

- 1 (a) (i) Manganese(IV) oxide, MnO_2 is the most common starting material for the production of compounds of manganese of other oxidation states.

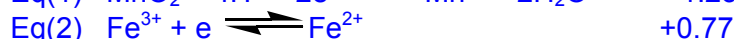
With reference to the *Data Booklet*, state which of the following ions would convert manganese(IV) oxide to manganese(II) sulfate in an acidic solution.

$\text{Pb}^{4+}(\text{aq}) / \text{Pb}^{2+}(\text{aq})$	$E^\theta = +1.69\text{V}$
$\text{Co}^{3+}(\text{aq}) / \text{Co}^{2+}(\text{aq})$	$E^\theta = +1.82\text{V}$
$\text{Fe}^{3+}(\text{aq}) / \text{Fe}^{2+}(\text{aq})$	$E^\theta = +0.77\text{V}$

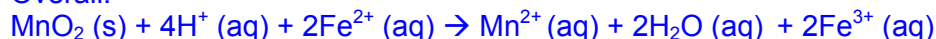
$\text{Co}^{3+}(\text{aq}) / \text{Co}^{2+}(\text{aq})$	$E^\theta = +1.82\text{V}$
$\text{Pb}^{4+}(\text{aq}) / \text{Pb}^{2+}(\text{aq})$	$E^\theta = +1.69\text{V}$
$\text{MnO}_2(\text{s}) / \text{Mn}^{2+}(\text{aq})$	$E^\theta = +1.23\text{V}$
$\text{Fe}^{3+}(\text{aq}) / \text{Fe}^{2+}(\text{aq})$	$E^\theta = +0.77\text{V}$

Only can choose $\text{Fe}^{2+}(\text{aq})$

- (ii) Calculate the E^θ_{cell} value to prove that the reaction between MnO_2 and the ion you have chosen in **a(i)** is feasible and write a balanced equation for the reaction.



Overall:



$$E^\theta_{\text{cell}} = (+1.23) - (+0.77) = +0.46\text{V}$$

Since $E^\theta_{\text{cell}} > 0$, reaction is feasible.

- (iii) What would be the colour of the final solution observed?

Orange (Pale pink + Yellow)

Also accept yellow

[5]

- (b) (i) Write the full electronic configuration of Zn^{2+} and Mn^{2+} .



- (ii) Explain why manganese forms compounds that are often coloured whereas compounds of zinc are usually white.

Compounds of Mn is coloured due to the presence of incompletely filled 3d-orbitals in the Mn^{2+} metal ions. In the complex ion, the electrostatic field produced by the donated lone pairs on the ligands, splits the five orbitals into a group of three and a group of two.

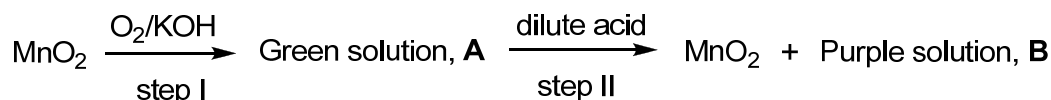
An electron in a lower d orbital energy can absorb radiation and be promoted into the higher orbital energy level by absorbing photons of light in the visible light region (d-d transitions).

The colour seen is the complement of those absorbed in the visible region of the spectrum.

Zn^{2+} is colourless because its d orbitals are completely filled. It is not possible to promote an electron to the higher energy level.

[5]

- (c) MnO_2 undergoes the following reaction as shown in the schematic diagram below:



Step I: Oxidation of MnO_2 in molten KOH with oxygen from the air produces a green compound, **A**.

Step II: Reaction of **A** with dilute acid produced 0.174 g of MnO_2 and a purple solution of compound **B** was observed. A solution of compound **B** is just decolourised by 40.0 cm^3 of $0.500 \text{ mol dm}^{-3}$ iron(II) sulphate.

- (i) **B** contains potassium, manganese and oxygen only. Suggest the chemical formula of compound **B** that causes the solution to appear purple.



- (ii) Calculate the number of moles of MnO_2 produced in step II.

No. of moles of $\text{MnO}_2 = 0.174 / (54.9 + 16 \times 2) = \underline{0.002 \text{ mol}}$

- (iii) Calculate the number of moles of compound **B** produced in step II, given that compound **B** and iron(II) sulphate reacted in a 1:5 mole ratio.

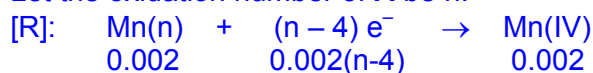
No. of moles of compound **B** = $40/1000 \times 0.5 \times 1/5 = \underline{0.004 \text{ mol}}$

- (iv) With reference to step II of the above reaction scheme, let the oxidation number of manganese in **A** be n , i.e. Mn^{n+} . Using your answer to **c(ii)** and **c(iii)**, write an expression in n to show

(I) the no. of moles of electrons gained by Mn^{n+} when Mn^{n+} is reduced to MnO_2

(II) the no. of moles of electrons lost by Mn^{n+} when Mn^{n+} is oxidised to **B**

Let the oxidation number of **A** be n .



