PAPER 2

1 Planning (P)

Eggshells are rich in calcium carbonate and make good plant fertilisers to replenish calcium, an essential nutrient in plant growth. The eggshells are normally crushed and sprinkled around the plants. The shells will slowly decompose and enrich the soil. The decomposition of $CaCO_3(s)$ may be represented as:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

In the laboratory, all Group II carbonates, $\boldsymbol{M}CO_3$, can be decomposed by heating to give the corresponding oxide, $\boldsymbol{M}O$, and carbon dioxide, CO_2.

You are to design an experiment to investigate how the rate of decomposition of Group II carbonates varies down the group.
In addition to the standard apparatus available in a school laboratory for gas collection, you are provided with the following materials,

- samples of carbonates of magnesium, calcium, strontium and barium,
- a stopwatch

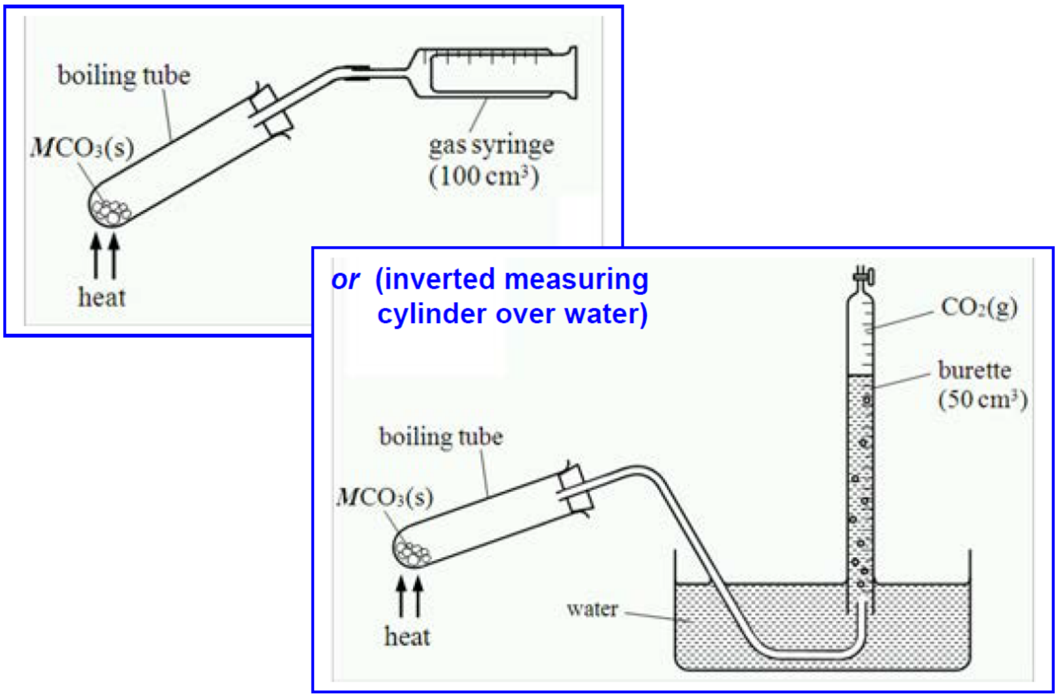
(a) Briefly describe how you would measure the rate of decomposition of the different carbonates in order to enable comparison.

- **measure time taken to produce (collect) the same volume of $CO_2(g)$ from each carbonate**
- **rate $\propto \frac{1}{\text{time}}$** [1]

(b) Draw a diagram of the apparatus and experimental set up that you would use to carry out the experiment. Show clearly the following:

- the apparatus used to heat the carbonate, and
- how the carbon dioxide will be collected.

Label each piece of apparatus used, indicating its size or capacity.



***or* (inverted measuring cylinder over water)**

[2]

(c) The temperature of the Bunsen flame varies depending on the ratio of the fuel to oxygen burnt. Besides keeping to the same fuel to oxygen ratio, suggest how you would control another factor in the heating to ensure a fair comparison of the rate of decomposition of different carbonates.

- **Bunsen burner at *same distance* from the reaction vessel.**

[1]

(d) Other than the use of safety goggles, state one hazard that must be considered when planning the experiment and suggest how you would keep this risk to a minimum.

