YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	TEACHERS' COPY

CG		INDEX NO	

CHEMISTRY

9729/02

Paper 2 Structured Questions

30 August 2021

2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
Paper 1	
	/30
Paper 2	
1	**/7**
2	**/5**
3	**/7**
4	**/17**
5	**/11**
6	**/22**
7	**/6**
Penalty	
	/75
Paper 3	
	/80
Paper 4	
	/55
Overall Percentage (%)	

This document consists of **19** printed pages and **3** blank pages.

[Turn over

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

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

This question is about period 3 elements.

(a) **(i)** State the electronic configuration of argon.

[1]

$1s^2 2s^2 2p^6 3s^2 3p^6$

(ii) Using the Cartesian axes shown in Fig. 1.1, draw a fully labelled diagram of the valence orbitals of argon.

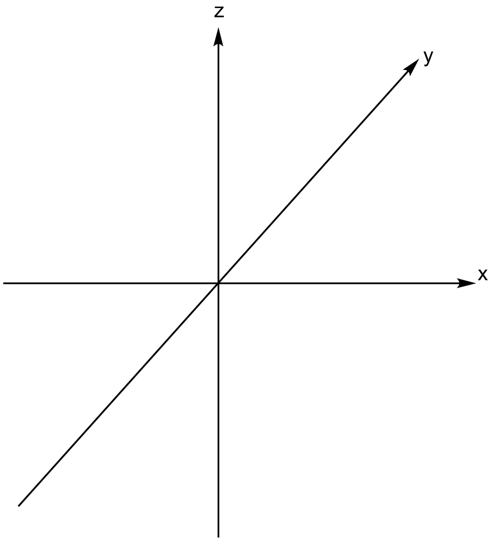
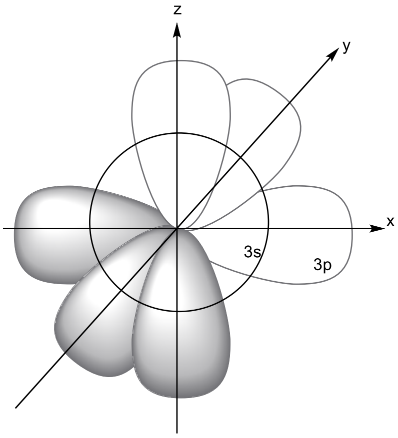


Fig 1.1

[1]



(iii) Two glass vessels **B** and **C** are connected by a closed valve as shown in Fig 1.2.

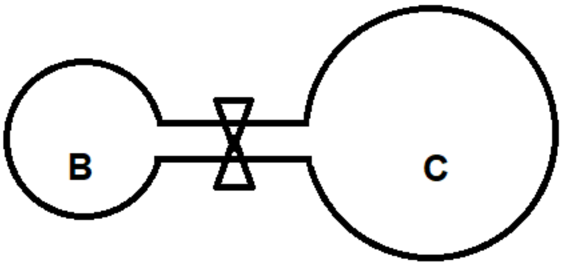


Fig. 1.2

B contains argon at 20 °C at a pressure of 1 x 10^5 Pa. **C** has been evacuated and has three times the volume of **B**. In an experiment, the valve was opened and the temperature of the whole apparatus was raised to 100 °C. Calculate the final pressure in the system.

Since amount of argon is the same throughout,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{1\ x\ 10^5 x\ V}{20+273} = \frac{P_2 x\ 4V}{100+273}$$

P_2(1172V) = 3.73 x 10^7V

P_2 = 31825.9
= 31800 Pa (3 sf)

[2]

(b) Fig 1.3 shows the fifth, sixth, seventh, eighth and ninth ionisation energies of another element **T** in Period 3.

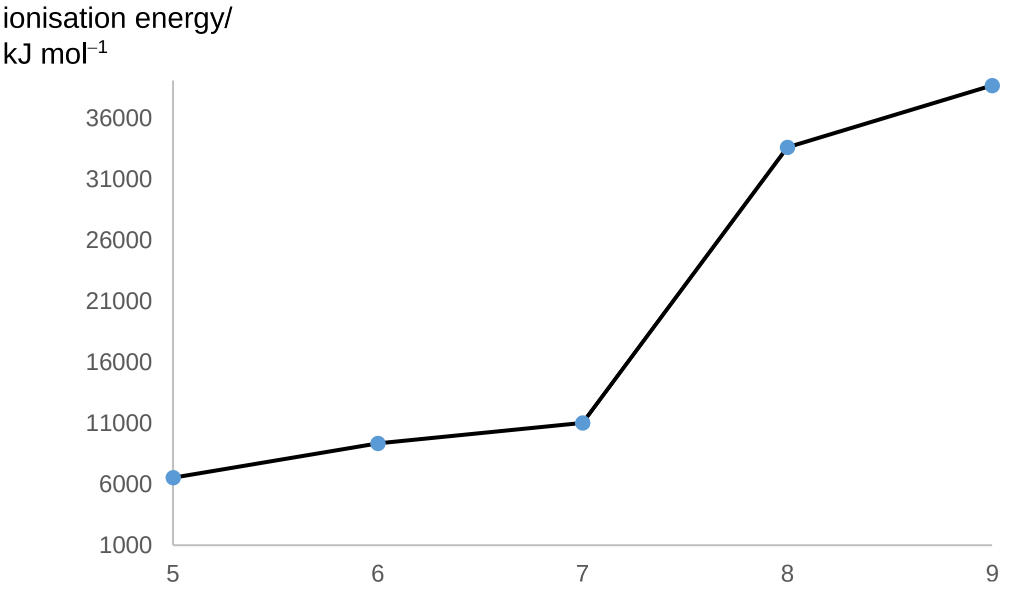


Fig.1.3

(i) State and explain which period 3 element has these ionisation energy values.

[2]

Chlorine as it has a **large increase in ionisation energy from the removal of 7th to 8th** electron, indicating that there are **7 valence electron** in the outermost shell (OR and the **8th electron is removed from an inner quantum shell**).

(ii) Element **U** is directly below element **T** in the periodic table. Explain how the 7th ionisation energy of element **U** is compared to element **T**.

