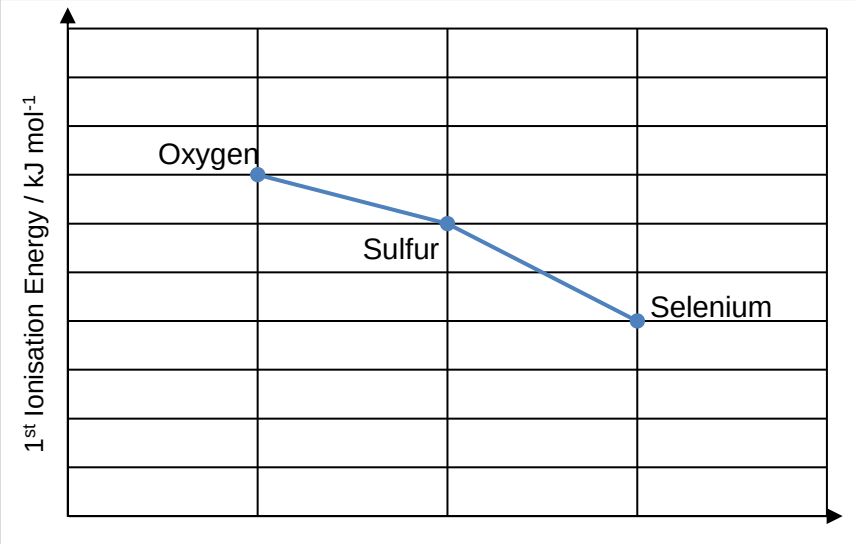
Answer **all** questions in the spaces provided.

1 The chalcogens, or the oxygen family, are the elements in group 16 of the Periodic Table. These elements are common in both organic and inorganic compounds.

(a) The graph below shows the trend in the first ionisation energies of oxygen, sulfur and selenium.



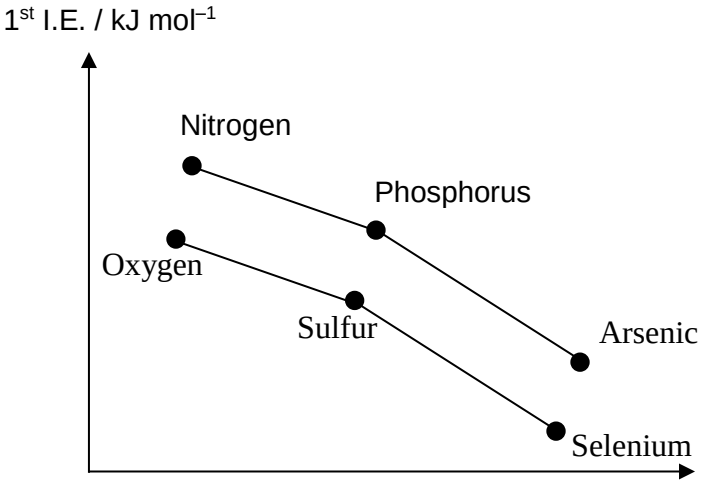
(i) Explain the trend in the first ionisation energies of oxygen, sulfur and selenium.

The first ionisation energy decreases from oxygen to selenium. This is because down the group while the nuclear charge increases, number of quantum shells increases and valence electrons are further away from the nucleus.

Hence, down the group, the valence electrons experience weaker attraction to the nucleus and a smaller amount of energy is required to remove this electron from the atom.

[2]

(ii) On the same grid above, sketch the trend in the first ionisation energies of nitrogen, phosphorus and arsenic.



[1]

(b) A common chalcogen-containing reagent used in both organic and inorganic synthesis is hydrogen peroxide, H_2O_2. Hydrogen peroxide readily decomposes at room temperature.

Iodide ions, I^-, catalyse this decomposition, as shown below:

Step I: $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)
Step II: $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$