1. **"hot" apparatus – use heat-proof gloves or let apparatus cool before handling**
2. **potential suck back (if water allowed to suck back, hot boiling tube would crack and shatter) – remove delivery tube from water when heating is stopped.**

[2]

(e) With reference to the apparatus in **(b)**, show how you would calculate the mass of each carbonate used in the experiment.
[M_r: $MgCO_3$ = 84.3; $CaCO_3$ = 100.1; $SrCO_3$ = 147.6; $BaCO_3$ = 197.0]

Note: 1. Vol of CO_2(g) collected *must not exceed* capacity of collection device.

2. Mass of each carbonate used must contain the *same number of moles*.

Let volume of CO_2(g) collected = 40 cm^3

Since molar gas volume at r.t.p. = 24 dm^3,

mol of CO_2 = $\frac{40}{24000}$ = 1.67×10^{-3} mol

[*vol and mol of CO_2(g)*]

MCO_3 ® $MO + CO_2$

\ minimum mol of MCO_3 = mol of CO_2 = 1.67×10^{-3} mol

M_r of MCO_3 = (A_r of M) + [12.0 + 3(16.0)] = (A_r of M) + 60.0

Let mol of carbonate = 2.00×10^{-3} mol

mass of MCO_3 = nM_r = 2.00×10^{-3} × [(A_r of M) + 60.0]

[*same mol of each carbonate*]

\ mass of $MgCO_3$ = (2.00×10^{-3}) × 84.3 = 0.169 g

mass of $CaCO_3$ = (2.00×10^{-3}) × 100.1 = 0.200 g

mass of $SrCO_3$ = (2.00×10^{-3}) × 147.6 = 0.295 g

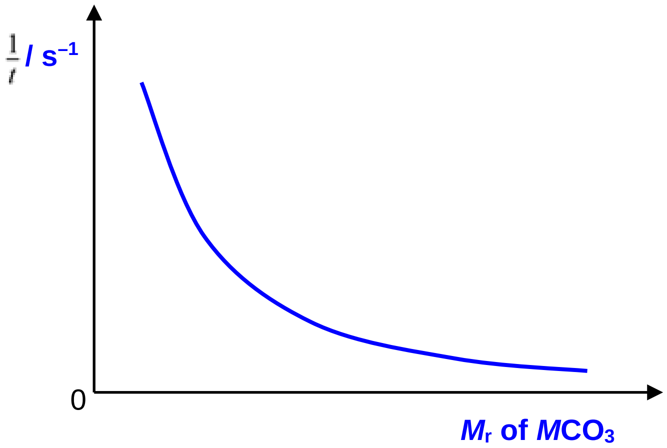
mass of $BaCO_3$ = (2.00×10^{-3}) × 197.0 = 0.394 g

[2]

(f) Draw a table with appropriate headings (and units) to show the data you would record and the values you would calculate in order to plot a suitable graph to show the variation in the rates of decomposition of the carbonates.

	M_r	**time / s**	**$\frac{1}{\text{time}}$ / s^{-1}**
$MgCO_3$	**84.3**		
$CaCO_3$	**100.0**		
$SrCO_3$	**147.6**		
$BaCO_3$	**197.0**		

Sketch, and explain, the shape of the graph you would expect from your results. Label clearly the axes.



Explanation:

- **Down the group, as the cation *increases in size* (while the charge remains unchanged), the *charge density decreases* and the polarising power of the cation also *decreases*.**
- **Hence, the larger cations *polarise* (*distort*) the carbonate anion less and the compound is thus relatively stable to heat.]**

[decrease in charge density of cation; less polarisation of anion]

[4]

[Total: 12]

2 **(a)** Carbon dioxide is useful in beverage carbonation. Cylinders of pressurised carbon dioxide are used to produce carbonated drinks. One such cylinder has an internal volume of 3.0 dm^3 and contains 4.6 kg of carbon dioxide.

(i) Calculate the pressure (in Pascals) the carbon dioxide gas would exert inside the cylinder at 28 °C.

$pV = nRT$

$$p\,(3 \times 10^{-3}) = \frac{4.6\times10^{3}}{44}(8.31)(28+273)$$

$p = 8.72 \times 10^{7}$ Pa

(ii) To find the pressure of a fixed amount of carbon dioxide gas under certain conditions, the van der Waals' equation should be used.

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Without further calculation, explain how the pressure obtained using the above equation would differ from that in **(a)(i)**.

The pressure obtained would be lower since intermolecular forces of attraction exist between CO_2 molecules.

