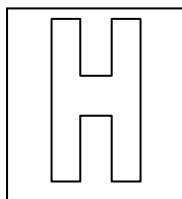


Candidate Name: \_\_\_\_\_

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## 2025 Preliminary Examination Pre-University 3

### H2 CHEMISTRY

Paper 3 Free Response

**9729/03**

**15 Sep 2025**

**2 hours**

Candidates answer on separate paper.

Additional materials: Data Booklet

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## 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.

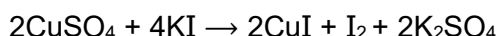
- (ii) When copper(I) oxide solid,  $\text{Cu}_2\text{O}$  was added to sulfuric acid,  $\text{H}_2\text{SO}_4(\text{aq})$ , and warmed, a blue solution and a pink solid were observed. Identify the blue solution and the pink solid and write a balanced chemical equation for the reaction. [2]

Blue solution:  $\text{CuSO}_4$  - Pink solid:  $\text{Cu}$  [1]

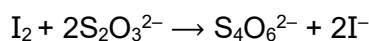
$\text{Cu}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{Cu} + \text{CuSO}_4 + \text{H}_2\text{O}$  [1]

- (iii) Ethylenediaminetetraacetic acid (EDTA) is a compound used in chelation therapy. Suggest why  $[\text{Cu}(\text{EDTA})]^{2-}$  and  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  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 of aqueous potassium iodide to make a  $250 \text{ cm}^3$  solution.



The amount of iodine produced can be found by titrating a sample of this solution with sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ , solution.  $25.0 \text{ cm}^3$  of the iodine-containing solution required  $20.00 \text{ cm}^3$  of  $0.10 \text{ mol dm}^{-3}$  sodium thiosulfate solution for complete reaction.



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

Comparing mole ratio,

$2 \text{ mol S}_2\text{O}_3^{2-} : 1 \text{ mol I}_2$

$2 \text{ mol Cu}^{2+} : 1 \text{ mol I}_2$

Hence,  $1 \text{ mol Cu}^{2+} : 1 \text{ mol S}_2\text{O}_3^{2-}$

Amount of  $\text{Cu}^{2+}$  in  $25 \text{ cm}^3 = (20/1000) \times 0.10 = 2.00 \times 10^{-3} \text{ mol}$  ;

Amount of  $\text{Cu}^{2+}$  in the original solution =  $(250/25) \times 2.00 \times 10^{-3} = 2.00 \times 10^{-2} \text{ mol}$  ;

- (c) Chromium is also a transition metal. Potassium dichromate(VI),  $\text{K}_2\text{Cr}_2\text{O}_7$ , is commonly used as an oxidising agent in organic chemistry reactions. For example, a solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  can be used to oxidise 1-butanol to butanoic acid.

(i) State the oxidation number of the underlined carbon in 1-butanol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ .

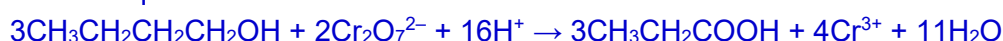
[1]

-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]



Overall Equation



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]



(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]

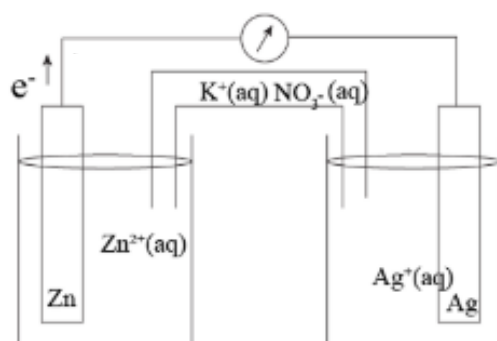
Zn – Ag electrochemical cell 1m

Best oxidising agent:  $\text{Ag}^+$  (most positive  $E^\circ$  value, +0.80 V)

Best reducing agent: Zn (less positive  $E^\circ$  value, –0.76 V) 1m

$$E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = +0.80 - (-0.76) = +1.56 \text{ V} \quad 1\text{m}$$

- (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<sup>+</sup> is toxic

[Total: 21]

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



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]



$\Delta H_c$  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<sup>-1</sup>

- (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,  $\text{H}_2\text{O}(\text{g})$  and concentrated  $\text{H}_3\text{PO}_4$  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