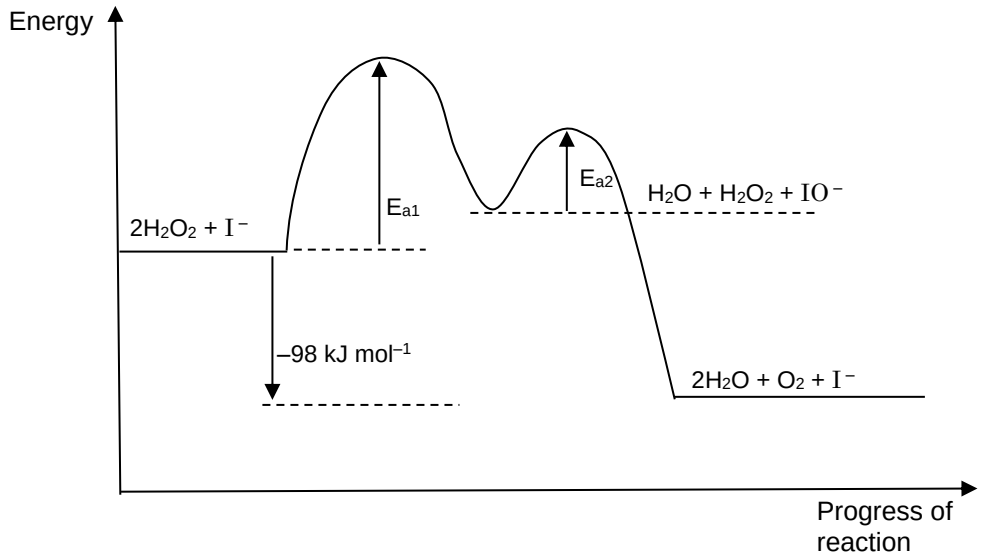
The overall equation for the decomposition of hydrogen peroxide is shown below:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The enthalpy and entropy changes for the reaction above are shown in the table below:

Enthalpy change / kJ mol^{-1}	–98
Entropy change / J K^{-1} mol^{-1}	+71

(i) Using the data above, complete the diagram below to show the energy profile diagram for the decomposition of hydrogen peroxide in the presence of iodide ions.



[2]

(ii) An unknown amount of hydrogen peroxide was allowed to decompose in a 5 dm^3 closed vessel at 120 ºC. When all the hydrogen peroxide was decomposed, a pressure of 177 kPa was measured in the vessel.

Determine the amount of hydrogen peroxide that decomposed in the vessel.
(Assume that H_2O and O_2 are ideal gases under the above reaction conditions)

$pV = nRT$

Total moles of gas in vessel, $n = \frac{177000 \times 5 \times 10^{-3}}{8.31 \times (273+120)}$ = **<u>0.27098 mol</u>**

Hence, moles of hydrogen peroxide that decomposed
= 0.27098 ÷ 3 × 2
= **<u>0.181 mol</u>**

[2]

(c) Chalcogens are also very commonly found in organic compounds. Table 1 below shows some common oxygen or sulfur containing organic functional groups.

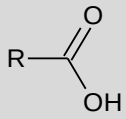
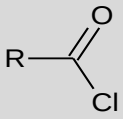
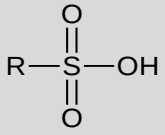
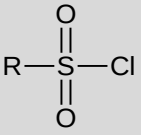
Oxygen-containing functional groups	Alcohols R–OH	Carboxylic Acids 	Acyl chlorides 
Sulfur-containing functional groups	Thiols R–SH	Sulfonic Acids 	Sulfonyl chlorides 

Table 1

(i) Explain why carboxylic acids are generally more acidic than alcohols.

This is because the lone pair of electrons on the negatively charged oxygen of the carboxylate anion is able to delocalise over two oxygen atoms. This results in the dispersal of the negative charge and hence, the conjugate base of carboxylic acids are more stable than that of alcohols.

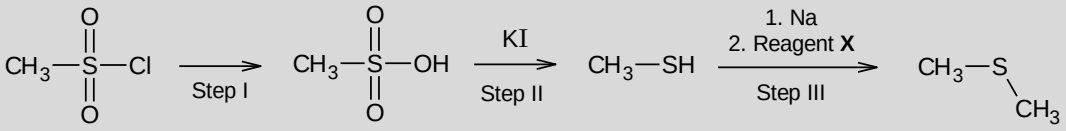
[1]

(ii) Hence, suggest a reason why carboxylic acids are generally less acidic than their corresponding sulfonic acids.

The conjugate base of the sulfonic acids are more stable due to the presence of an additional (electronegative) oxygen atom, which allows the delocalisation of electrons over more atoms.This reduces the intenisty of the negative charge on a single atom.

[1]

(iii) A reaction scheme for the synthesis of dimethyl sulfide (CH_3SCH_3) from methylsulfonyl chloride (CH_3SO_2Cl) is shown below:



Given that sulfur-containing functional groups undergo similar reactions as their corresponding oxygen-containing functional groups (Table 1), suggest:

I. The reagent(s) and condition(s) required for Step I.

H_2O

[1]

II. The role of KI in Step II.

Reducing agent

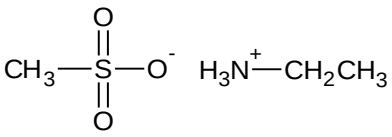
[1]

III. The identity of reagent **X** in Step III.

CH_3Cl or CH_3Br or CH_3I

[1]

IV. The structure of the product(s) formed when methylsulfonic acid (CH_3SO_3H) is reacted with ethylamine ($CH_3CH_2NH_2$) at room temperature.



