YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
CG		INDEX NO	

CHEMISTRY

9729/01

Paper 1 Multiple Choice

16 September 2021

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name and class on the Answer Sheet in the spaces provided unless this has been done for you.

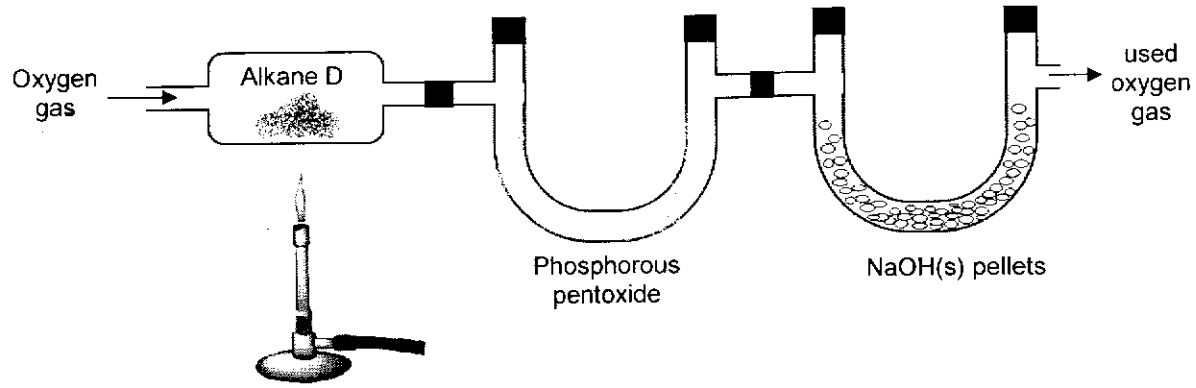
There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **16** printed pages.

1 A 1.00 g alkane D was burnt in an excess of oxygen, and the gases that were produced were first passed through a U-tube containing phosphorus pentoxide and another U-tube containing NaOH(s) as shown in the diagram. The phosphorus pentoxide U-tube increased in mass by 1.55 g, and the NaOH(aq) bottle increased in mass by 3.03 g. All volumes were measured at room temperature and pressure. What is the molecular formula of the alkane D?



A CH_4 **B** C_2H_5 **C** C_2H_6 **D** C_4H_{10}

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

What do the ions $^{36}S^{2-}$ and $^{37}Cl^-$ have in common?

A Both ions have more electrons than neutrons.

B Both ions have the same electronic configuration.

C Both ions contains the same number of nucleons.

D $^{36}S^{2-}$ has a smaller angle of deflection than $^{37}Cl^-$ in an electric field.

3 Boyle's law states that at constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure.

Which of the following statements shows application of Boyle's law?

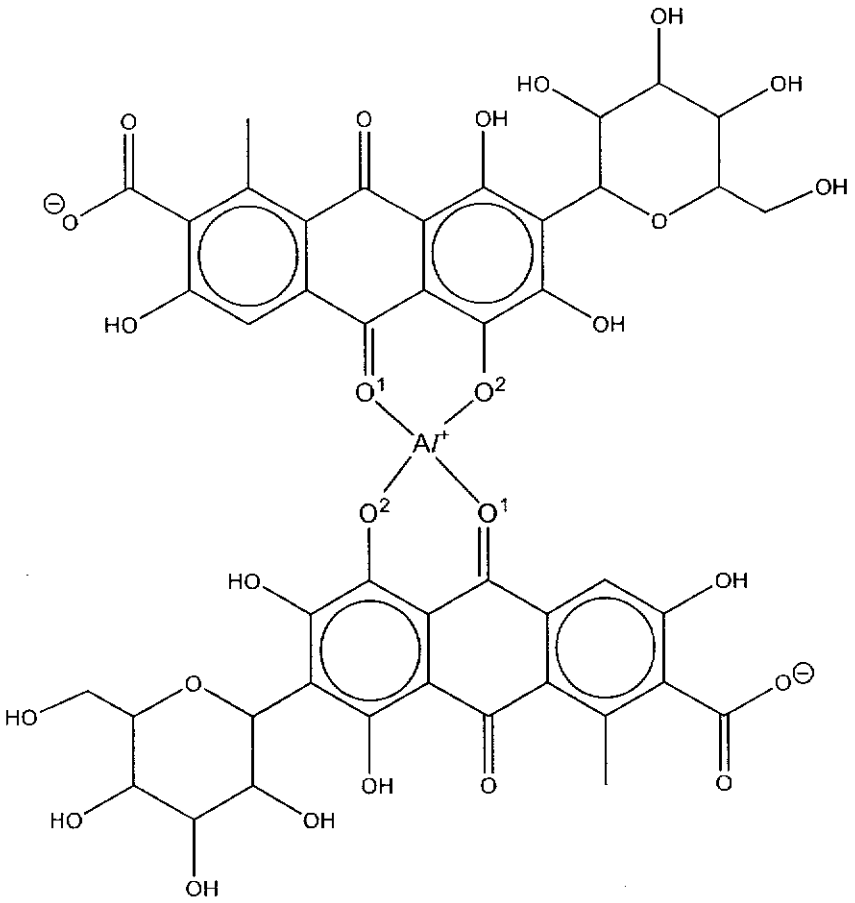
1 Human lungs, inhalation and exhalation.

2 Spraying paint from a can.

3 Working of hot air balloon.

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

4 Carmine is a red colorant extracted from the bodies of dead female insects, used in food colouring and lipsticks. The proposed structure of carmine is as shown.



The Al^{+} ion is situated in the centre of a planar arrangement of numbered oxygen atoms.
Which of the following descriptions of the bonds between Al^{+} and the numbered O atoms is most likely to be correct?

	O atoms numbered 1	O atoms numbered 2
A	co-ordinate	co-ordinate
B	co-ordinate	ionic
C	ionic	co-ordinate
D	ionic	ionic

5 The table shows the boiling point of some halogenoalkanes.

compound	boiling point/ °C
CH_3CH_2Cl	12.3
CH_3CH_2Br	34.8
CH_3CH_2I	70.0

Which of the following correctly explains the difference in the boiling point?

1 the electronegativity difference between the halogen and carbon increases from C–Cl to C–I

2 the strength of permanent dipole-permanent dipole attraction increases from C–Cl to C–I

3 the strength of instantaneous dipole-induced dipole attraction increases from CH_3CH_2Cl to CH_3CH_2I

4 the bond energy of C–X bond decreases from C–Cl to C–I

A 1 and 2 only **B** 2 and 4 only **C** 3 only **D** 4 only

6 The radioactive decay of element X is a first-order reaction. It take 16 days for element X to decay to 25% of its initial value.

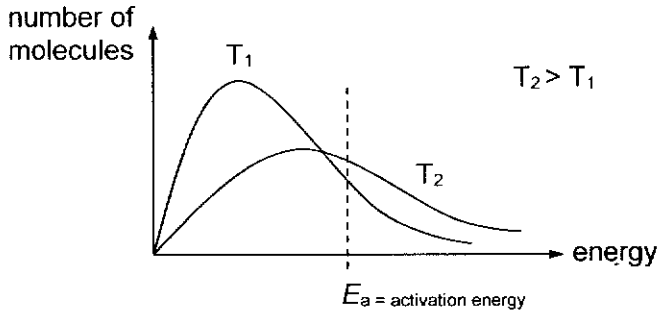
What fraction of element X would remain after 800 days?

A $\frac{1}{2^{10}}$ **B** $\frac{1}{2^{50}}$ **C** $\frac{1}{2^{80}}$ **D** $\frac{1}{2^{100}}$

7 The Boltzmann distribution of kinetic energies for the following equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57 \text{ kJ mol}^{-1}$$

is shown graphically below as temperature is increased.



Which statements can be drawn from the graph?

1 At all energies, the number of molecules of N_2O_4 of a given value increases.

2 The maximum of the curve lowers and shifts to the right.

3 The reaction is first order with respect to $[N_2O_4]$.

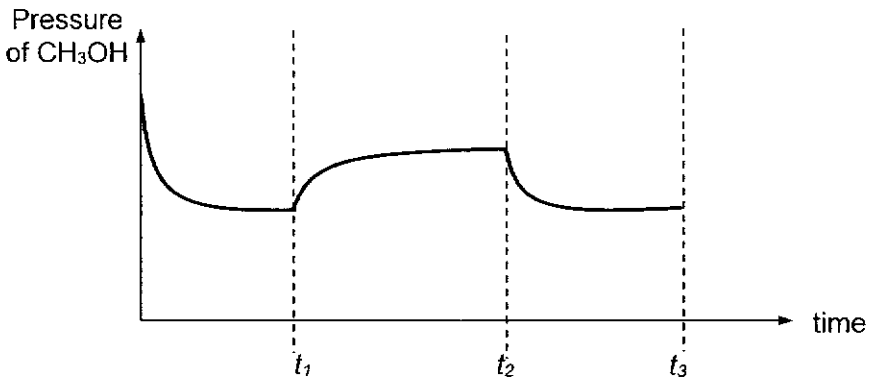
4 The number of molecules with energies equal or greater than *Ea* increases.

A 1, 2 and 3 only **B** 1 and 2 only **C** 2 and 4 only **D** 3 and 4 only

8 Methanol can be synthesised from hydrogen and carbon monoxide using a suitable catalyst at 480 K and a pressure of 3×10^6 Pa.

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -90.6 \text{ kJ mol}^{-1}$$

The reaction mixture reached equilibrium under the above conditions. The graph below shows how the pressure of CH_3OH varied with time.



What could be the changes made to the system at t_1 and t_2?

	t_1	t_2
A	CH_3OH was added	Temperature was decreased
B	CO was added	Temperature was increased
C	Temperature was decreased	CO was added
D	Temperature was increased	CH_3OH was added

9 A quantity of ethanol was burned underneath a copper can containing 400 g of water at 30 °C. The temperature of the water rose to 85 °C after the complete combustion of 5 g of ethanol (M_r = 46.0).

The efficiency of heat transfer to the water will not be 100% after taking into considerations the heat capacity of the copper can and heat loss to surroundings.

Given that the specific heat capacity of water is 4.2 J g^{-1} K^{-1} and the enthalpy change of combustion of ethanol is –1367 kJ mol^{-1}, what is the efficiency of heat transfer to the water?

A 27% **B** 39% **C** 62% **D** 96%

10 Which equation corresponds to the enthalpy change stated?

A	$2Al^{3+}(g) + 3O^{2-}(g) \rightarrow Al_2O_3(s)$	$2\Delta H^{\ominus}_{\text{lattice energy}}(Al_2O_3(s))$
B	$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$	$\Delta H^{\ominus}_{\text{neutralisation}}(H_2O(l))$
C	$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$	$\Delta H^{\ominus}_{\text{solution}}(CaCl_2(s))$
D	$\frac{1}{4}P_4(s) + \frac{5}{2}O_2(g) \rightarrow \frac{1}{4}P_4O_{10}(s)$	$\Delta H^{\ominus}_{\text{formation}}(P_4O_{10}(s))$

11 Calcium reacts with water to form calcium hydroxide and hydrogen.

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$$

The standard enthalpy change for this reaction can be measured in the laboratory.

What further information is needed in order to calculate the standard enthalpy change of formation of calcium hydroxide, $\Delta H_f^{\ominus}$?

1 $\Delta H_f^{\ominus}$ for $H_2O(l)$

2 $\Delta H_f^{\ominus}$ for $H_2(g)$

3 $\Delta H_{\text{atomisation}}^{\ominus}$ for Ca(s)

4 first and second ionisation energies of Ca(s)

A 1, 3 and 4 only **B** 2, 3 and 4 only **C** 3 and 4 only **D** 1 only

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

Water undergoes self–ionisation according to the equation:

$$H_2O\ (l) \rightleftharpoons H^+(aq) + OH^-\ (aq)$$

At 60 °C, the ionic product of water, K_w, has the value of 9.5×10^{-14} mol^2 dm^{-6}.

Which statement concerning water at 60°C is correct?

A The pH is 6.51.

B $[OH^-] = 4.75 \times 10^{-7}$ mol dm^{-3}

C The water is slightly acidic.

D Heating water from 25 °C to 60 °C causes water to ionise to a lesser extent.

13 Values of two solubility products are given

	K_{sp} value at 25 °C
$CaCO_3$	8.7×10^{-9}
CaF_2	4.0×10^{-11}

Solid $CaCO_3$ is shaken with water. The remaining solid is filtered off, leaving behind a saturation solution X.

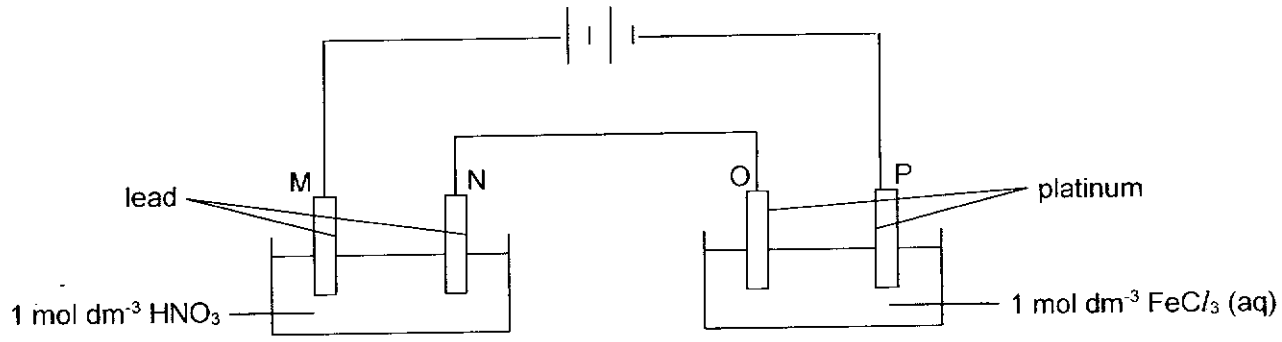
Drops of $F^-(aq)$ are added to solution X until CaF_2 just precipitates. Which row of the table is correct?

	$[Ca^{2+}(aq)]$ in solution X / mol dm^{-3}	$[F^-(aq)]$ when CaF_2 just precipitates / mol dm^{-3}
A	9.33×10^{-5}	6.55×10^{-4}
B	9.33×10^{-5}	9.67×10^{-3}
C	2.15×10^{-4}	6.55×10^{-4}
D	2.15×10^{-4}	4.31×10^{-4}

14 Which factors determine the number of atoms of copper deposited on the cathode of an electrolytic cell?

	current	time	$[Cu^{2+}(aq)]$	size of electrode
A	✓	✓	✓	✓
B	×	×	✓	✓
C	✓	✓	×	×
D	×	✓	✓	×

15 Two cells are connected in series as shown in the diagram where M, N, O and P are the electrodes.



Which of the following correctly shows the products formed at each electrode?

	M	N	O	P
A	O_2	H_2	O_2	Fe^{2+}
B	O_2	Pb	Cl_2	H_2
C	Pb^{2+}	H_2	Cl_2	H_2
D	Pb^{2+}	H_2	O_2	Fe^{2+}

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

An excess of zinc reacts with a warm solution containing VO_2^+ ions.

What will be the final oxidation state of vanadium?

A +2 **B** +3 **C** +4 **D** +5

17 What is the lowest number of carbon atoms a ketone molecule must contain to have chiral carbon atom?

A 5 **B** 6 **C** 7 **D** 8

18 When alkane G, C_6H_{14}, was reacted with bromine under ultraviolet light, it produced only three isomeric monobromo compounds.

What is the likely identity of alkane G?