[1]

Element U would have a **lower** 7th ionisation energy compared to element T as it has **one more inner quantum shell of electrons.** (OR **increase in shielding effect outweighs increase in nuclear charge** hence effective nuclear charge decreases and less energy is required to remove the 7th electron).

[Total: 7]

2 Diamine can ionise in stages.

$$H_2N(CH_2)_nNH_2 \xrightarrow[pK_1]{+\ H^+} H_2N(CH_2)_nNH_3^+ \xrightarrow[pK_2]{+\ H^+} H_3N^+(CH_2)_nNH_3^+$$

(a) Table 2.1 compares the pK_b values of ethylamine and 1,2-ethanediamine at 25 °C.

Table 2.1

Base	Formula	pK_1	pK_2
ethylamine	$CH_3CH_2NH_2$	3.19	-
1,2–ethanediamine	$H_2NCH_2CH_2NH_2$	4.11	7.39

(i) Suggest a reason why the pK_1 value of ethylamine is less than the pK_1 value of 1,2–ethanediamine.

[1]

Ethylamine is a stronger base (smaller pK_1 value) as the **lone pair of electron is more available** to accept a proton as compared to 1,2–ethanediamine, where there is **electron withdrawing nitrogen atom** OR there is **intramolecular hydrogen bonding** between the amine groups. This makes the lone pair of electron on another N atom less available to accept a proton, hence weaker base (larger pK_1 value).

(ii) Suggest why the pK_2 value of 1,2–ethanediamine is higher than its pK_1 value.

[1]

The second ionisation of 1,2–ethanediamine is less favourable than the first ionisation because the second ionisation of 1,2–ethanediamine involved **accepting H^+ ion to a positively charged** $CH_3CH_2NH_3^+$**(repulsion),** while the first ionisation involves **accepting H^+ to a uncharged** 1,2-ethanediamine **(less repulsion).**

(iii) 0.10 mol dm^{-3} of HC*l* (aq) was added to ethylamine solution at 25 °C.

$$CH_3CH_2NH_2\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CH_2NH_3^+\,(aq) + OH^-(aq)$$

Deduce without calculation, what happens to the position of equilibrium and the value of pK_1.

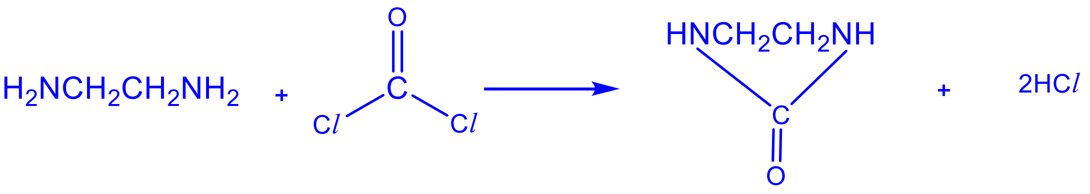
[2]

Addition of acid will cause the **concentration of OH^- to decrease**. **The equilibrium position will shift to the right** so as to **increase the concentration of OH^-** OR to **remove excess H^+**.

Value of pK_1 remains **constant** at 3.19 as **temperature is constant** or it is **temperature dependent.**

(b) Adding equimolar of 1,2–ethanediamine and phosgene, COC*l*$_2$ produced a cyclic compound **V** with molecular formula $C_3H_6ON_2$. Suggest the structure of compound **V.**

[1]

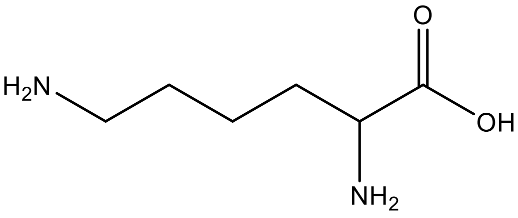


Compound **V**

[Total: 5]

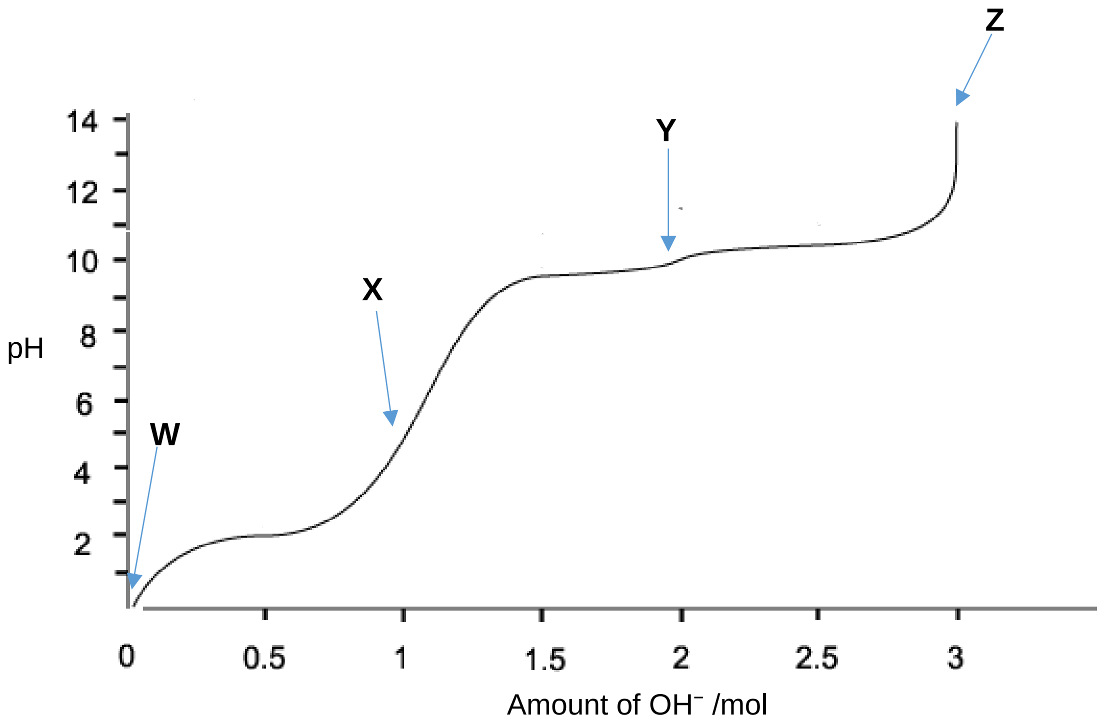
3 Lysine is an essential amino acid that cannot be synthesised by the human body and must be obtained from the diet. It is found in legumes such as peas, and animal products such as beef and fish.