[1]
[Total: 13]

2 The electrolysis of dilute sulfuric acid was carried out using two different currents at room temperature and pressure.

	Current / A	Duration / min
Experiment 1	0.75	90
Experiment 2	0.45	90

Oxygen gas is collected at one of the electrodes.

(a) (i) Calculate the final volume of oxygen produced in experiment 2.

$Q = I\,t$

$= 0.45 \times (90 \times 60) = 2430$ C

At the anode, $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

$4F \equiv 1O_2$

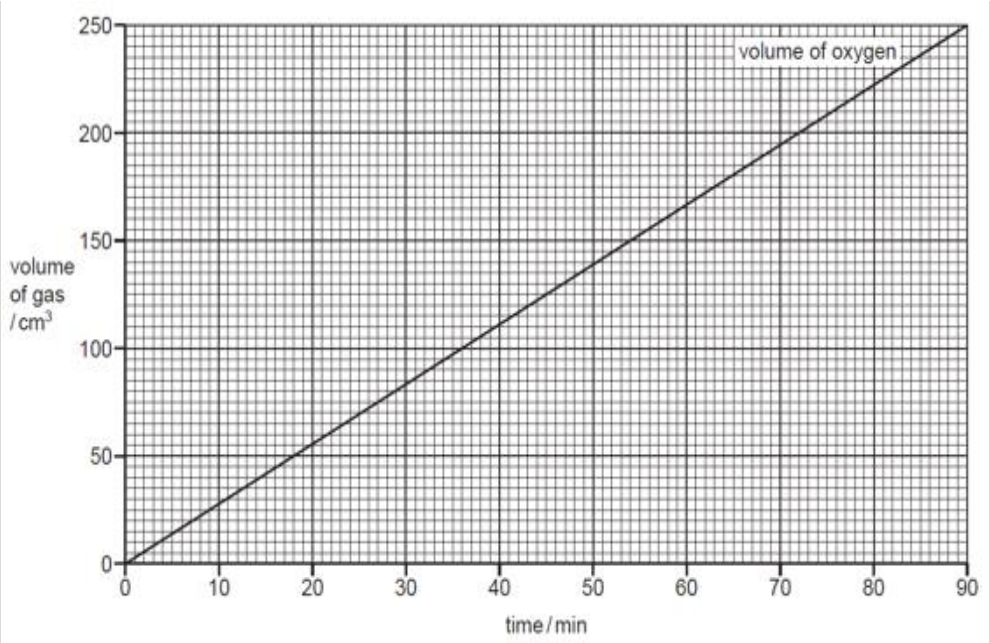
Moles of oxygen produced = $\frac{Q}{nF} = \frac{2430}{4 \times 96500}$

$= 6.30 \times 10^{-3}$

Final volume of O_2 produced = $(6.30 \times 10^{-3}) \times 24\,000$ cm^3 = **151 cm^3**

[2]

(ii) The volume of oxygen collect at one of the electrodes for experiment 1 is shown below.



On the graph above, draw a line to show each of the following:

I. the volume of H_2 gas that would be given off in experiment 1 (Label this line **1**)

II. the volume of oxygen that would be produced in experiment 2 (Label this line **2**)

[2]

I. A straight line from the origin which has double the oxygen volume at a given time.

II. A straight line from the origin which has 0.45/0.75 of the volume of oxygen at a given time.

(b) In another experiment, electrolysis of aqueous potassium butanedioate, $(OOCCH_2CH_2COO)K_2$ as the electrolyte was carried out. It was found that two gases, **Y** and **Z**, were liberated at the anode in a 2:1 ratio by volume.

Gas **Y** formed is absorbed by soda lime while gas **Z** is able to decolourise bromine water.

(i) Suggest the identities of gases **Y** and **Z**. [1]

Gas **Y** is CO_2 Gas **Z** is C_2H_4

(ii) Construct the half-equation for the reaction that occurs at the anode and the cathode respectively. [2]

Anode $^{-}OOCCH_2CH_2COO^{-} \rightarrow 2CO_2 + CH_2CH_2 + 2e^{-}$

Cathode $2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$

(iii) Predict the main organic product that would be obtained at the anode when a solution of potassium pentanedioate is electrolysed. [1]