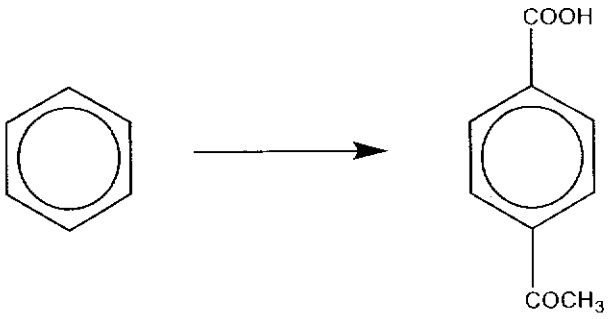
1 $CH_3(CH_2)_4CH_3$

2 $CH_3CH_2CH(CH_3)CH_2CH_3$

3 $CH_3C(CH_3)_2CH_2CH_3$

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

19 4-acetylbenzoic acid can be produced from benzene in three steps.



Which is the best method for this synthesis?

	step 1	step 2	step 3
A	CH_3COCl, anhydrous $FeCl_3$	CH_3Cl, anhydrous $FeCl_3$	dilute H_2SO_4, $KMnO_4$, heat
B	CH_3COCl, anhydrous $FeCl_3$	CH_3Cl, anhydrous $FeCl_3$	dilute H_2SO_4, $K_2Cr_2O_7$, heat
C	CH_3Cl, anhydrous $FeCl_3$	CH_3COCl, anhydrous $FeCl_3$	dilute H_2SO_4, $KMnO_4$, heat
D	CH_3Cl, anhydrous $FeCl_3$	dilute H_2SO_4, $KMnO_4$, heat	CH_3COCl, anhydrous $FeCl_3$

20 Which of the following property does benzene have because of the delocalised π electrons?

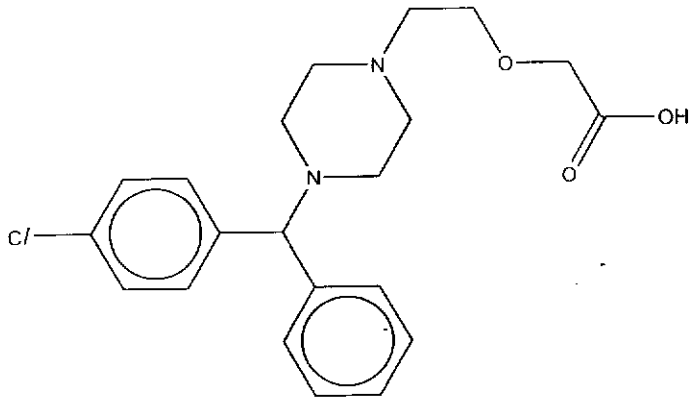
A Benzene is a good electrical conductor.

B Benzene undergoes addition reactions more readily than substitution reactions.

C Substitution in benzene occurs at one particular carbon atom.

D The carbon-carbon bond lengths are between those of C–C bonds and C=C bonds.

21 Cetirizine is an antihistamine that is used to relieve allergy symptoms such as runny nose and itching.



cetirizine

The C-O-C bond is inert.
Which of the following statements about cetirizine are correct?

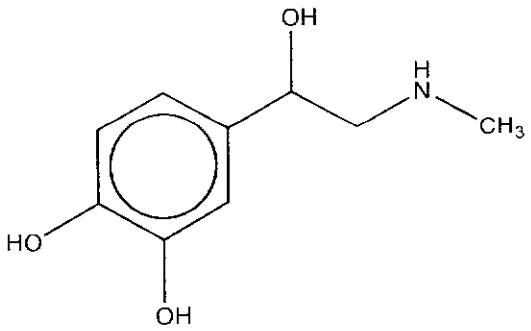
1 After heating with dilute sulfuric acid, 2 organic products are formed.

2 A white precipitate is observed when cetirizine is heated with ethanolic $AgNO_3$.

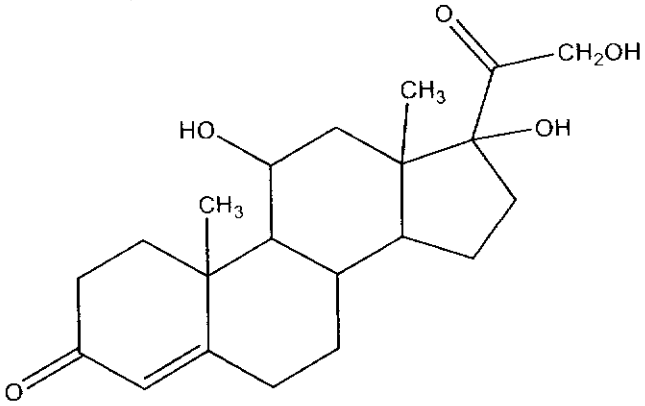
3 The purple colour of acidified $KMnO_4$ is discharged after heating with cetirizine.

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

22 Adrenaline and cortisol are hormones that are produced by the adrenal glands.



adrenaline



cortisol

Which of the following reagents can be used to distinguish the two hormones?

1 neutral iron(III) chloride solution

2 bromine in tetrachloromethane

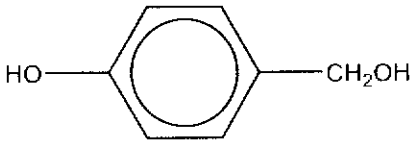
3 hot aqueous potassium dichromate(VI)

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

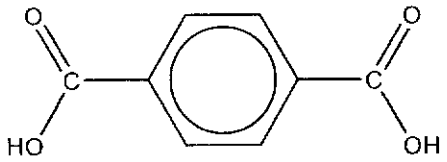
23 1 mole of compound Z reacts with 1 mole of NaOH. 1 mole of Z also reacts with PCl_5 to form 1 mole of HCl.

Which compounds can be Z?

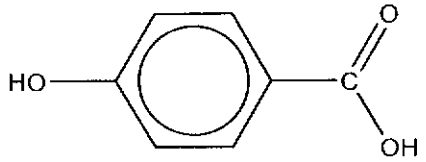
A



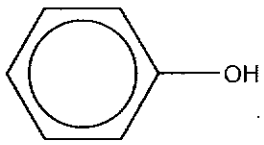
B



C



D



24 The dehydration of butan–2–ol to form but–2–ene is thought to involve the following steps.

step 1 $CH_3CH(OH)CH_2CH_3 + H_2SO_4 \rightleftharpoons CH_3CH(^+OH_2)CH_2CH_3 + HSO_4^-$

step 2 $CH_3CH(^+OH_2)CH_2CH_3 \xrightarrow{\text{slow}} CH_3\overset{+}{C}HCH_2CH_3 + H_2O$

step 3 $CH_3\overset{+}{C}HCH_2CH_3 + HSO_4^- \longrightarrow CH_3C{=}CHCH_3 + H_2SO_4$

Which of the following statements is incorrect?

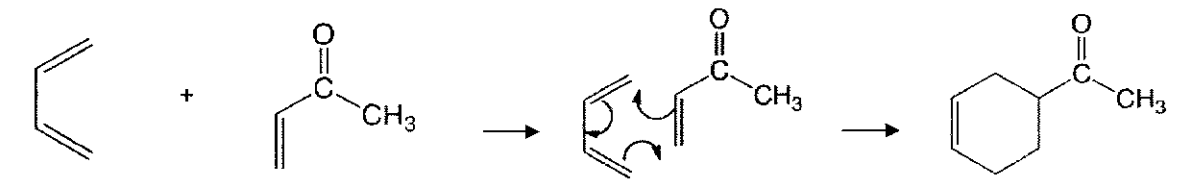
A Butan–2–ol serves as a base in step 1.

B H_2SO_4 is a catalyst in the dehydration reaction.

C A possible side product is $CH_3C(OSO_3H)CH_2CH_3$.

D Primary alcohols are more likely to proceed via this mechanism than tertiary alcohols.

25 The Diels–Alder reaction is an organic reaction between a conjugated diene and a substituted alkene to form a substituted cyclohexene system. One such reaction between buta–1,3–diene and but–3–en–2–one is shown below.

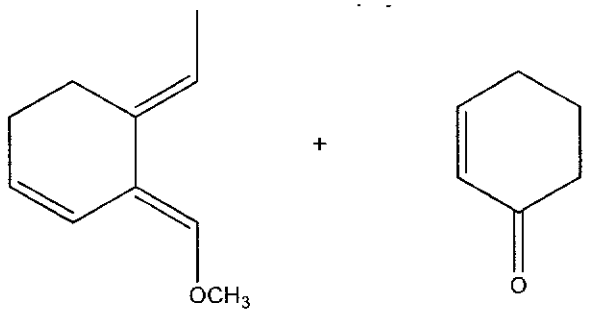


buta–1,3 –diene

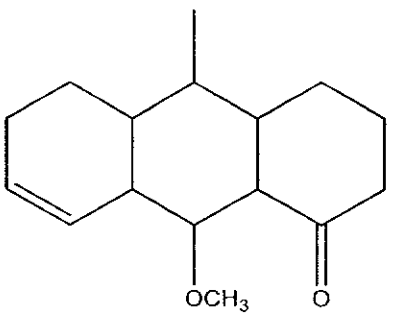
but–3–en–2–one

substituted cyclohexene

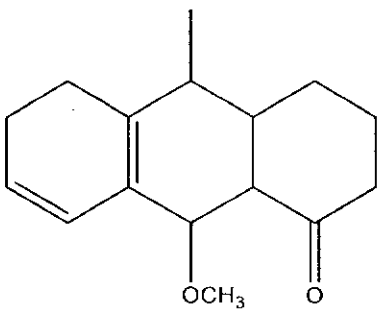
What would be the product formed when the following diene and substituted alkene reacts in a 1:1 ratio?



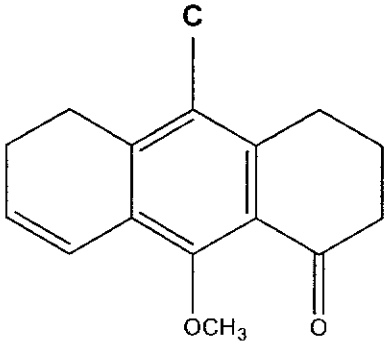
A



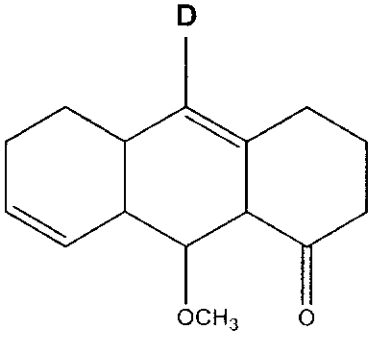
B



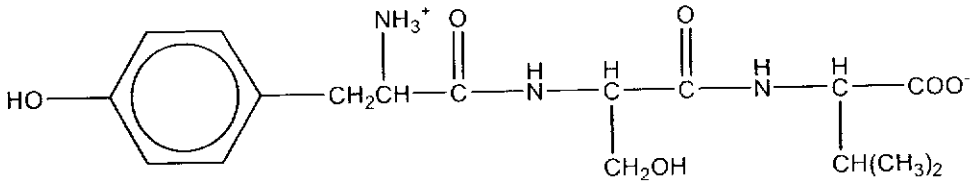
C



D

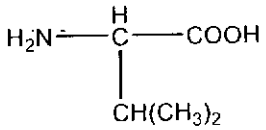


26 The therapeutic effect of tyroserleutide on lung cancer is currently being studied. It has the following structure:

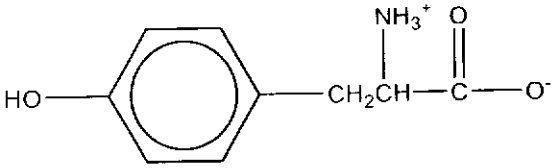


Which compound can be obtained when tyroserleutide reacts with hot dilute NaOH?

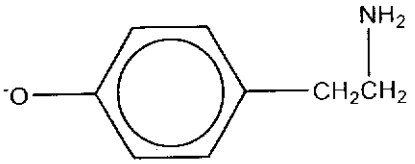
A



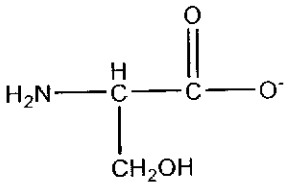
B



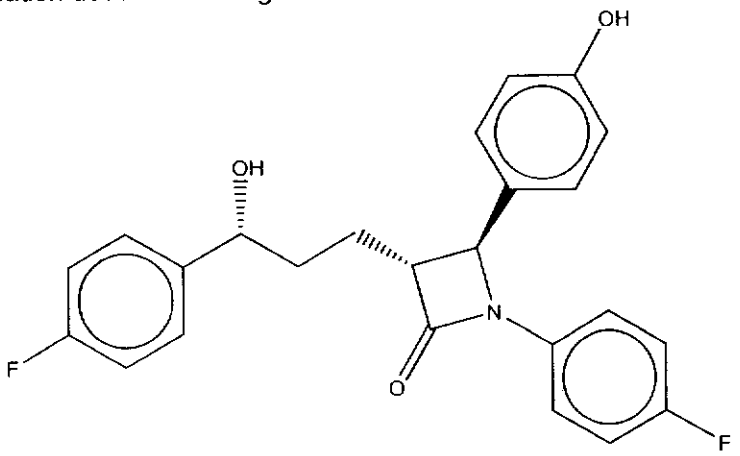
C



D



27 Ezetimibe is a medication used to treat high blood cholesterol.



Ezetimibe

When Ezetimibe is reacted with anhydrous $SOCl_2$, which groups will react?

A phenolic OH group

B halogenoarene

C alcoholic OH group

D amide group

28 Compounds of Period 3 elements dissolve in water to form aqueous solutions that are acidic, basic or neutral.

Which of the following sequence shows the order of increasing resultant pH when the compounds are added to water?

A $NaCl$, $MgCl_2$, $SiCl_4$

B $AlCl_3$, $SiCl_4$, PCl_5

C Al_2O_3, MgO, SO_2

D P_4O_{10}, SiO_2, MgO

29 Element Z is in Period 3 of the Periodic Table. The oxide of Z has a giant molecular structure while the chloride of Z is a simple molecule.

Which of the following statements about element Z and its compounds are correct?

1 Element Z is a solid at room temperature.

2 The oxide of Z reacts with water to give an acidic solution.

3 Element Z forms two chlorides with different oxidation states.

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

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

Some data relating to calcium and calcium chloride are as follows:

$Ca^{2+} + 2e^- \rightleftharpoons Ca$	$E^\ominus = -2.87$ V
Melting point of calcium chloride	782 °C

Which of the following is the most suitable method for extracting calcium metal from its ore?

A Electrolysis of aqueous calcium chloride.

B Electrolysis of molten calcium chloride.

C Reduction of calcium chloride with hydrogen.

D Reduction of calcium chloride with aluminium.