No of moles of electrons gained = $0.002(n-4)$



No. of moles of electrons lost = $0.004(7-n)$

- (v) Hence, using your answer to **c(iv)**, calculate the oxidation number of manganese in compound **A**.

No. of moles of electrons gained = No. of moles of electrons lost

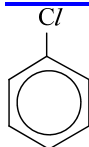
$$0.002(n-4) = 0.004(7-n)$$

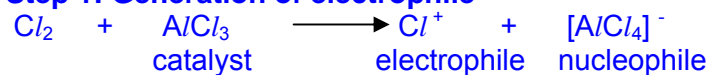
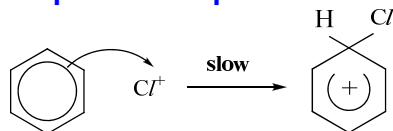
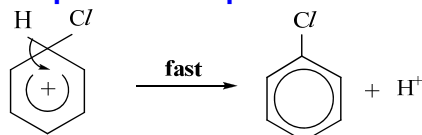
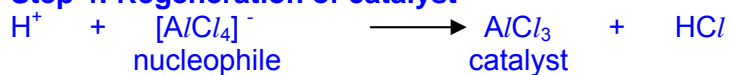
$$n = \underline{+6}$$

[5]

- (d) (i) Cl_2 reacts with benzene in the presence of a suitable catalyst. Describe the mechanism and suggest the product obtained.

Product



Mechanism: Electrophilic Substitution**Step 1: Generation of electrophile****Step 2: Electrophilic attack on benzene ring****Step 3: Loss of proton****Step 4: Regeneration of catalyst**

- (ii) The reaction in **d(i)** can only take place under anhydrous conditions. Suggest a reason to explain why it is so.

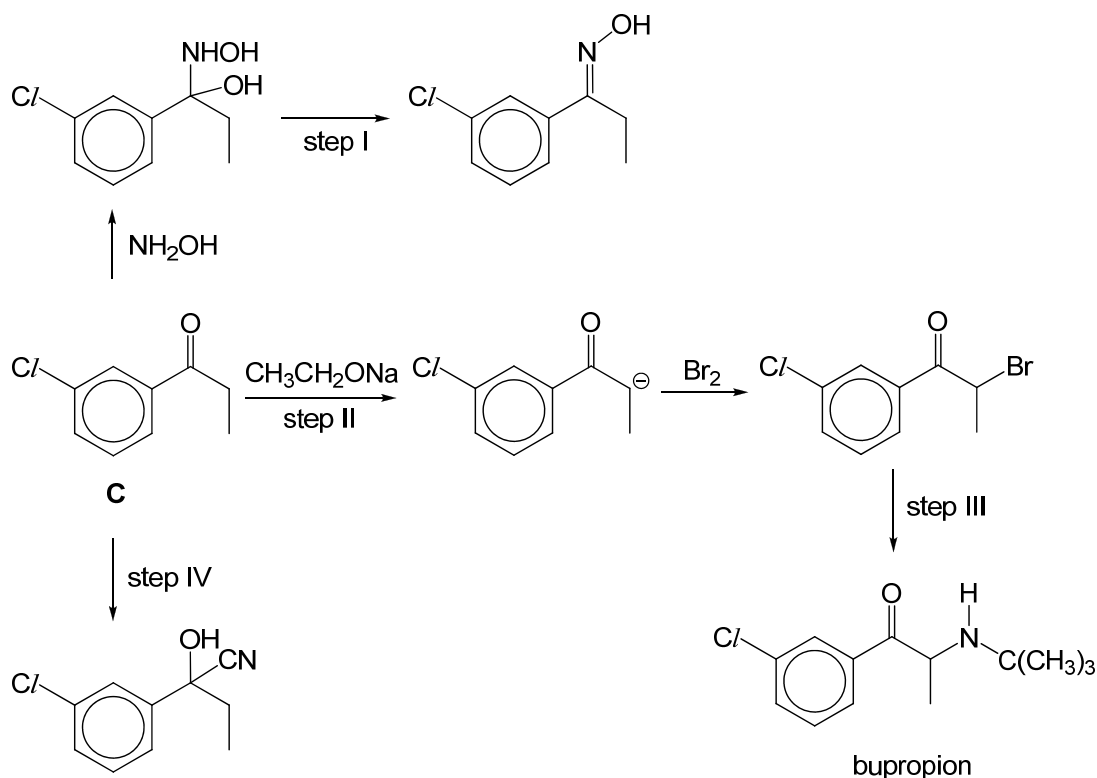
In the presence of water, AlCl_3 ionises to form Al^{3+} and Cl^- **OR** hydrolyses in water to form acidic solution **OR**

Hence under hydrated conditions, AlCl_3 cannot act as Lewis acid **OR** catalyst **OR** halogen carrier to accept a lone pair of electrons from BrCl **OR** electrophile Br^+ cannot be generated to brominate benzene. Thus the condition need to be anhydrous.

[5]
[Total:20]

- 2 (a) This question is related to the chemistry of carbonyl compounds to form nitrogen-containing compounds.

