BP-789

Paper- 1

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

Class	Adm No

Candidate Name: ____________________

H

millennia institute

2025 Preliminary Examination
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions

3 September 2025

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

Suggested answers

1 The fire triangle (Fig 1.1), shows the three components necessary for combustion. Disrupting any one of these components can suppress or extinguish a fire.

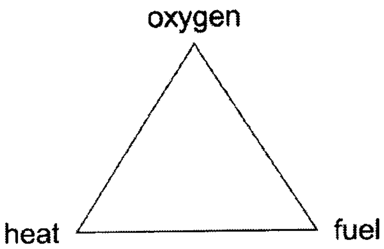


Fig 1.1

Fire retardants are substances added to materials to reduce flammability by disrupting the fire triangle.

(a) Magnesium hydroxide, $Mg(OH)_2$, is an example of an inorganic fire retardant. It undergoes thermal decomposition upon heating and releases water vapour in the process.

(i) Write a balanced equation for the thermal decomposition of magnesium hydroxide. State symbols are **not** required. [1]

$Mg(OH)_2 \rightarrow MgO + H_2O$

(ii) With reference to the components in Fig 1.1, suggest two ways in which this decomposition reaction helps to suppress a fire. [1]

The decomposition process is endothermic, which removes the heat component from the fire triangle.

Water (vapour) released dilutes the oxygen that is available, reducing the amount of oxygen in the fire triangle.

Magnesium oxide forms a protective barrier over the fuel, keeping oxygen and the fuel separated.

Any 1 for [1]

Aluminium hydroxide, $Al(OH)_3$ is also a good fire retardant. It undergoes thermal decomposition in the same way as magnesium hydroxide.

(iii) Explain why the thermal decomposition temperature of $Al(OH)_3$ is lower than that of $Mg(OH)_2$. [2]

Al^{3+} has a higher charge density than Mg^{2+} and polarises the O–H bond and weakens it to a larger extent, hence it decomposes at a lower temperature.

[1] higher charge density

[1] polarises O–H bond and weakens to a larger extent

(iv) Hence, explain whether $Al(OH)_3$ would be a better fire retardant compared to $Mg(OH)_2$. [1]

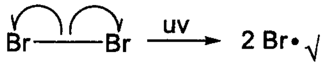
Better since the decomposition will occur at the lower temperature and release water vapour earlier in a fire.

(b) Halogenated fire retardants often use bromine or chlorine derivatives and they release hydrogen halides or halogen radicals upon decomposition which disrupt free radical chain reactions that sustain combustions.

(i) One method of preparing brominated organic compounds is free radical substitution.

Draw the mechanism for the formation of bromomethane from methane. [3]

Initiation √



Propagation √

$CH_4 + Br\bullet \rightarrow \bullet CH_3 + HBr$ √

$\bullet CH_3 + Br_2 \rightarrow CH_3Br + Br\bullet$ √

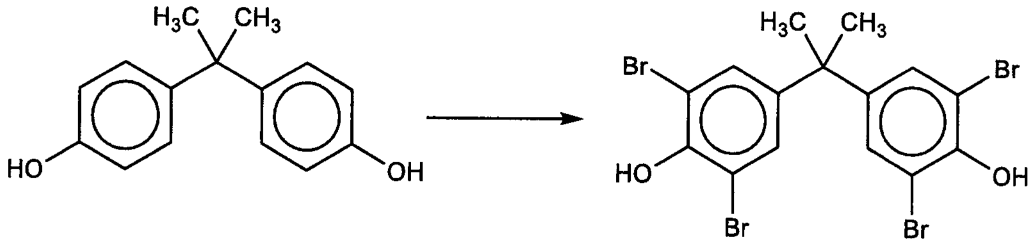
Termination √

$2\ \bullet CH_3 \rightarrow C_2H_6$ √

$\bullet CH_3 + Br\bullet \rightarrow CH_3Br$ √

8 ticks – [3]
5 – 7 ticks – [2]
3 – 4 ticks – [1]

Tetrabromobisphenol A (TBBPA) is a common brominated flame retardant. It can be made from bisphenol A (BPA) in a single step reaction, as shown in Fig. 1.2.

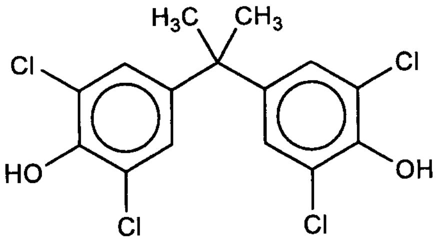


BPA TBBPA

Fig 1.2

(ii) State the reagent and conditions required to convert BPA to TBBPA. [1]

$Br_2(aq)$



TCBPA

Tetrachlorobisphenol (TCBPA) is the chlorinated analogue of TBBPA, where the bromine atoms are replaced with chlorine.

(iii) Using relevant data from the *Data Booklet*, explain the difference in strength between C–C*l* and C–Br. [2]

C–C*l* bond: 340 kJ mol^{-1}
C–Br bond: 280 kJ mol^{-1}
[1] for both values

The C–Br bond is weaker than the C–C*l* bond because the Br atom is larger than the C*l* atom, resulting in a longer bond and lower extent of orbital overlap. [1]

(iv) Hence, explain whether TCBPA would be a better flame retardant than TBBPA. [1]

No it will be less effective because the C-Cl bond requires more energy to break and hence will not produce HCl or Cl radical as easily as TBBPA to suppress the fire.

Link bond energy to ease of formation of HX or X radical which suppresses fire.

(c) Despite their effectiveness, halogenated fire retardants such at TBBPA are being phased out due to concerns over the release of toxic persistent organic pollutants during fires.

Suggest one reason why $Mg(OH)_2$ is considered a safer alternative to halogenated fire retardants. [1]

The products of $Mg(OH)_2$ decomposition (MgO and H_2O) are non–toxic.

[Total: 13]

2 **(a)** Lead(II) sulfate, $PbSO_4$, is a sparingly soluble white solid that was historically used as a pigment in paints.

(i) Write an expression for the solubility product, K_{sp}, of $PbSO_4$, stating its units. [1]

$K_{sp} = [Pb^{2+}][SO_4^{2-}]$, units: $mol^2\ dm^{-6}$

(ii) Calculate the solubility of $PbSO_4$ in pure water, given the value of K_{sp} is 1.60×10^{-8}. [1]

Let solubility of $PbSO_4$ be x $mol\ dm^{-3}$
$x^2 = 1.60 \times 10^{-8}$
$x = 1.26 \times 10^{-4}\ mol\ dm^{-3}$ [1]

(iii) A common method used by early artists to prepare $PbSO_4$ was to mix solutions of Na_2SO_4 and $Pb(NO_3)_2$.

A solution of $0.0200\ mol\ dm^{-3}$ $Pb(NO_3)_2$ was mixed with an equal volume of Na_2SO_4 to prepare $PbSO_4$.

Calculate the minimum concentration of Na_2SO_4 required for $PbSO_4$ to be formed. [2]

Upon mixing, $[Pb^{2+}] = 0.0200 / 2 = 0.0100\ mol\ dm^{-3}$
Hence $[SO_4^{2-}]$ at equilibrium $= 1.60 \times 10^{-8} / 0.0100 = 1.60 \times 10^{-6}\ mol\ dm^{-3}$ [1]

However, before mixing, the concentration is double.