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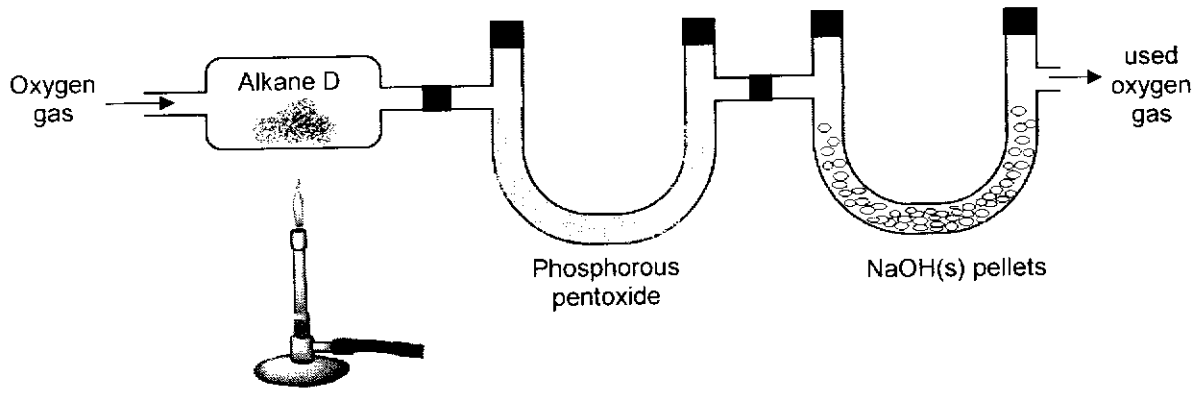
MCQ Answer Key:

1	2	3	4	5	6	7	8	9	10
D	B	B	A	C	D	C	B	C	C
11	12	13	14	15	16	17	18	19	20
D	A	A	C	D	A	B	B	C	D
21	22	23	24	25	26	27	28	29	30
A	A	A	D	B	D	C	D	A	B

1 A 1.00 g alkane D was burnt in an excess of oxygen, and the gases that were produced were first passed through a U-tube containing phosphorus pentoxide and another U-tube containing NaOH(s) as shown in the diagram. The phosphorus pentoxide U-tube increased in mass by 1.55 g, and the NaOH(aq) bottle increased in mass by 3.03 g. All volumes were measured at room temperature and pressure. What is the molecular formula of the alkane D?



A CH_4 **B** C_2H_5 **C** C_2H_6 **D** C_4H_{10}

Answer: D

Amount of H atoms = $2 \times 0.0861 = 0.1722$ mol
Amount of C atoms = 0.0689 mol
Ratio of H : C = 0.1722 0.0689 = 2.4992 : 1 = **5 : 2**

Since the molecular formula of an alkane is C_nH_{2n+2}, the molecular formula of alkane D must be $\mathbf{C_4H_{10}}$.

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

What do the ions $^{36}S^{2-}$ and $^{37}Cl^-$ have in common?

A Both ions have more electrons than neutrons.

B Both ions have the same electronic configuration.

C Both ions contains the same number of nucleons.

D $^{36}S^{2-}$ has a smaller angle of deflection than $^{37}Cl^-$ in an electric field.

Answer: B

Option A:
$^{36}S^{2-}$ has 16 protons, 20 neutrons and 18 electrons,
$^{37}Cl^-$ has 17 protons, 20 neutrons and 18 electrons.

Option B: Both ions are $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Option C:
$^{36}S^{2-}$ has 16 protons + 20 neutrons = 36 nucleons
$^{37}Cl^-$ has 17 protons + 20 neutrons = 37 nucleons

Option D:
angle of deflection = charge/mass,
$^{36}S^{2-}$ = 0.0556 > $^{37}Cl^-$, 0.0270

[Turn over

3 Boyle's law states that at constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure.

Which of the following statements shows application of Boyle's law?

1 Human lungs, inhalation and exhalation.

2 Spraying paint from a can.

3 Working of hot air balloon.

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

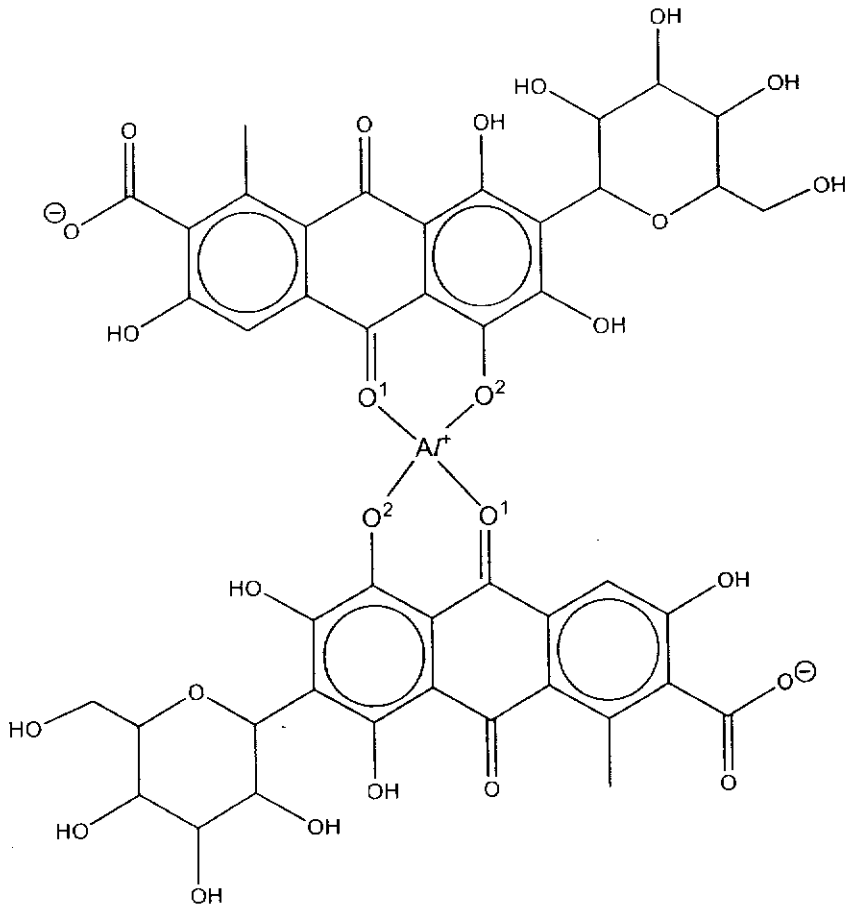
Answer: B

Option 1: correct. While inhaling, the lungs are filled with air; therefore, they expand. The volume increases hence, the pressure level goes down. Similarly, when the lungs are evacuated of air, they shrink; therefore, the volume reduces and the pressure increases.

Option 2: correct. When the top of the can is pressed, the volume inside the can gets reduced and the paint is thrown out with great pressure. Since the pressure has an inverse relationship with the volume, Boyle's law can be observed in action.

Option 3: Incorrect. On ignition of the fuel, the air inside the envelope heats up. This hot air expands as per Charles's law. As the temperature of the air increases, the volume of the air also increases and consequently, the density decreases. This makes the envelope lighter than the atmospheric air surrounding it. The buoyant force pushes the lighter envelope up in the air, and it flies.

4 Carmine is a red colorant extracted from the bodies of dead female insects, used in food colouring and lipsticks. The proposed structure of carmine is as shown.



The Al^{+} ion is situated in the centre of a planar arrangement of numbered oxygen atoms.
Which of the following descriptions of the bonds between Al^{+} and the numbered O atoms is most likely to be correct?

	O atoms numbered 1	O atoms numbered 2
A	co-ordinate	co-ordinate
B	co-ordinate	ionic
C	ionic	co-ordinate
D	ionic	ionic

Answer: A

Oxygen (in period 2) has 6 valence electrons and it cannot expand its octet. Oxygen 1 has lone pair available to form co-ordinate bond with Al^{3+}, hence oxygen has full octet. Oxygen 2 comes from O^{-}(phenoxide), forms co-ordinate bond with Al^{3+}*(high charge density)* , hence overall charge on *Al* is 1+. +3 -2(-1)= +1

5 The table shows the boiling point of some halogenoalkanes.

compound	boiling point/ °C
CH_3CH_2Cl	12.3
CH_3CH_2Br	34.8
CH_3CH_2I	70.0

Which of the following correctly explains the difference in the boiling point?

1 the electronegativity difference between the halogen and carbon increases from C–Cl to C–I

2 the strength of permanent dipole-permanent dipole attraction increases from C–Cl to C–I

3 the strength of instantaneous dipole-induced dipole attraction increases from CH_3CH_2Cl to CH_3CH_2I

4 the bond energy of C–X bond decreases from C–Cl to C–I

A 1 and 2 only **B** 2 and 4 only **C** 3 only **D** 4 only

Answer: C

N.B. H-bonding > pd-pd> id-id only if size of electron cloud of molecules are similar.

1 the electronegativity difference between the halogen and carbon should **decrease** from C–Cl to C–I. Statement **does not** explain for the trend of increasing boiling point from CH_3CH_2Cl to CH_3CH_2I.

2 the strength of permanent dipole-permanent dipole attraction **decreases** from C–Cl to C–I. The statement of option 2 is **incorrect** and **does not** explain for the trend of **increasing** boiling point from CH_3CH_2Cl to CH_3CH_2I.

3 the strength of instantaneous dipole-induced dipole attraction increases from CH_3CH_2Cl to CH_3CH_2I. Statement is **correct** as the total number of electrons increases from CH_3CH_2Cl to CH_3CH_2I and due to the increase in id-id attraction, the boiling point increases from CH_3CH_2Cl to CH_3CH_2I.

4 the bond energy of C-X bond decreases from C–Cl to C– I. Statement is correct but boiling does not break the C–X bond, so this **does not** explain for the trend of **increasing** boiling point from CH_3CH_2Cl to CH_3CH_2 I.

6 The radioactive decay of element X is a first-order reaction. It take 16 days for element X to decay to 25% of its initial value.

What fraction of element X would remain after 800 days?

A $\frac{1}{2^{10}}$ **B** $\frac{1}{2^{50}}$ **C** $\frac{1}{2^{80}}$ **D** $\frac{1}{2^{100}}$

Answer: D

Half-life = 8 days (1→0.5→0.25, 16 days 2 half-lives)

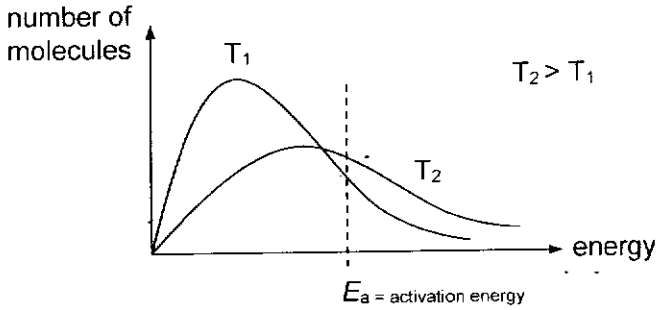
80 days = 100 x 8 days = 100 half-lives

Fraction of isotope remaining = $\left(\frac{1}{2}\right)^{100} = \frac{1}{2^{100}}$

7 The Boltzmann distribution of kinetic energies for the following equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57 \text{ kJ mol}^{-1}$$

is shown graphically below as temperature is increased.



Which statements can be drawn from the graph?

1 At all energies, the number of molecules of N_2O_4 of a given value increases.

2 The maximum of the curve lowers and shifts to the right.

3 The reaction is first order with respect to $[N_2O_4]$.

4 The number of molecules with energies equal or greater than *Ea* increases.

A 1, 2 and 3 only **B** 1 and 2 only **C** 2 and 4 only **D** 3 and 4 only

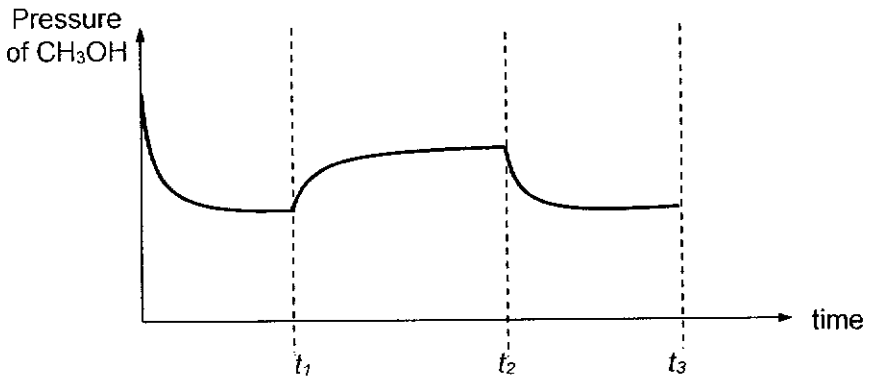
Answer: C

1 Incorrect as at the lower energy regions the number of molecules decreases when the temperature increases.
2 Correct as seen for the graph, at higher temperature, T2, the maximum of the curve lowers and shifts to the right.
3 Incorrect as you cannot deduce order of reaction from Boltzmann curve.
4 Correct. The number of molecules with energies above E_a increases as represented by area under the curve for T_2 is greater than T_1.

8 Methanol can be synthesised from hydrogen and carbon monoxide using a suitable catalyst at 480 K and a pressure of 3×10^6 Pa.

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -90.6 \text{ kJ mol}^{-1}$$

The reaction mixture reached equilibrium under the above conditions. The graph below shows how the pressure of CH_3OH varied with time.



What could be the changes made to the system at t_1 and t_2?

	t_1	t_2
A	CH_3OH was added	Temperature was decreased
B	CO was added	Temperature was increased
C	Temperature was decreased	CO was added
D	Temperature was increased	CH_3OH was added

Answer: B

At t_1: There was an increased in pressure of CH_3OH, indicating the position of equilibrium shifts right. This can be caused by either adding CO (POE shift right to remove excess CO) or decrease in temperature (POE shift right to increase heat as right, being exothermic, releases heat). Hence only Option B and C are correct for t_1.

At t_2: There was a decrease in pressure of CH_3OH, indicating the position of equilibrium shifts left. This can be caused by either adding CH_3OH (POE shift left to remove excess CH_3OH) or increase in temperature (POE shift left to decrease heat as left, being endothermic, absords heat). Hence only Option B and D are correct for t_2.

Hence, the answer is B as it is correct for both t_1 and t_2.

9 A quantity of ethanol was burned underneath a copper can containing 400 g of water at 30 °C. The temperature of the water rose to 85 °C after the complete combustion of 5 g of ethanol (M_r = 46.0).

The efficiency of heat transfer to the water will not be 100% after taking into considerations the heat capacity of the copper can and heat loss to surroundings.

Given that the specific heat capacity of water is 4.2 J g^{-1} K^{-1} and the enthalpy change of combustion of ethanol is –1367 kJ mol^{-1}, what is the efficiency of heat transfer to the water?

A 27% **B** 39% **C** 62% **D** 96%

Answer: C

Theoretical heat transferred = ΔH x amount of ethanol

= 1367 x 5/46

= 148.58 kJ

Experimental heat released = mcΔT

= 400 x 4.2 x 55

=92400 J = 92.4 kJ

% efficiency of heat transfer = 92.4/148.58 x 100% = 62%

10 Which equation corresponds to the enthalpy change stated?

A	$2Al^{3+}(g) + 3O^{2-}(g) \rightarrow Al_2O_3(s)$	$2\Delta H^{\ominus}_{\text{lattice energy}}(Al_2O_3(s))$
B	$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$	$\Delta H^{\ominus}_{\text{neutralisation}}(H_2O(l))$
C	$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2Cl^{-}(aq)$	$\Delta H^{\ominus}_{\text{solution}}(CaCl_2(s))$
D	$\frac{1}{4}P_4(s) + \frac{5}{2}O_2(g) \rightarrow \frac{1}{4}P_4O_{10}(s)$	$\Delta H^{\ominus}_{\text{formation}}(P_4O_{10}(s))$

Answer: C

A represents $\Delta H^{\ominus}_{\text{lattice energy}}(Al_2O_3(s))$.

B represents 2 × $\Delta H^{\ominus}_{\text{neutralisation}}$

D represents ¼ $\Delta H^{\ominus}_{\text{formation}}(P_4O_{10}(s))$

11 Calcium reacts with water to form calcium hydroxide and hydrogen.

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$$

The standard enthalpy change for this reaction can be measured in the laboratory.