[3]

(b) Real gases like carbon dioxide can be liquefied at low temperatures just by applying pressure. Gases can be liquefied by pressure alone if their temperature is below their critical temperature, T_c. The critical temperature of carbon dioxide is 31.1 °C.

(i) Explain why real gases like carbon dioxide can be liquefied just by applying pressure.

At high pressure, the molecules are very close together, and the intermolecular forces of attraction become significant.

(ii) By considering structure and bonding, suggest a value for the critical temperature of methane and give a reason for your choice.

Any value less than that of carbon dioxide will be accepted as the answer. The van der Waals' forces of attraction between methane molecules is weaker compared to that between carbon dioxide molecules because CH_4 has a smaller electron cloud.

[2]

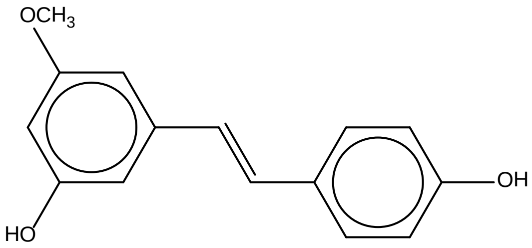
(c) Beyond the critical temperature and pressure, carbon dioxide exists as a supercritical fluid, a state that resembles a gas but has density closer to that in the liquid phase. Carbon dioxide is now well established as a solvent for use in extraction.

(ii) Suggest why supercritical carbon dioxide is preferred as a solvent to extract caffeine from solid coffee over organic solvents like benzene.

Carbon dioxide is non-toxic while benzene is toxic and should be kept away from food and beverages. OR

The carbon dioxide can be easily removed as a gas by depressurizing.

(iii) Suggest why small amounts of ethanol need to be added to supercritical carbon dioxide in the extraction of polyphenols. An example of a polyphenol is shown below.

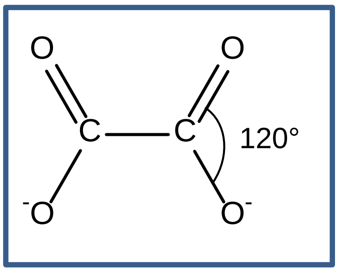


The ethanol molecules added can form hydrogen bonds with the phenol groups present and this increase the solubility of polyphenols.

[2]

(d) Ethanedioate ions, $C_2O_4^{2-}$, can be oxidised by hot acidified aqueous potassium manganate(VII) to form carbon dioxide.

(i) Draw the structure of ethanedioate ions, $C_2O_4^{2-}$, and give the bond angle around the central carbon atom.



(ii) Construct a balanced equation for the reaction between ethanedioate ions and hot acidified potassium manganate(VII).

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Overall equation: $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

(iii) 1.63 g of a salt, $KHC_2O_4{\cdot}H_2C_2O_4$, was dissolved in distilled water and made up to 250 cm³ solution. Calculate the volume of 0.020 mol dm⁻³ of $KMnO_4$ required to react with 20.0 cm³ of the $KHC_2O_4{\cdot}H_2C_2O_4$ solution.
[M_r of $KHC_2O_4{\cdot}H_2C_2O_4$ = 218.1]

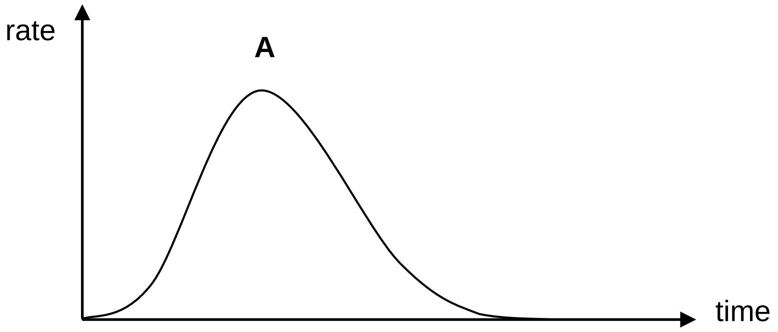
Amount of $C_2O_4^{2-}$ ions present $= 2 \times \frac{1.63}{218.1} \times \frac{20}{250} = 0.0011958$ mol

Amount of MnO_4^- required $= \frac{2}{5} \times 0.0011958 = 0.0004783$ mol

Volume of MnO_4^- required $= \frac{0.0004783}{0.020} = 0.0239\ dm^3 = 23.9\ cm^3$

[4]

The graph of rate against time for the reaction between acidified potassium manganate(VII) and ethanedioate ions is shown below.