Hence $[Na_2SO_4]$ required $= 1.60 \times 10^{-6} \times 2 = 3.20 \times 10^{-6}\ mol\ dm^{-3}$ [1]

(b) Due to the increased awareness of the toxicity of lead compounds, titanium dioxide, TiO_2, is now widely used as a non-toxic alternative to $PbSO_4$ in white pigments by modern artists.

(i) Write the full electronic configuration of the titanium ion in TiO_2. [1]

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

(ii) Explain what is meant by the term *transition element*. [1]

A transition element is a **d–block element** which forms **one or more stable ions**, in compounds, with a **partially filled d–subshell**.

(iii) Explain why TiO_2 appears white despite containing a transition element. [2]

TiO_2 has no electrons in the 3d subshell. [1]
Hence no wavelength of light is absorbed [1] and all are reflected hence it appears white.

(c) Copper obtained from the extraction of copper ores is often impure and contains small amounts of other metals such as zinc, silver and lead.

To obtain high purity copper for electrical use, impure copper is placed at the anode and a pure copper rod is placed at the cathode in an electrolytic cell. The electrolyte used is aqueous copper(II) sulfate.

(i) Write the half equation for the reaction occurring at the anode for copper. [1]

$Cu \rightarrow Cu^{2+} + 2\,e^-$

(ii) Using relevant data from the *Data Booklet*, explain how zinc and silver impurities are removed during the purification process. [3]

$E^\ominus(Zn^{2+}/Zn)$: –0.76 V

$E^\ominus(Ag^+/Ag)$: +0.80 V

$E^\ominus(Cu^{2+}/Cu)$: +0.34 V

Since $E^\ominus(Zn^{2+}/Zn)$ is more negative than $E^\ominus(Cu^{2+}/Cu)$, Zn will be oxidised before Cu and forms Zn^{2+} in the electrolyte. [1]

$E^\ominus(Ag^+/Ag)$ is less negative than $E^\ominus(Cu^{2+}/Cu)$, hence it will not be oxidised and be found at the bottom of the anode as Ag metal. [1]

At the cathode, since $E^\ominus(Zn^{2+}/Zn)$ is more negative than $E^\ominus(Cu^{2+}/Cu)$, it will not be reduced and remain as Zn^{2+} in the electrolyte. [1]

While the lead impurity was expected to dissolve into the electrolyte as Pb^{2+} ions, it was instead found in the anodic sludge as a compound.

(iii) State the identity of the compound and explain how it was formed. [2]

$PbSO_4$. [1]

When Pb^{2+} is formed, it reacts with the SO_4^{2-} present in the electrolyte to form $PbSO_4$ and hence is deposited in the anodic sludge. [1]

[Total: 14]

3 Advanced Oxidation Processes (AOPs) are used to degrade organic pollutants in wastewater through the formation of highly reactive hydroxyl radicals (•OH).

Two examples of AOPs are the Fenton reaction and the UV/H_2O_2 process which generate hydroxyl radicals (•OH) from H_2O_2 that is mixed in with the wastewater.

In the Fenton reaction, hydrogen peroxide reacts with iron(II) ions in acidic solution to generate hydroxyl radicals (•OH) as well as hydroperoxyl radicals (•OOH).

step 1: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH$

step 2: $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + \bullet OOH$

It is known that •OH is much more reactive than •OOH and is mainly responsible for the oxidation of organic pollutants.

In fact, •OH is so reactive that it reacts with hydrogen peroxide to form •OOH (reaction 3.1).

reaction 3.1 $\bullet OH + H_2O_2 \rightarrow \bullet OOH + H_2O$

(a) Write the overall equation for the Fenton reaction. [1]

$2H_2O_2 \rightarrow \bullet OH + \bullet OOH + H_2O$

(b) It is said that Fe^{2+} acts as a catalyst in the Fenton reaction.

(i) Explain how you can tell that Fe^{2+} is acting as a catalyst in this reaction. [1]

Fe^{2+} reacts in step 1 and is regenerated in step 2 of the reaction.

(ii) State whether Fe^{2+} acts as a homogeneous or heterogeneous catalyst in the Fenton reaction. Explain your answer. [1]

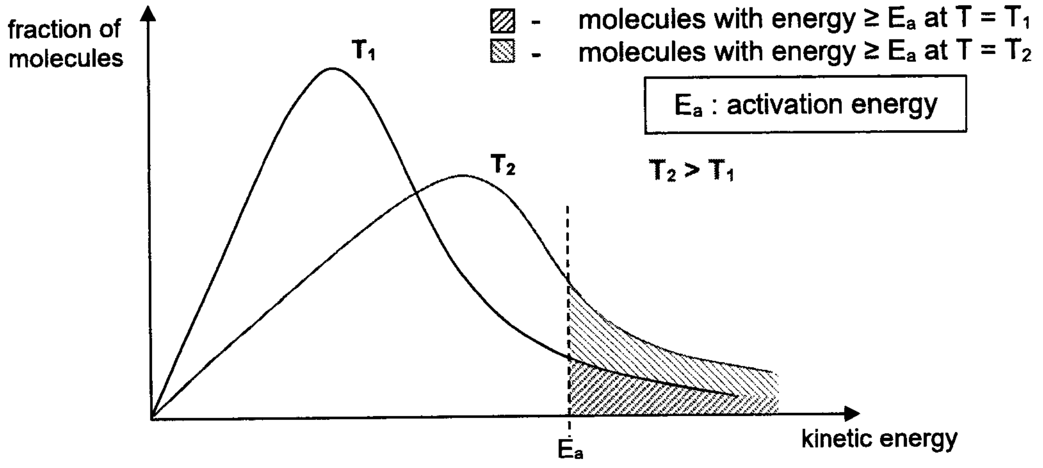
Homogeneous because the catalyst and the reactants are in the same phase.

(c) Suggest a reason why the Fenton reaction is less effective at high pH values. [1]

At higher pH values, Fe^{2+} or Fe^{3+} precipitate out as $Fe(OH)_2$ or $Fe(OH)_3$, decreasing their availability for the Fenton reaction.

Idea that the ions precipitate out and hence the catalyst can no longer function

(d) Explain, with the aid of a labelled Boltzmann distribution curve, how increasing the temperature increases the effectiveness of the Fenton reaction. [3]



[1] for graph (axes, start from origin, shape of graph T_2 flatter than T_1, shading, single E_a)

When temperature increases from T_1 to T_2, the average kinetic energy of H_2O_2 particles increase and the fraction of H_2O_2 particles having energy ≥ E_a increases. [1]

The frequency of effective collisions is higher hence more •OH radicals are generated and the reaction is more effective. [1]

(e) It was observed that the effectiveness of the degradation decreased when the concentration of H_2O_2 exceeded its optimal level.

Suggest a reason for this observation. [1]

When the concentration of H_2O_2 is too high, it reacts with the reactive •OH radical to form the •OOH radical, which is less effective at degrading the organic pollutants.

Idea that H_2O_2 reacts with the •OH radical instead of the pollutant, generating the weaker •OOH radical.

In the UV/H_2O_2 process, short wavelength UV C radiation produced by UV lamps penetrates the solution and decomposes H_2O_2 to form hydroxyl radicals (reaction 3.2).

reaction 3.2 $H_2O_2 \rightarrow 2\ \bullet OH$

(f) State the type of bond fission that occurs in reaction 3.2 when hydrogen peroxide is decomposed by UV light to form hydroxyl radicals. [1]

Homolytic fission

(g) At times, the wastewater may be turbid due to the presence of suspended particles.

Explain why the UV/H_2O_2 process may be less effective in turbid water. [1]

The suspended particles block the UV from reaching the H_2O_2 and decreases the amount of hydroxyl radicals formed.