What further information is needed in order to calculate the standard enthalpy change of formation of calcium hydroxide, $\Delta H_f^\ominus$?

1 $\Delta H_f^\ominus$ for $H_2O(l)$

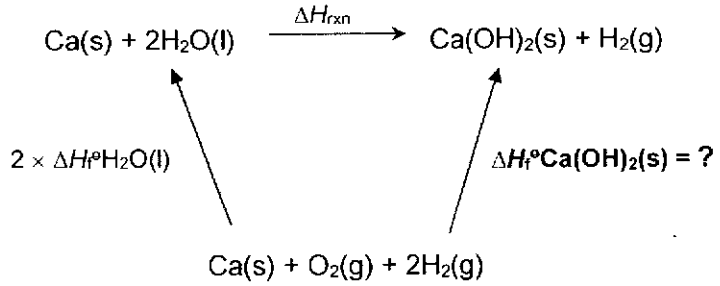
2 $\Delta H_f^\ominus$ for $H_2(g)$

3 $\Delta H_{atomisation}^\ominus$ for Ca(s)

4 first and second ionisation energies of Ca(s)

A 1, 3 and 4 only **B** 2, 3 and 4 only **C** 3 and 4 only **D** 1 only

Answer: D



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

Water undergoes self–ionisation according to the equation:

$$H_2O\ (l) \rightleftharpoons H^+(aq) + OH^-\ (aq)$$

At 60 °C, the ionic product of water, K_w, has the value of 9.5×10^{-14} mol^2 dm^{-6}.

Which statement concerning water at 60°C is correct?

A The pH is 6.51.

B $[OH^-] = 4.75 \times 10^{-7}$ mol dm^{-3}

C The water is slightly acidic.

D Heating water from 25 °C to 60 °C causes water to ionise to a lesser extent.

Answer: A

A is correct as $pH = -\log_{10}[H^+] = -\log_{10}(3.08 \times 10^{-7}) = 6.51$
B is incorrect as $[OH^-] = \sqrt{(9.5 \times 10^{-14})} = 3.08 \times 10^{-7}$ mol dm^{-3}
C is incorrect as water is still neutral as $[OH^-] = [H^+]$
D is incorrect as the ionisation of water is an endothermic process. An increase in temperature causes equilibrium position of $H_2O \rightleftharpoons H^+ + OH^-$ to shift right, causing water to ionise more instead.

13 Values of two solubility products are given

	K_{sp} value at 25 °C
$CaCO_3$	8.7×10^{-9}
CaF_2	4.0×10^{-11}

Solid $CaCO_3$ is shaken with water. The remaining solid is filtered off, leaving behind a saturation solution X.

Drops of $F^-(aq)$ are added to solution X until CaF_2 just precipitates. Which row of the table is correct?

	$[Ca^{2+}(aq)]$ in solution X / mol dm^{-3}	$[F^-(aq)]$ when CaF_2 just precipitates / mol dm^{-3}
A	9.33×10^{-5}	6.55×10^{-4}
B	9.33×10^{-5}	9.67×10^{-3}
C	2.15×10^{-4}	6.55×10^{-4}
D	2.15×10^{-4}	4.31×10^{-4}

Answer: A

$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

Let the solubility of $CaCO_3(s) = x$ mol dm^{-3}

$[Ca^{2+}(aq)] = x$ mol dm^{-3}; $[CO_3^{2-}(aq)] = x$ mol dm^{-3}

$K_{sp} = [Ca^{2+}][CO_3^{2-}] = (x) \times (x) = x^2 = 8.7 \times 10^{-9}$

$x = \sqrt{8.70 \times 10^{-9}} = 9.33 \times 10^{-5}$ mol dm^{-3}

$K_{sp} = [Ca^{2+}][F^-]^2 = 4.0 \times 10^{-11}$

$[9.33 \times 10^{-5}]\ [F^-]^2 = 4.0 \times 10^{-11}$

$[F^-] = 6.55 \times 10^{-4}$

14 Which factors determine the number of atoms of copper deposited on the cathode of an electrolytic cell?

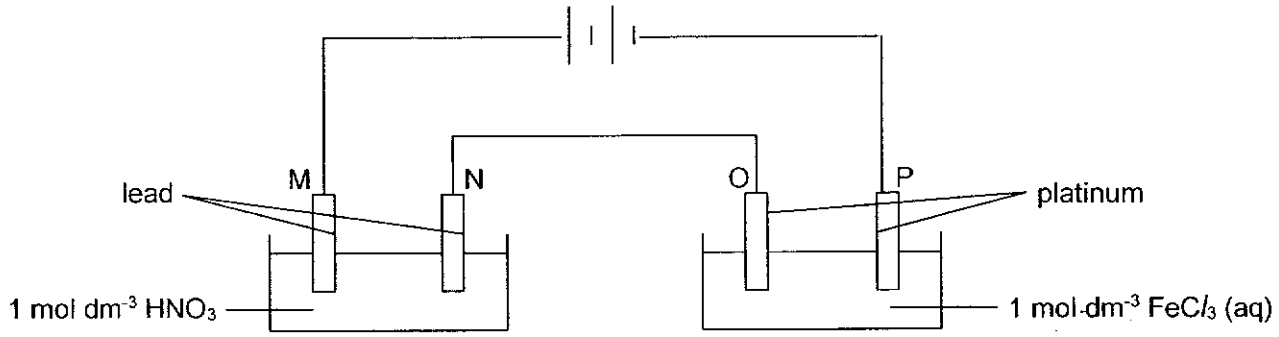
	current	time	$[Cu^{2+}(aq)]$	size of electrode
A	✓	✓	✓	✓
B	×	×	✓	✓
C	✓	✓	×	×
D	×	✓	✓	×

Answer: C

The amount of copper deposited depends on the amount of current and the time duration for the electrical charge to flow into the cathode, hence the formula Q = It.

It is not dependent on $[Cu^{2+}(aq)]$ and the size of electrode.

15 Two cells are connected in series as shown in the diagram where M, N, O and P are the electrodes.



Which of the following correctly shows the products formed at each electrode?

	M	N	O	P
A	O_2	H_2	O_2	Fe^{2+}
B	O_2	Pb	Cl_2	H_2
C	Pb^{2+}	H_2	Cl_2	H_2
D	Pb^{2+}	H_2	O_2	Fe^{2+}

Answer: D

From the battery, we can deduce that M and O are anode, N and P are cathode.

Oxidation will occur at M and O.
At M, Pb will be preferentially oxidised to form Pb^{2+} compared to water.

$Pb^{2+} + 2e^- \rightleftharpoons Pb$	– 0.13
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23

At O, water will be preferentially oxidised to from oxygen gas compared to chloride ions.

$Cl_2 + 2e^- \rightleftharpoons 2\ Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23

Reduction will occur at N and P.
At N, H^+ will be reduced to form hydrogen gas.

$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	– 0.83

At P, Fe^{3+} will be preferentially reduced to form Fe^{2+} compared to water molecules.

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	– 0.83

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

An excess of zinc reacts with a warm solution containing VO_2^+ ions.

What will be the final oxidation state of vanadium?

A +2 **B** +3 **C** +4 **D** +5

Answer: A

Excess Zn is the reducing agent which can reduce $VO_2^+(aq)$ to $V^{2+}(aq)$

$\mathbf{VO_2^+} + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$ +1.00
$Zn^{2+} + 2e^- \rightleftharpoons Zn$ –0.76
Ecell = +1.00 – (–0.76) =1.76V > 0

Excess Zn can further reduce $VO^{2+}(aq)$ to $V^{3+}(aq)$:
$VO^{2+} + 2H^+ + e \rightleftharpoons V^{3+} + H_2O$ + 0.34
$Zn^{2+} + 2e^- \rightleftharpoons Zn$ –0.76
Ecell = +0.34 – (–0.76) = 1.10V >0

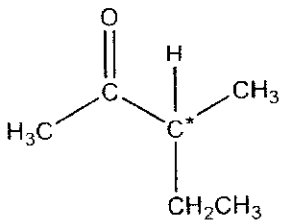
Excess Zn can further reduce $V^{3+}(aq)$ to $V^{2+}(aq)$:
$V^{3+} + e \rightleftharpoons V^{2+}$ -0.26
$Zn^{2+} + 2e^- \rightleftharpoons Zn$ –0.76
Ecell: –0.26 – (–0.76) = 0.50V > 0

Hence the final oxidation product of vanadium is V^{2+}.
i.e. final oxidation state of vanadium is **+2**.

17 What is the lowest number of carbon atoms a ketone molecule must contain to have chiral carbon atom?

A 5 **B** 6 **C** 7 **D** 8

Answer: B



18 When alkane G, C_6H_{14}, was reacted with bromine under ultraviolet light, it produced only three isomeric monobromo compounds.

What is the likely identity of alkane G?

1 $CH_3(CH_2)_4CH_3$

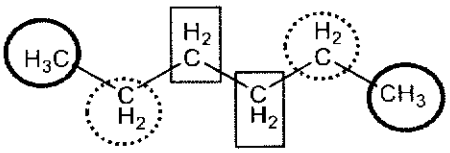
2 $CH_3CH_2CH(CH_3)CH_2CH_3$

3 $CH_3C(CH_3)_2CH_2CH_3$

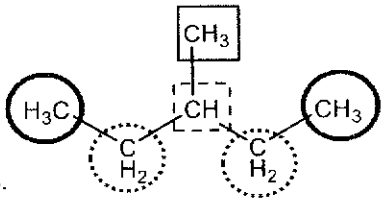
A 1 only **B** 1 and 3 only **C** 2 and 3 only **D** 1, 2 and 3

Answer: B

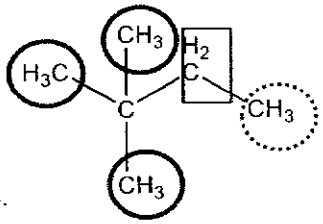
1. hexane can form 3 monobromo products.



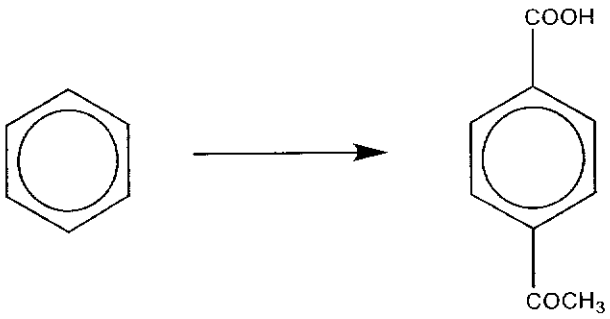
2. 3-methylpentane can form 4 monobromo products.



3. 2,2-dimethylbutane can form 3 monobromo products.



19 4-acetylbenzoic acid can be produced from benzene in three steps.



Which is the best method for this synthesis?

	step 1	step 2	step 3
A	CH_3COCl, anhydrous $FeCl_3$	CH_3Cl, anhydrous $FeCl_3$	dilute H_2SO_4, $KMnO_4$, heat
B	CH_3COCl, anhydrous $FeCl_3$	CH_3Cl, anhydrous $FeCl_3$	dilute H_2SO_4, $K_2Cr_2O_7$, heat
C	CH_3Cl, anhydrous $FeCl_3$	CH_3COCl, anhydrous $FeCl_3$	dilute H_2SO_4, $KMnO_4$, heat
D	CH_3Cl, anhydrous $FeCl_3$	dilute H_2SO_4, $KMnO_4$, heat	CH_3COCl, anhydrous $FeCl_3$

Answer: C

As the 2 substituents in 4-acetylbenzoic acid are on carbon 1 and 4, methyl group should be introduced onto the benzene ring first as it is 2,4-directing. The methyl group is only oxidised after CH_3CO- group is substituted as COOH group is 3-directing.

20 Which of the following property does benzene have because of the delocalised π electrons?

A Benzene is a good electrical conductor.

B Benzene undergoes addition reactions more readily than substitution reactions.

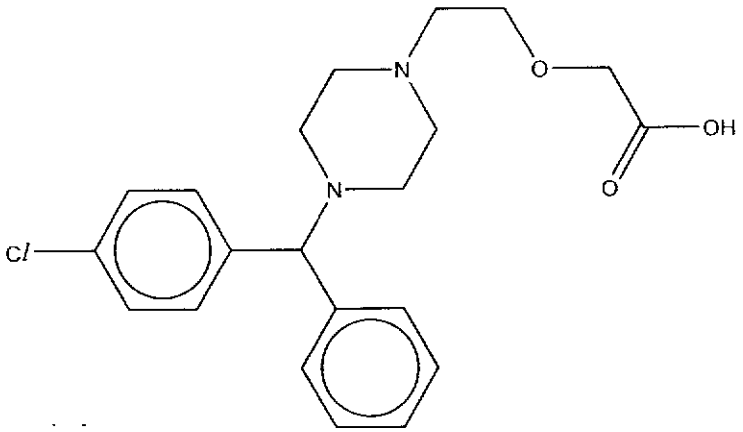
C Substitution in benzene occurs at one particular carbon atom.

D The carbon-carbon bond lengths are between those of C−C bonds and C=C bonds.

Answer: D

A: The electrons are only delocalised among the six carbon atoms, hence benzene cannot conduct electricity across molecules.
B: Benzene undergoes substitution reactions instead of addition to preserve the delocalised π electron cloud.
C: All six carbon atoms in benzene are identical and substitution can occur at any carbon atom.

21 Cetirizine is an antihistamine that is used to relieve allergy symptoms such as runny nose and itching.



cetirizine

The C-O-C bond is inert.
Which of the following statements about cetirizine are correct?

1 After heating with dilute sulfuric acid, 2 organic products are formed.

2 A white precipitate is observed when cetirizine is heated with ethanolic $AgNO_3$.

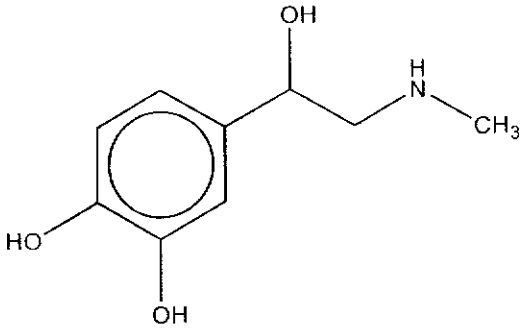
3 The purple colour of acidified $KMnO_4$ is discharged after heating with cetirizine.

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

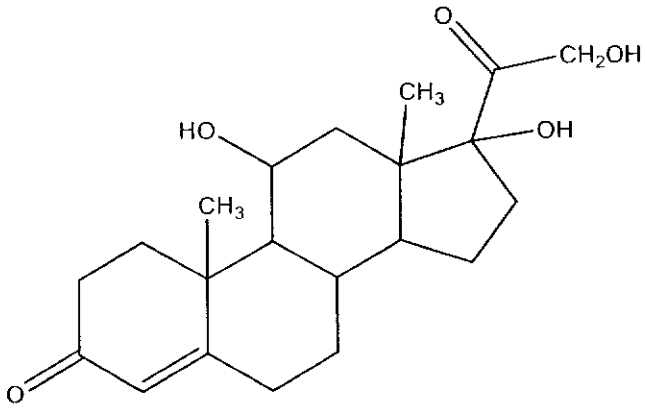
Answer: **A**

1: There are no functional groups that can undergo acidic hydrolysis.
2: Chlorobenzene is resistant towards hydrolysis and no precipitate will be formed.
3: There is a benzylic H that allows for side-chain oxidation to occur.

22 Adrenaline and cortisol are hormones that are produced by the adrenal glands.



adrenaline



cortisol

Which of the following reagents can be used to distinguish the two hormones?