The structure of lysine is given below.

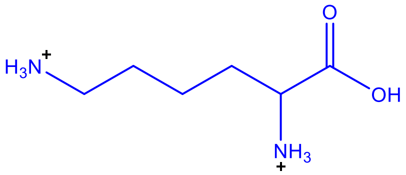
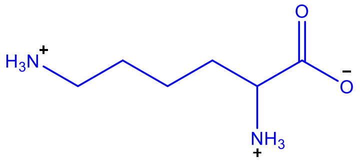
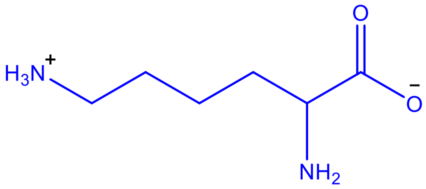
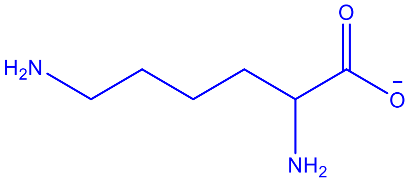


lysine

(a) A solution was prepared by reacting 1 mole of lysine with 2 moles of hydrochloric acid. This solution was titrated with aqueous sodium hydroxide to obtain the titration curve below.



(i) Draw the structure of the species present at points **W**, **X**, **Y** and **Z** on the titration curve. [4]

W	X
	
Y	**Z**
	

[4]

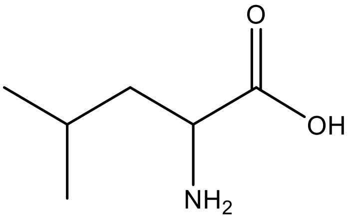
(ii) Explain why the melting point of lysine is high, in terms of structure and bonding.

[2]

Lysine exists as a **zwitterion** and has a **giant ionic structure** with strong **electrostatic** forces of **attraction** between the oppositely charged **$-COO^-$ and $-NH_3^+$** groups .

Since **a lot of energy** is required to overcome the (OR) **strong** ionic bonds, lysine has high melting point.

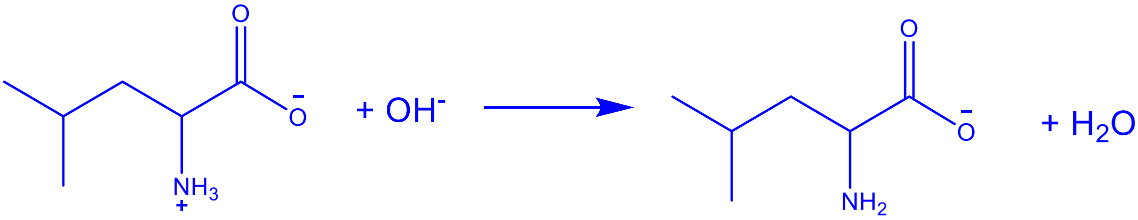
(b) Leucine is another essential amino acid that is mainly found in legumes.



leucine

Write an equation to explain how the zwitterionic form of leucine behaves as a buffer when a small amount of base is added.

[1]



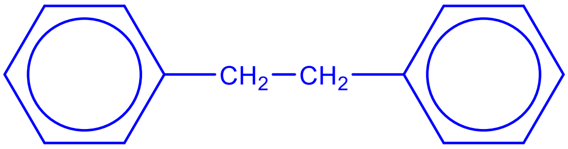
[Total: 7]

4 Benzene is a natural constituent of crude oil and is mainly used as an intermediate to produce other chemicals.

(a) In the presence of anhydrous $AlCl_3$, benzene can undergo Friedel-Crafts alkylation with CH_3Cl to form methylbenzene. The alkyl side chain can further react to form compound **A**, $C_{14}H_{14}$, along with side products like hydrogen chloride gas.

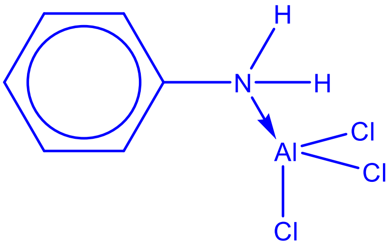
(i) Suggest the structure of compound **A**.

[1]

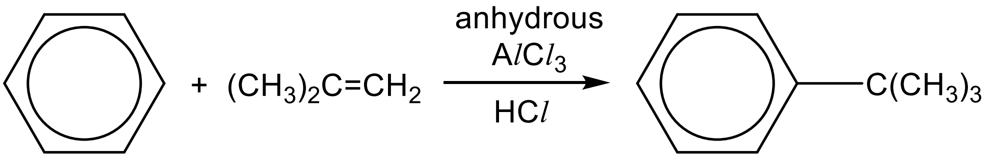


(ii) Unlike benzene, phenylamine does **not** undergo Friedel-Crafts alkylation with halogenoalkanes in the presence of $AlCl_3$. This is because the amine reacts with $AlCl_3$ to form a neutral compound **B**. Draw the **displayed** formula of **B**.

[1]



(b) Friedel-Crafts alkylation can also be achieved using alkenes, such as the example below.

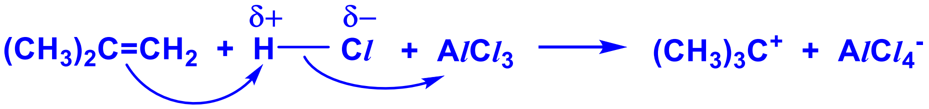


C

(i) In the first step, $(CH_3)_3C^+$ is produced in the presence of $AlCl_3$ and HCl.

Write an equation to show the formation of $(CH_3)_3C^+$.