Idea that the particles absorb/reflect the UV, preventing it from reacting with the H_2O_2

Table 3.1 compares selected characteristics of the two processes.

Table 3.1

process	reagents required	pH range	byproduct
Fenton	Fe^{2+} and H_2O_2	~2.8	$Fe(OH)_3$ sludge
UV/H_2O_2	H_2O_2	5–9	None

(h) State one advantage and one disadvantage that the UV/H_2O_2 process has over the Fenton reaction. [2]
advantage: can be used over a wider pH range, no byproducts

disadvantage: requires energy/electricity to power the UV lamps.

[Total: 12]

4 (a) The process of rusting begins with the formation of iron(II) hydroxide when iron is exposed to air and moisture. The iron(II) hydroxide is further oxidised to iron(III) hydroxide and eventually forms iron(III) oxide, Fe_2O_3, commonly known as rust.

(i) Explain why the Fe^{2+} ion is smaller than the Fe atom. [1]

Fe^{2+} ion has one less electron shell compared to the Fe atom, hence the attraction of the nucleus on the valence electrons is stronger, resulting in a smaller size.

(ii) Using relevant data from the ***Data Booklet***, explain why the oxidation of iron to iron(II) ions is spontaneous in the presence of air and moisture.

$$Fe^{2+} + 2e^- \rightleftharpoons Fe \qquad E^\ominus = -0.44\text{ V}$$
$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \qquad E^\ominus = +0.40\text{ V}$$

[2]

$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$

$= +0.40 - (-0.44)$

$= +0.84V > 0$

Since $E^\ominus_{cell}$ is positive, the reaction is spontaneous

[1] for quoting 2 correct $E^\ominus$ values

[1] for calculating $E^\ominus_{cell}$

(iii) Explain how the formation of $Fe(OH)_2$ causes the actual cell potential to be more positive than the value you calculated in **(a)(ii)**. [2]

$$Fe^{2+} + 2e^- \rightleftharpoons Fe \qquad E^\ominus = -0.44\text{ V} \text{--------}(1)$$
$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \qquad E^\ominus = +0.40\text{ V} \text{--------}(2)$$

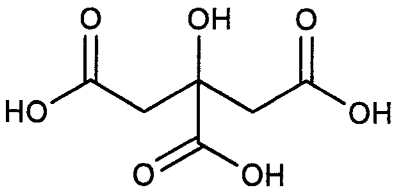
When $Fe(OH)_2$ is formed, $[Fe^{2+}]$ decreases, causing the POE of (1) to shift to the left. As a result, E_{anode} becomes more negative than -0.44 V. [1]

At the same time, $[OH^-]$ decreases as well, causing the POE of (2) to shift to the right. As a result, $E_{cathode}$ becomes more positive than +0.40 V. [1]

These two cause the actual E_{cell} to be more positive.

(b) A student investigates if lemon juice can be used to clean rusted iron surfaces.

Lemon juice contains citric acid, a weak acid.



citric acid

(i) Explain what is meant by a *weak acid.* [1]

A weak acid is an acid that **partially dissociate or ionise** in aqueous solution **to give H^+.**

(ii) Rust reacts with citric acid to form soluble iron(III) ions.

Write a balanced equation for the reaction of Fe_2O_3 with citric acid. Include state symbols in your equation. You may use H^+ to represent the acid from citric acid. [1]

$Fe_2O_3(s) + 6H^+(aq) \rightarrow Fe^{3+}(aq) + 3H_2O(l)$

Subsequently, citrate ions (Cit) act as tridentate ligands and bind to the iron(III) ions to form a soluble iron(III) citrate complex, $[Fe(Cit)_2]^{x-}$.

Fig 4.1 shows the structure of $[Fe(Cit)_2]^{x-}$.

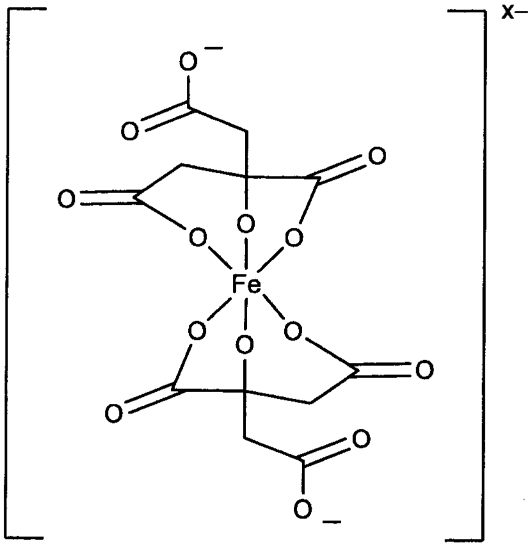


Fig. 4.1

(iii) Give two reasons why Fe^{3+} is able to form complexes with ligands such as citrate ions. [2]

Fe^{3+} has a high charge density which draws lone pairs of electrons from the ligands [1] and has energetically accessible vacant orbitals to accept lone pairs of electrons to form dative bonds. [1]

(iv) State the coordination number of Fe^{3+} in $[Fe(Cit)_2]^{x-}$. [1]

6

(v) State the charge on the citrate ligand in $[Fe(Cit)_2]^{x-}$. [1]

4–

accept –4

(vi) Hence, determine the value of x in $[Fe(Cit)_2]^{x-}$. [1]

Charge = $+3+2(-4) = -5$

$x = 5$

Each Cit ligand has a charge of 4–. There are two of them bound to Fe^{3+} hence the overall charge is –5

[Total: 12]

5 **(a)** Ring strain in cycloalkanes arises when the bond angles in the molecules deviate from their ideal tetrahedral angle of 109.5°.

Cyclohexane, C_6H_{12}, is considered largely strain free while smaller cycloalkanes like cyclopropane, C_3H_6, experience significant ring strain.

The ring strain represents stored potential energy that contributes to the molecule's enthalpy change of combustion, a factor of significant interest in fuel research aimed at identifying high-energy-density compounds.

Table 5.1 shows the enthalpy change of combustion of gaseous cyclohexane and cyclopropane.

Table 5.1

compound	enthalpy change of combustion, ΔH_c / kJ mol^{-1}
cyclohexane(g)	–3887
cyclopropane(g)	–2091

(i) Write a balanced equation for the complete combustion of gaseous cyclohexane. [1]

$C_6H_{12}(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

(ii) Using the information given in Table 5.1, calculate the average heat released per CH_2 group for gaseous cyclohexane in kJ mol^{-1} . [1]

In C_6H_{12}, there are 6 CH_2 groups

average heat released per CH_2 group = 3887 ÷ 6 = 648 kJ mol^{-1}

(iii) Using your answer to **(a)(ii)**, calculate the theoretical enthalpy change of combustion of cyclopropane, assuming it has no ring strain. [1]

In C_3H_6, there are 3CH_2 groups.

Theoretical ΔH_c (C_3H_6) = 3 x –647.833 = –1940 kJ mol^{-1}

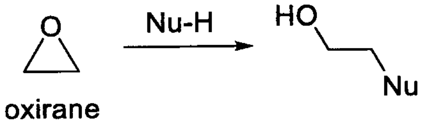
(iv) Hence, calculate the ring strain energy present in one mole of cyclopropane. [1]

Ring strain energy = 2091 – 1943.5 = 148 kJ

(b) An epoxide contains a three-membered ring compound consisting of two carbon atoms and one oxygen atom. Since it experiences the same ring strain as cyclopropane, it is highly reactive towards nucleophiles. The simplest epoxide is oxirane, C_2H_4O.

