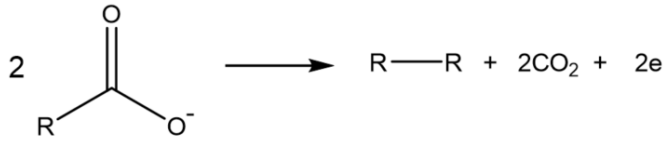
Section A

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

1 Electrosynthesis in organic chemistry is the synthesis of compounds in an electrolytic cell using inert electrodes. One important process is the Kolbe reaction. The Kolbe reaction is the decarboxylative dimerization of two carboxylate ions. Alkanes can be formed at the anode by the following reaction.



(a) Explain why alkanes are generally unreactive. **[1]**

Alkanes have C-C and C-H bonds which are strong and non-polar.

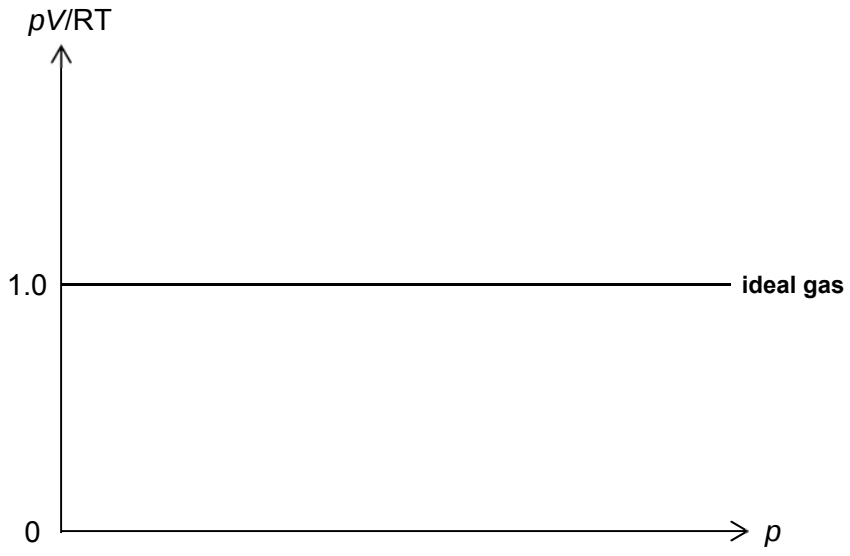
(b) **(i)** Calculate the volume of carbon dioxide produced when a steady current of 5A is passed through the electrolyte for 32 minutes at standard temperature and pressure. **[2]**

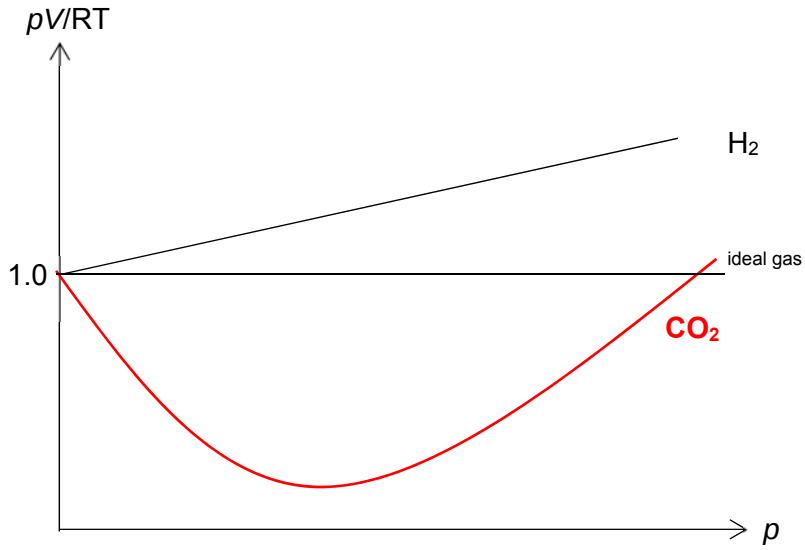
$Q = It = 32 \times 60 \times 5 = 9600$ C

Amt of CO_2 = Amt of e = Q/F = 9600/(96500) = 0.09948 mol

Vol of CO_2 collected = $0.09948 \times 22.7 = 2.26$ dm^3

(ii) Methanoate ions undergo the Kolbe reaction to form only 2 gases. Using the axes given below, sketch the variation of *pV*/RT against *p* for one mole of **each** gas at the same temperature. Briefly explain your answer. **[2]**





CO_2 deviates more from ideal behaviour because it experiences stronger instantaneous dipole-induced dipole interactions / intermolecular forces between the molecules compared to H_2 which has a smaller electron cloud.