1 neutral iron(III) chloride solution

2 bromine in tetrachloromethane

3 hot aqueous potassium dichromate(VI)

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

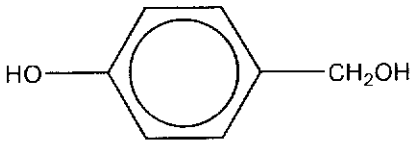
Answer: A

1: Only the phenol in adrenaline will give positive test.
2: The phenol in adrenaline will decolourise orange-red bromine while alkene in cortisol will also decolourise bromine.
3: Both adrenaline and cortisol contain primary or secondary alcohols that will be oxidised by potassium dichromate(VI).

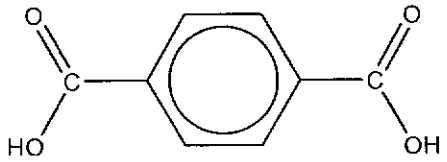
23 1 mole of compound Z reacts with 1 mole of NaOH. 1 mole of Z also reacts with PCl_5 to form 1 mole of HCl.

Which compounds can be Z?

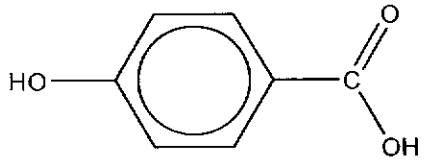
A



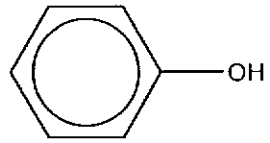
B



C



D

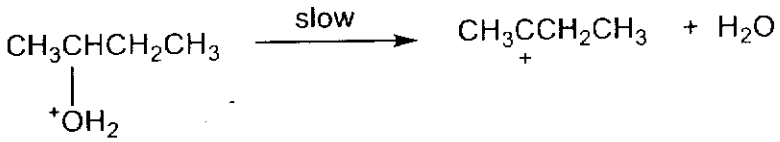


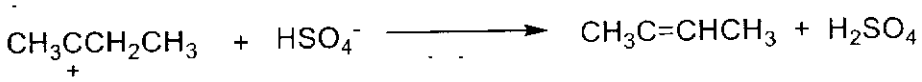
Answer: A

There is only 1 mole of phenol or carboxylic acid to undergo acid-base reaction with 1 mole of NaOH. There is only 1 mole of alcohol or carboxylic acid to undergo nucleophilic substitution with PCl_5.

24 The dehydration of butan–2–ol to form but–2–ene is thought to involve the following steps.

step 1 

step 2 

step 3 

Which of the following statements is incorrect?

A Butan–2–ol serves as a base in step 1.

B H_2SO_4 is a catalyst in the dehydration reaction.

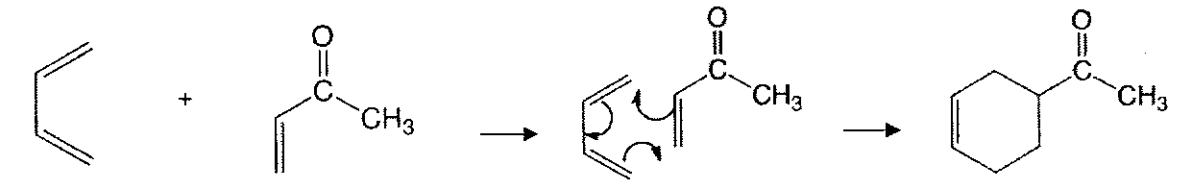
C A possible side product is $CH_3C(OSO_3H)CH_2CH_3$.

D Primary alcohols are more likely to proceed via this mechanism than tertiary alcohols.

Answer: D

A: Butan-2-ol acts as a Brønsted base and accepts a H^+ from H_2SO_4.
B: H_2SO_4 is reacted in step 1 and regenerated at the end of step 3, acting as a catalyst.
C: HSO_4^- can act as a nucleophile and be attracted to the carbocation $CH_3C^+CH_2CH_3$ to form the side product.
D: Tertiary carbocations are more stable than primary carbocations due to the presence of more electron-donating alkyl groups to disperse the positive charge on C^+, hence tertiary alcohols are more likely to react via this mechanism (E1).

25 The Diels–Alder reaction is an organic reaction between a conjugated diene and a substituted alkene to form a substituted cyclohexene system. One such reaction between buta–1,3–diene and but–3–en–2–one is shown below.

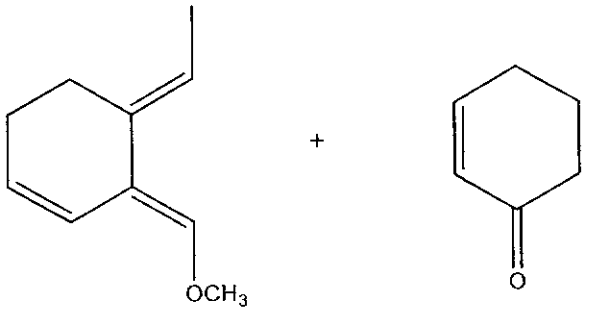


buta–1,3 –diene

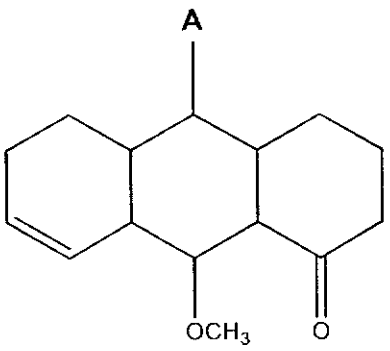
but–3–en–2–one

substituted cyclohexene

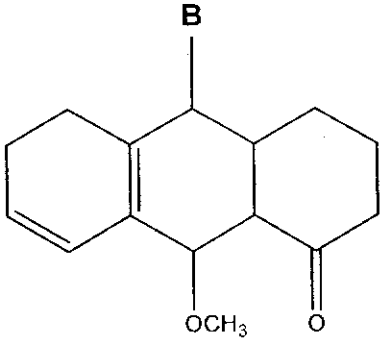
What would be the product formed when the following diene and substituted alkene reacts in a 1:1 ratio?



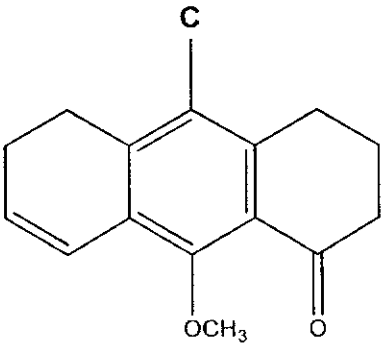
A



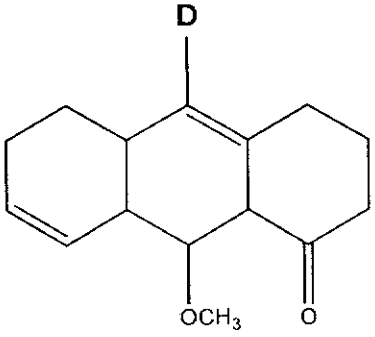
B



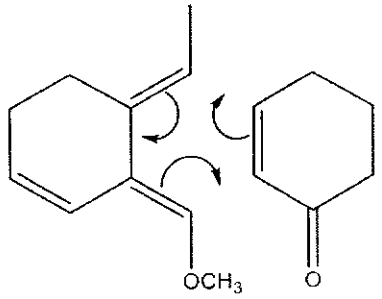
C



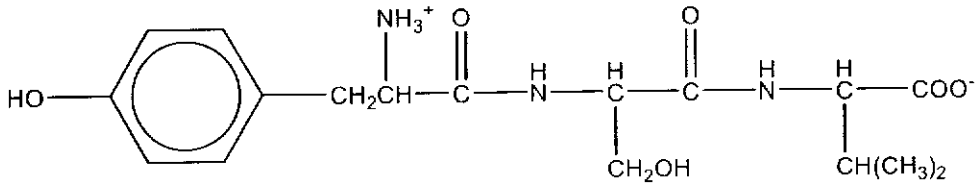
D



Answer: B

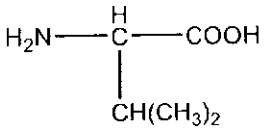


26 The therapeutic effect of tyroserleutide on lung cancer is currently being studied. It has the following structure:

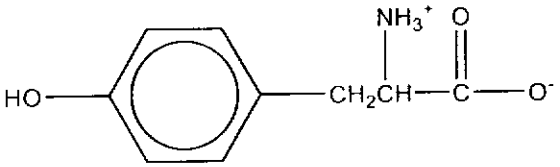


Which compound can be obtained when tyroserleutide reacts with hot dilute NaOH?

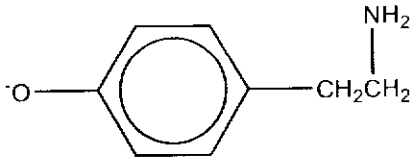
A



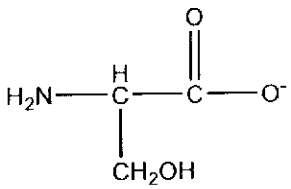
B



C

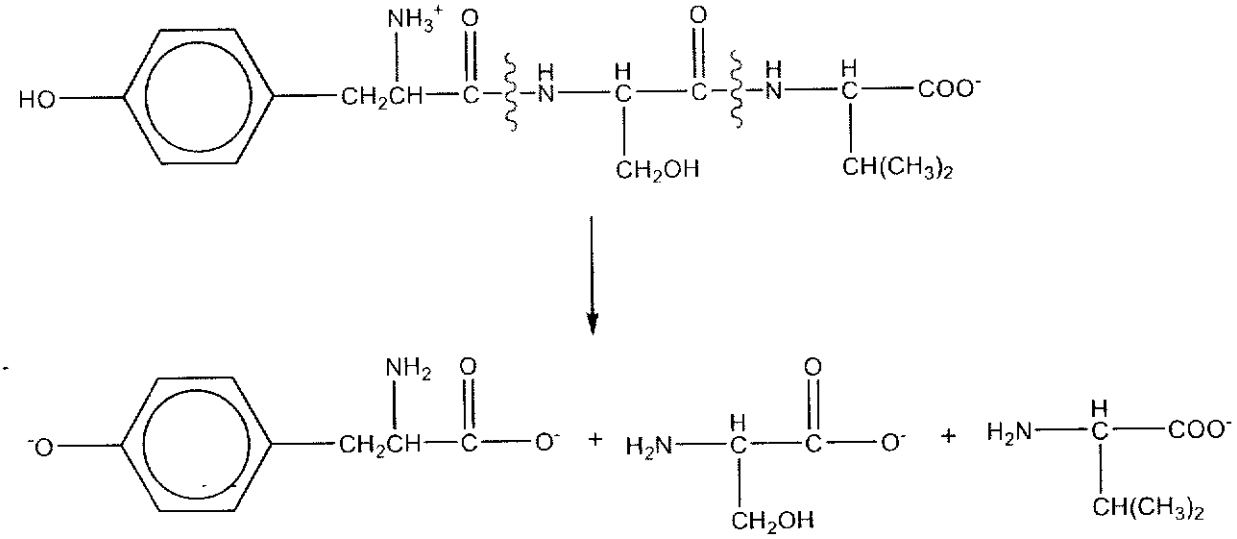


D

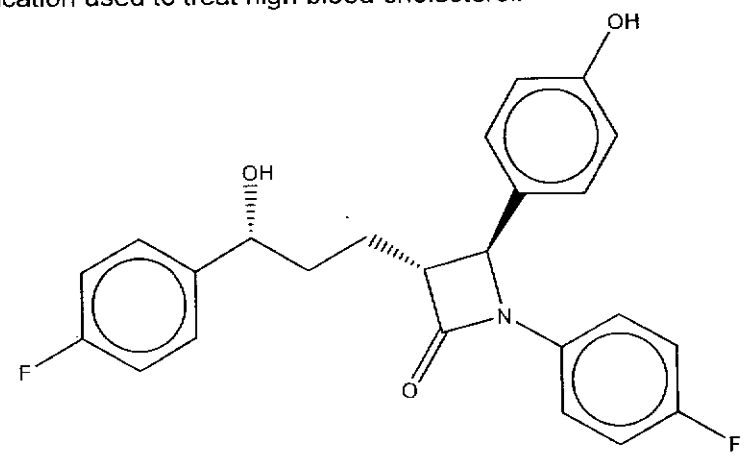


Answer: D

The amide functional groups will undergo alkaline hydrolysis to form amine and carboxylate ion. Phenol will undergo acid-base reaction to form phenoxide while alcohol is too weak of an acid and will not react with NaOH.



27 Ezetimibe is a medication used to treat high blood cholesterol.



Ezetimibe

When Ezetimibe is reacted with anhydrous $SOCl_2$, which groups will react?

A phenolic OH group

B halogenoarene

C alcoholic OH group

D amide group

Answer: C

The phenolic OH group does not undergo nucleophilic substitution as the C-O bond is strong.
The alcoholic OH undergoes nucleophilic substitution.
The halogenoarene and amide does not react.

28 Compounds of Period 3 elements dissolve in water to form aqueous solutions that are acidic, basic or neutral.

Which of the following sequence shows the order of increasing resultant pH when the compounds are added to water?

A $NaCl$, $MgCl_2$, $SiCl_4$

B $AlCl_3$, $SiCl_4$, PCl_5

C Al_2O_3, MgO, SO_2

D P_4O_{10}, SiO_2, MgO

Answer: D
pH 2, pH 7, pH 9

29 Element Z is in Period 3 of the Periodic Table. The oxide of Z has a giant molecular structure while the chloride of Z is a simple molecule.

Which of the following statements about element Z and its compounds are correct?

1 Element Z is a solid at room temperature.

2 The oxide of Z reacts with water to give an acidic solution.

3 Element Z forms two chlorides with different oxidation states.

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

Answer: A

Since the oxide of **Z** has a giant molecular structure, **Z** must be **silicon**. Hence, the chloride of **Z** is silicon tetrachloride which is indeed a simple molecule.

Silicon has a high melting point so it is a solid at room temperature.
Silicon oxide is insoluble in water.
Silicon forms only one chloride, $SiCl_4$.
Thus, statements 2 and 3 are incorrect.

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

Some data relating to calcium and calcium chloride are as follows:

$Ca^{2+} + 2e^- \rightleftharpoons Ca$	$E^e = -2.87$ V
Melting point of calcium chloride	782 °C

Which of the following is the most suitable method for extracting calcium metal from its ore?

A Electrolysis of aqueous calcium chloride.

B Electrolysis of molten calcium chloride.

C Reduction of calcium chloride with hydrogen.

D Reduction of calcium chloride with aluminium.

Answer: B

The large negative electrode potential of Group 2 elements makes it difficult to reduce their positive ions into metal by chemical agents since the group 2 metals are strong reducing agents.

	$E^{\ominus}$/V
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	– 2.87
$Al^{3+} + 3e^- \rightleftharpoons Al$	– 1.66
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	– 0.83

Electrolysis of aqueous solution of calcium chloride results in preferential discharge of water at the cathode instead of calcium since reduction potential of water occurs with more positive standard $E^{\ominus}$ value, $E^{\ominus}H_2O/H_2$= -0.83V

YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

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 **1** 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]

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

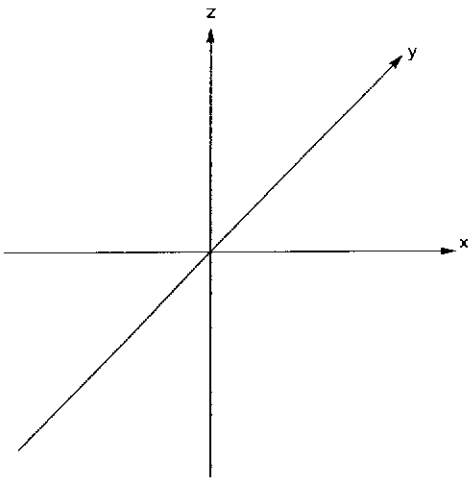


Fig 1.1

[1]

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

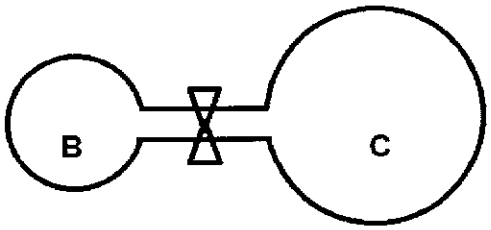


Fig. 1.2

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.