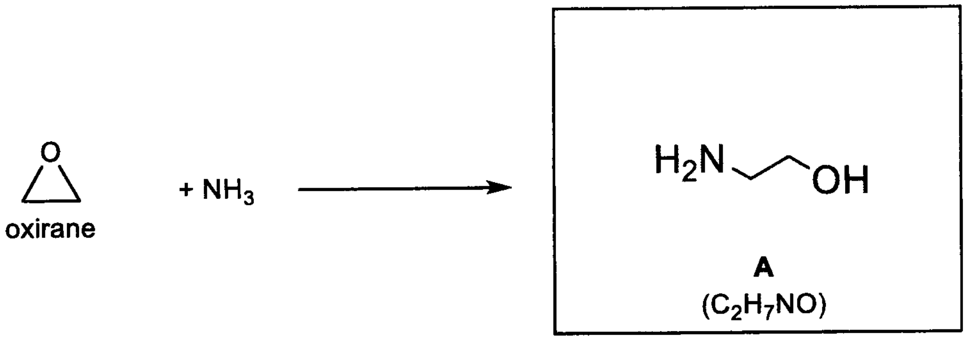
When oxirane reacts with nucleophiles, the ring opens as shown in reaction 5.1.

reaction 5.1

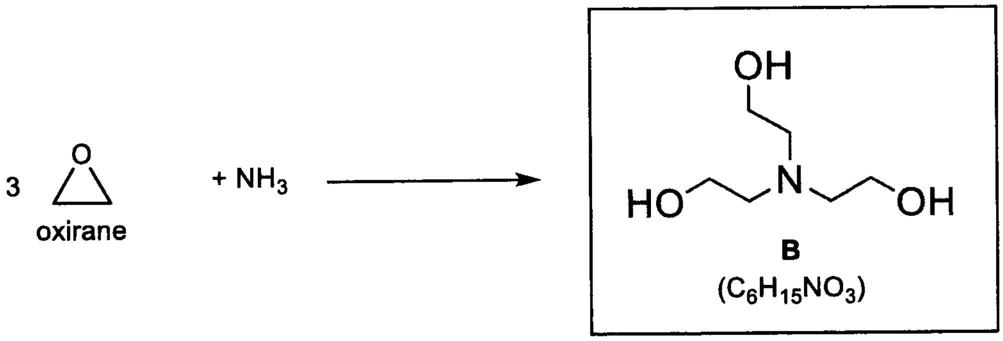


(i) When oxirane reacts with NH_3 in a 1:1 ratio, compound **A** (C_2H_7ON) is formed. However, when oxirane reacts with NH_3 in a 3:1 ratio, compound **B** ($C_6H_{15}NO_3$) is formed.

Draw the structures of **A** and **B**.



A
(C_2H_7NO)



B
($C_6H_{15}NO_3$)

[2]

Epichlorohydrin is a useful epoxide used in the manufacture of epoxy resins. It can be prepared from 3-chloro-1-propene by a sequence of reactions as shown in Fig 5.1.

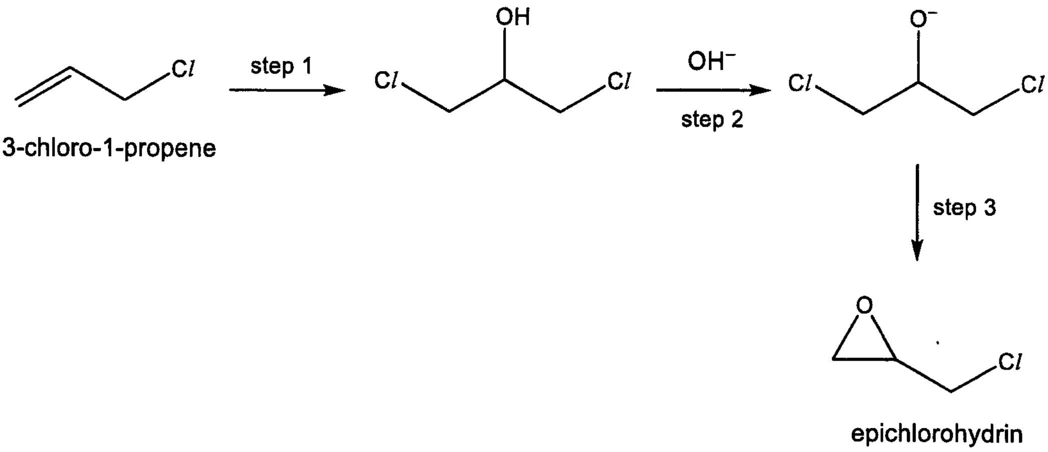


Fig 5.1

(ii) State the reagent and conditions required for step 1. [1]

Cl_2(aq)

(iii) State the type of reaction for step 2 and step 3. [2]

step 2 : acid – base

step 3 : nucleophilic substitution

(c) The acid–catalysed hydrolysis of styrene epoxide forms 1-phenyl-1,2-ethanediol as seen in Fig 5.2.

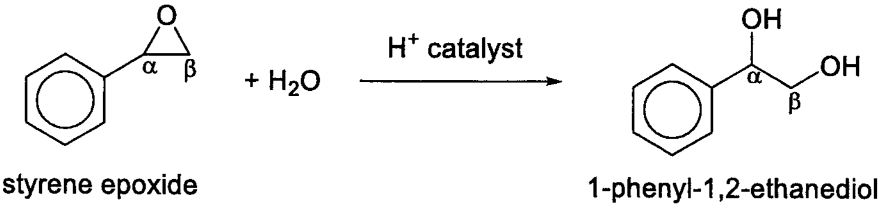


Fig 5.2

A student proposed that the reaction proceeds via the following mechanism:

step 1: The protonation of the O atom in the epoxide by H^+ catalyst.

step 2: A nucleophilic attack by H_2O on the carbon of the epoxide leading to the opening of the ring.

step 3: The deprotonation of the H_2O^+ group forming the diol and regenerating the H^+ catalyst.

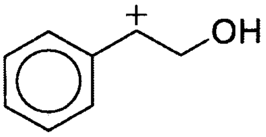
(i) Based on your understanding of steric hindrance, circle the carbon, α or β, of the epoxide that would be attacked by the H_2O nucleophile in Fig 5.2. [1]

Circle β

Isotopic labelling is used in kinetic studies to learn about the mechanisms of a reaction. $H_2{}^{18}O$ is a water molecule that contains ^{18}O instead of ^{16}O. The hydrolysis reaction was carried out with $H_2{}^{18}O$ as the nucleophile.

A study of the hydrolysis products revealed that all ^{18}O were incorporated in the α-position. The conclusion drawn was that a stable carbocation intermediate must have formed before the nucleophilic attack by $H_2{}^{18}O$.

(ii) Suggest the structure of the carbocation intermediate formed and explain why it is stable. [2]



As the α carbon is bonded to the benzene ring, the electrons from the benzene ring delocalise to the carbocation and stabilise the positive charge.

(d) Nitrocellulose is produced by reacting cellulose with a nitrating mixture of concentrated nitric acid and concentrated sulfuric acid.

Sulfuric acid donates a proton to nitric acid from to form an intermediate, $H_2NO_3^+$. This intermediate then decomposes to form the nitronium ion, NO_2^+. The NO_2^+ generated then reacts with the alcohol groups of cellulose to form nitrocellulose.