(c) The cathodic reaction for the Kolbe reaction can be represented by the following half equation: $2H_2O + 2e \rightarrow H_2 + 2OH^-$.

Write an overall equation for the Kolbe reaction involving ethanoate ions. Hence, calculate ΔG^Θ for the Kolbe reaction given that the E^Θ_{cell} value for the reaction is +2.28 V. **[2]**

$2CH_3COO^- \rightarrow CH_3\text{-}CH_3 + 2CO_2 + 2e$

$2H_2O + 2e \rightarrow H_2 + 2OH^-$

Overall: $2CH_3COO^- + 2H_2O \rightarrow CH_3\text{-}CH_3 + 2CO_2 + H_2 + 2OH^-$

$\Delta G^\Theta = -nFE = -(2)(96500)(2.28) = -440\ kJ\ mol^{-1}$

(d) The reaction mechanism of the Kolbe reaction involves a 4-step reaction mechanism as described below:

Step 1: Dissociation of carboxylic acid to form a carboxylate ion.

Step 2: Oxidation of carboxylate ion to form a carboxyl radical, RCOO•.

Step 3: Decomposition of the carboxyl radical to form carbon dioxide gas and an alkyl radical, R•.

Step 4: Formation of a covalent bond between two alkyl radicals.

(i) Using ethanoic acid as a starting reagent, suggest suitable equations for **Steps 1, 2** and **4** on how ethane can be produced using the Kolbe reaction. **[3]**

Step 1: $CH_3COOH \rightarrow CH_3COO^- + H^+$

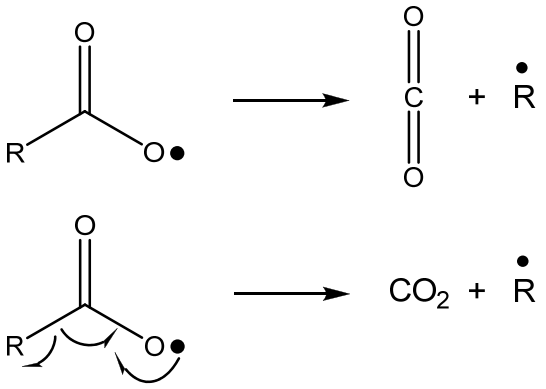
Also accept "$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$".

Step 2: $CH_3COO^- \rightarrow CH_3COO\bullet + e$

Step 4: $CH_3\bullet + CH_3\bullet \rightarrow CH_3CH_3$ (accept C_2H_6 also)

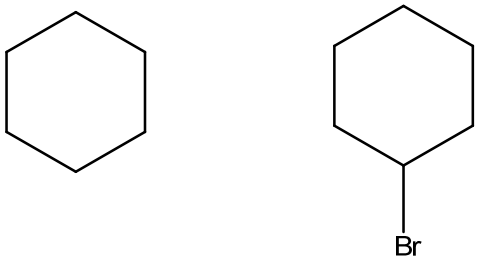
(ii) The decomposition of the carboxyl radical to form carbon dioxide gas and an alkyl radical, R•, in **Step 3** can be represented by the following equation: $RCOO\bullet \rightarrow CO_2 + R\bullet$

Outline the mechanism of this step by copying the diagram below and include relevant curly half arrows.



[1]

(e) In another separate experiment, a new alkane **A**, C_6H_{12}, was produced. When reacted with bromine under ultraviolet light, **A** produced only **one isomeric monobromo** compound, **B**, which does not have a chiral centre. Draw the skeletal formulae of **A** and **B**. **[2]**



(f) **(i)** Using monohalogenoethane, C_2H_5X, as examples, describe and explain the relative reactivities of chloro- and bromo-compounds in hydrolysis reactions. **[2]**

The hydrolysis of C_2H_5X will increases in reactivity (C_2H_5Cl < C_2H_5Br) . This is because the bond length / bond energy of C-Cl <C-Br, hence, it is most difficult to overcome C-Cl bond > C-Br bond.

(ii) Halogenoalkanes such as chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer. Explain how CFCs destroy the ozone layer and suggest one potential hazard of using alkanes instead of CFCs. **[2]**

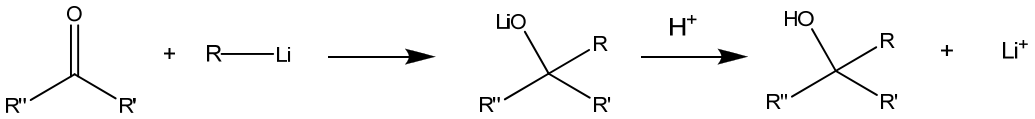
CFCs produce chlorine radicals, which in turn initiate the chain reaction breaking down ozone molecules, O_3 to O_2.