Bupropion is an anti-depressant that was subsequently found to be useful as a smoking cessation aid. It reduces the severity of nicotine cravings and withdrawal symptoms. It can be synthesised from compound **C**, from which many derivatives of bupropion can also be synthesised.



- (i) Suggest the type of reaction occurring in step I.
 Step 1 is an elimination/dehydration reaction.
- (ii) Name the type of reaction in step III and state the reagent(s) and condition(s) involved.
 Nucleophilic substitution
 Reagents: ethanolic $(\text{CH}_3)_3\text{CNH}_2$
 Conditions: Heat with reflux
- (iii) Given that bupropion is basic, without using fractional distillation, suggest a reagent and a suitable separation technique that you will use to isolate the product bupropion from the reaction mixture. Describe what you will observe in the process.
- 1) Add conc HCl / aqueous HCl to the liquid product.
 - 2) A white ppt will be formed.
 - 3) Obtain the crystals of bupropion hydrochloride through filtration.

- (iv) Suggest the reagents and conditions required in step IV and state and describe the mechanism of this step.

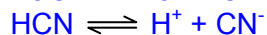
Reagents: HCN , trace amount of NaOH(aq)

OR HCN , trace amount of NaCN

Conditions: $10 - 20^\circ\text{C}$ / Cold

Mechanism: Nucleophilic Addition

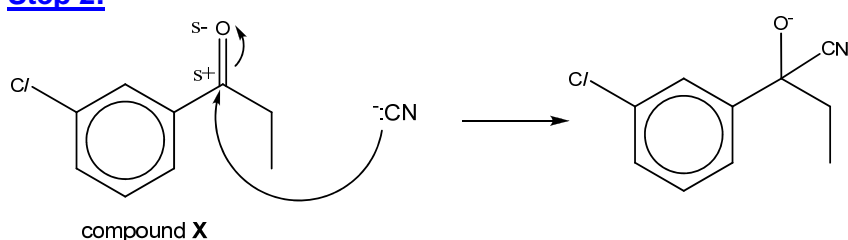
Step 1:



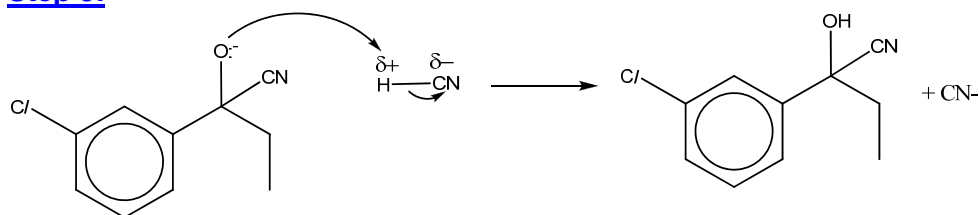
OR



Step 2:



Step 3:



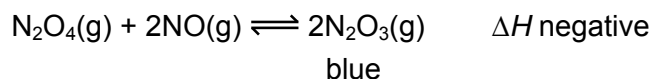
- (vi) Based on your answer in **a(iv)**, suggest and explain whether the product of step IV is optically active or optically inactive.

The product of step 5 is optically inactive.

In the mechanism, the nucleophile/ CN^- can attack the planar carbonyl carbon from the top and bottom with equal probability. So the product exists as a racemic mixture, where the optical activity of the optical isomers cancel out.

[12]

- (b) When two colourless gases dinitrogen tetraoxide and nitrogen monoxide are mixed at room temperature, the two gases react slowly to form the blue compound dinitrogen trioxide according to the following equilibrium.



A gas syringe is filled with the colourless gases and sealed. When the gases are compressed, the blue colour becomes more intense. When the system is warmed, the blue colour fades.

- (i) Use Le Chatelier's Principle to explain the above observations.
When the gases are compressed, total pressure increased. The equilibrium position will shift to the right where there are lesser gaseous molecules. Hence, concentration of N_2O_3 increases/ there are more N_2O_3 molecules and the blue colour becomes more intense.

When the system is warmed, the equilibrium position will shift to the left to favour the endothermic reaction to absorb additional heat. Hence concentration of N_2O_3 decreases/ there are less N_2O_3 molecules and the blue colour fades.

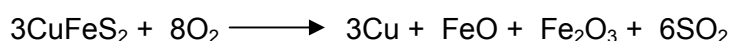
- (ii) At low temperatures, N_2O_3 exists as a deep blue liquid. Using your knowledge of the chemistry of P_4O_6 , state the acid-base nature of N_2O_3 and write an equation with state symbols to illustrate your answer.

N_2O_3 is acidic.