[2]

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

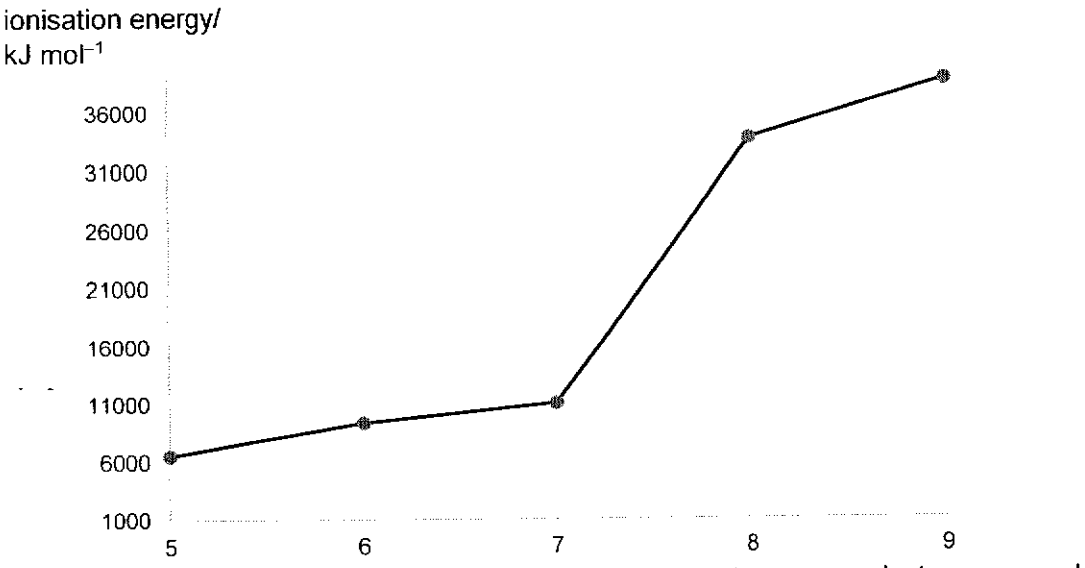


Fig.1.3

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

.....

.....

..... [2]

(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]

[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]

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

.....

..... [1]

(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]

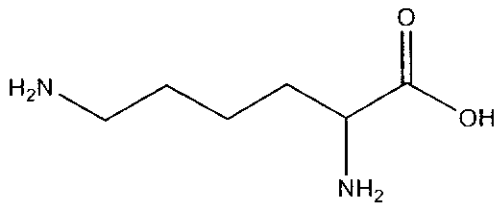
(b) Adding equimolar of 1,2–ethanediamine and phosgene, $COCl_2$ produced a cyclic compound **V** with molecular formula $C_3H_6ON_2$. Suggest the structure of compound **V**.

[1]

[Total: 5]

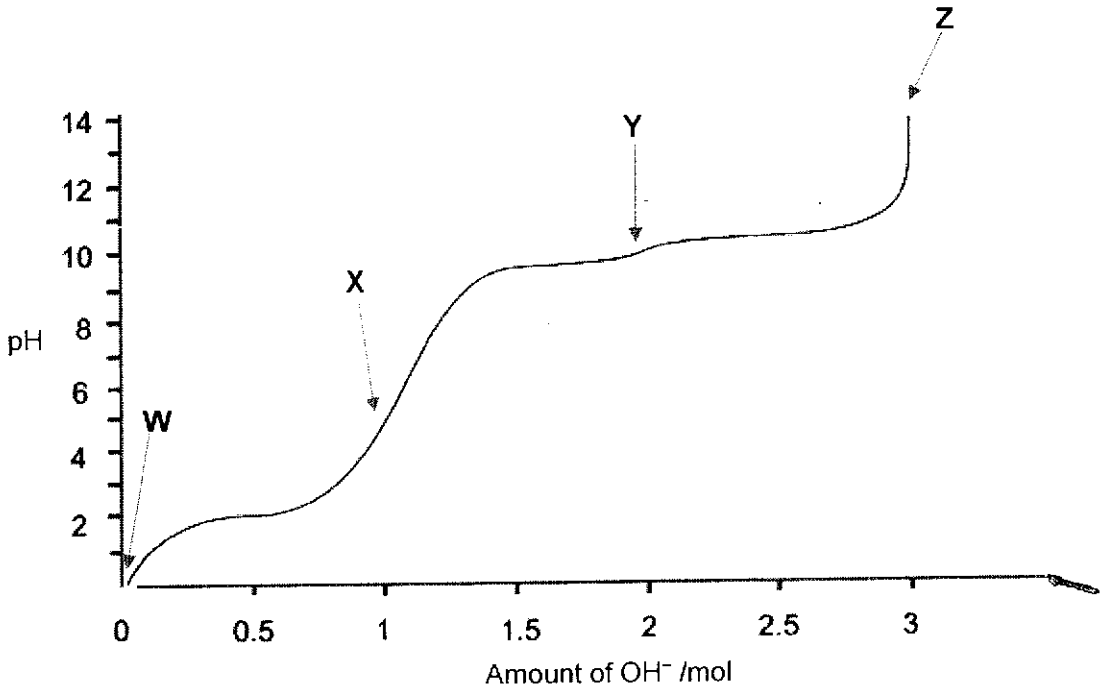
3 Lysine is an essential amino acid that cannot be synthesised by the human body and must be obtained from the diet. It is found in legumes such as peas, and animal products such as beef and fish.

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.

W	X
Y	**Z**

[4]

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

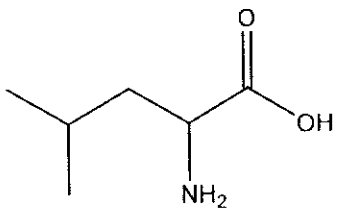
.....

.....

.....

..... [2]

(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.

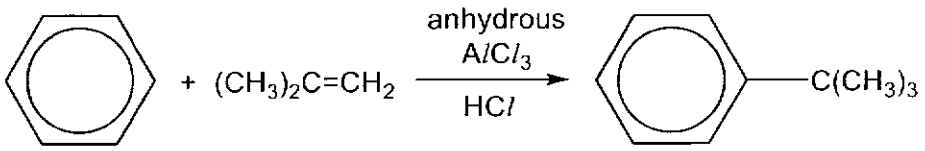
(i) Suggest the structure of compound **A**.

[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]

(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]

(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]

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

..... [1]

(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}.

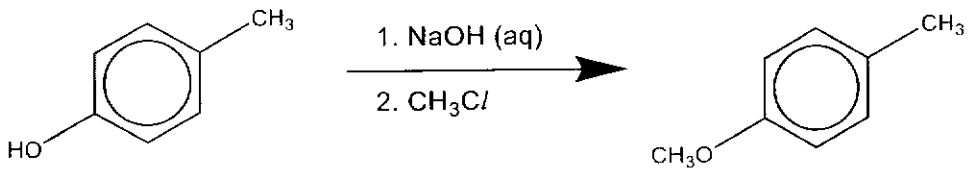
[2]

(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 $Cu(OH)_2$.

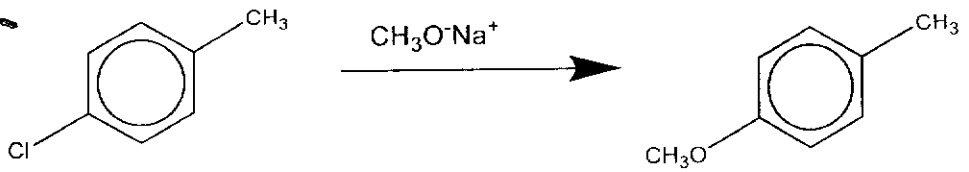
[1]

(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]

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

.....

.....

..... [2]

[Total: 17]

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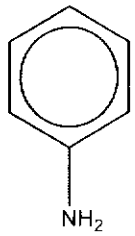
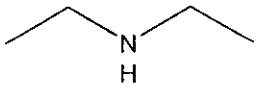
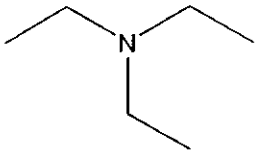
5 (a) Table 5.1 below gives the pK_b values of some weak bases.

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.

.....

.....

.....

.....

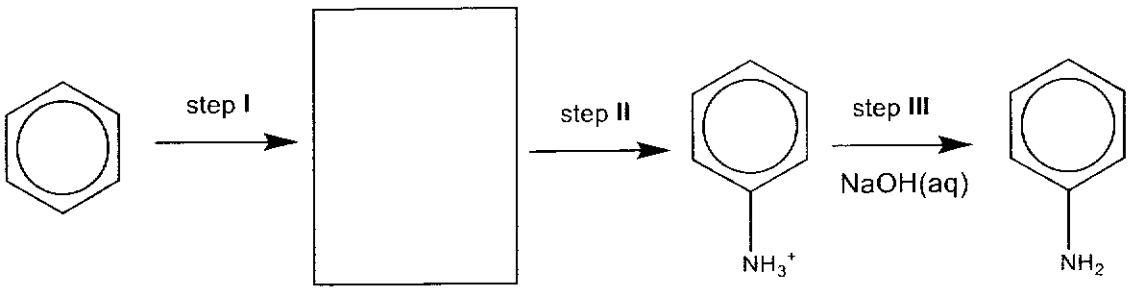
.....

..... [3]

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

[2]

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



E

(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.

type of reaction: .....

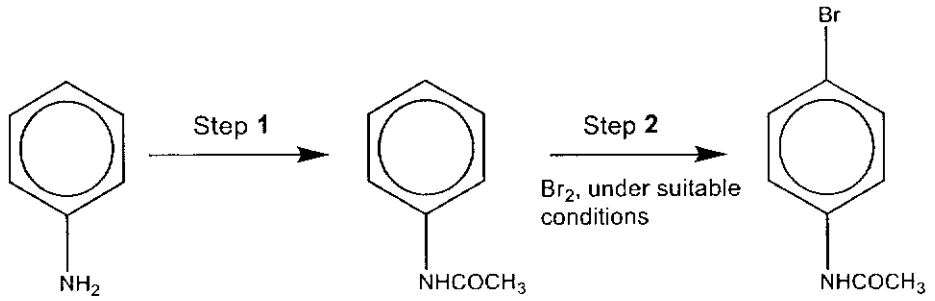
reagents and conditions: .....

[2]

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

..... [1]

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



F

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

..... [1]

(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, NaOCl as oxidising agent in an aqueous alkaline medium.

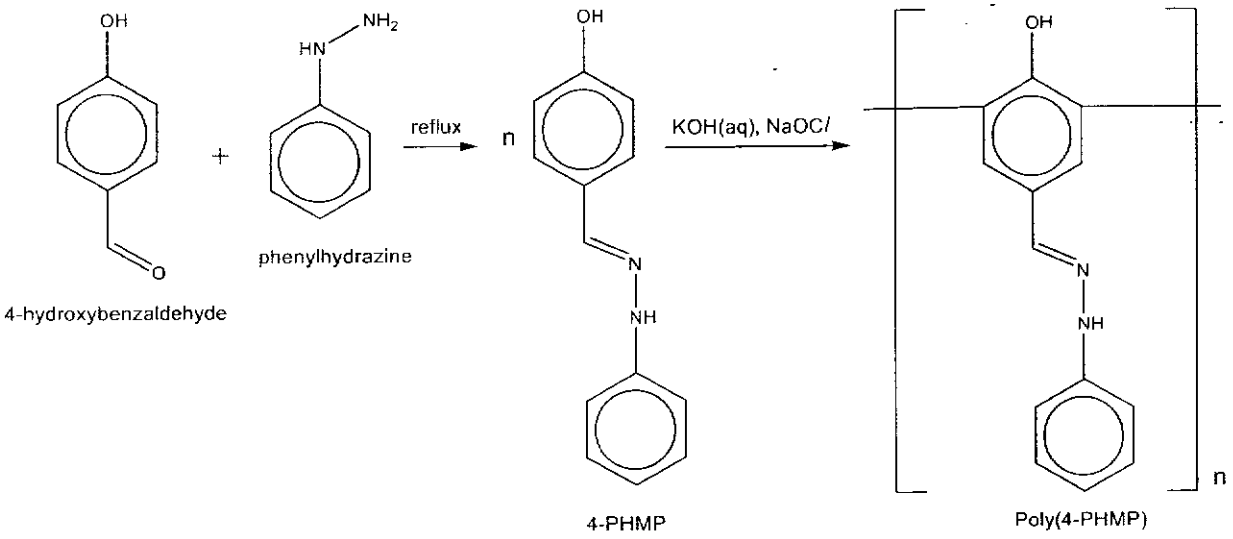


Fig. 6.1

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]

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

[2]

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

[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 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 NaOC*l*.

2. After heating to 50°C, 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 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]

(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]

(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]

(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]

(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).

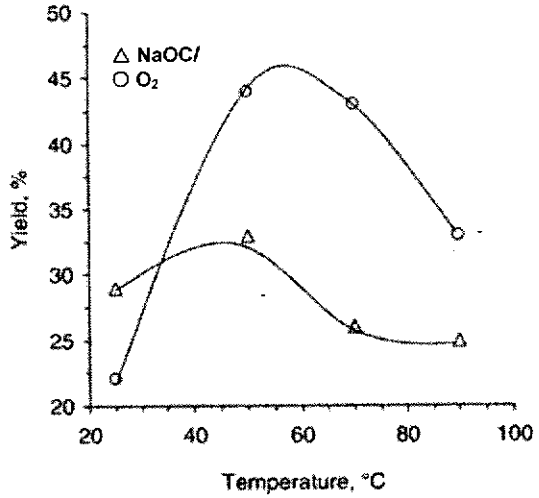


Fig 6.2a

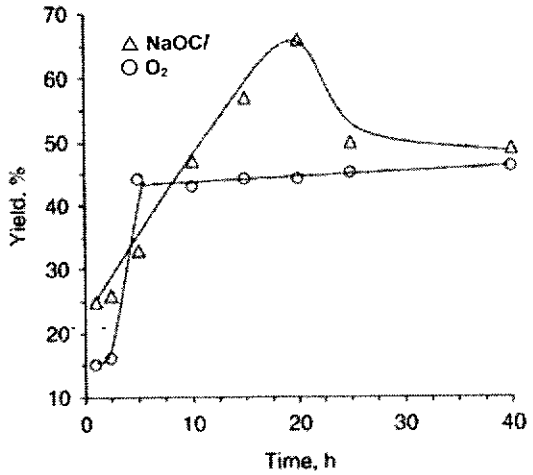


Fig 6.2b

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*.