Alkanes are flammable.

(iii) Halogenoalkanes can react with lithium to give organolithium compounds.

$$R\text{-}Br + 2Li \rightarrow R\text{-}Li + LiBr$$

These organolithium compounds can react with carbonyl compounds to form alcohols.



(R is alkyl, R' and R'' are either alkyl or H)

Using the above reaction sequence, deduce the structure of a suitable bromoalkane, R-Br, and a suitable carbonyl compound to synthesise hexan-2-ol. **[2]**

Ethanal, 1-bromobutane

OR Bromomethane, Pentanal

[Total: 19]

2 Wastewater has to be treated carefully to remove all harmful contaminants before it can be released into water bodies.

(a) Industrial wastewater contains high levels of heavy metal ions. Electrocoagulation is used to remove heavy metal ions from wastewater. In this method, heavy metal ions are oxidised to form hydroxides, so that they can coagulate easily and be removed easily in subsequent steps.

A sample of wastewater containing Fe^{2+} is treated by electrocoagulation.

$$4Fe^{2+}\ (aq) + 10H_2O\ (l) + O_2\ (g) \qquad 4Fe(OH)_3\ (s) + 8H^+\ (aq)$$

(i) By considering the interaction it forms with water, explain why Fe^{2+} cannot be easily removed from wastewater. **[1]**

It forms ion-dipole interaction with water. Hence, it is soluble in water and cannot be easily removed.

OR

It forms dative bond with water to form a soluble complex of $[Fe(H_2O)_6]^{2+}$. Hence it cannot be easily removed.

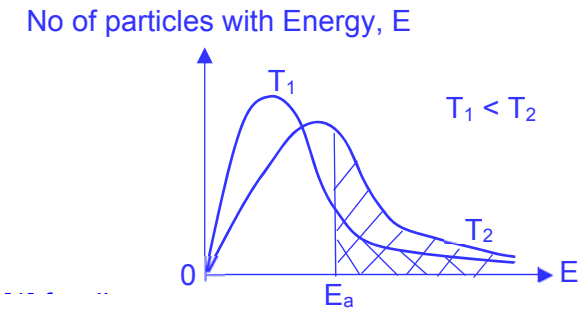
(ii) State a suitable physical method to remove $Fe(OH)_3$ from the wastewater. **[1]**

filtration

(iii) Using *Le Chatelier's Principle*, suggest why the wastewater has to be kept alkaline for a more effective removal of Fe^{2+}. **[1]**

As $[OH^-]$ is high / $[H^+]$ is low, the position of the equilibrium shifts right to increase $[H^+]$. Hence, more Fe^{2+} would be oxidised/removed as $Fe(OH)_3$.

(iv) With an appropriate sketch of the Boltzmann distribution, explain how an increase in temperature would affect the rate of removal of Fe^{2+}. **[3]**



When T increases, the KE of the reacting particles increases. Hence, there are more particles with $E \geq E_a$ and the frequency of effective collision increases. The rate of removal of Fe^{2+} would increase.

(b) Ammonia is a toxic substance present in wastewater from the mining industry. Nitrification is a common biological treatment method to convert ammonia into less toxic nitrate.

$$NH_3\,(aq) + 2O_2\,(g) \rightleftharpoons NO_3^-\,(aq) + H^+\,(aq) + H_2O\,(l)$$

(i) Write the expression for the equilibrium constant, K_c, for this reaction given that K_c has units of $mol^{-1}\ dm^3$. **[1]**

$K_c = [NO_3^-][H^+] / [NH_3]\,[O_2]^2$

(ii) 12 mol of oxygen gas was pumped into 1000 dm^3 of wastewater containing 5 mol of NH_3. After nitrification, the resulting treated wastewater had a pH of 4.2. Calculate the value of K_c. Leave your answer to 3 significant figures. **[3]**

	$NH_3(aq)$	$+ 2O_2$	$\rightleftharpoons$	$NO_3^-(aq)$	$H^+(aq)$	H_2O
Initial conc / mol dm^{-3}	0.005	0.012		0	0	
Eqm conc / mol dm^{-3}	$0.005 - 10^{-4.2}$ = 0.0049369	$0.012 - 2 \times 10^{-4.2}$ = 0.011873		$10^{-4.2}$	$10^{-4.2}$	

$$K_c = \frac{(10^{-4.2})^2}{(4.9369 \times 10^{-3})(1.1873 \times 10^{-2})^2} = 5.72 \times 10^{-3}\ mol^{-1}\ dm^3\ (3sf)$$

(iii) State how the K_c in **(ii)** would change when the amount of NH_3 in wastewater is increased to 10 mol. **[1]**

K_c would remain the same.