[5]

- (c) (i) A large portion of the copper produced in the world is obtained by the *smelting of chalcopyrite*. It is an iron-containing mineral with the molecular formula of CuFeS_2 . Smelting of chalcopyrite can be represented by the following equation:



Calculate the volume of sulfur dioxide gas released into the atmosphere at r.t.p. if 1 tonne of the rock sample is smelted. It is estimated that the rock contains 1.5% by mass of chalcopyrite. [1 tonne = 1000 kg]

$$\text{Mass of CuFeS}_2 \text{ smelted} = \frac{1.50}{100} \times 1 \times 10^6 = 1.5 \times 10^4 \text{ g}$$

$$\text{Amount of CuFeS}_2 \text{ smelted} = \frac{1.50 \times 10^4}{[63.5 + 55.8 + 2(32.1)]} = 81.744 \text{ mol}$$

$$\text{Mole ratio of CuFeS}_2 : \text{SO}_2 = 3 : 6$$

$$\text{Hence mole of SO}_2 = 2 \times 81.744 = 163.488 \text{ mol}$$

$$\text{Vol. of SO}_2 = 163.488 \times 24.0 \text{ dm}^3 = 3.92 \times 10^4 \text{ dm}^3$$

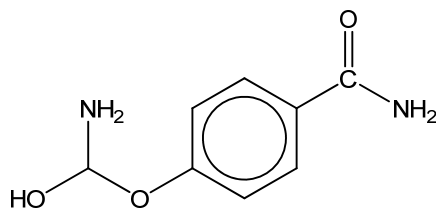
- (ii) Why is it important to remove SO_2 from the products of smelting before release into the atmosphere?

SO_2 in the atmosphere will result in the formation of acid rain, which is detrimental to living things and will corrode buildings / cause air pollution / cause global warming.

[3]

Total: [20]

- 3 (a) Atenolol is a drug used mainly to prevent hypertension and coronary heart disease.

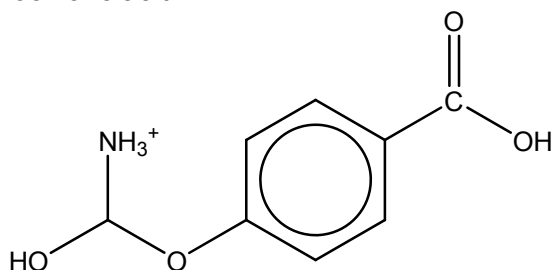


Atenolol

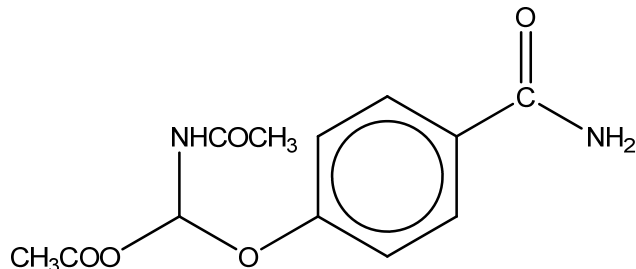
[Assume that the ether functional group is inert and does not undergo any reaction.]

Draw the structural formula of the organic product formed when Atenolol is treated with the following reagents:

- (i) Hot aqueous hydrochloric acid

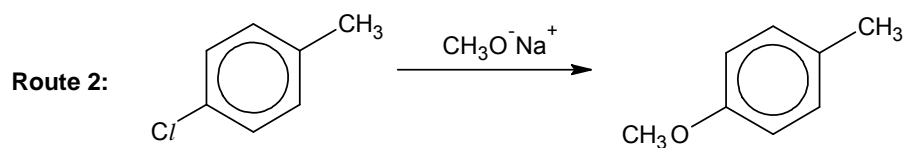
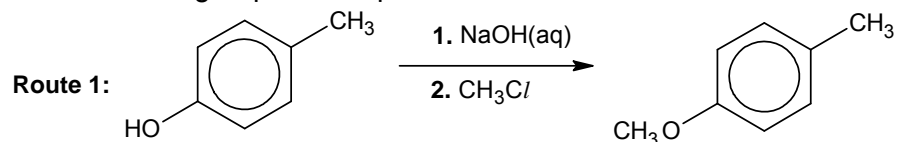


- (ii) Ethanoyl chloride



[4]

- (b) Part of the reaction scheme for the formation of Atenolol involves the synthesis of the ether functional group via two possible routes:



- (i) Which route will give a greater yield of the product? Explain your reasoning.

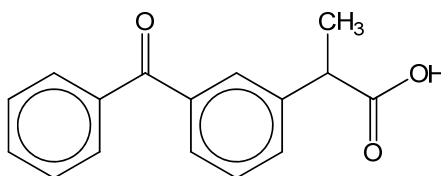
Route 1 will give greater yield.

Route 1 can form a better OR stronger nucleophile for subsequent attack on CH_3Cl

Or

Route 2 has a lower yield, because the lone pair of electrons on Cl atom interacts with the π electrons of the benzene ring, hence strengthening the C – Cl bond. Thus hydrolysis of the C – Cl bond is slower in Route 2.

- (ii) Another drug, Ketoprofen, commonly used in painkillers, has the structure as shown below. Describe a simple chemical test which would enable you to distinguish between Atenolol and Ketoprofen.



Ketoprofen

Reagent : 2,4-DNPH and room temperature

Observation: For Ketoprofen, orange ppt formed

No ppt formed for Atenolol

Reagent : Na_2CO_3 solid and room temperature

Observation:

For Ketoprofen, effervescence observed, evolved forms white ppt with $\text{Ca}(\text{OH})_2$ (aq)

No effervescence formed for Atenolol

Reagent : $\text{NaOH}(\text{aq})$ and heat

Observation:

For Atenolol, pungent gas evolved turned moist red litmus paper blue

For Ketoprofen, moist red litmus remained

[4]

- (c) (i) Group II carbonates decompose in a similar manner as Group II nitrates. The following table shows the temperature at which Group II carbonates decompose.