(e) **(i)** The reaction between acidified potassium manganate(VII) and ethanedioate ions is usually carried out at a higher temperature of 60 °C. Suggest why the rate of this reaction is slow at room temperature.

Both $C_2O_4^{2-}$ and MnO_4^- are <u>negatively charged</u> and the <u>activation energy for the reaction is high</u> due to <u>repulsion between the ions.</u>

(ii) Suggest the species responsible for the increase in rate of reaction before point **A**, and identify the property which enables it to act as a catalyst in this reaction.

Mn^{2+}. It can exist in variable oxidation states.

……………………………………………………………………………………………

[2]

[Total: 13]

3 Iron is the fourth most common element in the Earth's crust, and has many applications throughout the history of mankind. In nature, iron exists in many different mineral ores, consisting of iron in either +2 or +3 oxidation state. In prehistoric era, iron compounds were more commonly used as pigment without further purification. Limonite, which has the general formula of $FeO(OH){\cdot}nH_2O$, was used as a yellow pigment as early as 10 000 B.C.

(a) **(i)** Complete the electronic configuration of Fe^{3+}.

$1s^2$ …**$2s^2\,2p^6\,3s^2\,3p^6\,3d^5$**…………………

(ii) Briefly explain why iron in mineral ores are found in variable oxidation states, but for s-block elements, for example calcium, there is usually only one oxidation state.

Iron has valence electrons of similar energy in both the 3d and 4s orbitals, thus it can lose electrons from both the 4s and 3d orbitals, giving rise to *variable oxidation states*. However s-block elements can only lose valence electrons in the s orbitals, resulting in only 1 oxidation state.

[3]

(b) A mineralogist dissolved 100 g of a certain pure limonite in concentrated HC*l* to form a yellow solution. It was found that 3.2 mol of HC*l* had reacted based on the equation,

$$FeO(OH).nH_2O + 4HCl \text{ ® } FeCl_4^- + (n+2)H_2O + H^+$$

(i) State the formula of this limonite (with n as an integer): **$FeO(OH).2H_2O$**……………………

Suggest the shape of $FeCl_4^-$: …**Tetrahedral** **[or square planar]**

(ii) Explain, with reference to $FeCl_4^-$, why transition element complexes are coloured.

When Cl^- ligands are bonded to the Fe^{3+} they will cause the originally partially-filled degenerate d-orbitals to split into 2 energy levels with small energy gap.

When electron from the lower d-orbitals absorbs energy in the visible light region, it will be excited to the higher d* orbital. Such transition is d-d* electronic transition.

Complementary colours, yellow, which is not absorbed will be observed as the colour of $FeCl_4^-$. [5]

(c) In recent times, with much better understanding of chemistry, iron and its compounds are widely used as catalysts and reagents in synthesis of chemicals. In particular, the ferrate(VI) ion, FeO_4^{2-} , is a strong oxidising agent that is used in green chemistry and water purification due to its non-toxic by-products.

Ferrate(VI) ions are not stable in acidic conditions and easily oxidise water to give oxygen. Hence they are often produced in an alkaline medium.

Some E^e data of chlorate(I) and ferrate(VI) are given below.

$FeO_4^{2-} + 8H^+ + 3e^- \rightleftharpoons Fe^{3+} + 4H_2O$	$E^\ominus = +2.20$ V
$FeO_4^{2-} + 4H_2O + 3e^- \rightleftharpoons Fe(OH)_3 + 5OH^-$	$E^\ominus = +0.80$ V
$2ClO^- + 4H^+ + + 2e^- \rightleftharpoons Cl_2 + 2H_2O$	$E^\ominus = +1.63$ V
$ClO^- + H_2O + 2e- \rightleftharpoons Cl^- + 2OH^-$	$E^\ominus = +0.89$ V

(i) By selecting relevant $E^\ominus$ data from the *Data Booklet* and using the information above, explain with suitable calculation,

I why ferrate(VI) ions are not stable in acidic conditions.

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^\ominus$ = +1.23V

$E^\ominus_{rxn}$ = +2.20 -1.23 = +0.99 V

As $E^\ominus_{rxn}$ is positive, the reaction is feasible, and ferrate will oxidise water to give oxygen.

II why it is feasible to form potassium ferrate(VI), K_2FeO_4, by reacting KC*l*O with $Fe(OH)_3$ in the presence of KOH.