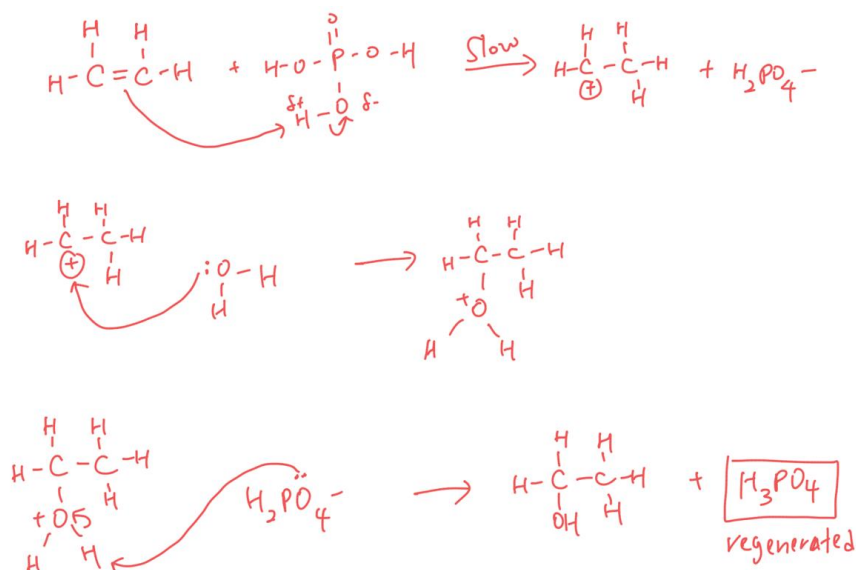
- (ii) The reaction mechanism for the synthesis of ethanol from ethene takes place in the following steps.

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 ( $\text{H}_2\text{PO}_4^-$ )
- 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

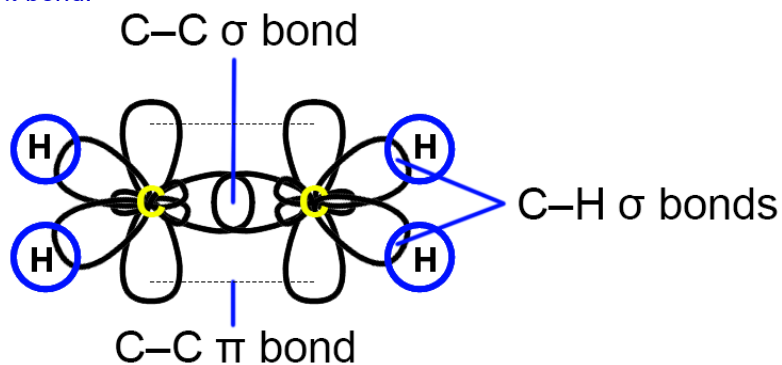
1m for 2 correct points (1 x 4)

- (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  $\sigma$  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  $\sigma$  bond.

the **unhybridised p orbitals** of the two adjacent carbon atoms **overlap sideways** forming a C–C  $\pi$  bond.



[Total: 16]

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.

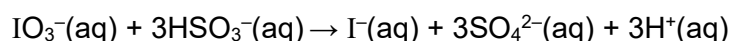
(a) One such ion, the iodate ion,  $\text{IO}_3^-$ , contains iodine in an oxidation state of +5, and acts as an oxidising agent in chemical reactions.

(i) Draw the 'dot-and-cross' diagram of an iodate ion,  $\text{IO}_3^-$ , stating the shape clearly. [2]

3BP, 1LP (1m)

trigonal pyramidal (1m)

The reaction between potassium iodate,  $\text{KIO}_3$ , and sodium bisulfite,  $\text{NaHSO}_3$ , in acidic solution was studied.



(ii) The reaction was found to be first order with respect to iodate and had a rate constant of  $3.10 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  at a particular temperature.

Deduce the rate equation for the reaction between iodate and bisulfite ions. [2]

Since the units of  $k$  is  $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ,

units of concentrations = units of Rate / units of rate constant

$$= \text{mol dm}^{-3} \text{ s}^{-1} / \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

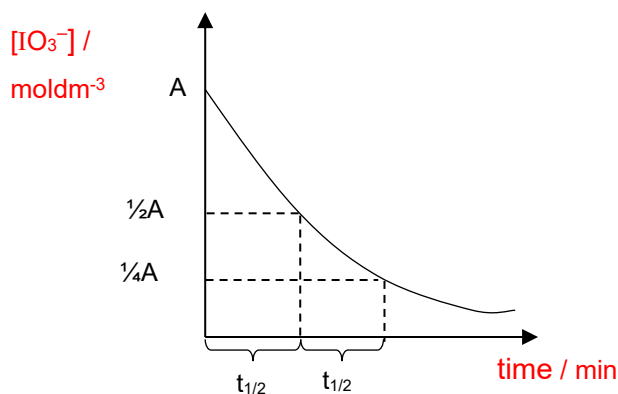
$$= \text{mol}^2 \text{ dm}^{-6}$$

Hence rate =  $k[\text{IO}_3^-][\text{HSO}_3^-]$

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]



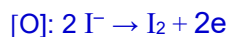
1m for shape and labelled axis

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,  $\text{I}^-$ .