Carbonate	Decomposition temperature / K
MgCO_3	523
CaCO_3	1098
SrCO_3	1373
BaCO_3	1573

Based on the above data, state and explain the trend of thermal stabilities of Group II carbonates down the group.

The decomposition temperature increases down the group and hence the thermal stability increases down the group.

Down the group, size of cation increases. This results in a decrease in its charge density and polarising power, hence extent of polarization of electron cloud of carbonate ion decreases. More energy required to break down the group II carbonate/ carbonate ion.

- (ii) One of the products in the thermal decomposition of magnesium carbonate is magnesium oxide. It is used as a refractory material as it is able to withstand high temperatures.

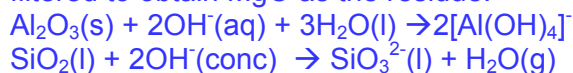
Relate this use of magnesium oxide to its structure and bonding.

Magnesium oxide has a giant ionic lattice where strong electrostatic forces of attraction exist between magnesium and oxide ions. These give it the strength to withstand the high temperature.

- (iii) A mixture of magnesium oxide, MgO, alumina, Al_2O_3 and silica, SiO_2 is usually used in the manufacture of such refractory material.

Suggest, using suitable equations with state symbols, how magnesium oxide can be separated from a mixture containing these three oxides.

Magnesium oxide is basic and hence has no reaction with alkali. To the mixture, add excess NaOH (concentrated/aqueous) and both amphoteric Al_2O_3 and acidic SiO_2 will dissolve. Hence, the resulting mixture can be filtered to obtain MgO as the residue.

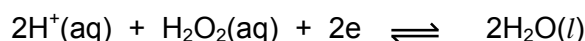
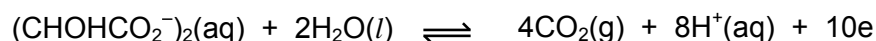


[9]

- (d) (i) One of the important uses of transition metals or their compounds is their role as catalysts in industrial processes.

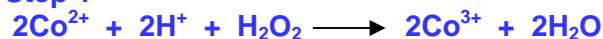
Tartrate ions, $(\text{CHOHCO}_2^-)_2$ are oxidised by hydrogen peroxide to carbon dioxide and water. The reaction is catalysed by $\text{Co}^{2+}(\text{aq})$. The solution is pink at the beginning and end of the reaction, but green during it.

The redox reaction between tartrate ions and hydrogen peroxide is represented by the following half-equations:

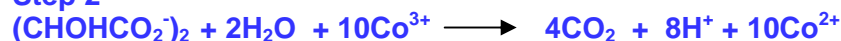


Suggest a **two-step** mechanism by which $\text{Co}^{2+}(\text{aq})$ ions catalyse this reaction.

Step 1



Step 2



- (ii) Besides the example in **d(i)**, give another example of a reaction that uses a transition metal or its compound as a homogenous catalyst and state the identity of this catalyst.

[3]

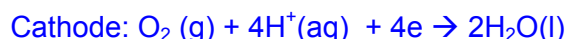
FeBr_3 as homogenous catalyst for halogenation of benzene OR
 Fe^{3+} ions / Fe^{2+} ions reaction between $\text{S}_2\text{O}_8^{2-}$ and I^-

[Total:20]

- 4 (a) Since its invention in 1950 by John Hopps, the heart pacemaker has saved the lives of many cardiac patients by regulating their heartbeat.

In this device, electrical energy is generated by implanting zinc and platinum electrode in body tissues. These electrodes in the oxygen-containing body fluid will form a bioelectric battery in which zinc is oxidized and oxygen is reduced to water.

- (i) Write balanced half equations, with state symbols, for the reactions that occur at the anode and cathode of the bioelectrical battery.



- (ii) Calculate the time taken for a 6.5 g of zinc electrode to be used up, given that a current of 4×10^{-5} A is generated.

No of moles of zinc = $6.5 / 65.4 = 0.09939$ mol

No of moles of electrons given out = $0.09939 \times 2 = 0.1988$ mol

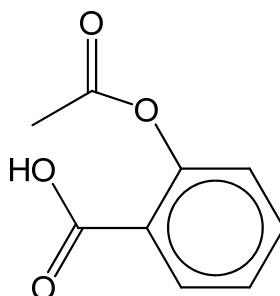
$n_e F = It$

$0.1988 \times 96500 = 4 \times 10^{-5} \times t$

$t = 480\,000\,000$ s OR 4.80×10^8 sec OR 15.2 years OR 1.33×10^5 hours OR time in other units (weeks, days, etc)

[3]

- (b) Acetylsalicylic acid is known for its ability to ease pains and reduce fevers since ancient times. It is an active component found in aspirin, an anti-inflammatory drug. Acetylsalicylic acid is a monobasic acid with $K_a = 1.56 \times 10^{-5} \text{ mol dm}^{-3}$.