[1]



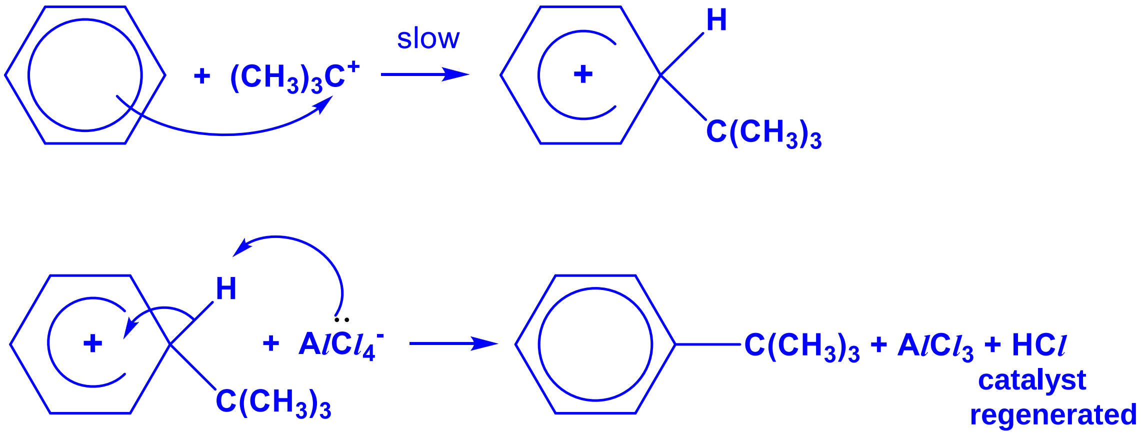
$$(CH_3)_2C{=}CH_2 + \overset{\delta+}{H}—\overset{\delta-}{Cl} + AlCl_3 \longrightarrow (CH_3)_3C^+ + AlCl_4^-$$

(ii) Name and outline the mechanism of the reaction to form compound **C**.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

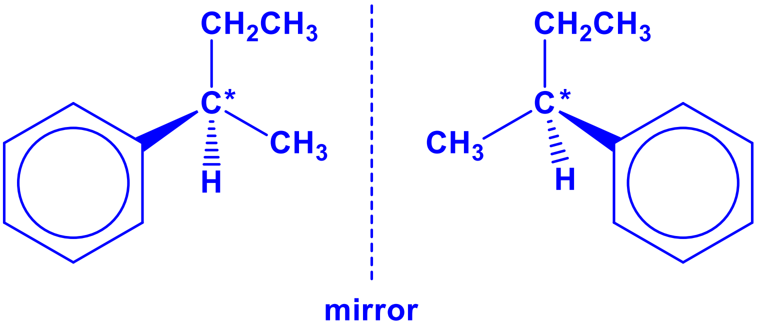
[2]

Name of mechanism: Electrophilic substitution



(iii) Compound **D** is a constitutional isomer of compound **C** and it can exhibit stereoisomerism. Draw diagrams to illustrate the type of stereoisomerism present in **D**.

[2]

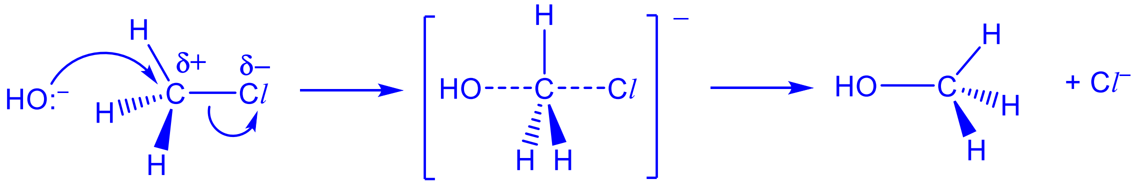


(c) Chloromethane, CH_3Cl, can be hydrolysed by aqueous sodium hydroxide. The rate equation was experimentally determined to be rate = k $[CH_3Cl]$ $[OH^-]$

(i) Outline the mechanism of this hydrolysis reaction that is consistent with the rate equation.

[3]

Name: Nucleophilic substitution, S_N2 [√]



(ii) Explain why the mechanism in **(c)(i)** is consistent with the rate equation.

[1]

There is **one** (mole of) **CH_3Cl** and **one** (mole of) **OH^-** involved in the **rate-determining / slow step**.

(d) When aqueous sodium hydroxide is added dropwise to aqueous copper(II) nitrate, a pale blue precipitate, $Cu(OH)_2$, is formed.

The numerical value of the solubility product, K_{sp}, of $Cu(OH)_2$ is 2.2×10^{-20} at 25 °C.

(i) Calculate the solubility of $Cu(OH)_2$ in g dm^{-3}.

[2]

$K_{sp} = [Cu^{2+}][OH^-]^2$

$$Cu(OH)_2(s) \rightleftharpoons \underset{x}{Cu^{2+}(aq)} + \underset{2x}{2OH^-(aq)}$$

$(x)(2x)^2 = 4x^3 = 2.2 \times 10^{-20}$

$x = 1.7652 \times 10^{-7}$ mol dm^{-3}

solubility in g dm^{-3} = $(1.7652 \times 10^{-7}) \times 97.5$ = **1.72×10^{-5} g dm^{-3}**

(ii) If equal volumes of a sample of copper(II) nitrate solution and 0.250 mol dm^{-3} aqueous sodium hydroxide are mixed, calculate the minimum concentration, in mol dm^{-3}, of copper(II) ions that must be present in the sample to cause precipitation of $Cu(OH)_2$.