(iv) The nitrification process was carried out at room temperature. It was observed that the outer surface of the reaction vessel was cold after some time. **[2]**

By considering the effect of temperature on the equilibrium, suggest and explain how you can change the reaction temperature to increase the conversion of ammonia.

The (forward) reaction is endothermic. Hence, we can increase the temperature to shift the equilibrium position right, so as to absorb the excess heat, which allows more NH_3 to be converted.

(v) Construct a suitable energy cycle using the following equations to show how the enthalpy change of reaction, ΔH_r, can be determined. **[3]**

$NH_3\ (aq) + 2O_2\ (g)$ $\quad$ $NO_3^-\ (aq) + H^+\ (aq) + H_2O\ (l)$ $\quad$ ΔH_r

$NH_3(aq) + O_2(g) + H_2(g)$ $\quad$ $NH_2OH(aq) + H_2O(l)$ $\quad$ ΔH_1

$NH_2OH(aq) + H_2O(l) + ½O_2(g)$ $\quad$ $NO_3^-(aq) + 2H_2(g) + H^+(aq)$ $\quad$ ΔH_2

$2H_2O(l)$ $\quad$ $2H_2(g) + O_2(g)$ $\quad$ ΔH_3

ΔH_r

$NH_3(aq) + 2O_2(g) + H_2(g)$ $\quad$ $NO_3^-\ (aq) + H^+\ (aq) + H_2O\ (l) + H_2\ (g)$

$\downarrow \Delta H_1$

$NH_2OH\ (aq) + H_2O\ (l) + O_2\ (g)$ $\quad$ $½\Delta H_3$

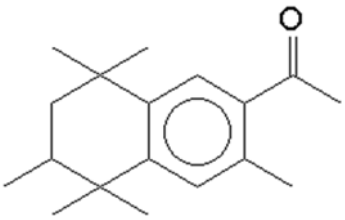
$\downarrow \Delta H_2$ $\quad$ ΔH_3

$NO_3^-\ (aq) + 2H_2\ (g) + H^+\ (aq) + ½\ O_2\ (g)$

$\Delta H_r + ½\ \Delta H_3 = \Delta H_1 + \Delta H_2$

$\Delta H_r = \Delta H_1 + \Delta H_2 - ½\ \Delta H_3$

(c) Wastewater treatment plants that treat pharmaceutical wastewater produces sludge that contains a high amount of organic substances. These organic substances can be combusted to harness energy for other processes. Tonalide, $C_{18}H_{26}O$, is one such organic compound found commonly in sludge. It has a melting point of 54.5^{o}C.



tonalide

(i) Write an equation which describes the standard enthalpy change of combustion of tonalide. **[1]**

$C_{18}H_{26}O\ (s) + 24O_2\ (g) \rightarrow 18CO_2\ (g) + 13H_2O\ (l)$

(ii) The enthalpy change of combustion of tonalide is −865 kJ mol^{-1}. **[2]**
Given that the combustion is 70% efficient, determine the amount of energy that can be harnessed from the combustion of sludge, which contains 900 g of tonalide.

Amt of tonalide = 900 / (18 X 12.0 + 26 X 1.0 + 16.0) = 3.4883 mol

Amt of heat released (100%) = 865 X 3.4883 = 3017.4 kJ

Amt of energy harnessed (70%) = 3017.4 X 0.7 = 2110 kJ (3sf)

(iii) The sign of the entropy change of combustion of tonalide is positive. Briefly explain the effect of temperature on the spontaneity of combustion of tonalide. **[1]**

$\Delta G = \Delta H - T\Delta S$

$T\Delta S > 0$

$\Delta H < 0$

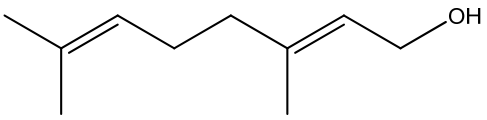
ΔG becomes more negative at higher temperatures. Hence, the combustion is more feasible.

OR

ΔG is always negative at all temperatures. Hence, the combustion is feasible at all temperatures.

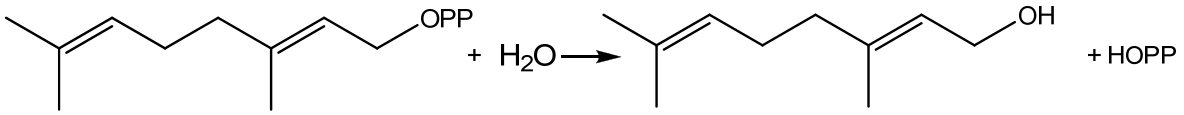
[Total: 20]

3 Geraniol, $C_{10}H_{18}O$, is commonly used in perfumes and food flavourings.



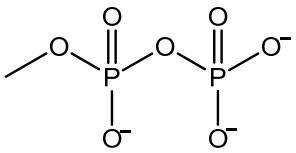
Geraniol

It is produced from geranyl diphosphate as shown in the following equation.