Acetylsalicylic acid

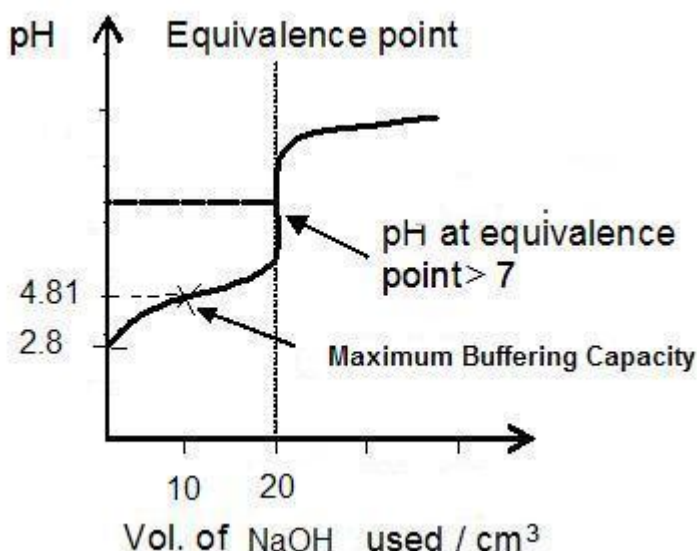
A 25.0 cm^3 sample of acetylsalicylic acid with a pH of 2.8 was titrated with 0.20 mol dm^{-3} of aqueous sodium hydroxide. 20.00 cm^3 of aqueous sodium hydroxide was needed for complete reaction.

- (i) Calculate the pH at maximum buffering capacity.

Maximum Buffering Capacity

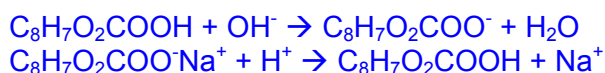
$\text{pH} = \text{p}K_a = -\log(1.56 \times 10^{-5}) = 4.81$

- (ii) Sketch and label the titration curve obtained, clearly indicating the following:
- the initial pH
 - equivalence point
 - maximum buffering capacity



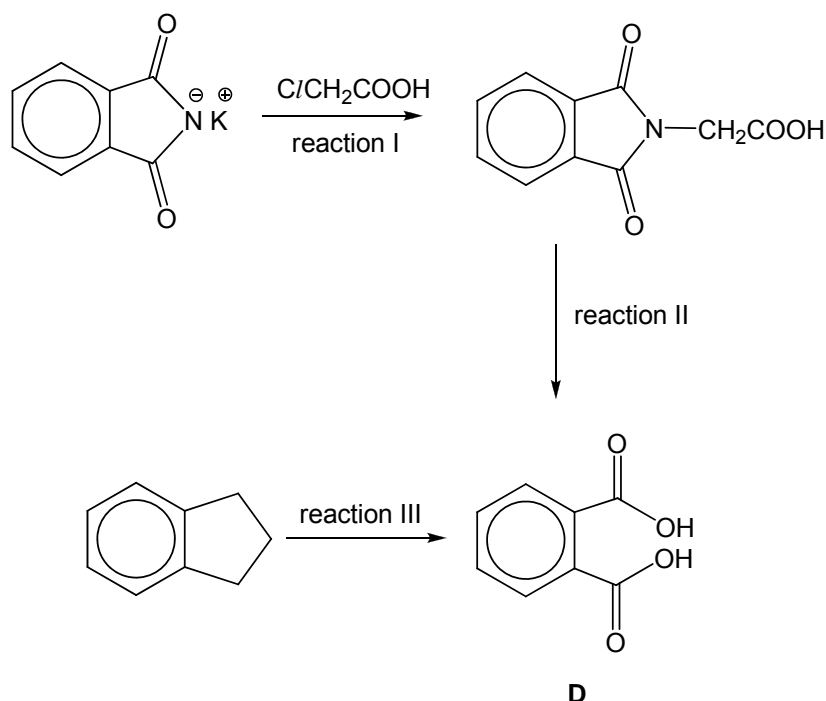
- (c) A mixture of acetylsalicylic acid, $\text{C}_8\text{H}_7\text{O}_2\text{COOH}$ and its salt, sodium acetylsalicylate, $\text{C}_8\text{H}_7\text{O}_2\text{COO}^-\text{Na}^+$ is used as a buffer solution in biochemical studies. Write equations to illustrate how the above mixture acts as a buffer when small amounts of acid or alkali are added to it.

[3]



[2]

- (d) The following reaction scheme involves Compound **D**, benzene 1,2-dicarboxylic acid which is a derivative of acetylsalicylic acid.



- (i) State the type of reactions for reaction I and III.

Reaction I: Nucleophilic Substitution, $\text{S}_{\text{N}}2$

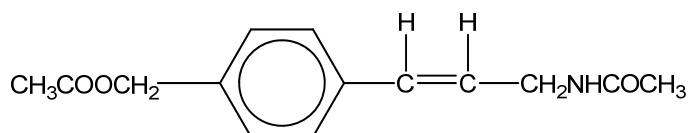
Reaction III: Side-chain Oxidation (Accept oxidation)

- (ii) Suggest reagent(s) and condition(s) for reaction II and III.