[1]

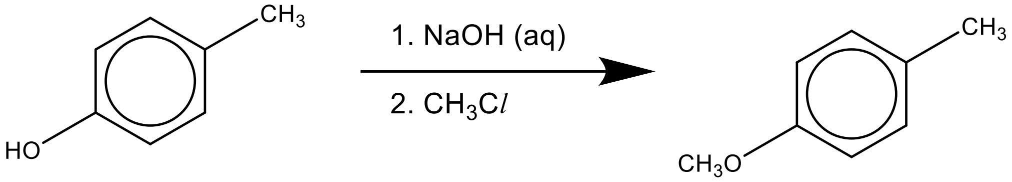
$$\left[Cu^{2+}\right]\left[\frac{0.250}{2}\right]^2 \geq 2.2 \times 10^{-20}$$

minimum $[Cu^{2+}]$ in mixed solution = 1.41×10^{-18} mol dm^{-3}

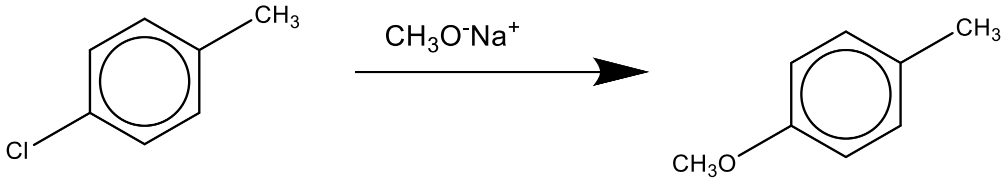
minimum $[Cu^{2+}]$ in sample = $2 \times 1.41 \times 10^{-18}$ = **2.82×10^{-18} mol dm^{-3}**

(e) A student suggested two methods to prepare 4-methoxymethylbenzene.

Route 1:



Route 2:



(i) State the role of NaOH (aq) in **Route 1**.

[1]

NaOH acts as a (Bronsted) **base**.

(ii) Which route will give a higher yield? Explain your answer.

[2]

Route 1 will give a higher yield.

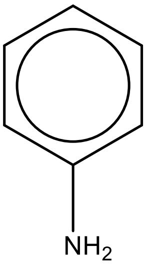
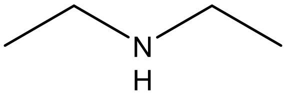
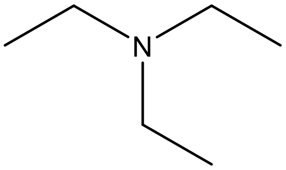
In Route 2, the **delocalisation of the lone pair of electrons on the C*l* atom into the benzene ring** resulted in the **C–C*l* bond having a partial double bond character**/**becoming stronger**,
OR
The (π electron cloud of the) **benzene ring will repel** (the lone pair of electrons of) **an incoming nucleophile**,
OR
Benzene causes **steric hindrance** or **blocks / hinders** the approach of the nucleophile from the **rear / back side** of the C-C*l* bond.

thus causing chlorobenzene to be **resistant to nucleophilic substitution** or
hard to break the bond or
rendering approach of the nucleophile difficult under the given conditions.

[Total: 17]

5 **(a)** Table 5.1 below gives the pK_b values of some weak bases.

Table 5.1

base	phenylamine	diethylamine	triethylamine
			
pK_b	9.38	3.16	3.28

(i) Arrange the bases in ascending order of base strength, explaining your reasoning.

[3]

Base strength: phenylamine < triethylamine < diethylamine

Phenylamine is the weakest base because the **lone pair of electrons on the N atom is delocalised into the benzene ring**. This **decreases the electron density on the N atom** and hence the **lone pair of electrons on the nitrogen** atom is **less available to accept a H^+** ion.

Diethylamine is a stronger base than triethylamine as triethylamine has a **greater number of alkyl groups** and hence **increasing steric hindrance**, making the **lone pair of electrons on the nitrogen** atom is **less available to accept a H^+** ion.

(ii) Calculate the pH of 0.200 mol dm^{-3} phenylamine.

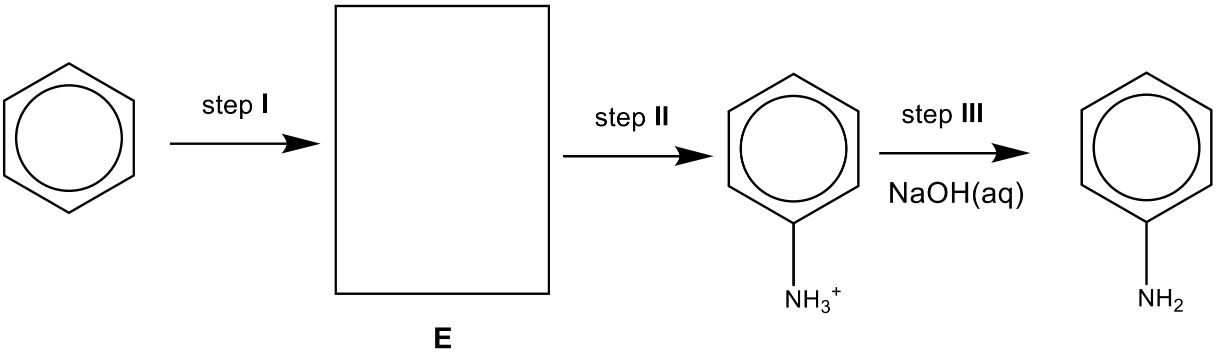
[2]

pOH$= -\,log\sqrt{K_b \times c_{phenylamine}}$

$= -log\sqrt{10^{-9.38} \times 0.200}$ = 5.0395

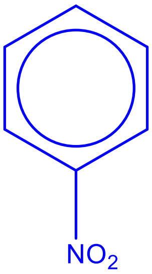
pH = 14 – pOH = **8.96**

(b) Phenylamine can be synthesised from benzene in a three-step process as shown below.



(i) Draw the structure of intermediate **E** in the box above.

[1]



(ii) Identify the type of reaction in step **II**, and name the reagents and conditions used.