(i) Write the equation for the decomposition of the intermediate to form the nitronium ion. [1]

$H_2NO_3^+ \rightarrow NO_2^+ + H_2O$

(ii) Draw the dot-and-cross diagram of the nitronium ion and hence state its shape.

shape:.. [2]

[1]

Linear [1]

The empirical formula of nitrocellulose is $C_6H_7O_{11}N_3$. Complete combustion of nitrocellulose produces carbon dioxide, water vapour and nitrogen.

(iii) Balance the combustion equation of nitrocellulose with the correct stoichiometric coefficients.

$$\ldots\ldots C_6H_7O_{11}N_3 + \ldots\ldots O_2 \rightarrow \ldots\ldots CO_2 + \ldots\ldots H_2O + \ldots\ldots N_2$$

[1]

$2C_6H_7O_{11}N_3 + 4\tfrac{1}{2}O_2 \rightarrow 12CO_2 + 7H_2O + 3N_2$

(iv) During magic performances, magicians often use nitrocellulose as flash paper to produce dramatic flashes of flame without leaving a mess.

Suggest why nitrocellulose is suitable for this purpose. [1]

The combustion products are all gaseous and there is no residue left.

(v) State two main assumptions of the kinetic theory as applied to an ideal gas. [2]

The gas particles have negligible volume when compared with the volume of the container. [1]

The gas particles have negligible intermolecular forces of attraction. [1]

(vi) Complete Table 5.2 by identifying the most significant type of intermolecular force of attraction present between each of the gas molecules formed during the combustion of nitrocellulose.

Table 5.2

Gas	most significant intermolecular force of attraction
CO_2	instantaneous dipole – induced dipole
H_2O	hydrogen bonding
N_2	instantaneous dipole – induced dipole

[2]

[2] for all 3 [1] for any 2

(vii) Arrange the three gases, CO_2, H_2O and N_2, in order of increasing deviation from ideal gas behaviour at 400 K. Explain your answer. [3]

[1] for correct order N_2, CO_2, H_2O

[1] for H_2O having the most significant IMF (hydrogen bond) hence deviates the most.

[1] for CO_2 having more significant id–id than N_2 because it has a larger electron cloud size.

[Total: 24]

BP~809

Class	Adm No

Candidate Name: ____________________

millennia
institute

2025 Preliminary Examination
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response

15 Sep 2025

2 hours

Candidates answer on separate paper.

Additional materials: Data Booklet

Suggested answers

Section A

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

1 Copper and iron are transition metals that form a wide array of complexes due to their ability to exhibit multiple oxidation states. Copper and iron complexes showcase diverse chemical and biological roles, ranging from catalysis to electrochemical processes.

(a) **(i)** State two physical properties of transition metals which differ from that of main group elements. [2]

They have high melting and boiling points.

They have higher densities.

(ii) When copper(I) oxide solid, Cu_2O was added to sulfuric acid, $H_2SO_4(aq)$, and warmed, a blue solution and a pink solid were observed. Identify the blue solution and the pink solid and write a balanced chemical equation for the reaction. [2]

Blue solution: $CuSO_4$ - Pink solid: Cu [1]

$Cu_2O + H_2SO_4 \rightarrow Cu + CuSO_4 + H_2O$ [1]

(iii) Ethylenediaminetetraacetic acid (EDTA) is a compound used in chelation therapy. Suggest why $[Cu(EDTA)]^{2-}$ and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complexes have different colours. [1]
Presence of ligands in the solution cause the degenerate 3d orbitals to split into two different energy levels. Different ligands split the d-orbitals to different extents.

(b) A sample of copper(II) sulfate solution was added to an excess o f aqueous potassium iodide to make a 250 cm^3 solution.

$$2CuSO_4 + 4KI \rightarrow 2CuI + I_2 + 2K_2SO_4$$

The amount of iodine produced can be found by titrating a sample of this solution with sodium thiosulfate, $Na_2S_2O_3$, solution. 25.0 cm^3 of the iodine-containing solution required 20.00 cm^3 of 0.10 mol dm^{-3} sodium thiosulfate solution for complete reaction.

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

Calculate the amount of copper(II) sulfate present in the original sample. [2]

Comparing mole ratio,
2 mol $S_2O_3^{2-}$: 1 mol I_2
2 mol Cu^{2+} : 1 mol I_2
Hence, 1 mol Cu^{2+}: 1 mol $S_2O_3^{2-}$
Amount of Cu^{2+} in 25 cm^3 = (20/1000) x 0.10 = 2.00 x10^{-3} mol ;
Amount of Cu^{2+} in the original solution = (250/25) x 2.00 x10^{-3} = 2.00 x 10^{-2} mol ;

(c) Chromium is also a transition metal. Potassium dichromate(VI), $K_2Cr_2O_7$, is commonly used as an oxidising agent in organic chemistry reactions. For example, a solution of $K_2Cr_2O_7$ can be used to oxidise 1-butanol to butanoic acid.

(i) State the oxidation number of the underlined carbon in 1-butanol, $CH_3CH_2CH_2\underline{C}H_2OH$. [1]

-1

(ii) By writing the oxidation and reduction half equations, construct an ionic equation for the reaction between potassium dichromate(VI) and 1-butanol in an acidic solution. [3]

[R]: $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ x2
[O]: $CH_3CH_2CH_2CH_2OH + H_2O \rightarrow CH_3CH_2CH_2COOH + 4H^+ + 4e^-$ x3

Overall Equation

$3CH_3CH_2CH_2CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3CH_2COOH + 4Cr^{3+} + 11H_2O$

A student proposed a reaction mechanism for the oxidation of 1-butanol and suggested that steps 1 and 2 of the mechanism are as follows:

Step 1: Protonation of 1-butanol to form a better leaving group.

Step 2: Breaking of the C–O bond to form a carbocation.

(iii) Draw the structure of the protonated intermediate in step 1. [1]
$CH_3CH_2CH_2CH_2OH_2^+$

(iv) It was found that the proposed mechanism was not feasible as the carbocation formed in step 2 was unstable. Suggest why the carbocation formed was unstable. [1]
The carbocation in step 2 is unstable as it is a primary carbocation. There is only one electron donating group present hence the positive charge is less dispersed, resulting in an unstable carbocation.

(d) A team of scientists is designing a power source for field sensors. The aim is to develop a sustainable electrochemical cell using abundant and recyclable materials. After consideration, the team narrows their choice of materials to zinc, copper, iron, and silver electrodes.

(i) Propose a combination of two materials that will give rise to the most efficient electrochemical cell with the highest voltage. Explain your answer and justify by means of a calculation. [3]

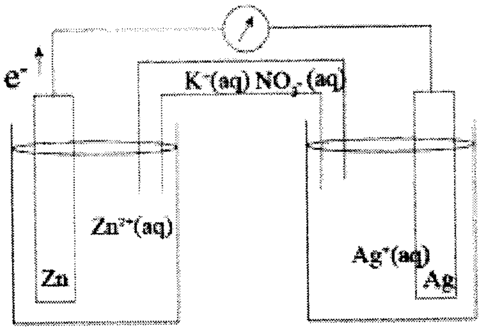
Zn – Ag electrochemical cell 1m

Best oxidising agent: Ag^+ (most positive E° value, +0.80 V)

Best reducing agent: Zn (less positive E° value, –0.76 V) 1m

E°cell = E°(cathode) – E°(anode) = +0.80 – (–0.76) = **+1.56 V** 1m

(ii) Draw a fully labelled diagram of the electrochemical cell proposed in **(d)(i)**, indicating clearly the direction of electron flow. [3]



1m metal electrodes
1m electrolyte solution + salt bridge
1m direction of electron flow

(iii) State the observations observed over time as the electrochemical cell is allowed to run. [1]

The Zn electrode decreases in size (dissolves) and the Ag electrode thickens / increase in size as Ag metal deposits on it.