Propene

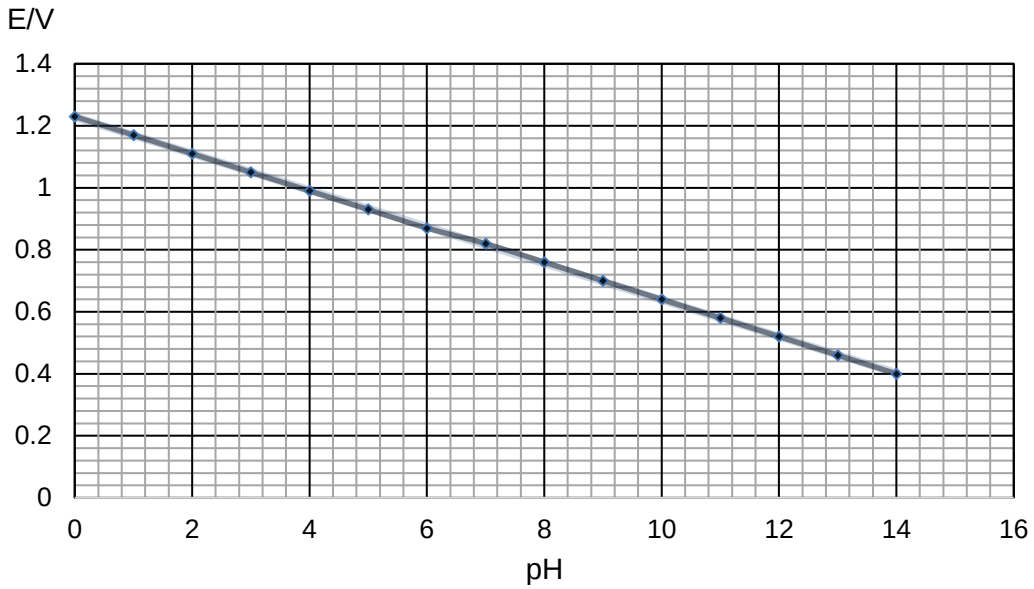
(c) Nicotinamide adenine dinucleotide (NAD^+) is involved in redox chemistry throughout the respiratory system. Aerobic respiration is the process of producing cellular energy involving oxygen.

The electrode potential for the reduction of NAD^+ in a *biological* system, E(pH 7), at 1 mol dm^{-3}, 25 °C and pH 7, is as shown.

Its oxidised and reduced forms are represented as NAD^+ and NADH respectively.

$$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH \qquad E(\text{pH } 7) = -0.320 \text{ V}$$

The reduction electrode potential of oxygen at different pH is given below.



(i) With reference to the *Data Booklet* and the graph given above, calculate the value of E_{cell} for aerobic respiration. Write a balanced equation for this reaction. [3]

At pH 7, reduction potential of oxygen is **+0.82 V**. That is,

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E(\text{pH } 7) = +0.82 \text{ V}$
OR
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$

$E_{cell} = E_{cathode} - E_{anode} = +0.82 - (-0.32)$
$= +1.14 \text{ V}$

Equation:

$2NADH + O_2 + 2H^+ \rightarrow 2H_2O + 2NAD^+$
OR
$2NADH + O_2 \rightarrow 2NAD^+ + 2OH^-$

(ii) State how will the E_{cell} differ if the aerobic reaction is performed at a pH of 7.4. [1]

At a higher pH, i.e. lower $[H^+(aq)]$, the aerobic respiration reaction is *less* favourable and so E_{cell} will be less positive.

(iii) Based on your answer in **(c)(i),** calculate ΔG(pH 7) for the aerobic respiration process. [1]

ΔG(pH 7) = $-nFE$(pH 7)
= –(4)(96500)(+1.14)
= –440 040 J mol^{-1}
= **–440 kJ mol^{-1}**

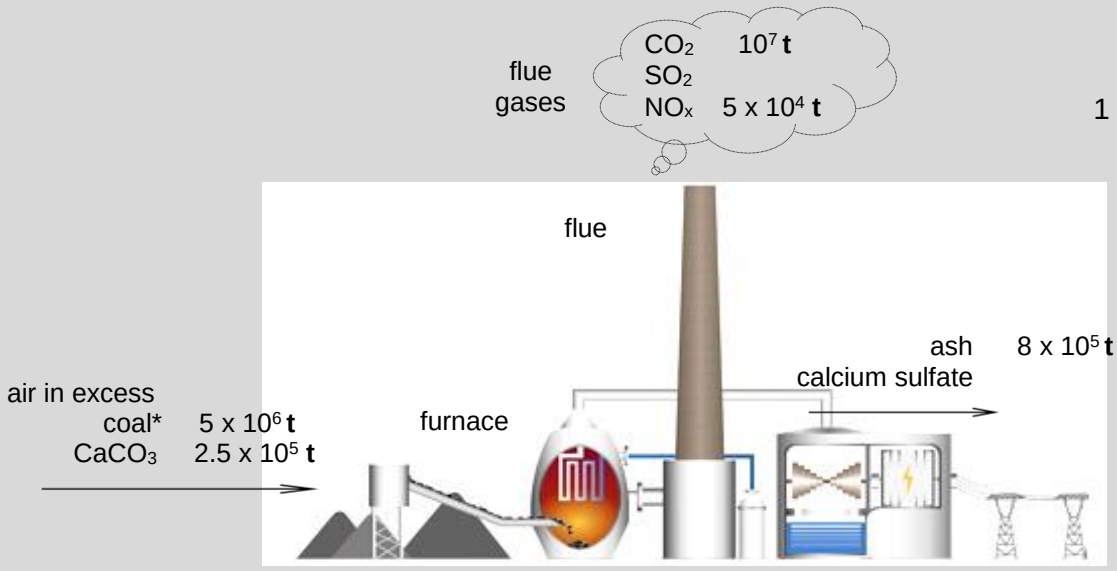
[correct answer + units]