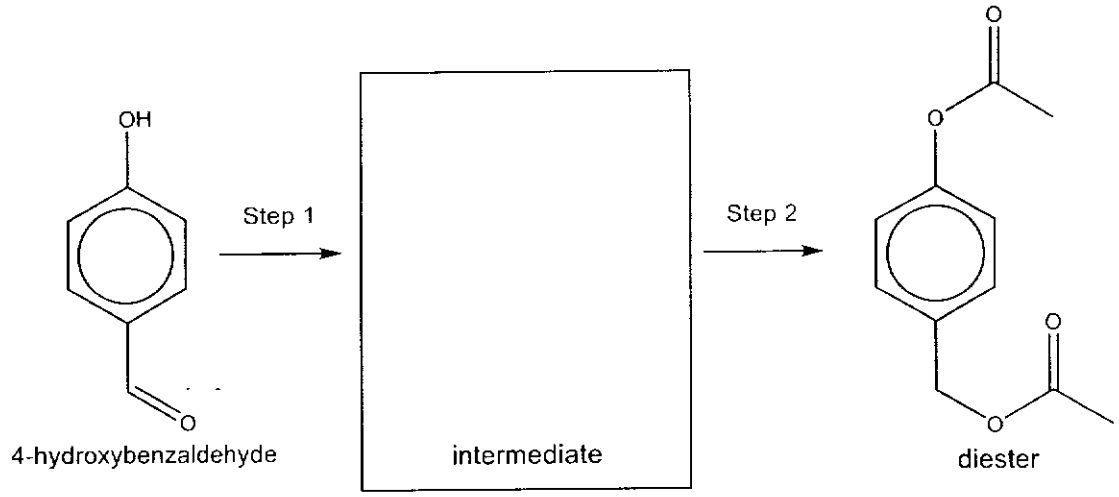
Using NaOC*l*: ..... [1]

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

.....

..... [1]

(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]

(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]

(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 **(d)(i)**, calculate the oxygen saturation in blood for a man who has the same $[O_2]$ as in **(d)(i)**.

[1]

(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.

Based on you answer in **(e)(ii)**, suggest whether the man needs to seek doctor's advice based on his oxygen saturation in blood.

.....

..... [1]

[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.

Shape: ..... [2]

(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]

(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]

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

..... [1]

[Total: 6]

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.

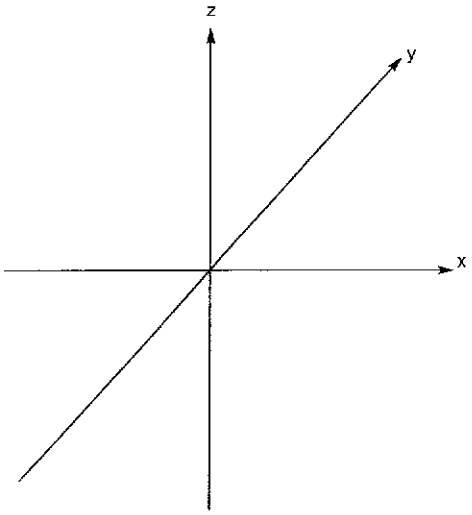
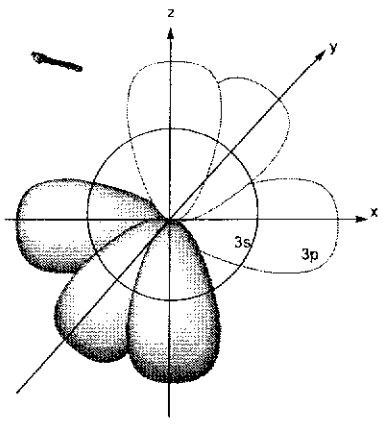


Fig 1.1

[1]



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

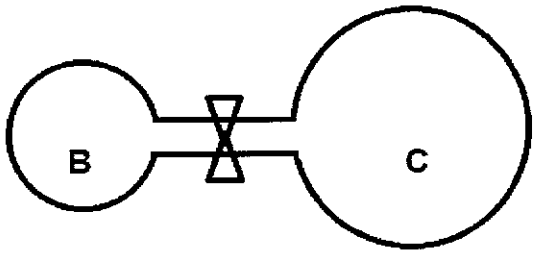


Fig. 1.2

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,

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

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

$P_2(1172V) = 3.73 \times 10^7 V$

$P_2 = 31825.9$
$= 31800$ 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.

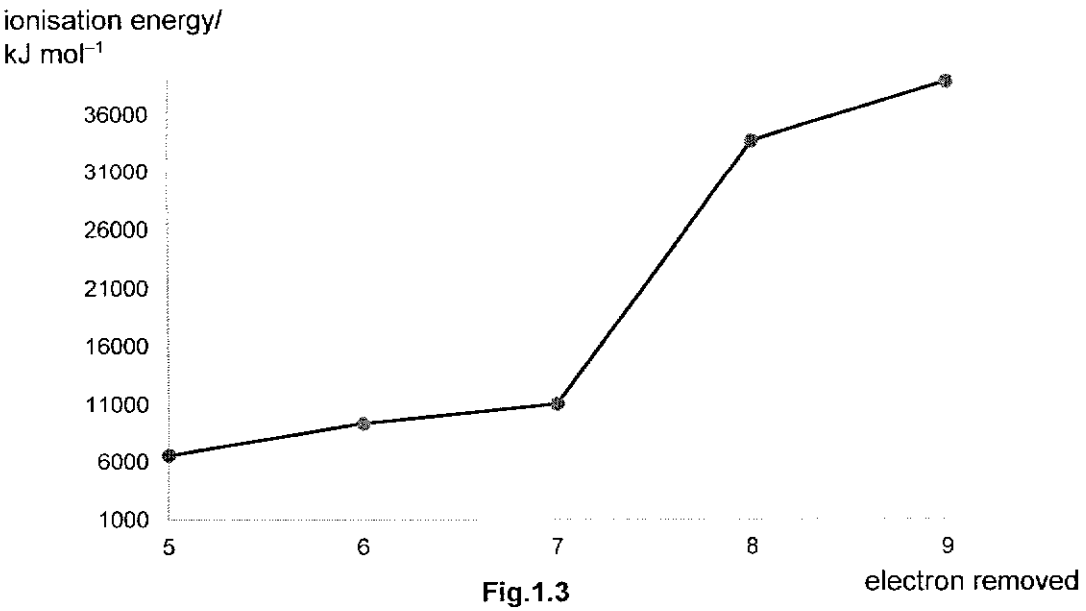


Fig.1.3

(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.

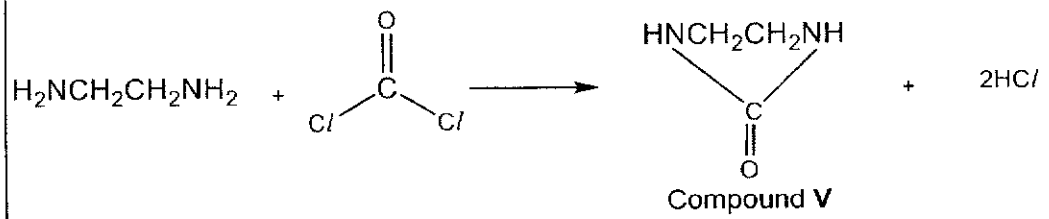
[2]

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, $COCl_2$ produced a cyclic compound **V** with molecular formula $C_3H_6ON_2$. Suggest the structure of compound **V.**

[1]

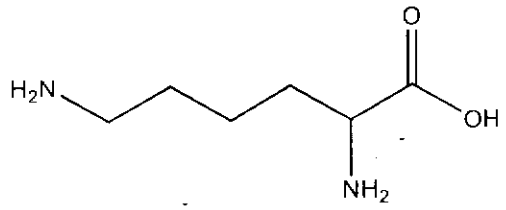


Compound **V**

[Total: 5]

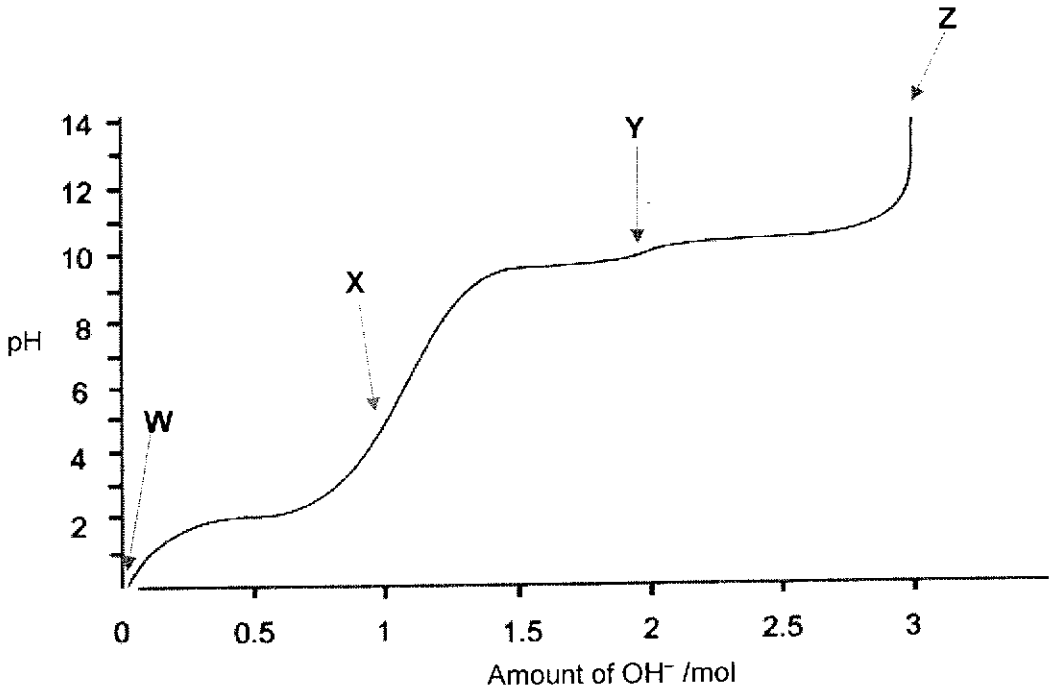
3 Lysine is an essential amino acid that cannot be synthesised by the human body and must be obtained from the diet. It is found in legumes such as peas, and animal products such as beef and fish.

The structure of lysine is given below.

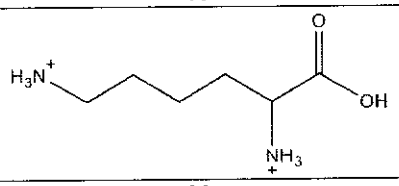
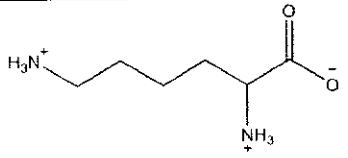
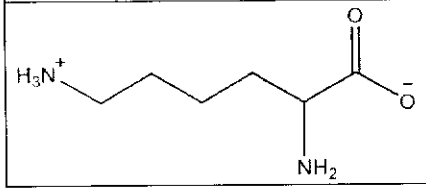
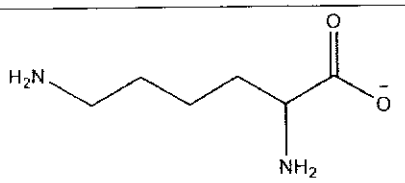


lysine

(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]

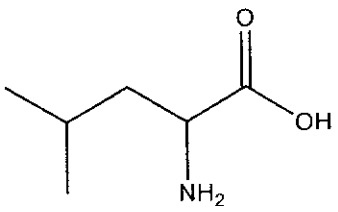
(ii) Explain why the melting point of lysine is high, in terms of structure and bonding.

[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.

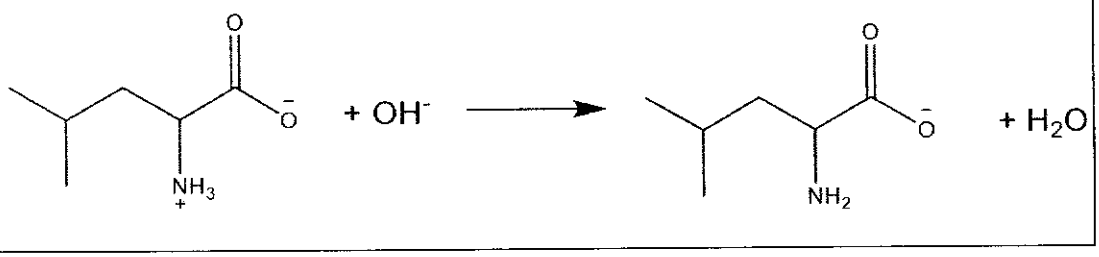
(b) Leucine is another essential amino acid that is mainly found in legumes.



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]



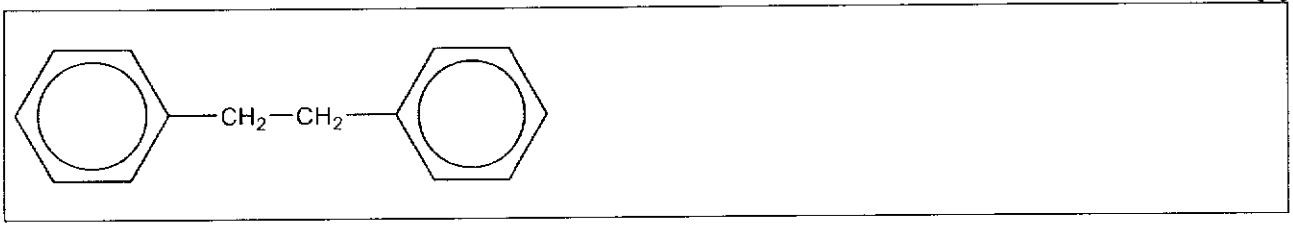
[Total: 7]

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.

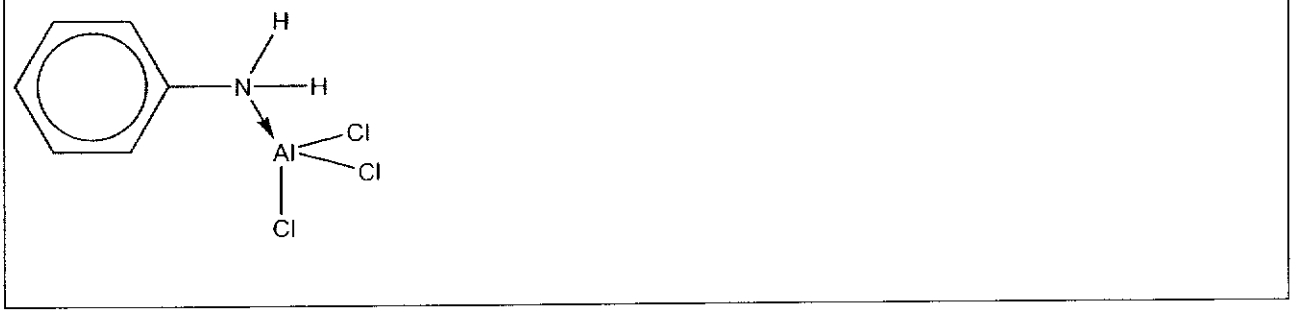
(i) Suggest the structure of compound **A**.

[1]

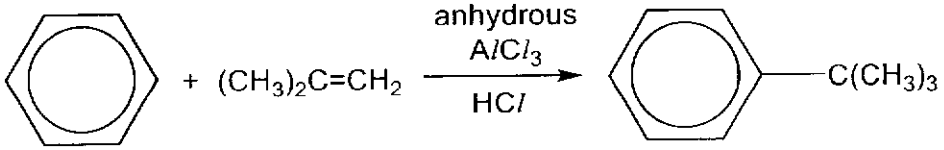


(ii) Unlike benzene, phenylamine does **not** undergo Friedel-Crafts alkylation with halogenoalkanes in the presence of $AlCl_3$. This is because the amine reacts with $AlCl_3$ to form a neutral compound **B**. Draw the **displayed** formula of **B**.