(iv) Suggest one potential challenge the team of scientists might face should they proceed with large scale productions of the electrochemical cells proposed in **(d)(i)**. [1]

High production costs as Ag is expensive
Or
Environmental concerns – Ag / Ag^+ is toxic

[Total: 21]

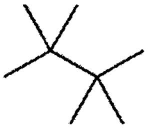
2 The cracking of decane, $C_{10}H_{22}$, produces octane and ethene, as shown in the equation below.

$$C_{10}H_{22} \rightarrow C_8H_{18} + C_2H_4$$

Octane is a key chemical component of gasoline, while ethene is a common starting material for the synthesis of many two-carbon containing organic compounds. The straight-chain isomer of octane is known as n-octane and exists in the liquid state at room temperature.

(a) Highly branched alkanes are favoured in gasoline, because the branched structure makes them more resistant to 'knocking' in combustion engines compared to n-octane. This resistance to 'knocking' leads to smoother engine operation.

(i) Draw the skeletal structure and state the IUPAC name of the most highly branched isomer of n-octane. [2]



2,2,3,3-tetramethyl butane or tetramethylbutane

(ii) State and explain if the branched isomer in **(a)(i)** will have a higher or lower boiling point compared to n-octane. [2]

The branched isomer will have a lower boiling point as it is more spherical, with lesser surface area for contact. Hence, less extensive instantaneous dipole–induced dipole forces of attractions exists between the branched molecules, therefore less energy is required to overcome the forces of attraction.

(iii) Using bond energy values from the *Data Booklet*, calculate the enthalpy change of combustion of n-octane. [3]

$C_8H_{18} + 25/2\ O_2 \rightarrow 8CO_2 + 9H_2O$

ΔH_c of octane

= bonds broken – bonds form

= 7 (C-C) + 18 (C-H) + 25/2 (O=O) – [16 (C=O) + 18(O-H)]

= 7(350) + 18(410) + 25/2(496) – [16(805) + 18(460)]

= 16030 – 21160

= – 5130 kJ mol^{-1}

(iv) Suggest why the method in **(a)(iii)** will not be able to give an accurate value of the enthalpy change of combustion of n-octane. [1]

Bond energy values are approximate. OR

Octane exists in the liquid state.

(b) Ethene is a useful starting material for the synthesis of ethanol. The reagent for the formation of ethanol from ethene includes steam, $H_2O(g)$ and concentrated H_3PO_4 as the acid catalyst. The reaction takes place under conditions of high temperature and pressure. The ethanol produced can subsequently be used to synthesise ethyl ethanoate, in a reversible chemical reaction.

(i) Name the type of reaction when ethanol is synthesised from ethene. [1]

Electrophilic addition

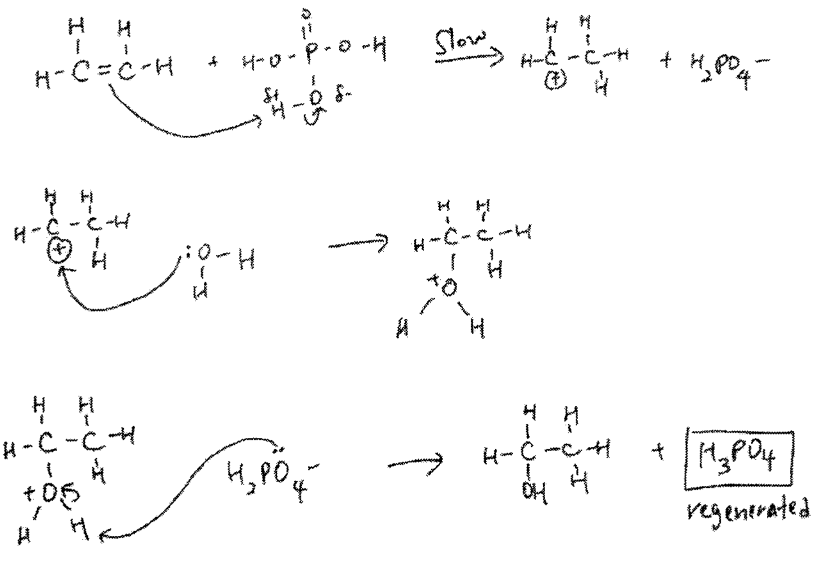
(ii) The reaction mechanism for the synthesis of ethanol from ethene takes place in the following steps.

Step 1: the ethene molecule acts as a nucleophile and attacks a proton from the acid catalyst, forming a carbocation intermediate.

Step 2: the water molecule attacks the carbocation, forming an oxonium ion intermediate, where an oxygen atom carries a positive charge.

Step 3: the oxonium ion from step 2 is unstable and loses a proton, resulting in the formation of ethanol. The acid catalyst is regenerated in the process.

Draw the mechanism of the synthesis reaction based on the steps above, including all curly arrows and intermediates drawn clearly. [4]



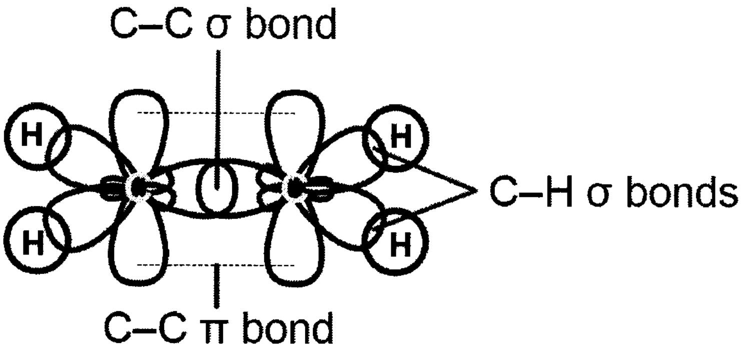
Marking points

- Ethene attacking proton
- Electron transfer from proton to O and indication of delta + and –
- Correct carbocation
- Correct conjugate base ($H_2PO_4^-$)
- Lone pair from water attacking carbocation
- Correction oxonium intermediate
- Lone pair on O attacking oxonium ion and electron transfer for deprotonation
- Formation of ethanol and regeneration of acid catalyst

1m for 2 correct points (1 x 4)

(iii) By reference to the hybridisation of the carbon atoms and orbital overlap, describe the covalent bonding in ethene with the aid of a labelled diagram. [3]

two of the *sp*^{2} hybrid orbitals **overlap head-on** with the s orbital of two hydrogen atoms to give two C–H σ bonds.
one of the *sp*^{2} hybrid orbitals **overlaps head-on** with the *sp*^{2} orbital of the adjacent carbon atom to give one C–C σ bond.
the **unhybridised p orbitals** of the two adjacent carbon atoms **overlap sideways** forming a C–C π bond.



[Total: 16]

[Turn over

3 Iodine is a Group 17 element that can form several ions with varying oxidation states. Iodine also plays important roles in organic and inorganic reactions.

(a) One such ion, the iodate ion, IO_3^-, contains iodine in an oxidation state of +5, and acts as an oxidising agent in chemical reactions.