[Total:13]

3 A coal-fired power station is fitted with a Flue Gas Desulfurisation (FGD) plant, which removes some of the sulfur dioxide from flue (waste) gases.

In the FGD plant, the flue gases are treated with powdered limestone, $CaCO_3$, where sulfur dioxide is absorbed and reacted to produce calcium sulfite, $CaSO_3$, which is oxidised by air to form solid calcium sulfate, $CaSO_4$.

The diagram below shows the amounts of substances used, and produced, by such a coal-fired power station with an FGD plant in **one** year.



Power station & FGD plant

**coal is chiefly hydrocarbons*

(a) (i) State the process that produces the energy in the power station. [1]

Combustion of coal.

(ii) Identify a gas, not listed in the diagram, which will be a chief component of the flue gases. [1]

H_2O(g) or water vapour.

(iii) Explain why oxides of nitrogen (NO_x) are present in the flue gases. [1]

NO_x is likely formed from reaction of oxygen and nitrogen in the air at high temperatures during combustion of coal.

(b) Write a balanced equation in each case to show how

- sulfur dioxide is removed from flue gases;

$SO_2 + CaCO_3 \rightarrow CaSO_3 + CO_2$

- calcium sulfate is formed. [2]

$CaSO_3 + ½ O_2 \rightarrow CaSO_4$

(c) Using your answer in **(b)**, determine the maximum mass of sulfur dioxide which could be removed in the FGD plant.
[1**t** = 1 tonne = 1000 kg] [1]

Mass of SO_2 that could be removed in FGD plant depends on mass of $CaCO_3$ used.

Moles of $CaCO_3$ used = $2.5 \times 10^5 \times 10^6 / 100.1 = 2.4975 \times 10^9$ mol
Maximum moles of SO_2 can be removed = Moles of $CaCO_3$ used

Maximum mass of SO_2 removed = $2.4975 \times 10^9 \times 64.1$
$= 1.60 \times 10^{11}$ g or 1.60×10^8 kg or 1.60×10^5 t

(d) Given that your answer in **(c)** was only 90% of the sulfur dioxide removed from the flue gases, calculate the mass of sulfur dioxide which is released into the atmosphere in **five** years by this power station when the same mass of coal is burnt each year. [1]

Mass of SO_2 released in 5 years = $(1.6009 \times 10^{11} \text{ g} \times \frac{0.10}{0.90}) \times 5$
$= 8.89 \times 10^{10}$ g or 8.89×10^7 kg or 8.89×10^4 t

(e) Another method for removing sulfur dioxide from the flue gases is to absorb it in a slurry of magnesium oxide, to produce magnesium sulfite, $MgSO_3$.

(i) Explain why magnesium oxide can also be used to remove sulfur dioxide. [1]

Magnesium oxide is basic and can undergo acid-base reaction with (acidic) sulfur dioxide.

(ii) Magnesium sulfite decomposes readily, upon heated, to give magnesium oxide and sulfur dioxide. Magnesium oxide could be recycled, while sulfur dioxide could be used to make sulfuric acid.

Explain whether it would be easier to obtain magnesium oxide or calcium oxide from its respective sulfite. [3]

It will require less energy to decompose magnesium sulfite as magnesium sulfite is less thermally stable, due to the higher charge density, hence higher polarising power, of Mg^{2+} ion. The electron cloud of SO_3^{2-} ion will be polarised to a larger

extent by Mg^{2+}, resulting in $MgSO_3$ decomposing more readily to give MgO. Therefore it will be easier to obtain magnesium oxide from its respective sulfite.

(f) When 1 mol of magnesium oxide, calcium oxide and other Group 2 metal oxides were separately dissolved in 1 dm^3 of deionised water, the pH of the resulting solutions were obtained.