$3e^- + 4H_2O + FeO_4^{2-} \rightleftharpoons Fe(OH)_3 + 5OH^-$ $E^\ominus = +0.80$ V

$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$ $E^\ominus = +0.89$ V

$E^\ominus_{rxn} = +0.89 - 0.80 = \underline{+0.09\ V} > 0$, hence the reaction is feasible.

(ii) Hence write a balanced overall equation for the formation of K_2FeO_4**.**

$4KOH + 2Fe(OH)_3 + 3KClO \rightarrow 3KCl + 5H_2O + 2K_2FeO_4$……………………………………

(iii) Would you expect an acidified solution of K_2FeO_4 to be a stronger or weaker oxidising agent compared to an acidified solution of $KMnO_4$? Support your answer with relevant $E^\ominus$ values from the *Data Booklet*.

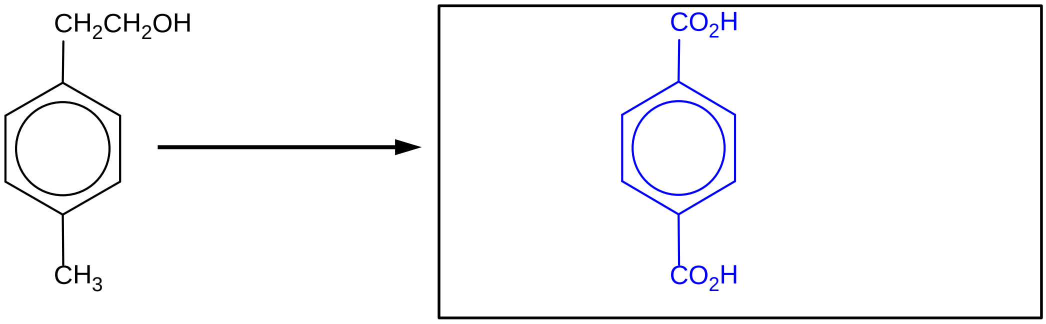
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ $E^\ominus = +1.52$ V

……………………………………………………………………………………………

Comparing the $E^\ominus$ values of +1.52 V and + 2.20V, <u>FeO_4^{2-} undergoes reduction more readily</u>, thus it is a stronger oxidising agent compared to MnO_4^-

……………………………………………………………………………………………

(iv) Hence draw the structure of the possible organic product formed when hot acidified purple K_2FeO_4 reacts with the following compound and suggest the expected observations.



Observations :……………………………………………………………………………

Efferversence of carbon dioxide is observed, and the solution changes <u>from purple FeO_4^{2-} to yellow Fe^3.</u>

……………………………………………………………………………………………

[8]

(d) White light contains all the colours in the visible spectrum. Each of these colours is associated with a certain wavelength, l . The formula relating energy and wavelength is,

$E = hc/l$, where $h = 6.626 \times 10^{-34}$ J s,
$c = 3.00 \times 10^{8}$ m s^{-1}
l has the units of m.

Wavelength, l (10^{-9} m)	**Colour of light**
400	Violet
450	Blue
500	Green
550	Yellow
600	Orange
650	Red

(i) By considering the appearance of green iron(II) compounds and yellow iron(III) compounds, state the colour of light absorbed for these compounds.

Iron(II):…**Red**……………… Iron(III)…**Violet**……………………

(ii) Hence, with the information above, calculate the energy associated with the respective colours absorbed.

For Red absorbed by iron (II), E = $(6.626 \times 10^{-34})(3.00 \times 10^{8})/(650 \times 10^{-9})$
$= 3.06 \times 10^{-19}$ J

For Violet absorbed by iron (III), E = $(6.626 \times 10^{-34})(3.00 \times 10^{8})/(400 \times 10^{-9})$
$= 4.97 \times 10^{-19}$ J