(i) Draw the 'dot-and-cross' diagram of an iodate ion, IO_3^-, stating the shape clearly. [2]

3BP, 1LP (1m)
trigonal pyramidal (1m)

The reaction between potassium iodate, KIO_3, and sodium bisulfite, $NaHSO_3$, in acidic solution was studied.

$$IO_3^-(aq) + 3HSO_3^-(aq) \rightarrow I^-(aq) + 3SO_4^{2-}(aq) + 3H^+(aq)$$

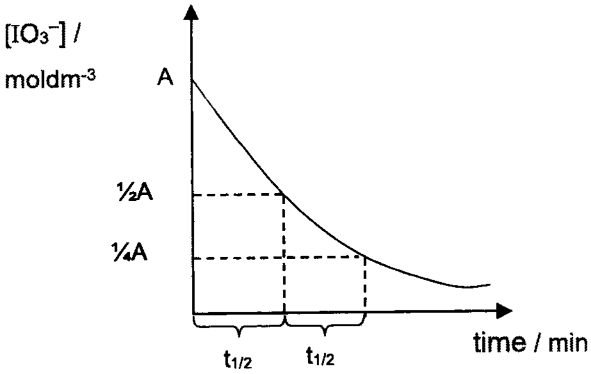
(ii) The reaction was found to be first order with respect to iodate and had a rate constant of 3.10 $mol^{-1}\ dm^3\ s^{-1}$ at a particular temperature.
Deduce the rate equation for the reaction between iodate and bisulfite ions. [2]

Since the units of *k* is $mol^{-1}\ dm^3\ s^{-1}$,
units of concentrations = units of Rate / units of rate constant
$= mol\ dm^{-3}\ s^{-1} / mol^{-1}\ dm^3\ s^{-1}$
$= mol^2\ dm^{-6}$

Hence rate = $k[IO_3^-][HSO_3^-]$

1m for rate equation
1m for working

(iii) In a separate experiment, the bisulfite ions were present in excess. Sketch a labelled graph of concentration of iodate against time for this experiment. [2]



1m for shape and labelled axis
1m for construction lines indicating constant half-lives

(b) Iodine can also exhibit the oxidation state of -1, in the form of the iodide ion, I^-.

A solution containing potassium iodide, KI, was electrolysed using inert electrodes. Calculate the mass of iodine, I_2, produced at the anode when a current of 3.2 A is passed through the solution for 45 minutes. [3]

[O]: $2\,I^- \rightarrow I_2 + 2e$

Q = It = nF = (3.2)(45x60) = n_e(96500) 1m
Amount of electrons = 0.08953 mol
Amount of iodine produced = 0.08953 / 2 = 0.04477 mol 1m
Mass of iodine produced = 0.04477 x (126.9 x 2) = 11.4 g (3 s.f.) 1m

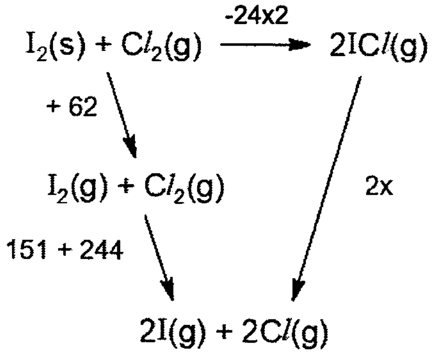
(c) Use of the *Data Booklet* is relevant to this question.

Iodine reacts with chlorine to form gaseous iodine monochloride, ICl.

(i) Construct an energy cycle to determine the average bond energy of the I–Cl bond in iodine monochloride, using the data given below and other data from the *Data Booklet*.

Enthalpy change of formation of ICl (g)	- 24 kJ mol^{-1}
Enthalpy change of sublimation of I_2 (s)	+ 62 kJ mol^{-1}

[4]



By Hess' law,
2x = –(–24x2) + 62 + 151 + 244 = +505 kJ mol^{-1}

BE(I–Cl) = 505 / 2 = +253 kJ mol^{-1}

1m for each pair of correctly constructed arrows in the cycle (2m)
1m for hess' law
1m for final ans

(ii) State and explain the sign of ΔS for the sublimation of iodine. [2]

$\Delta S > 0$, positive.

Entropy increases when iodine sublimes. The number of moles of gaseous particles increases from 0 to 1. There are more ways to arrange the particles, hence the system becomes more disordered.

(d) Iodine also reacts with hydrogen to form hydrogen halides. When sparked, the reaction takes place and eventually reaches an equilibrium.

$$I_2(g) + H_2(g) \rightleftharpoons 2HI(g) \qquad \Delta H = -11 \text{ kJ mol}^{-1}$$

(i) Platinum could be used as a heterogeneous catalyst for this reaction. Outline the mode of action of platinum in this reaction. [3]

Platinum allows the gaseous reactant molecules to adsorb onto it.

As a result, the surface concentration of the reactant molecules increased, and activation energy is lowered as the chemical bonds in the reactant molecules are weakened. Hence, the rate of reaction is increased.

The products formed then desorb from the surface, freeing the active sites for adsorption by new reactant molecules.

(ii) In addition to HI, other hydrogen halides such as HBr and HC*l* can also be produced from the reaction in **(d)**. State and explain the trend in thermal stability of the Group 17 hydrogen halides. [3]

Thermal stability decreases down the group: HC*l* > HBr > HI.

This is because the atomic radius of the halogens increases down the group, resulting in decreasing extent of effective overlapping of p-orbitals. Thus, covalent bond strength and hence bond energy of H**X** decreases down the group.

(e) Iodine can react with alkenes via electrophilic addition reactions. The reactivity of iodine with alkenes is lower than that of bromine in electrophilic addition reactions with alkenes. Suggest two reasons why this is so. [2]

1. The C-I bond formed is weaker than the C-Br bond formed (due to larger atomic radius of I, resulting in poorer overlapping of orbitals). Hence, the iodo-alkane product formed is less stable, resulting in lower reactivity.
2. Bromine is more electronegative than iodine. This results in bromine being able to form a stronger electrophile, hence reactivity increases.

[Total: 23]

Section B

Answer **one** question from this section.

4 **(a)** Sodium fluoride reacts with concentrated sulfuric acid to form hydrogen fluoride which dissolves in water to form hydrofluoric acid, HF(aq).

(i) An aqueous solution of HF with a concentration of 0.0100 mol dm^{-3} has a pH of 3.2 at 25 °C. Show that HF(aq) is a weak acid. Explain your answer. [2]

$[H^+] = 10^{-3.2} = 6.31 \times 10^{-4}$ mol dm^{-3}

Since $[H^+] << [HF]$, HF is a weak acid which partially ionises in aqueous solutions.

(ii) Suggest how the addition of sodium fluoride, NaF(s), to a solution of hydrofluoric acid, HF(aq), affects the pH of the resulting solution. [2]

By LCP, the addition of NaF increases the concentration of the common ion F^-.

This shifts the equilibrium $HF \rightleftharpoons H^+ + F^-$. to the left, reducing the concentration of H^+. Thus, the resulting solution becomes less acidic, and pH increases.

(iii) A buffer solution can be made from sodium fluoride and hydrofluoric acid.

Write two equations to show how this buffer solution will react when small amount of acid or alkali are added separately to two portions of the buffer solution. [2]

When a small amount of acid is added,
$F^- + H_3O^+ \rightarrow HF + H_2O$

When a small amount of base is added,
$HF + OH^- \rightarrow F^- + H_2O$

(iv) Suggest why a mixture of NaC*l*(aq) and HC*l*(aq) cannot form a buffer solution. [1]

When small amount of H^+ is added, Cl^- being the conjugate base of HC*l*, is unable to react with H^+ to form HC*l* as the HC*l* is a strong acid which will completely dissociated into H^+ and Cl^-.
Hence the mixture is unable to control the changes in the pH and cannot be called a buffer solution.

