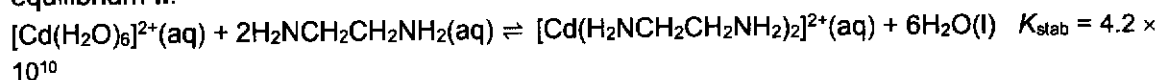
[Total: 20]

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

equilibrium I:



equilibrium II:



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

(i)
$$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}}{[\text{Cd}(\text{H}_2\text{O})_6]^{2+} [\text{CH}_3\text{NH}_2]^4}; \text{ units : } \underline{\text{mol}^{-4} \text{ dm}^{12}}$$

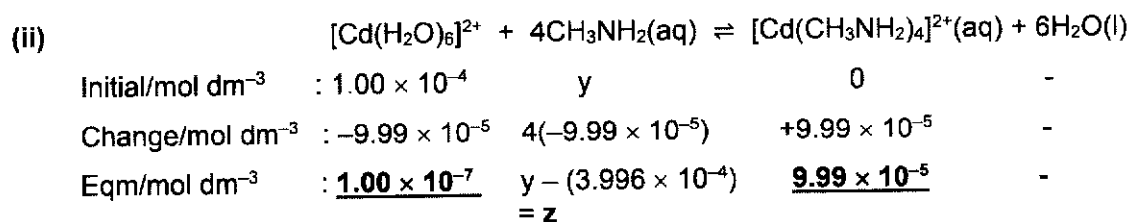
Examiner's comments:

This was not well answered. Common mistakes:

- Including water in the expression when it is an aqueous system
- Not including [] to represent concentration
- Units are often incorrect.

Cadmium ions are toxic and need to be removed from some water supplies. This is often done by adding a complexing agent such as $\text{CH}_3\text{NH}_2(\text{aq})$.

(ii) A sample of ground water contains $1.00 \times 10^{-4} \text{ mol dm}^{-3}$ of $\text{Cd}^{2+}(\text{aq})$. Calculate the concentration of $\text{CH}_3\text{NH}_2(\text{aq})$ needed to reduce the concentration of $\text{Cd}^{2+}(\text{aq})$ in the sample of ground water to $\frac{1}{1000}$ of its original concentration. [2]



$$K_{\text{stab}} = \frac{9.99 \times 10^{-5}}{(1 \times 10^{-7})(z)^4} = 3.6 \times 10^6$$

$$z^4 = 2.775 \times 10^{-4} \therefore \underline{z = 0.129}$$

$$y - (3.996 \times 10^{-4}) = 0.129$$

$$\Rightarrow \underline{y = 0.129} \quad \Rightarrow [\text{CH}_3\text{NH}_2] \text{ needed is } \underline{0.129 \text{ mol dm}^{-3}}$$

Examiner's comments:

This was not well answered. Most students are only able to calculate the concentration of $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ and unable to proceed further or they calculated the concentration of $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$ and presented that as concentration of CH_3NH_2 .

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

[1]

- (iii) Coordination no. is 4.

Geometry is **tetrahedral or square planar**.

Examiner's comments:

This was not well answered. Many students gave the coordination number as 2 and shape as linear by looking at the number of ligands bonded without considering that the ligand is bidentate.

- (b) The structure picolinic acid is shown.

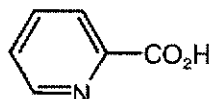


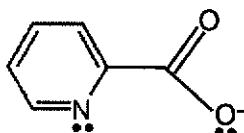
Fig. 5.1

When picolinic acid is placed in basic solution, a bidentate ligand, **V** in Fig. 5.1, is formed.

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

[1]

- (i)



Examiner's Comments:

A significant number of students did not complete this part question. The lone pair on N is often missing.