Reaction IIReagent and condition: Dilute H_2SO_4 or HCl or aq NaOH , heat with refluxReaction IIIReagent and condition: KMnO_4 , dilute H_2SO_4 , heat with reflux

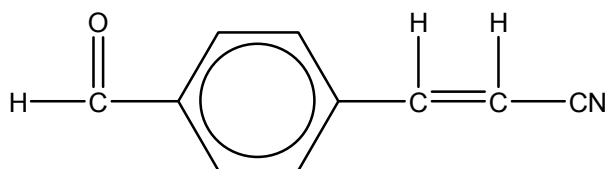
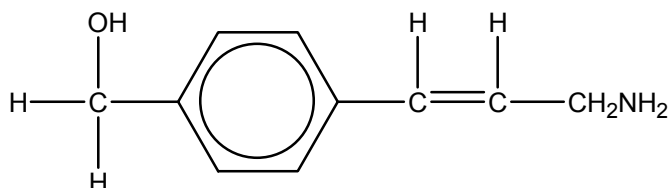
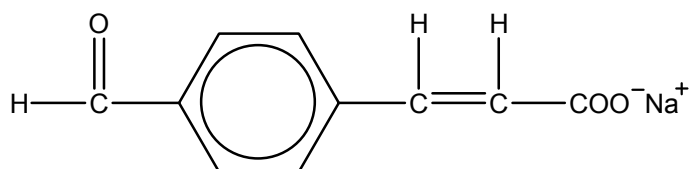
[4]

- (e) Compound **E**, $\text{C}_{10}\text{H}_7\text{NO}$ can exhibit geometric isomerism. **E** can react with silver diamine but not Fehling's solution. On reacting **E** with lithium aluminium hydride, **F**, $\text{C}_{10}\text{H}_{13}\text{NO}$ is formed. **F** is readily soluble in acid. 1 mole of **F** reacts with 2 moles of ethanoyl chloride to give the compound below:



When **E** is heated with dilute sodium hydroxide, the dried product is a white crystalline solid, **G**, $\text{C}_{10}\text{H}_7\text{O}_3\text{Na}$.

Deduce the structural formula of **E**, **F** and **G**, explaining your reasoning.

E:**F:****G:**

E has comparable hydrogen and carbon ratio and hence has a benzene ring.

E has $\text{C}=\text{C}$ bond / alkene since it can display geometric isomerism.

E undergoes mild oxidation in presence of Tollen's reagent and has an aromatic aldehyde functional group.

E undergoes reduction to form **F** which has a primary alcohol functional group.

F has an amine functional group since it is soluble in acid.

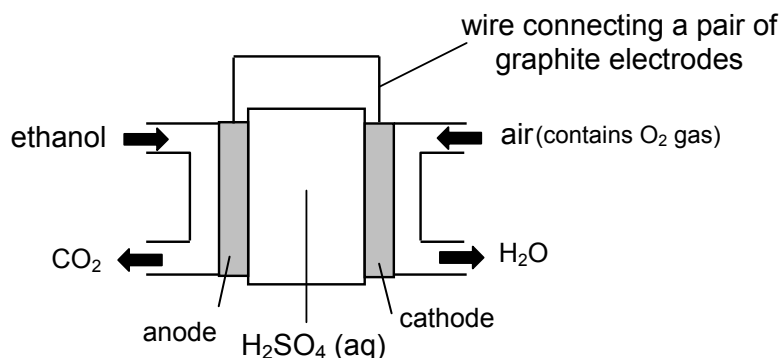
F undergoes nucleophilic substitution to form **G**.

E undergoes alkaline hydrolysis to form **G** which is a sodium carboxylate salt.

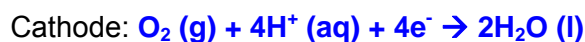
[7]

[Total:20]

- 5 Ethanol fuel cells are a more practical and viable source of energy as compared to hydrogen fuel cells.

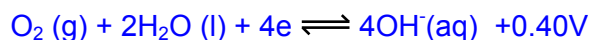
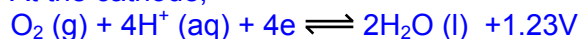


- (a) (i) Write balanced half-equations, with state symbols, for the reactions taking place at the anode and cathode when the fuel cell is in operation.



- (ii) Use appropriate data from the *Data Booklet* to explain why an acidic electrolyte is often preferred over an alkaline or neutral electrolyte.

At the cathode,



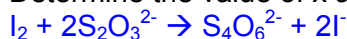
In acidic medium, O_2 is more easily reduced as it has a more positive standard reduction potential or $E^\ominus_{\text{O}_2/\text{H}_2\text{O}}$. Thus the E^\ominus_{cell} generated is larger.

[4]

- (b) A metallic salt containing the anion I_xCl_y^- decomposed when heated to form iodine vapour and the metallic chloride. When 0.270g of this compound was heated, the iodine evolved was bubbled into excess potassium iodide solution.

The dissolved iodine required 21.30 cm^3 of $0.0600 \text{ mol dm}^{-3}$ of aqueous sodium thiosulfate for complete reaction. When the residue was dissolved in water, the resultant solution required 6.40 cm^3 of $0.100 \text{ mol dm}^{-3}$ aqueous silver nitrate for complete reaction.