(b) **(i)** Propose a synthesis route to synthesise phenylethylamine, $C_6H_5CH_2CH_2NH_2$, from benzene and CH_3CH_2Cl. Include all reagents and conditions used in each step and draw the structures of the intermediates clearly. [5]

$C_6H_6 \rightarrow C_6H_5CH_2CH_3$ 1m
R&C: CH_3CH_2Cl, $AlCl_3$ catalyst, heat 1m

$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH_2CH_2Br$ 1m
R&C: Br_2 / CCl_4, uv light 1m

$C_6H_5CH_2CH_2Br \rightarrow C_6H_5CH_2CH_2NH_2$
R&C: excess concentrated NH_3, heated in a sealed tube. 1m

(ii) Based on your answer in **(b)(i)**, suggest one reason why the yield of phenylethylamine tends to be low. [1]

Other products can be formed in the 2nd stage (FRS), e.g. $C_6H_5CHBrCH_3$

Or a di-substituted amine in the 3rd stage: $C_6H_5CH_2CH_2–NHCH_2CH_2C_6H_5$

(c) **(i)** Describe the reactions of the chlorides of silicon and aluminium with water. Include the pH value of the resulting solutions and write equations where appropriate. [4]

$SiCl_4$ hydrolyses completely in water to give an acidic solution of pH 1. Steamy white fumes are also observed. 1m

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl\,(aq)$ 1m

$AlCl_3$, dissolves to give $[Al(H_2O)_6]^{3+}$ which hydrolyses partially in water to give an acidic solution of pH 3. 1m

Hydration : $AlCl_3(s) + 6H_2O(l) \rightarrow [Al\,(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

Hydrolysis : $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$ 1m for both

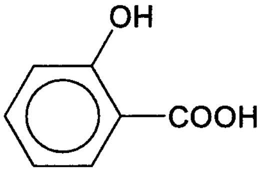
(ii) Predict and explain the difference in melting points between Na_2O and MgO. [3]

$LE \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$

Anion is the same
Charge on Mg^{2+} is two times that of Na^+
Size of Mg^{2+} is smaller than that of Na^+
Thus the LE of MgO should be more exothermic than Na_2O.
MgO will have a higher melting point than Na_2O

[Total: 20]

5 2-hydroxybenzoic acid, commonly known as salicylic acid, is primarily used in medicine as a key ingredient in skincare.



2-hydroxybenzoic acid

(a) Describe two simple chemical tests and state the positive observations expected, to confirm the presence of the two functional groups present in 2-hydroxybenzoic acid. [3]

Test for phenol – neutral $FeCl_3$, violent colouration observed.

Test for carboxylic acid – add Na_2CO_3. Effervescence observed. Colourless, odourless gas evolved formed white ppt in lime water.

1m for both test, 1m (x2) for each observation

(b) 2-hydroxybenzoic acid reacts with ethanol, in the presence of concentrated H_2SO_4 catalyst in an esterification process. The esterification process is reversible and results in low yield of the ester product.

(i) Write a balanced chemical equation for the esterification process. [1]

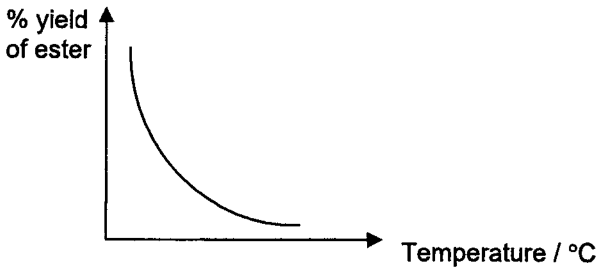
$HOC_6H_4COOH + CH_3CH_2OH \rightleftharpoons HOC_6H_4COOCH_2CH_3 + H_2O$

(ii) Suggest two **different methods** to increase the yield of the ester product. Explain the chemistry behind the methods. [3]

Addition of a drying agent (e.g. calcium chloride) to remove the water produced. 1m
Increasing the concentration of the reactants (ethanol or 2-hydroxybenzoic acid). 1m

In both methods, by LCP, the position of equilibrium will shift to the right (to remove excess ethanol / to produce more water), hence increasing the yield of the ester product. 1m

(iii) The thermodynamics of the esterification process was investigated, and the following graph was obtained.

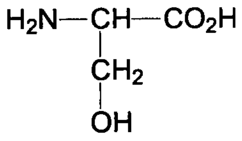
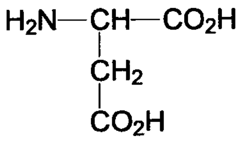


Use Le Chatelier's Principle to explain if the esterification process was exothermic or endothermic. [2]

As temperature increases, the percentage yield decreases. This implies that the system absorbs the additional heat by favouring the backward reaction, and hence position of equilibrium shifts to the left. Thus the forward reaction is exothermic.

(c) The pK_a values of two amino acids are given in Table 5.1 below.

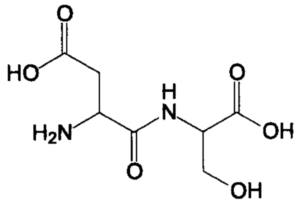
Table 5.1

	structure	pK_{a1}	pK_{a2}	pK_{a3}
ethanoic acid	CH_3COOH	4.7	–	–
serine (ser)	 $H_2N{-}CH(CH_2OH){-}CO_2H$	2.2	9.2	–
aspartic acid (asp)	 $H_2N{-}CH(CH_2CO_2H){-}CO_2H$	1.9	3.7	9.6

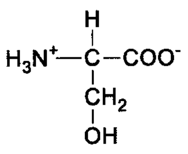
(i) Suggest one reason why the pK_{a1} of serine is smaller than the pK_{a1} of ethanoic acid. [1]

Serine has the electron-withdrawing NH_2 group that stabilises the conjugate base of the carboxyl group.

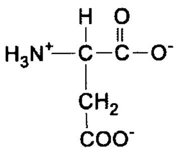
(ii) Draw the structure for the dipeptide, asp–ser. [1]



(iii) A sample consisting of serine and aspartic acid was analysed by electrophoresis using a gel buffered at pH 5.7. Draw the structures of the major species present in the buffer solution at pH 5.7. [2]


$H_3N^+{-}CH(CH_2OH){-}COO^-$

Ser


$H_3N^+{-}CH(CH_2COO^-){-}C(=O){-}O^-$

Asp

(d) **(i)** Al_2O_3 is an amphoteric oxide that can react with both acids and bases. By writing suitable balanced chemical equations, illustrate the amphoteric property of Al_2O_3 and explain why Al_2O_3 is amphoteric. [4]

$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$
$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq)$

Al_2O_3 has a giant ionic lattice structure with strong electrostatic forces of attraction between Al^{3+} and O^{2-} ions. The high charge density of Al^{3+} (1m) allows the electron cloud of O^{2-} ion to be polarised, resulting in covalent character in the ionic bond (1m).

(ii) Predict and explain the difference in melting points between NaCl and AlCl₃. [3]

NaCl has a higher melting point than $AlCl_3$. 1m

NaCl is held together by strong electrostatic forces of attraction between Na^+ and Cl^- which is stronger than the id-id between $AlCl_3$ molecules.

More energy needed to overcome the ionic bonds in NaCl than the IMF between $AlCl_3$ molecules.

[Total: 20]

End of Paper 3