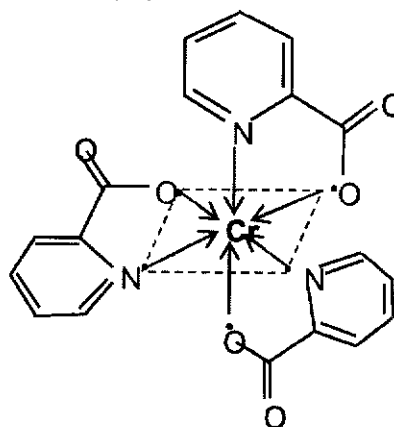
- (ii) **V** reacts with aqueous chromium(III) ions, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, in a 3 : 1 ratio to form a new neutral complex.

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]

- (ii) **Ligand exchange** reaction.



Examiner's Comments:

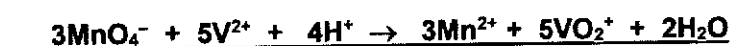
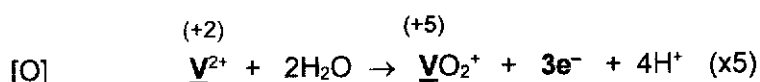
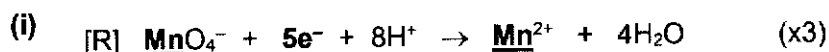
A significant number of students did not complete this part question.

- (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 $0.0250 \text{ mol dm}^{-3}$ 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]



Examiner's Comments:

This was not well answered. Many of the equation is not balanced correctly.

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

(ii) $n(\text{MnO}_4^-) = \frac{21.10}{1000} \times 0.0250 = \underline{5.275 \times 10^{-4} \text{ mol}}$

$n(\text{V}^{2+}) = \frac{5}{3} \times 5.275 \times 10^{-4} = \underline{8.792 \times 10^{-4} \text{ mol}}$

$= n(\text{VO}_2^+) \text{ present} = n(\text{NH}_4\text{VO}_3) \text{ in } 0.155 \text{ g impure sample.}$

Mass of NH_4VO_3 present = $8.792 \times 10^{-4} \times \underline{116.9} = \underline{0.1028 \text{ g}}$

$\therefore \% \text{ by mass of } \text{NH}_4\text{VO}_3 = \frac{0.1028}{0.155} \times 100 = \underline{66.3\%}$

Examiner's Comments:

This was not well answered. Many left this part blank. Some were able to gain some credit based on the equation given.

- (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.

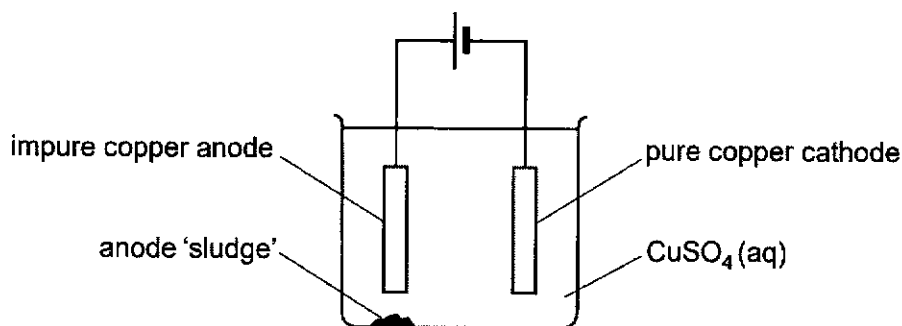
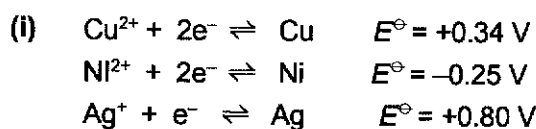


Fig. 5.2

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 relevant E^\ominus values from the *Data Booklet*, what happens to the nickel and silver impurities during this purification procedure. [2]



- Ni will be oxidised at the anode to Ni^{2+} as $E^\ominus(\text{Ni}^{2+}/\text{Ni})$ is more negative than $E^\ominus(\text{Cu}^{2+}/\text{Cu})$.
- Ni^{2+} will not be reduced to Ni at the cathode as $E^\ominus(\text{Ni}^{2+}/\text{Ni})$ is less positive (or more negative) than $E^\ominus(\text{Cu}^{2+}/\text{Cu})$. $\therefore \text{Ni}^{2+}$ will be remained in solution.
- Ag will not be oxidised at the anode to Ag^+ as $E^\ominus(\text{Ag}^+/\text{Ag})$ is less negative (or more positive) than $E^\ominus(\text{Cu}^{2+}/\text{Cu})$
- It will be collected as 'anode sludge' at the base of the cell.