A solution containing potassium iodide, KI, was electrolysed using inert electrodes. Calculate the mass of iodine,  $\text{I}_2$ , produced at the anode when a current of 3.2 A is passed through the solution for 45 minutes. [3]



$Q = It = nF = (3.2)(45 \times 60) = n_e(96500)$  1m

Amount of electrons = 0.08953 mol

Amount of iodine produced =  $0.08953 / 2 = 0.04477$  mol 1m

Mass of iodine produced =  $0.04477 \times (126.9 \times 2) = 11.4$  g (3 s.f.) 1m

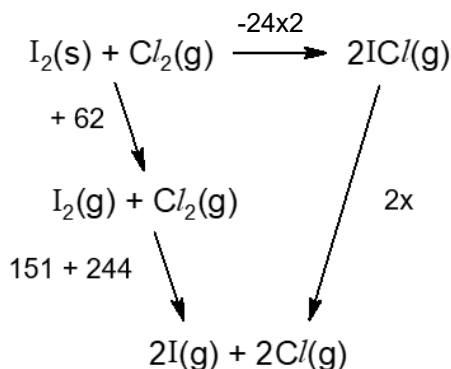
- (c) Use of the *Data Booklet* is relevant to this question.

Iodine reacts with chlorine to form gaseous iodine monochloride,  $\text{ICl}$ .

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

Enthalpy change of formation of $\text{ICl(g)}$	- 24 $\text{kJ mol}^{-1}$
Enthalpy change of sublimation of $\text{I}_2(\text{s})$	+ 62 $\text{kJ mol}^{-1}$

[4]



By Hess' law,

$2x = -(-24 \times 2) + 62 + 151 + 244 = +505 \text{ kJ mol}^{-1}$

$\text{BE}(\text{I}-\text{Cl}) = 505 / 2 = +253 \text{ kJ mol}^{-1}$

1m for each pair of correctly constructed arrows in the cycle (2m)

1m for hess' law

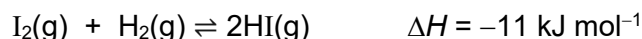
1m for final ans

- (ii) State and explain the sign of  $\Delta S$  for the sublimation of iodine. [2]

$\Delta S > 0$ , positive.

Entropy increases when iodine sublimates. 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) 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 HCl 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:  $\text{HCl} > \text{HBr} > \text{HI}$ .

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  $\text{HX}$  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  $0.0100 \text{ mol dm}^{-3}$  has a pH of 3.2 at  $25^\circ\text{C}$ . Show that HF(aq) is a weak acid. Explain your answer. [2]  
 $[\text{H}^+] = 10^{-3.2} = 6.31 \times 10^{-4} \text{ mol dm}^{-3}$

Since  $[\text{H}^+] \ll [\text{HF}]$ , 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  $\text{F}^-$ .

This shifts the equilibrium  $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$  to the left, reducing the concentration of  $\text{H}^+$ . 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,  
 $\text{F}^- + \text{H}_3\text{O}^+ \rightarrow \text{HF} + \text{H}_2\text{O}$

When a small amount of base is added,  
 $\text{HF} + \text{OH}^- \rightarrow \text{F}^- + \text{H}_2\text{O}$

- (iv) Suggest why a mixture of NaCl(aq) and HCl(aq) cannot form a buffer solution. [1]

When small amount of  $\text{H}^+$  is added,  $\text{Cl}^-$  being the conjugate base of HCl, is unable to react with  $\text{H}^+$  to form HCl as the HCl is a strong acid which will completely dissociated into  $\text{H}^+$  and  $\text{Cl}^-$ .

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,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2$ , from benzene and  $\text{CH}_3\text{CH}_2\text{Cl}$ . Include all reagents and conditions used in each step and draw the structures of the intermediates clearly. [5]

$\text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$  1m  
 R&C:  $\text{CH}_3\text{CH}_2\text{Cl}$ ,  $\text{AlCl}_3$  catalyst, heat 1m

$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br}$  1m  
 R&C:  $\text{Br}_2$  /  $\text{CCl}_4$ , uv light 1m

$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2$   
 R&C: excess concentrated  $\text{NH}_3$ , 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 2<sup>nd</sup> stage (FRS), e.g.  $\text{C}_6\text{H}_5\text{CHBrCH}_3$

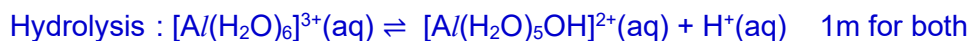
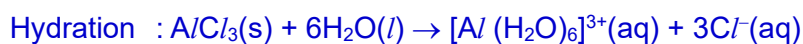
Or a di-substituted amine in the 3<sup>rd</sup> stage:  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{-NHCH}_2\text{CH}_2\text{C}_6\text{H}_5$

- (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]