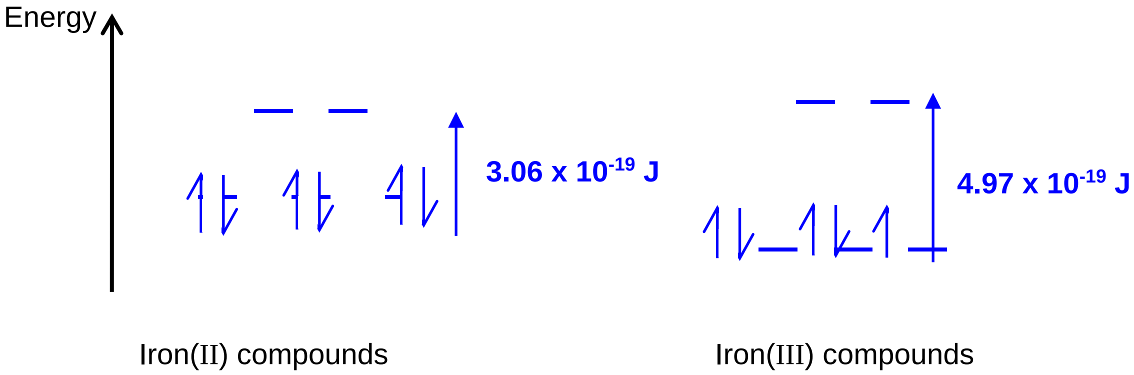
Energy of colour absorbed by

Iron(II) compounds: ……. **3.06×10^{-19} J**

Iron(III) compounds: ……………………… **4.97×10^{-19} J**

(iii) Using your answer in **(d)(ii)**, complete the diagram below to show the relative energies of the d orbitals, and the electronic distribution of the respective compounds. In each case, label clearly the energy difference required for the promotion of an electron upon absorption of light.

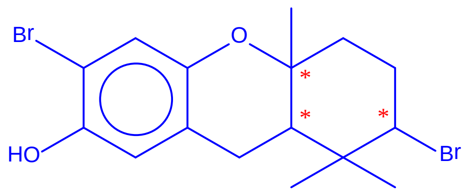
Assume all electrons occupy the lower energy orbitals before the higher energy orbitals.



[5]

[Total: 21]

4 Cymobarbatol is an antimutagenic agent isolated from the marine algae Cymopolia barbata. The structure of cymobarbatol is shown below.



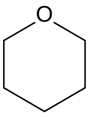
(a) Name **two** functional groups, other than phenyl and ether, that are present in the cymobarbatol molecule.

phenol, secondary bromoalkane, bromoarene

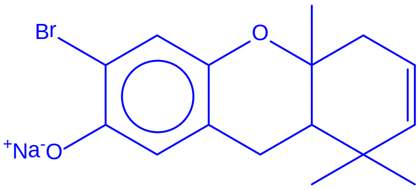
………………………………………… [2]

(b) Identify the chiral carbons in cymobarbatol molecule by placing an asterix (*) against each chiral carbon on the structure above. [1]

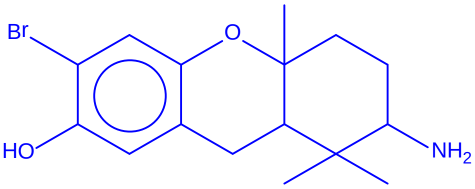
(c) Draw the structural formula of each organic product formed when cymobarbatol is treated with the following reagents.

In the following reactions, the  ring remains unaltered.

(i) ethanolic NaOH, heated under reflux



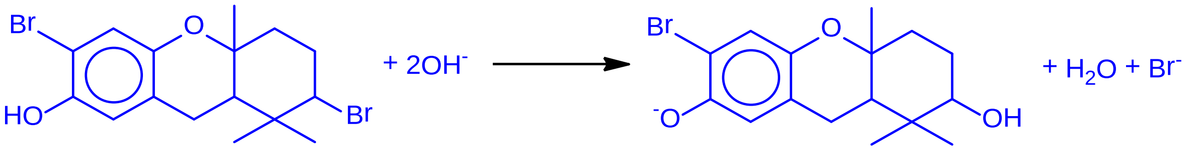
(ii) concentrated ethanolic NH_3, heated in a sealed tube



[2]

(d) Cymobarbatol will also react with aqueous NaOH under reflux condition.

(i) Given that one mole of cymobarbatol reacts with two moles of aqueous NaOH, write a balanced equation for this reaction.



(ii) When bromine in cymobarbatol is replaced by iodine, how would you expect the rate of its hydrolysis reaction to compare to that of cymobarbatol? Explain your answer.

…**When bromine in cymobarbatol is replaced by iodine, the rate of reaction is faster than cymobarbatol.**

…**This is because the C-I bond is longer and hence weaker than the C-Br bond (since I atom is larger than Br atom).**

……………………………………………………………………………………………

……………………………………………………………………………………………

(iii) Describe the expected observations when aqueous $AgNO_3$, followed by concentrated aqueous ammonia, is subsequently added to the resultant mixture in **(d)(i)**. Explain your answer with relevant equations.