Examiner's Comments:

This was not well answered. Many left this part blank. Many students did not compare the electrode potential with $E^\ominus(\text{Cu}^{2+}/\text{Cu})$ or state the electrode in which oxidation and reduction occur.

- (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]



$$Q = I \times t = n_e \times F$$

$$n_e = \frac{15 \times (5 \times 60 \times 60)}{96500} = \underline{2.798 \text{ mol}}$$

$$n(\text{Cu}) \text{ deposited} = \frac{1}{2} \times 2.798 \times 63.5 = \underline{88.8 \text{ g}}$$

Examiner's Comments:

This was not well answered. Many left this part blank. Common mistake is to omit the mole ratio of Cu.

(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]

- (i) Complex ion in **W** : CuCl_2^- Solid compound **X** : CuCl

Examiner's Comments:

This was not well answered. Many left this part blank.

- (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]

- (ii) When concentrated HCl is added to $\text{Cu}^{2+}(\text{aq})$,



high $[\text{Cl}^-]$ causes the position of equilibrium of (1) to shift right, forming yellow $[\text{CuCl}_4]^{2-}$.

Solution appeared yellow-green due to mixture of pale blue $[\text{Cu(H}_2\text{O)}_6]^{2+}$ and yellow $[\text{CuCl}_4]^{2-}$ presence in the solution.

Addition of water causes the concentrations of all aqueous ions to fall while $[\text{H}_2\text{O}]$ remains relatively constant. This causes the position of equilibrium of (1) to shift left since there are more aqueous concentration terms on the left-hand side, forming back the original blue $[\text{Cu(H}_2\text{O)}_6]^{2+}$.

2(✓) [1]

Examiner's Comments:

This was not well answered. Many left this part blank.

- (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.

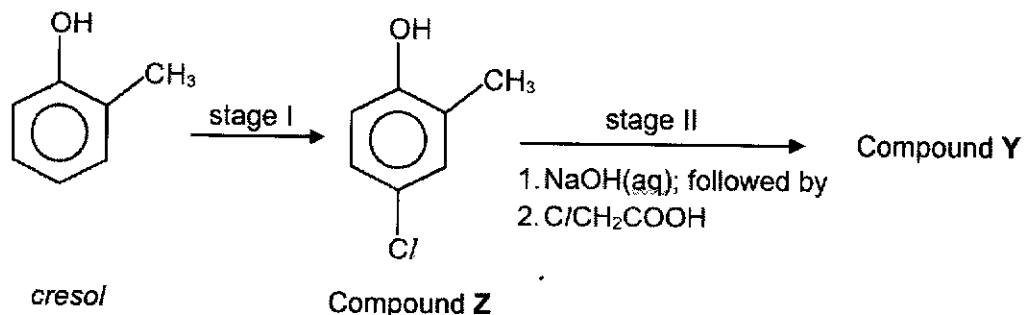
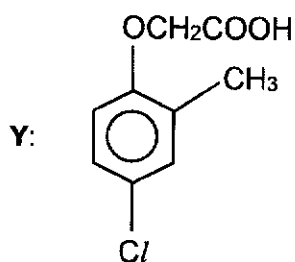


Fig. 5.3

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

(i)



Examiner's Comments:

This was not well answered. Many students thought that the product formed is an ester. They forgot that to form a phenyl ester, acyl chloride is required. Many did not consider nucleophilic substitution as the reaction that occur.

- (ii) Suggest why NaOH(aq) is added to compound Z in stage II before C/CH₂COOH is added. [1]
- (ii) NaOH(aq) is added to convert Z to phenoxide which is a better/stronger nucleophile with a full negative charge.

Examiner's Comments:

This was not well answered. Many left this part blank. Credit were given for students who drew the structure of the phenoxide.

[Total: 20]

A series of 30 horizontal dotted lines for writing.