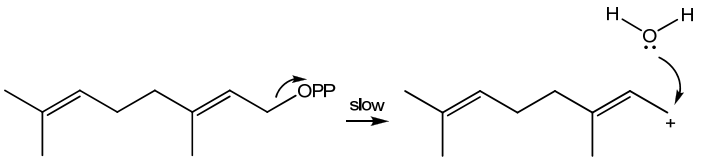
Geranyl diphosphate

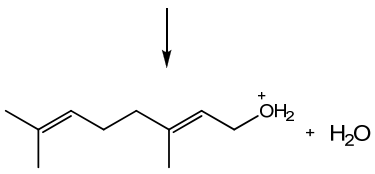
where OPP :



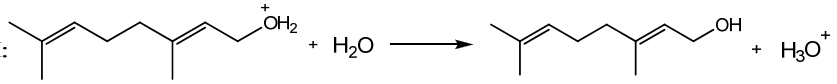
(a) The mechanism of this reaction consists of the following:

Reaction I:





Reaction II:



(i) State the mechanism in reaction I. **[1]**

Nucleophilic substitution

(ii) Explain why the mechanism in reaction **I** takes place in two steps instead of one step.

OPP is a **bulky group** which creates **steric hindrance** for the nucleophile to attack the carbon bonded to OPP / **transition state is unstable**.

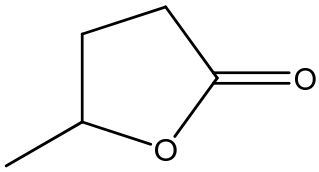
OR

OPP is negatively charged so it repels the approaching nucleophile (H_2O).

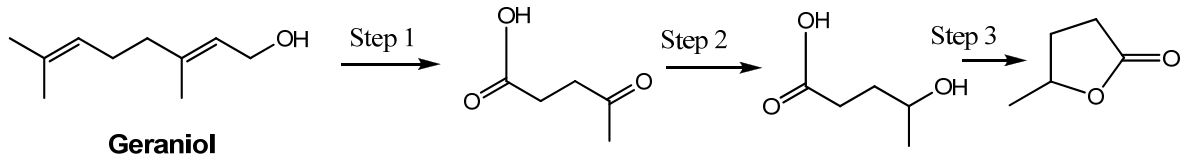
(iii) State the role of water in reaction **II**. **[1]**

It acts as a **Bronsted-Lowry / Lewis base** (as it accepts H^+ to form H_3O^+) or **nucleophile**.

(iv) The following compound can be synthesised from geraniol. **[4]**



Propose a reaction scheme for this synthesis.



Geraniol

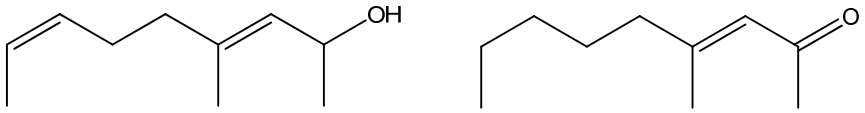
Step 1: $KMnO_4$, H_2SO_4 (aq), heat

Step 2: $NaBH_4$ or Hydrogen / Nickel, heat

Step 3: concentrated sulfuric acid, heat

(v) Explain what is meant by constitutional isomers and draw a constitutional isomer of geraniol that will form a yellow precipitate with alkaline aqueous iodine. **[2]**

They are compounds with the same molecular formula but different structural formulae



OR Any other structure with same molecular formula with R-$CO(CH_3)$ or R-$CH(OH)CH_3$

(b) Geranyl diphosphate can be synthesised using P_4O_{10}.

(i) Write an equation for the reaction of P_4O_{10} in water and describe the effect of the resulting solution on universal indicator solution. **[2]**

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

Universal indicator will turn red / orange.