[2]

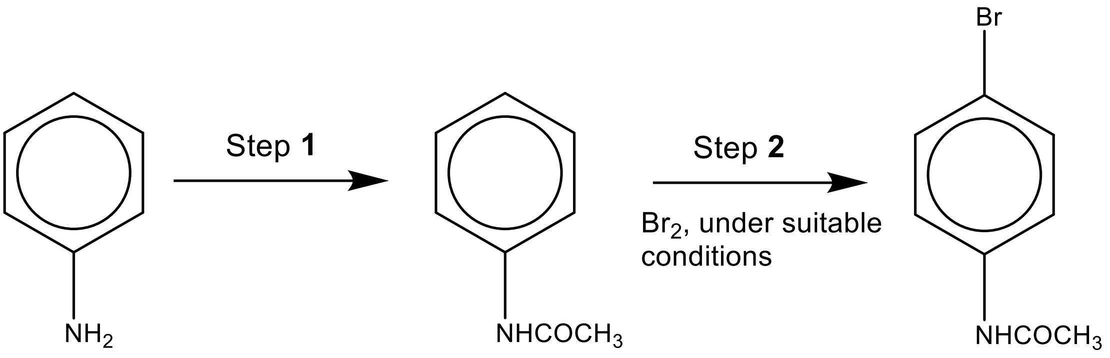
Reduction
Sn, concentrated HC*l*, heat

(iii) Explain why ammonia can be used in place of NaOH in step **III**.

[1]

Ammonia is a **stronger bases than phenylamine**, and can deprotonate the phenylammonium ion.

(c) Phenylamine can undergo the following reactions to form compound **F**.



F

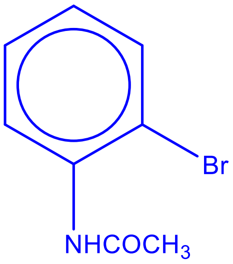
(i) State the reagent used in step **1**.

[1]

(anhydrous) CH_3COCl, (room temperature)

(ii) Besides **F**, another possible product **G** is also formed. Suggest the structural formula of **G**.

[1]



[Total: 11]

6 Wearing of masks can be used for either protection of healthy persons or to prevent onward transmission of Coronavirus disease, COVID-19.

Tea polyphenols extracted from green tea possess antiviral properties. A dip coating of nonwoven fabric mask into tea polyphenol extract can inactivate >99% of tested viruses.

The chemical synthesis of a new type of polyphenol was achieved by reaction of 4–((2–phenylhydrazono)methyl)phenol (4–PHMP) to form Poly(4–PHMP) using sodium hypochlorite, NaOC*l* as oxidising agent in an aqueous alkaline medium.

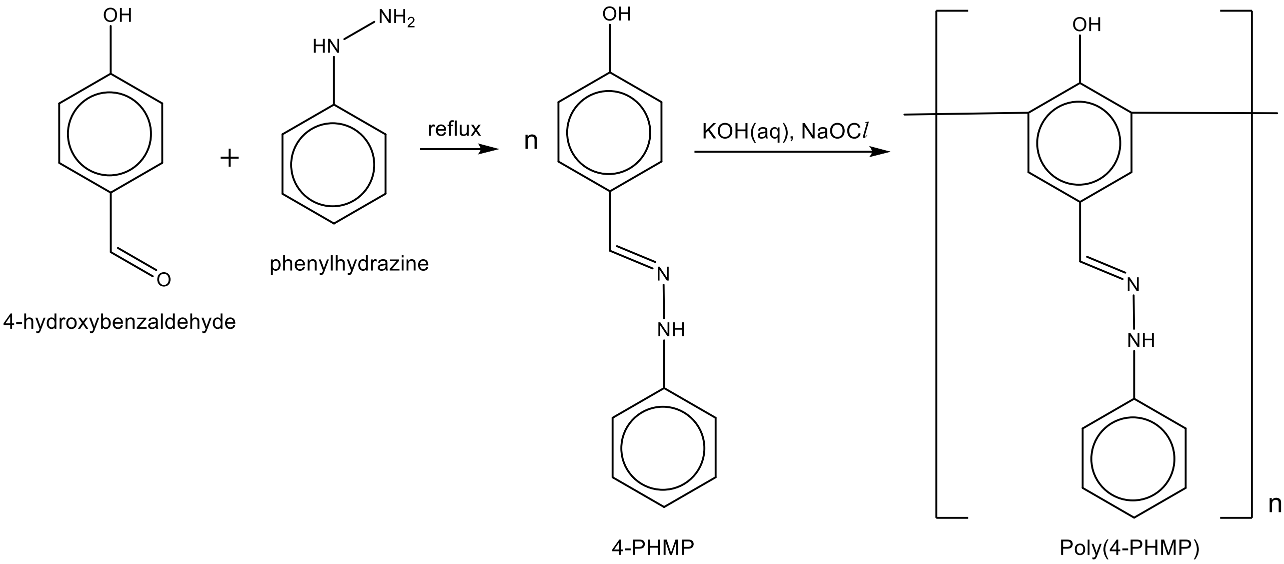


Fig. 6.1

Data about these 4 compounds are given in Table 6.1.

Table 6.1

	Molecular Mass /g mol^{-1}	Solubility in hexane / g cm^{-3}
4-hydroxybenzaldehyde	122.0	
phenylhydrazine	108.0	
4–PHMP	212.0	0.99
Poly(4–PHMP)	22065.0	0.00

(a) The monomer 4–PHMP was prepared by the reaction between 4–hydroxybenzaldehyde and phenylhydrazine in ethanol as shown in Fig.6.1.

1.221 g of 4–hydroxybenzaldehyde in 3 cm^3 of ethanol and 1.282 g of phenylhydrazine in 2 cm^3 of ethanol and were mixed and stirred for 30 mins at room temperature. The precipitated product was purified by recrystallisation to provide 2.06 g of product 4–PHMP.

(i) State the type of reaction occurring.

[1]

Condensation

(ii) Use the data above to determine, by calculation, whether 4–hydroxybenzaldehyde or phenylhydrazine is the limiting reagent.

[2]

Amount of phenyl hydrazine =1.282/108.0 = 0.0119 mol
Amount of 4-hydroxybenzaldehyde = 1.221/122.0 = 0.0100 mol
4-hydroxybenzaldehyde is the limiting reagent.

(iii) Using answer in **(a)(ii)**, calculate the percentage yield of 4–PHMP.

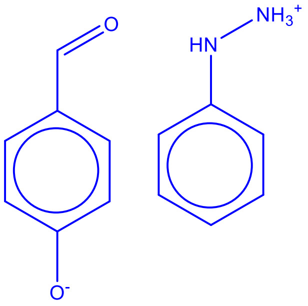
[2]

Amount of 4-PHMP = 0.0100 mol
Mass of 4-PHMP = 0.0100 x 212.0 = 2.12 g

% yield = 2.06/2.12 x 100% = 97.2%

(iii) Identify one possible by-product of this reaction in aqueous medium.