Some data regarding these Group 2 metal oxides, **M**O, and their resulting solutions are provided in the table below.

ion	ionic radius/ nm	$\Delta H_{hydration}$ / kJ mol^{-1}	pH of **M**O in water	Electronegativity difference (ΔEN) in **M**O
O^{2-}	0.140			
Be^{2+}	0.031	–2370	7.0	1.87
Mg^{2+}	0.065	–2024	9.0	2.13
Ca^{2+}	0.099	–1680	9.5	2.44
Sr^{2+}	0.113	?	11	2.49
Ba^{2+}	0.135	–1314	12	2.55

(i) Suggest why there is no value for $\Delta H_{hydration}$ of the oxide ion, O^{2-}. [1]

O^{2-} reacts with water to give OH^-.
OR equation: $O^{2-} + H_2O \rightarrow 2OH^-$

(ii) Using the data given, estimate $\Delta H_{hydration}$ of Sr^{2+}. [1]

enthalpy change of hydration of Sr^{2+} = **-1538 kJ mol^{-1}**

(iii) State and explain the trend in $\Delta H_{hydration}$ in the table, in terms of the interaction between cations and water. [2]

$\Delta H_{hydration}$ of cations becomes less exothermic (or its magnitude decreases) with increasing cationic radius. The increase in cationic radius results in decrease in charge density of cations. Cations will polarise the electron cloud of water molecules to a smaller extent, hence there is a decrease in strength of ion–dipole interactions formed between cations and water molecules. This results in less amount of energy evolved when cations are hydrated.

(iv) With reference to the relevant data given in **(f)**, suggest explanations for the increasing pH of the resulting solution from BeO to BaO in terms of:

(I) Lattice energy and enthalpy change of solution of **M**O [3]

Increasing cationic radius from Be^{2+} to Ba^{2+}, hence lattice energy becomes less exothermic (or magnitude decreases) resulting in a more exothermic (or increasing magnitude of) enthalpy change of solution from BeO to BaO.

Thus, solubility of Group 2 MO increases down the group.
As a result, $[OH^-]$ increases and pH of resulting solution increases.

(II) ΔEN and the nature of the bonding in **M**O [2]

ΔEN increases from BeO to BaO. This means that the metal-oxygen bond gets more ionic from BeO to BaO, thus MO gets more basic / [OH^-] increases, and the pH of the resulting solution becomes higher.

[Total: 20]

4 (a) Vitamin C is an essential nutrient also known as ascorbic acid. A deficiency of vitamin C leads to a disease known as scurvy.

Ascorbic acid is known to have a M_r of 176.0 and contains 40.9% of carbon and 54.5% of oxygen by mass.

(i) Determine the molecular formula of ascorbic acid.

	C	O	H
% mass	40.9	54.5	4.6
Divide by A_r	3.41	3.41	4.6
Simplest ratio	3	3	4

The empirical formula of ascorbic acid is $C_3O_3H_4$.
n[(3 x 12.0) + (3 x 16.0) + (4 x 1.0)] = 176.0
n = 2
The molecular formula of ascorbic acid is $C_6O_6H_8$.

[2]

(b) Ascorbic acid is a monobasic acid, H**A**, and has a pK_a of 4.10. The amount of ascorbic acid contained in dietary supplement tablets can be verified by titration. A tablet containing 500 mg of ascorbic acid was dissolved in 25.0 cm^3 of deionised water.

(i) Calculate the volume of 0.100 mol dm^{-3} sodium hydroxide required for complete neutralisation.

$$n_{acid} = \frac{0.500}{176.0} = 2.841 \times 10^{-3} mol$$
$$v_{NaOH} \times 0.100 = 2.841 \times 10^{-3}$$
$$v_{NaOH} = 28.4\ cm^3$$

[1]

(ii) Calculate the initial pH of the ascorbic acid solution.

$$[HA] = \frac{2.841 \times 10^{-3}}{(25.0) \div 1000} = 0.1136 \text{ mol dm}^{-3}$$
$$K_a = 10^{-4.10}$$
$$[H^+] = \sqrt{K_a \times [HA]} = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$$
$$pH = -\lg[3.00 \times 10^{-3}] = 2.52$$

[2]

(iii) Suggest a suitable indicator the titration. Describe the expected colour change at the endpoint.
Phenolphthalein (colorless to pink) or
Thymol blue (yellow to blue)

[1]

(iv) With the aid of a suitable equation, explain your choice of indicator in **(iii)**.

$A^- + H_2O \rightleftharpoons HA + OH^-$
At end point, the salt / conjugate base of ascorbic acid undergoes salt hydrolysis to form hydroxide ions. [1] with equation

The pH of the resultant solution is > 7.
The pH transition range of selected indicator lies within the range of rapid pH change over the equivalence point of the neutralisation reaction.

[2]

(c) When a vitamin C tablet is swallowed, it dissolves in the stomach. The pH of the stomach is 2.