(ii) Naturally occurring phosphorus contains the isotopes ^{31}P, ^{32}P and ^{33}P. Explain the term isotopes and calculate the relative atomic mass of phosphorus given that the relative abundance of each isotope is 91.1 %, 7.9% and 1.0 % respectively. **[2]**

Isotopes are elements with the same atomic number / same number of protons but different mass number / due to different number of neutrons.

relative atomic mass = (0.911 x 31) + (0.079 x 32) + (0.01 x 33) = 31.1

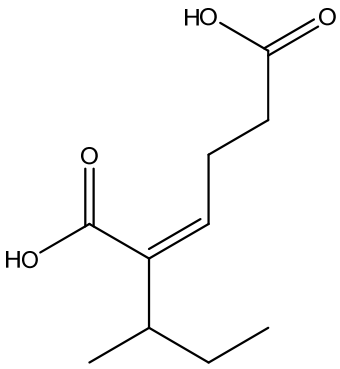
(c) Geraniol is a by-product of the metabolism of sorbic acid, C_5H_7COOH. Sorbic acid and its salt are used to prevent growth of mould and fungi and to regulate the pH in food and drinks. With the aid of relevant equations, explain how the pH of food and drinks can be regulated through the use of sorbic acid and its salt. **[3]**

$C_5H_7COOH + OH^- \rightarrow C_5H_7COO^- + H_2O$

$C_5H_7COO^- + H^+ \rightarrow C_5H_7COOH$

A large reservoir of acid and salt will help to remove a small amount of base and acid respectively to ensure that the pH remains **relatively/almost** constant/resists pH changes.

(d) Another constitutional isomer of geraniol is compound **X**. **X** does not react with 2,4-dinitrophenylhydrazine. **X** produces effervescence when sodium metal is added to it. When hot acidified $K_2Cr_2O_7$ is added to **X**, orange solution remains. On addition of aqueous bromine to **X**, the orange solution decolourises and compound **Y** is formed. **X** reacts with hot acidified $KMnO_4$ to form compound **Z** only. When **Z** is reacted with excess concentrated H_2SO_4 at 170 °C, the following product is obtained. **[5]**

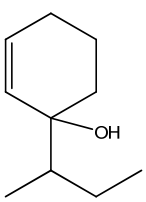


X, **Y** and **Z** are all able to rotate the plane of polarised light. Suggest the identities of **X**, **Y** and **Z**, explaining your reasoning.

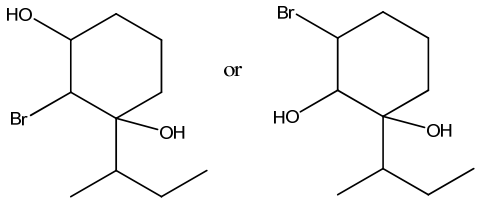
Observations	**Deductions**
X does not react with 2,4-DNPH.	**X** is not an aldehyde or ketone / not a carbonyl compound.
X produces effervescence when Na added.	Redox. Gas is H_2. **X** contains hydroxyl group (or –OH group or alcohol).
Orange solution remains when hot $K_2Cr_2O_7$ added to **X**.	**X** contains tertiary alcohol.
On addition of aqueous bromine to **X**, the orange solution turns colourless.	**X** undergoes electrophilic addition. **X** contains C=C (or alkene).
X reacts with hot acidified $KMnO_4$ to produce **Z** only.	Oxidation **X** is a cyclic compound
Z reacts with excess concentrated H_2SO_4 at 170 °C.	Elimination
X, **Y** and **Z** are all able to rotate the plane of polarised light.	All 3 compounds have chiral carbon.

Structures

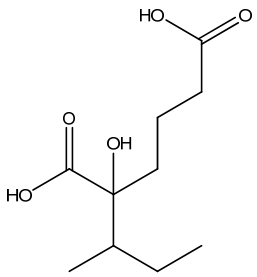
X:



Y:



Z:



[Total: 21]

Section B

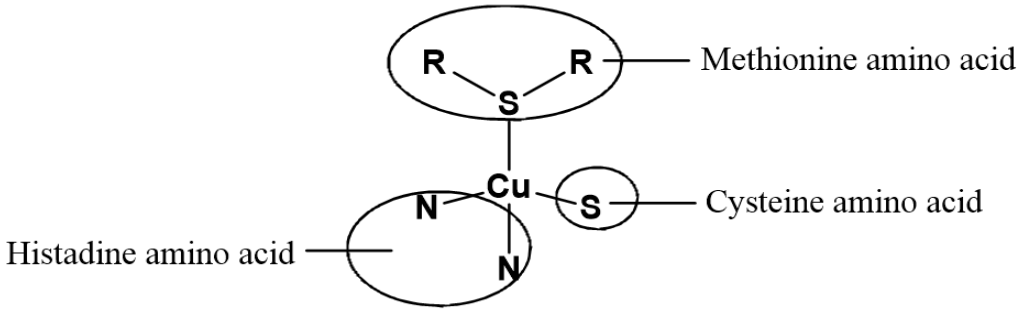
Answer **one** question in this section.