[1]



(b) The reaction of 4-PHMP to form Poly(4-PHMP) using $\text{NaOC}l$ was carried out as follows

1. 0.53 g of 4–PHMP was dissolved in 1 cm^3 of aqueous KOH and placed into a 25 cm^3 three-necked round-bottomed flask that was fitted with a condenser, a thermometer and a stirrer, in addition to a funnel containing $\text{NaOC}l$.

2. After heating to 50°C, $\text{NaOC}l$ was added dropwise over 30 min with stirring and the mixture was heated under reflux for 5 hours.

3. The mixture was allowed to cool to room temperature and 0.5 cm^3 of concentrated $\text{HC}l$ was added.

4. The mixture was filtered and washed with 25 cm^3 hot water three times, and the removal of mineral salts was confirmed using an $AgNO_3$ solution.

5. The unreacted 4-PHMP was separated from the reaction products by washing with hexane and dried in an oven at 105 °C.

(i) Suggest why 1 cm^3 of aqueous KOH is added to dissolve 4–PHMP in step 1.

[1]

KOH will react with the phenol group in 4–PHMP to form a **phenoxide ion** which will in turn form **ion-dipole interaction with water** and dissolves.

(ii) State the purpose of adding concentrated HC*l* in step 3 and suggest why the mixture was cooled to room temperature before addition.

[2]

The reaction mixture is alkaline, HC*l* is added to **neutralise** OH^-. As dilution/hydration of concentrated acid is **exothermic**, it is added to the mixture after it is cooled to room temperature.

(iii) Suggest the identity of the mineral salt which is removed when the mixture was washed with 25 cm^3 hot water three times after the reaction is completed in step 4.

[1]

KC*l*, NaC*l* (NaOC*l* → NaC*l*, KOH → KC*l*)

(iv) In step 5, the unreacted 4–PHMP was separated from the reaction products by washing with hexane. Using data from Table 6.1 and knowledge of structure and bonding, suggest how the product, Poly(4–PHMP) is separated from unreacted 4–PHMP. [3]

From table 6.1, Poly(4–PHMP) is **not soluble in hexane while 4–PHMP is soluble** (0.99 g cm^{-3}). Poly(4–PHMP) is **giant molecular with extensive network of strong covalent bonds, cannot form appreciable interaction** with hexane while monomer 4–PHMP is **simple molecular**, is able to form **significant instantaneous dipole-induced dipole interaction** with hexane. Hence when hexane is added into the reaction product, 4–PHMP will dissolve in hexane, separating from the product Poly(4–PHMP).

(c) A researcher carried out the reaction of 4-PHMP described in **(b)** by repeating the reaction with different parameters such as reaction temperature and reaction time, on the yield of poly 4-PHMP. He also decided to use O_2 instead of NaOC*l* as the oxidising agent. The results are summarised in Fig. 6.2a (reaction temperature) and Fig. 6.2b (reaction time).

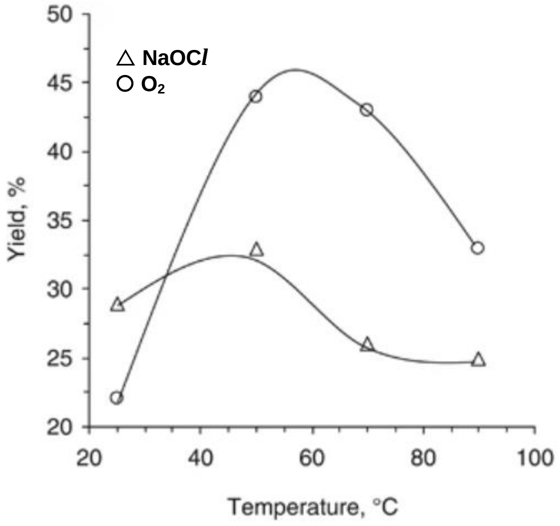


Fig 6.2a

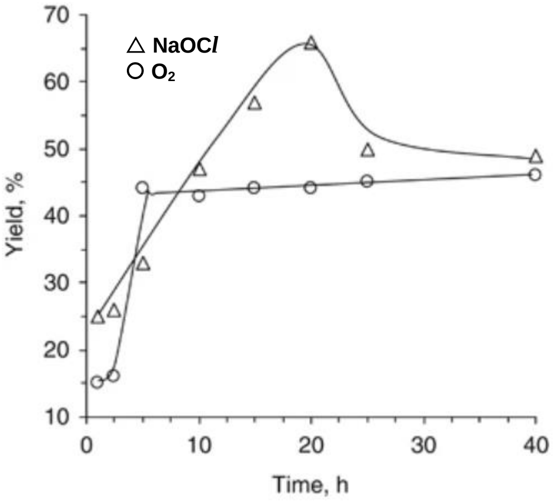


Fig 6.2b

Source: Demir, H. A novel polyphenol: synthesis, characterization and investigation of its thermal and electrochemical properties. *Polym J* **44,** 699–705 (2012). https://doi.org/10.1038/pj.2012.17

(i) From Fig. 6.2a and 6.2b, the optimal reaction condition for producing Poly(4-PHMP) using O_2 is 60 °C for 40 h.