(i) Determine the percentage of ascorbic acid that is ionised in the stomach.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$
$$10^{-4.10} = \frac{[10^{-2}][A^-]}{[HA]}$$
$$\frac{[A^-]}{[HA]} = 10^{-2.1} = 7.93 \times 10^{-3}$$

Alternative method:
$$pH = pK_a + lg\frac{[A^-]}{[HA]}$$
$$2 = 4.10 + lg\frac{[A^-]}{[HA]}$$
$$\frac{[A^-]}{[HA]} = 10^{-2.1} = 7.93 \times 10^{-3}$$

Let α represent the percentage ionisation.
$$\frac{\alpha}{100 - \alpha} = 7.93 \times 10^{-3}$$
$$\alpha = 0.788\%$$

Alternative method:
Since [HA]>>[A^-] or since K_a is small,
% ionisation = 0.793%

[2]

The pH of blood is maintained at 7.35 by a H_2CO_3/HCO_3^- buffer.

(ii) Using appropriate equations, explain how the buffer minimises changes in pH.

Excess acid in blood is removed by hydrogen carbonate.
$HCO_3^- + H^+ \rightarrow H_2CO_3$
Excess alkali in blood is removed by carbonic acid.
$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$

[2]

(d) Organic acids like ascorbic acid react with amines in aqueous medium.

(i) State the type of bond formed during the reaction.

Type of bond: Ionic

[1]

(ii) Account for the increasing basicity of primary, secondary and tertiary amines in gas phase.

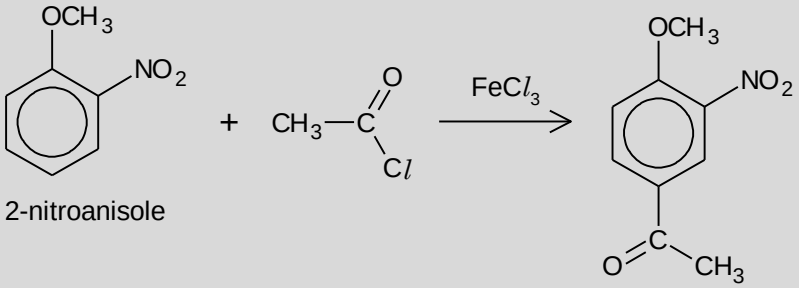
As the number of electron-donating alkyl groups increases, electron density on the N atom increases or lone pair of electrons is more available for donation.

[1]

[Total: 15]

5 **(a)** In Friedel-Crafts acylation, $FeCl_3$ is employed to attach an acyl group to an aromatic ring via electrophilic substitution.

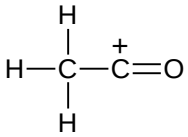
For example, compound **A** can be prepared by the reaction of 2-nitroanisole with ethanoyl chloride in the presence of $FeCl_3$.



2-nitroanisole

compound **A**

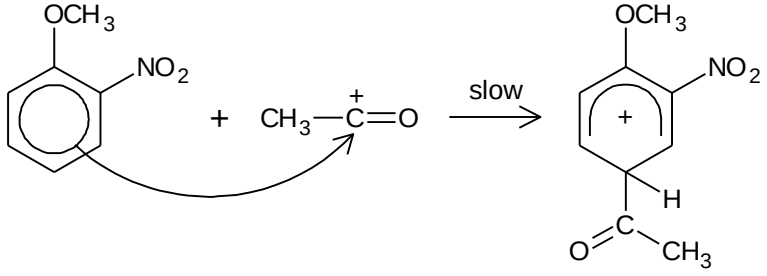
(i) Draw the displayed formula of the electrophile and write an equation to show how it is generated.

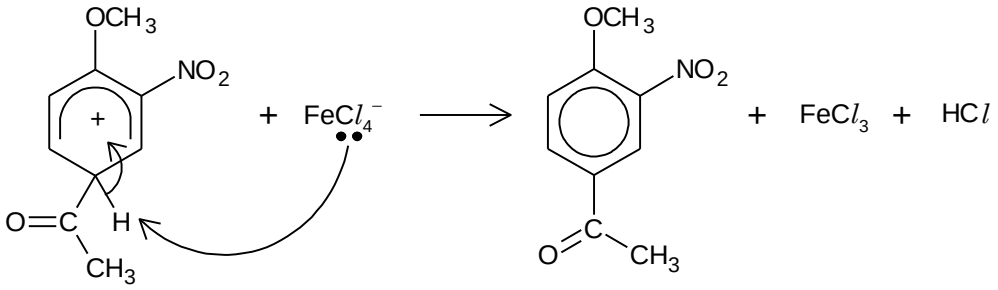


$CH_3COCl + FeCl_3 \rightarrow CH_3CO^+ + FeCl_4^-$

[2]

(ii) Using your answer in **(i)**, draw the mechanism of the acylation of 2-nitroanisole by ethanoyl chloride. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.