4 Transition elements and its compounds have various applications, such as in materials, catalysis and even in nature. An example of a transition element which has many uses and is widely researched on is copper.

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

It is a **d-block element** which forms **one or more stable ions** with **partially filled d subshells**.

(b) **(i)** Plastocyanin is a copper-containing protein found in vascular plants. The shape around Cu^{2+} in plastocyanin is tetrahedral and can be represented by the following simplified structure. The amino acids found around Cu^{2+} act as ligands.



Define the term *ligand*. **[1]**

It is an **ion or molecule** which contains **at least 1 atom bearing a lone pair of electrons** which can be **donated into a low-lying vacant orbital of a central metal atom or ion** by forming a **dative bond**.

(ii) Plastocyanin is commonly involved in electron transfer and this results in the formation of Cu^{+} complex which has a deep blue colour.

State the electronic configuration of Cu^{+}. **[1]**

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

(iii) The deep blue colour seen is considered to be unusual.

Suggest a reason why this is so. **[1]**

The **d orbitals in Cu^{+} are completely filled** and therefore, **no d-d transition** can occur and the complex should not be coloured.

(c) Azurite is a copper containing mineral that is deep blue in colour. The formula of azurite is $Cu_3(CO_3)_2(OH)_2$ and it can be inferred that azurite contained copper(II) carbonate and copper(II) hydroxide, which are sparingly soluble salts.

(i) To prepare small crystals of azurite in the lab, a few drops of copper(II) sulfate solution can be added into a saturated solution of sodium carbonate and leave to stand overnight.

With reference to the preparation method as described, write an equation to suggest how OH^- may be produced from a saturated solution of sodium carbonate. **[1]**

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

(ii) A student wishes to determine the percentage of azurite in a rock sample. He proposes to do so by performing a direct titration with dilute sulfuric acid.

Suggest an explanation why the proposed method is not ideal. **[1]**

The solid is **insoluble** and **cannot be directly titrated**.

OR

The solid hydroxide and carbonate (especially) will be **too slow to react** with the sulfuric acid.

OR

The **end-point will not be accurately determined**.

(iii) Another student proposed the following method which is ideal in determining the percentage of azurite in a rock sample.

Step 1: Add 7.00 g of the rock sample to 130 cm^3 of 0.550 mol dm^{-3} sulfuric acid. The resulting solution was topped up to 250 cm^3 using deionised water.

Step 2: 25.0 cm^3 of the solution required 15.55 cm^3 of 0.200 mol dm^{-3} sodium hydroxide for complete reaction.

Azurite reacts with sulfuric acid according to the following equation.

$$Cu_3(CO_3)_2(OH)_2 + \boldsymbol{a}\ H_2SO_4 \rightarrow \boldsymbol{a}\ CuSO_4 + \boldsymbol{b}\ H_2O + \boldsymbol{c}\ CO_2$$

Complete the balancing of the above equation by deducing values for ***a***, ***b*** and ***c***. Hence, calculate the percentage of azurite in the rock sample. **[3]**

$Cu_3(CO_3)_2(OH)_2 + 3\ H_2SO_4 \rightarrow 3\ CuSO_4 + 4\ H_2O + 2\ CO_2$

Amount of NaOH = Amount of excess H_2SO_4 = ½ x 15.55/1000 x 0.2 = 1.55×10^{-3} mol

Amount of excess H_2SO_4 in 250 cm^3 = $10 \times 1.55 \times 10^{-3} = 0.0155$ mol

Amount of H_2SO_4 reacted with azurite = (130/1000 x 0.55) – 0.0155
= 0.05595 mol
Amount of azurite = 0.05595 / 3 = 0.01865 mol
Mass of azurite = 0.01865 x 344.5 = 6.42 g
% azurite in rock sample = 6.425 / 7 x 100% = 91.8% (to 3 sf)

(iv) Using your knowledge on the thermal decomposition of carbonates and given that $Cu(OH)_2$ thermally decomposes to form CuO and H_2O, write an equation for the thermal decomposition of azurite.
Using the equation written and appropriate molar mass values, calculate the percentage loss in mass upon strongly heating a sample of azurite until no further changes. **[3]**

$Cu_3(CO_3)_2(OH)_2 \rightarrow 3\ CuO + H_2O + 2\ CO_2$
Mass of azurite in 1 mol = 344.5 g
Mass of H_2O in 1 mol = 18 g
Mass of CO_2 in 2 mol = 2 x 44 = 88 g
% loss in mass = (18+88) / 344.5 x 100% = 30.76% ≈ 30.8% (to 3 sf)

(v) In another instance, a student tried to synthesise azurite by adding copper(II) nitrate solution slowly to a solution containing 0.100 mol dm^{-3} sodium carbonate solution and 0.100 mol dm^{-3} potassium hydroxide solution. Calculate the concentration of Cu^{2+} required to begin precipitating $CuCO_3$ and $Cu(OH)_2$ respectively. Hence, state which compound precipitates first assuming that there is a negligible change in volume.