A cream ppt. of AgBr will be observed to form when aq. $AgNO_3$ is added. It will then dissolve in the concentrated aq. NH_3 solution to form a colourless solution.

$Ag^+(aq) + 2NH_3(aq)$ ® $[Ag(NH_3)_2]^+(aq)$ equation I

……………………………………………………………………………………………

Ag^+ (aq) reacts with NH_3(aq) to form a soluble complex, $[Ag(NH_3)_2]^+$ from equation I.

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ equilibrium II

As $[Ag^+]$ decreases, the position of equilibrium II shifts to the right and hence more AgBr dissolves

[OR]

When excess NH_3(aq) is added such that ionic product of AgBr < K_{sp} of AgBr, all the AgBr will dissolve completely.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[7]

[Total: 12]

5 There are a number of structural isomers of molecular formula $C_nH_nO_2$. In particular, one of the isomers, **B**, is used as a tincture in perfumes and as a food additive.

(a) To find the value of *n*, a 1.00 g sample of **B** was burned in an excess of oxygen, and the gases that were produced were first passed through a U-tube containing P_4O_{10} (to absorb the water vapour) and then bubbled through concentrated NaOH(aq). The P_4O_{10} in the U-tube **increased** in mass by 0.529 g.

(i) Write an equation for the reaction of P_4O_{10} with water vapour and state the pH of the resultant solution.

$P_4O_{10} + 6H_2O$ à $4H_3PO_4$. pH = 1 to 2

(ii) Suggest why anhydrous $CaCl_2$ **cannot** be used in place of P_4O_{10} in the U-tube.

Calcium chloride will absorb water vapour to form a neutral solution, and would absorb some of the CO_2 formed.

(iii) Calculate the number of moles of water produced.

Amount of H_2O = $\frac{0.529}{18}$ = 0.0294 mol

(iv) Use the above data to show that the value of $n = 8$.

Amount of B = $\frac{1.00}{12n + n + 32} = \frac{1.00}{13n + 32}$ **mol**

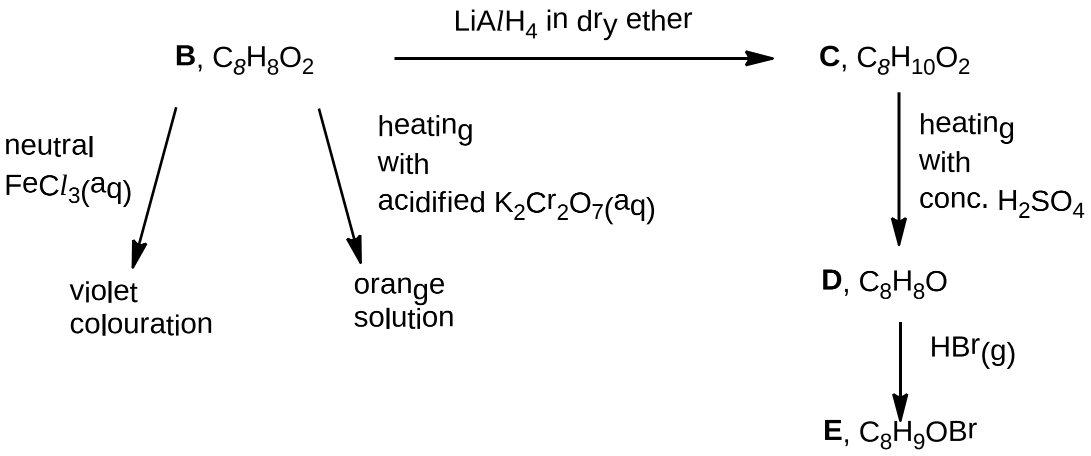
$C_nH_nO_2 \equiv \frac{n}{2} H_2O$

Thus $\frac{1.00}{13n + 32} \times \frac{n}{2} = 0.0294$

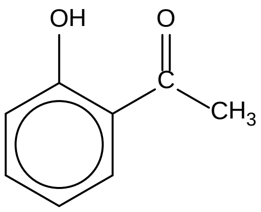
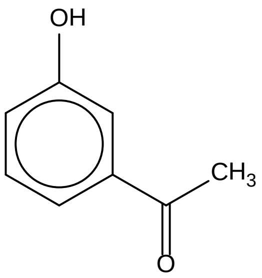
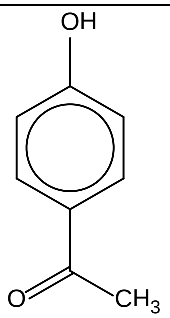
Therefore n = 8