[2]

Empirical evidence shows that the electrophile generated in **(i)** is not exceptionally reactive. As such, the Friedel-Crafts acylation of nitrobenzene by ethanoyl chloride does not take place under any conditions.

(iii) Explain why nitrobenzene does not undergo acylation but the presence of the $–OCH_3$ group in 2-nitroanisole permits acylation.

- The $–NO_3$ group is a highly deactivating substituent.
- It reduces the electron density of benzene ring such that it becomes less susceptible to an electrophilic attack by a rather unreactive electrophile like CH_3CO^+.

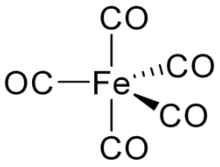
- The presence of a second strongly activating group like $–OCH_3$ increases the electron density of benzene ring sufficiently for it be susceptible to electrophilic attack by CH_3CO^+.

[2]

(b) Another iron compound, $Na_2[Fe(CO)_4]$, is used in the reaction between alkyl halides and carbon monoxide to synthesise ketones. This iron-based reagent is made as follows.

$$Fe(CO)_5 \xrightarrow{Na/Hg} \xrightarrow{-CO} 2Na^+ + [Fe(CO)_4]^{2-}$$

(i) Draw the structure of $Fe(CO)_5$ to show its shape clearly.



[1]

(ii) The oxidation state of Fe in $Fe(CO)_5$ is 0 and the CO ligands are neutral. Suggest the oxidation state of Fe in the $[Fe(CO)_4]^{2-}$ anion.

–2

[1]

(iii) Besides the oxidation states exhibited in the above reaction, iron also exists in other oxidation states like +2 and +3.

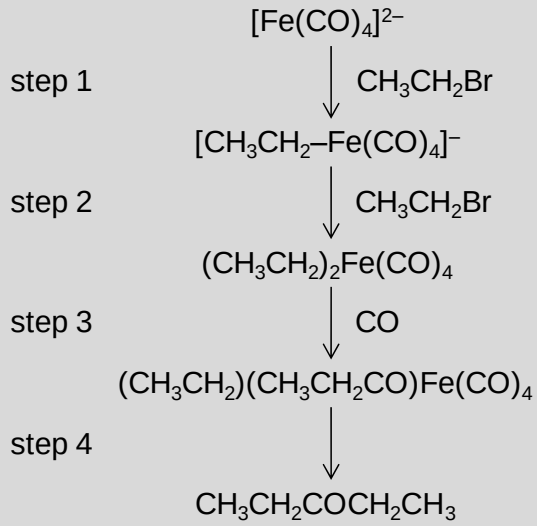
State a property of iron that allows its compounds to behave in this manner and give a reason why this property arises in iron.

- Fe exhibits variable oxidation states.

- In transition elements, 3d and 4s orbitals / electrons are similar in energy *OR* 3d orbitals which are partially filled, which allows the removal or accepting of electrons without requiring much more energy.

[2]

The reaction between $[Fe(CO)_4]^{2-}$ and bromoethane takes place under an applied pressure of carbon monoxide via the following steps.



(iv) Explain what is meant by the term *coordination number* in the context of a metal complex.

State the coordination number of iron in $[Fe(CO)_4]^{2-}$ and in $(CH_3CH_2)(CH_3CH_2CO)Fe(CO)_4$.

The coordination number is the number of dative covalent bonds formed between ligands and the central metal atom or ion.

	coordination number of iron
$[Fe(CO)_4]^{2-}$	4
$(CH_3CH_2)(CH_3CH_2CO)Fe(CO)_4$	6

[2]

(v) Studies show that steps 1 and 2 proceed via nucleophilic substitution.

If bromoethane were replaced by bromobenzene, the above reaction with $Na_2[Fe(CO)_4]$ would not work. With reference to the bonding and structure of bromobenzene, give **two** reasons why both S_N1 and S_N2 cannot occur.

- A p orbital of Br atom overlaps with the p orbitals of C atoms in benzene ring.
- The lone pair of electrons in this p orbital delocalises into the benzene ring to form a delocalised π electron cloud.
- This results in a partial double bond character in the C–Br bond.
- Large amount of energy is needed to break the C–Br bond, making it very difficult for both S_N1 and S_N2 o occur.

- The rear end of the C–Br bond in bromobenzene is sterically hindered by the

bulky benzene ring.
OR

- The π electron cloud repels the lone pair of electrons of the incoming nucleophile and hinders the rear end attack of the electrophilic C bearing the Br atom.
- This makes it difficult for S_N2 to occur.

[3]

[Total: 15]