State the optimal reaction condition in terms of temperature and time, for producing Poly(4-PHMP) using NaOC*l.*

Using NaOC*l*:

[1]

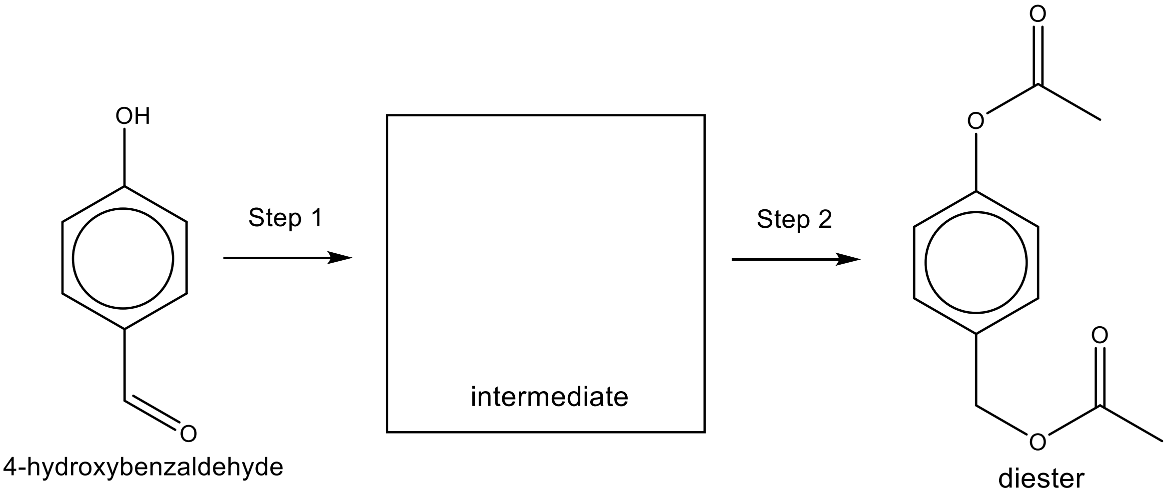
Using NaOC*l*: 45-50 °C for 20 h

(ii) Hence suggest with reasoning which oxidising agent should be more suitable for use in commercial large scale production of Poly(4-PHMP).

[1]

NaOC*l* as lower reaction temperature and heating duration is required. This saves time and cost in operation.
or
O_2 although higher temperature and longer duration is required for higher yield, it is more readily available/cheaper.

(d) 4-hydroxybenzaldehyde can also be used to synthesis a diester in several steps.



Describe the reagents and conditions needed for steps 1 and 2 and draw the structure of the intermediate formed in the box above.

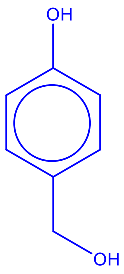
Step 1:

Step 2:

[3]

Step 1: $LiAlH_4$ in dry ether, (room temp) or $NaBH_4$ in methanol, (room temp) or H_2(g), Ni, Heat
Step 2: (NaOH(aq)), followed by (anhydrous) (excess) CH_3COCl, (room temp).

Structure of intermediate:



(e) Patients with COVID-19 may use a pulse oximeter to measure the oxygen level in their body. However, the oxygen level measured by a pulse oximeter is not the only way to know how sick someone is.

Pulse oximeters measure how much of the haemoglobin in blood is carrying oxygen (oxygen saturation). Oxygen saturation refers to the percentage of the available haemoglobin that carries oxygen.

(i) One molecule of haemoglobin molecule can bind up to four molecules of oxygen according to the following equation.

$$Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq) \qquad K_c = 3.00 \times 10^{20}$$

Write an expression for K_c for the reaction, and calculate the ratio of $[Hb(O_2)_4]$ to $[Hb]$, given that the $[O_2]$ is 9.6×10^{-6} mol dm^{-3}.

[2]

$$K_c = \frac{[Hb(O_2)_2]}{[Hb][O_2]^4}$$

$$3.00 \times 10^{20} = \frac{[Hb(O_2)_4]}{[Hb][9.6 \times 10^{-6}]^4}$$

$$\frac{[Hb(O_2)_4]}{[Hb]} = 2.54$$

(ii) Calculation of oxygen saturation (SaO_2) is given by the following formula:

$$SaO_2(\%) = \frac{[HbO_2]}{[Hb]+[HbO_2]} \times 100\%$$

where
$[HbO_2]$ is the concentration of haemoglobin
$[Hb]$ is the concentration of deoxyhaemoglobin
$[Hb] + [HbO_2]$ is the total concentration of haemoglobin capable of binding oxygen

Given that the $[Hb(O_2)_4] = [HbO_2]$, using answers in **(e)(i)**, calculate the oxygen saturation in blood for a man who has the same $[O_2]$ as in **(e)(i)**.

[1]

$[HbO_2] = 2.54[Hb]$

$$\frac{2.54[Hb]}{[Hb]+2.54[Hb]} \times 100\% = 71.8\%$$

(iii) A normal oxygen level measured by a pulse oximeter is around 97%. Doctors start to worry when this level drops under 90% because this can affect the amount of oxygen going to the brain and other vital organs. People can experience confusion and lethargy at low levels. Levels below 80% are considered dangerous and increase the risk of organ damage.

Using your answer in **(e)(ii)**, suggest whether the man needs to seek doctor’s advice.

[1]

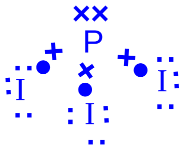
The man should seek doctor's advice since his oxygen level of 71.8% is below 80%, and is considered dangerous.

[Total: 22]

7 **(a)** Phosphorus triiodide, PI_3, is a red solid that is widely used in organic synthesis to convert alcohols into iodoalkanes.

(i) Draw a 'dot-and-cross' diagram of PI_3 and state its shape.

[2]



trigonal pyramidal

(ii) Unlike phosphorus pentachloride, PCl_5, phosphorus pentaiodide, PI_5, is highly unstable and cannot be prepared at room temperature. Suggest a reason for this.

[1]

Iodine is **bigger** than chlorine and there is high **steric hindrance** to arrange five big iodine atoms around a central P atom.

(b) The boiling points of PCl_5 and PI_3 are 167 °C and 200 °C respectively.

Explain, in terms of structure and bonding, the difference in boiling point between PCl_5 and PI_3.

[2]

Both PCl_5 and PI_3 have **simple molecular structure** with **intermolecular instantaneous dipole-induced dipole interactions** and permanent dipole-permanent dipole interactions.

Since PI_3 has a **larger electron cloud** that is **more polarisable** than PCl_5, PI_3 molecules form **stronger** id-id interactions that **require more energy to overcome**.

(c) Write an equation to describe the reaction of P_4O_{10} with water.

[1]

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

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