[5]

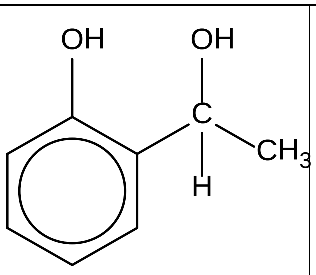
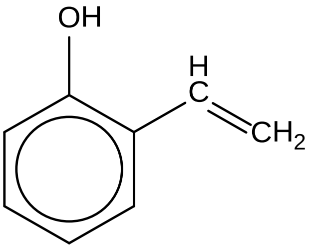
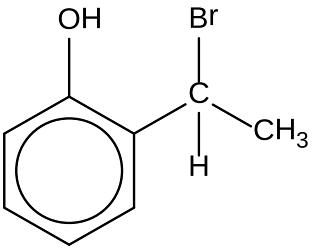
(b) A reaction scheme involving compound **B** and its related compounds, **C** to **E**, undergo the following reactions:



(i) Based on the above information, draw three possible structural isomers of **B**, which are labeled as **B1**, **B2** and **B3** in the boxes below.

		
B1	**B2**	**B3**

(ii) Based on your structure of **B1**, draw the structures of **C**, **D** and **E**.

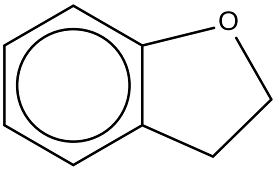
		
C	**D**	**E**

[6]

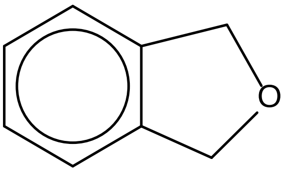
(c) A structural isomer of **D**, C_8H_8O, which is labelled as **F**, contains a C-O-C bond. **F** does **not** react with HBr(g).

(i) Suggest a structural formula of **F**.

F is

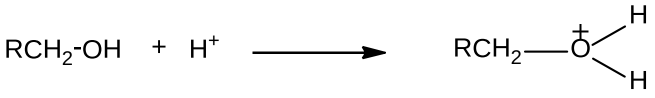


or



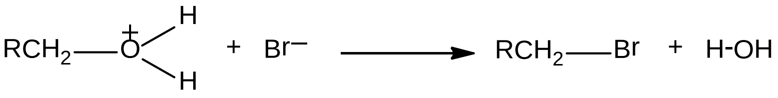
(ii) Although **F** does not react with HBr(g), it can react with concentrated HBr(aq). The reaction of **F** with concentrated HBr(aq) is similar to the reaction of primary alcohols with concentrated HBr(aq). The process involves two stages:

Stage I



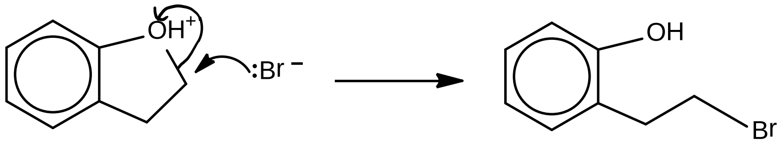
$$RCH_2\text{-}OH + H^+ \longrightarrow RCH_2-\overset{+}{O}H_2$$

Stage II

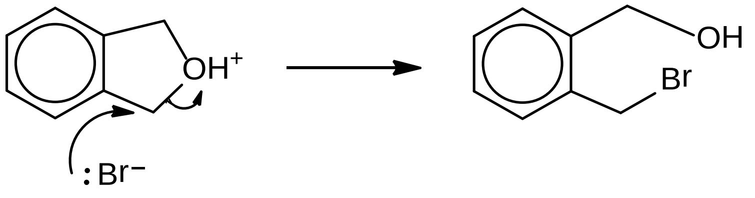


$$RCH_2-\overset{+}{O}H_2 + Br^- \longrightarrow RCH_2-Br + H\text{-}OH$$

Suggest a mechanism for the **Stage II** process in the reaction of **F** with concentrated HBr(aq), including curly arrows to denote movement of electrons, and all charges. You do **not** need to draw the 3-dimensional representation of the molecules involved.



OR



[arrows, lone pair on Br^- indicated, S_N2 mechanism]

[3]

[Total: 14]