[1]



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

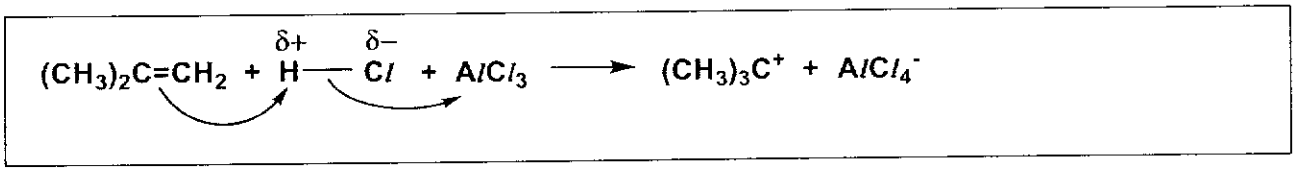


C

(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]

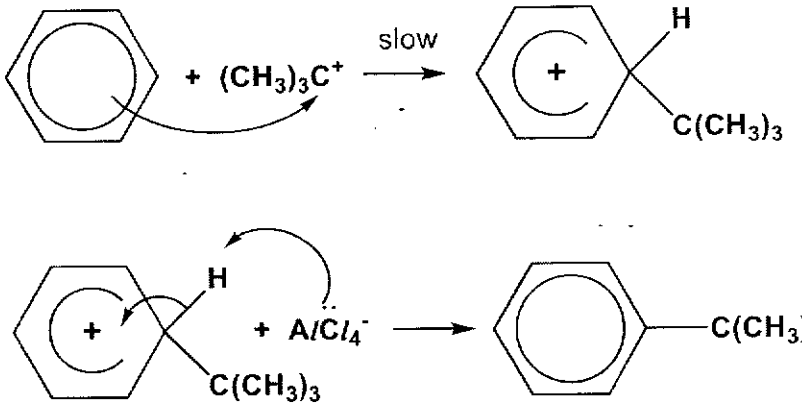


(ii) Name and outline the mechanism of the reaction to form compound **C**.

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

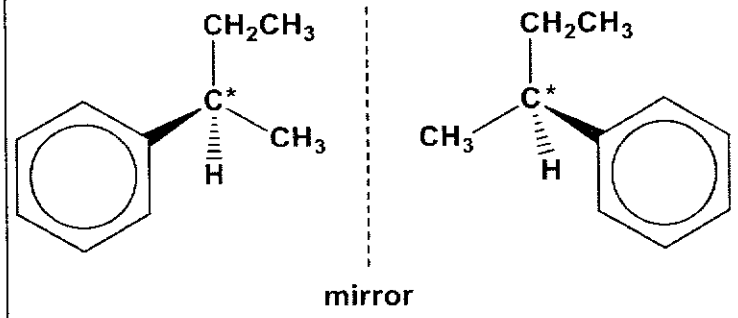
[2]

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]

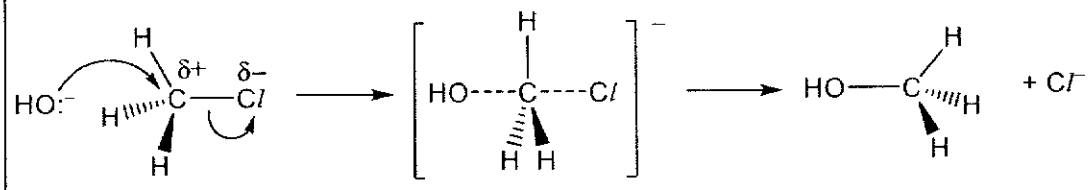


(c) Chloromethane, CH_3Cl, can be hydrolysed by aqueous sodium hydroxide. The rate equation was experimentally determined to be rate = k $[CH_3Cl]$ $[OH^-]$

(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]

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

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

$\quad\quad\quad\quad\quad\quad\quad\quad x \quad\quad 2x$

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

$x = 1.7652 \times 10^{-7}$ 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]

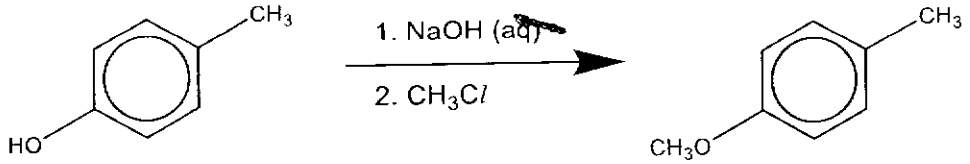
$$[Cu^{2+}][\frac{0.250}{2}]^2 \geq 2.2 \times 10^{-20}$$

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

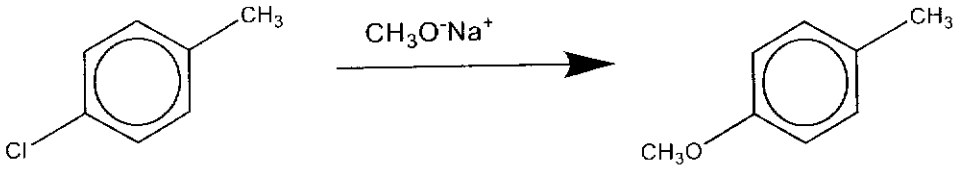
minimum $[Cu^{2+}]$ in sample = $2 \times 1.41 \times 10^{-18}$ = **2.82×10^{-18} mol dm^{-3}**

(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.

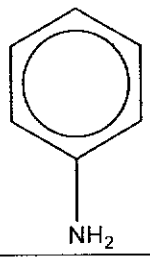
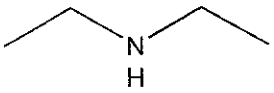
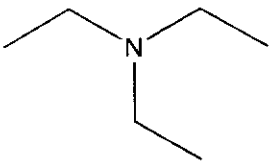
In Route 2, the **delocalisation of the lone pair of electrons on the C*l* atom into the benzene ring** resulted in the **C–C*l* bond having a partial double bond character/becoming stronger**,
OR
The (π electron cloud of the) **benzene ring will repel** (the lone pair of electrons of) **an incoming 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.

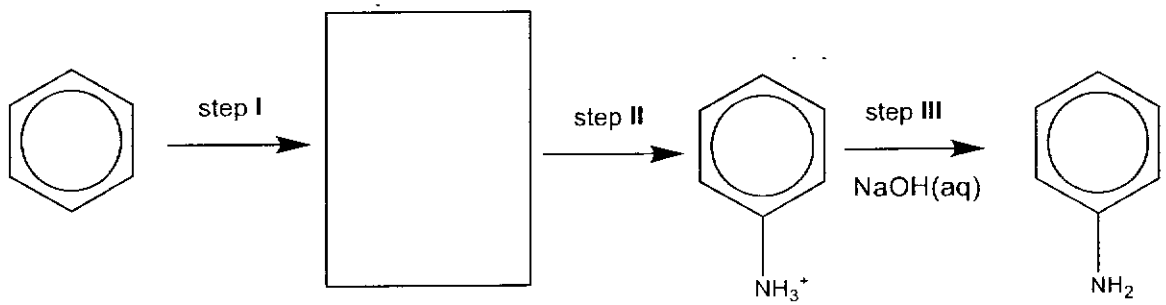
[2]

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

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

pH = 14 – pOH = **8.96**

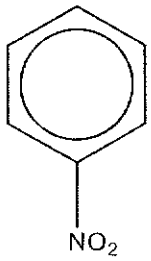
(b) Phenylamine can be synthesised from benzene in a three-step process as shown below.



E

(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]

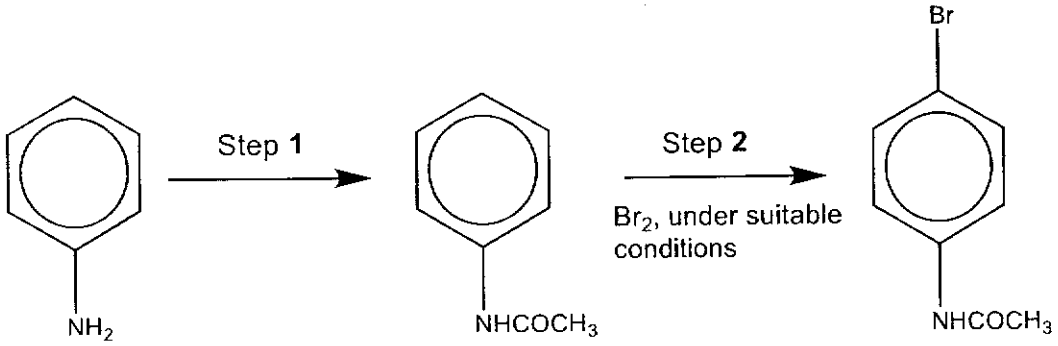
Reduction
Sn, concentrated HC*l*, heat

(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

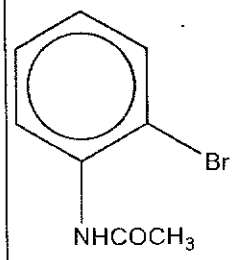
(i) State the reagent used in step **1**.

[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.

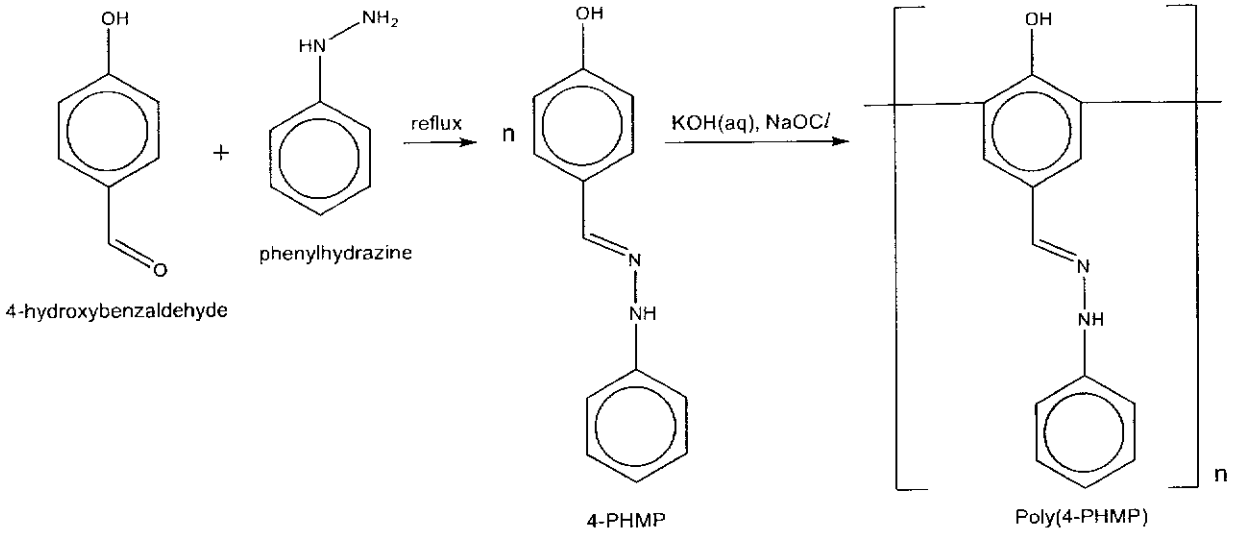


Fig. 6.1

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.

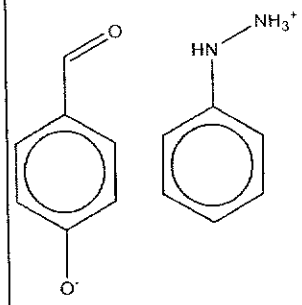
[2]

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 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 NaOC*l*.

2. After heating to 50°C, 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 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).

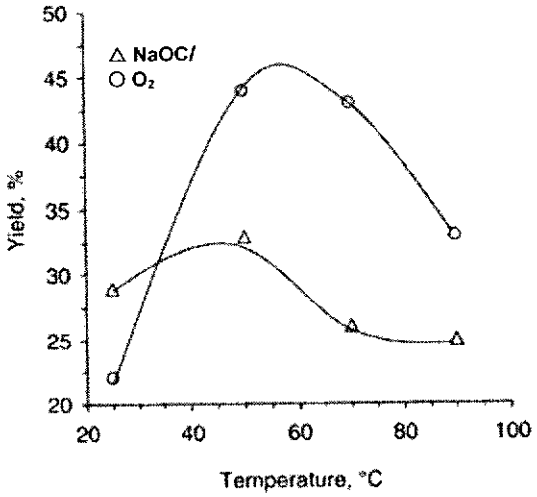


Fig 6.2a

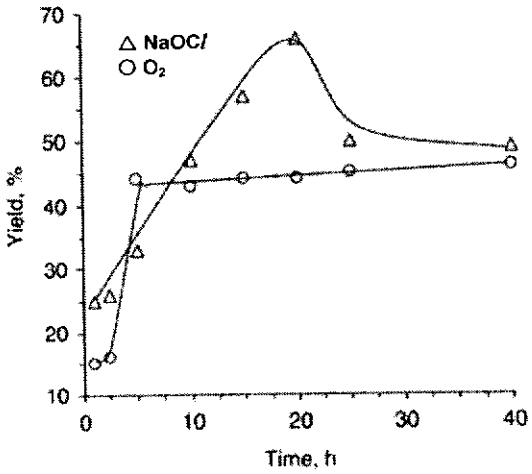


Fig 6.2b

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]

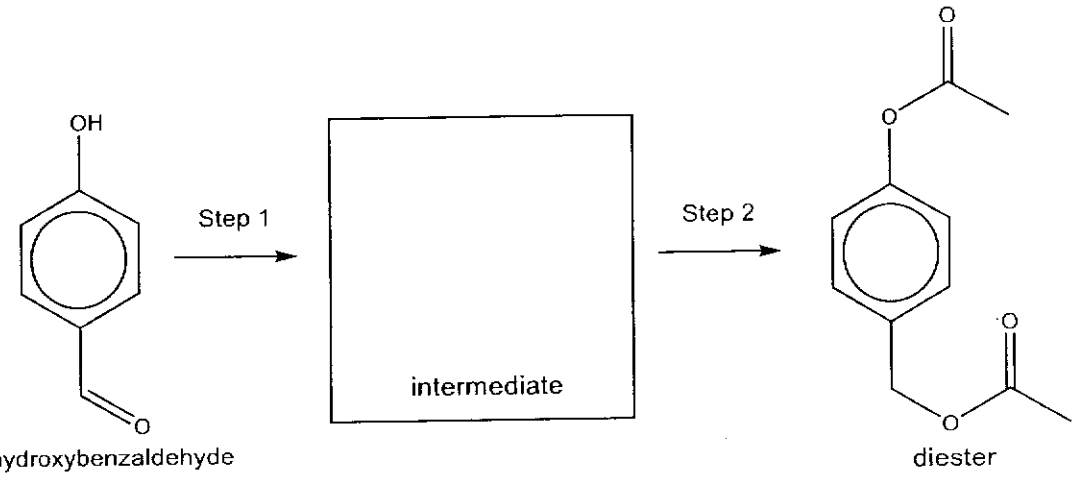
Using NaOC*l*: 45-50 °C for 20 h

(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.

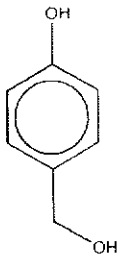
Step 1:

Step 2:

[3]

Step 1: LiA*l*H_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]

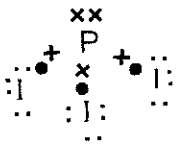
The man should seek doctor's advice since his oxygen level of 71.8% is below 80%, and is considered dangerous.

[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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