- (i) Determine the value of x and y in I_xCl_y^- .



$$\text{No. of moles of } \text{S}_2\text{O}_3^{2-} = \frac{0.0600}{1000} \times 21.30 = 1.278 \times 10^{-3} \text{ mol}$$

$$\text{No. of moles of } \text{I}_2 = \frac{1.278 \times 10^{-3}}{2} = 6.39 \times 10^{-4} \text{ mol}$$

$$\text{No. of moles of } \text{I}^- = 1.278 \times 10^{-3} \text{ mol}$$

$$\text{No. of moles of Silver nitrate} = \frac{0.100}{1000} \times 6.40 = 6.39 \times 10^{-4} \text{ mol}$$



$$\text{No. of moles of } \text{Cl}^- = 6.39 \times 10^{-4} \text{ mol}$$

$$\text{I}^- : \text{Cl}^-, x : y = 2 : 1$$

$$X = 2$$

$$Y = 1$$

- (ii) Hence, determine the identity of the metallic element.

$$\text{No. of moles of } I_xC/I_y^- = 6.39 \times 10^{-4} \text{ mol}$$

$$M_r \text{ of the metallic salt} = \frac{0.27}{6.4 \times 10^{-4}} = 421.9$$

$$A_r \text{ of metal} = 421.9 - (79.9 \times 2) - 35.5 = 133$$

Identity: Caesium / Cs

[6]

- (c) Predict the observations when aqueous silver nitrate is added to a solution containing both Cl^- and I^- , followed by an addition of excess aqueous ammonia to the resultant mixture.

The resultant mixture will contain a mixture of white solid, $AgCl$ and yellow solid AgI . When excess aqueous ammonia is added, the white solid will dissolve, leaving behind only yellow solid.

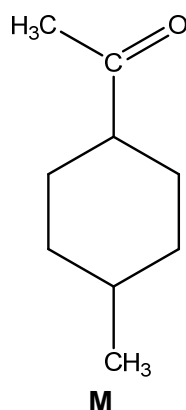
[2]

- (d) α -Terpineol, $C_{10}H_{18}O$, has a pleasant smell similar to lilac and is a common ingredient in perfumes, cosmetics, and flavours.

α -Terpineol contains a *cyclohexene ring* and an alcohol group which is not readily oxidised.

Heating α -Terpineol with concentrated acidified $KMnO_4$ gives H, $C_{10}H_{18}O_4$, which gives a yellow precipitate on warming with alkaline aqueous iodine. On hydrogenation in the presence of palladium catalyst, α -Terpineol gives J, $C_{10}H_{20}O$.

J reacts readily in the presence of a few drops of concentrated sulfuric acid to give K, $C_{10}H_{18}$. K is oxidised by warm acidified $KMnO_4$ to give M, $C_9H_{16}O$ along with the evolution of CO_2 gas.



Deduce the structural formulae for H, J, K and α -Terpineol. Explain your reasoning.

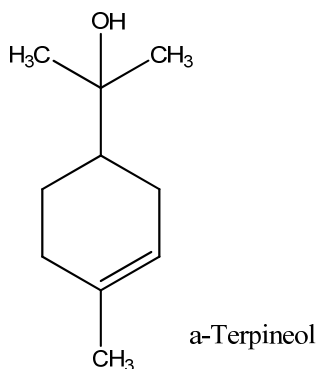
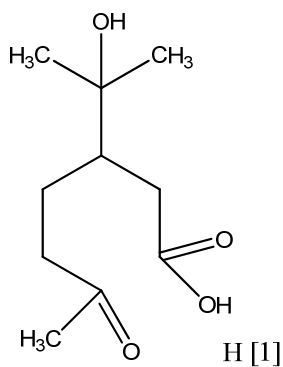
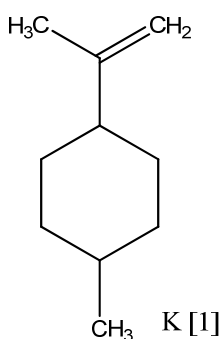
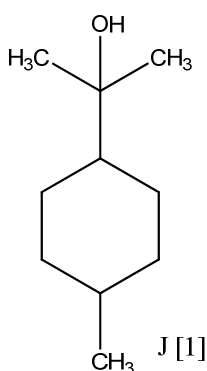
α -Terpineol has a tertiary alcohol as it is not easily oxidised. It does not have benzene ring as the C:H ratio is not 1:1.

Hydrogenation of α -Terpineol will reduce the double bond **OR** it undergoes electrophilic addition. **J** undergoes dehydration/elimination with concentrated sulfuric acid to give an alkene, **K**

α -Terpineol undergoes oxidative cleavage with concentrated acidified KMnO_4 . Compound **H** contains $-\text{CH}_3\text{CO}$. **H** undergoes mild oxidation with alkaline aqueous iodine.

K undergoes oxidative cleavage with concentrated acidified KMnO_4 to form compound **M**.

K contains terminal $\text{C}=\text{C}$ double bond as **M** contains one less carbon after oxidative cleavage.



[8]
[Total:20]