$\text{SiCl}_4$  hydrolyses completely in water to give an acidic solution of pH 1. Steamy white fumes are also observed. 1m



$\text{AlCl}_3$  dissolves to give  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  which hydrolyses partially in water to give an acidic solution of pH 3. 1m



- (ii) Predict and explain the difference in melting points between  $\text{Na}_2\text{O}$  and  $\text{MgO}$ . [3]

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

Anion is the same

Charge on  $\text{Mg}^{2+}$  is two times that of  $\text{Na}^+$

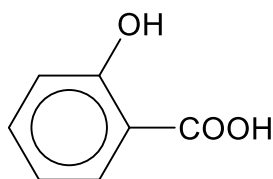
Size of  $\text{Mg}^{2+}$  is smaller than that of  $\text{Na}^+$

Thus the LE of  $\text{MgO}$  should be more exothermic than  $\text{Na}_2\text{O}$ .

$\text{MgO}$  will have a higher melting point than  $\text{Na}_2\text{O}$

[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  $\text{FeCl}_3$ , violent colouration observed.

Test for carboxylic acid – add  $\text{Na}_2\text{CO}_3$ . 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  $\text{H}_2\text{SO}_4$  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]

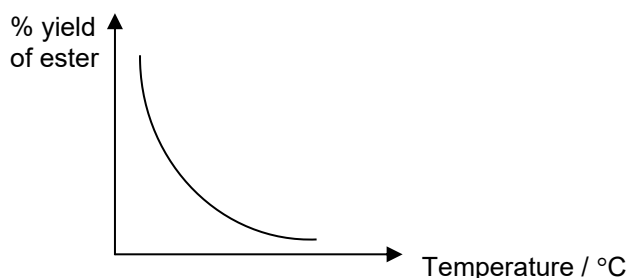


- (ii) Suggest two **different methods** to increase the yield of the ester product. Explain the chemistry behind the methods. [3]

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.

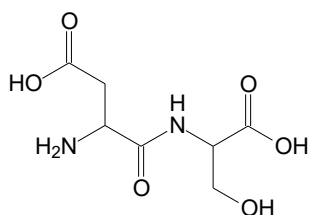
**Table 5.1**

	structure	$pK_{a1}$	$pK_{a2}$	$pK_{a3}$
ethanoic acid	$\text{CH}_3\text{COOH}$	4.7	—	—
serine (ser)	$\begin{array}{c} \text{H}_2\text{N}-\text{CH}-\text{CO}_2\text{H} \\   \\ \text{CH}_2 \\   \\ \text{OH} \end{array}$	2.2	9.2	—
aspartic acid (asp)	$\begin{array}{c} \text{H}_2\text{N}-\text{CH}-\text{CO}_2\text{H} \\   \\ \text{CH}_2 \\   \\ \text{CO}_2\text{H} \end{array}$	1.9	3.7	9.6

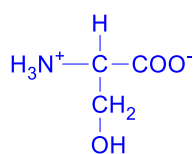
(i) Suggest one reason why the  $pK_{a1}$  of serine is smaller than the  $pK_{a1}$  of ethanoic acid. [1]

Serine has the electron-withdrawing  $\text{NH}_2$  group that stabilises the conjugate base of the carboxyl group.

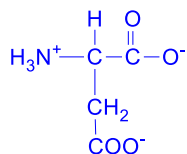
(ii) Draw the structure for the dipeptide, asp-ser. [1]



(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]

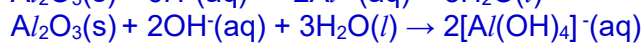


Ser



Asp

- (d) (i)  $\text{Al}_2\text{O}_3$  is an amphoteric oxide that can react with both acids and bases. By writing suitable balanced chemical equations, illustrate the amphoteric property of  $\text{Al}_2\text{O}_3$  and explain why  $\text{Al}_2\text{O}_3$  is amphoteric. [4]



$\text{Al}_2\text{O}_3$  has a giant ionic lattice structure with strong electrostatic forces of attraction between  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  ions. The high charge density of  $\text{Al}^{3+}$  (1m) allows the electron cloud of  $\text{O}^{2-}$  ion to be polarised, resulting in covalent character in the ionic bond (1m).

- (ii) Predict and explain the difference in melting points between  $\text{NaCl}$  and  $\text{AlCl}_3$ . [3]

$\text{NaCl}$  has a higher melting point than  $\text{AlCl}_3$ . 1m

$\text{NaCl}$  is held together by strong electrostatic forces of attraction between  $\text{Na}^+$  and  $\text{Cl}^-$  which is stronger than the id-id between  $\text{AlCl}_3$  molecules.

More energy needed to overcome the ionic bonds in  $\text{NaCl}$  than the IMF between  $\text{AlCl}_3$  molecules.

[Total: 20]

**End of Paper 3**