K_{sp} of $CuCO_3$ = 7.08 x 10^{-9} mol^2 dm^{-6}
K_{sp} of $Cu(OH)_2$ = 4.8 x 10^{-20} mol^3 dm^{-9}

[3]

When $Cu(OH)_2$ first precipitates,
$[Cu^{2+}] = 4.8 \times 10^{-20} / (0.1)^2 =$ **4.8 x 10^{-18} mol dm^{-3}**
When $CuCO_3$ first precipitates,
$[Cu^{2+}] = 7.08 \times 10^{-9} / 0.1 =$ **7.08 x 10^{-8} mol dm^{-3}**
$Cu(OH)_2$ will precipitate first.

(vi) When sufficient ammonia is added to copper(II) hydroxide precipitate, the precipitate dissolves. Explain this observation with the aid of relevant equations.

[2]

$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons$ **$Cu(OH)_2(s)$** $+ 6H_2O\ (l)$ **---- eqm (1)**

blue solution **blue precipitate**

When excess aqueous NH_3 is added, **ligand exchange** occurs to form a deep blue solution.

$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4\ H_2O$ --- eqm (2)

deep blue solution

The formation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ decreases the concentration of $[Cu(H_2O)_6]^{2+}$ causing **position of equilibrium (1) to shift to the left in order to replenish $[Cu(H_2O)_6]^{2+}$**. Hence, blue ppt of $Cu(OH)_2$ dissolves, forming the deep blue solution.

(d) Copper metal is obtained from copper ore and is widely used in electrical wiring. To prevent short circuit, the metal used must have high purity. Outline how the impure copper ore is purified industrially to remove impurities such as zinc and silver metals.

[3]

Impure copper ore can be purified using electrolysis. The impure copper is placed at the anode, while pure copper is used as the cathode. The electrolyte used is aqueous $CuSO_4$.

When an electric current is applied, copper at the **anode (+)**, together with Zn are oxidised to their ions owing to their relatively less positive $E^\ominus$ values. Hence, Cu^{2+} and Zn^{2+} then migrate to the cathode / remain in solution.

Ag will not be oxidised as it has a relatively positive $E^\ominus$ values and it falls off the electrode and accumulate at the bottom as anodic sludge.

At the cathode, only Cu^{2+} ions are reduced to Cu, which is deposited on the pure copper electrode, due to its more positive $E^\ominus$.

Zn^{2+} remain as ions in the solution as they do not reduce to metals easily.

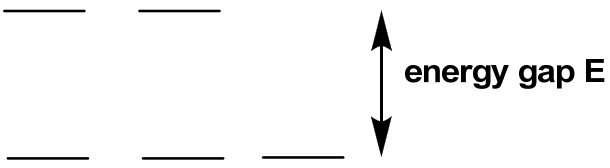
[Total: 20]

5 Iron is an important transition element and the second most abundant metal in Earth's crust. Iron containing compounds have various uses and the element itself can also be found in a number of proteins within living things. Iron and its compounds have been widely researched on as they are relatively cheap and non-toxic.

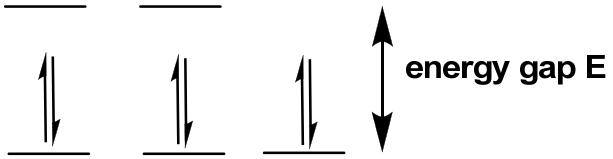
(a) Haemoglobin is a protein found in red blood cells. Within haemoglobin, it contains an Fe^{2+} ion which has an octahedral shape as it is surrounded by five nitrogen-containing ligands and one oxygen-containing ligand, which is H_2O in deoxyhaemoglobin and O_2 in oxyhaemoglobin.

(i) A species with unpaired electrons is paramagnetic and can be attracted by an externally applied magnetic field. On the other hand, a species with no unpaired electrons is diamagnetic and is unaffected by a magnetic field.

Oxyhaemoglobin is found to be diamagnetic. Based on the information provided and using the diagram below, show the electronic distribution of the 3d electrons of Fe^{2+} in oxyhaemoglobin.

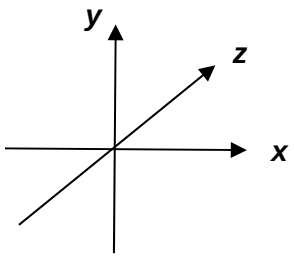


[1]



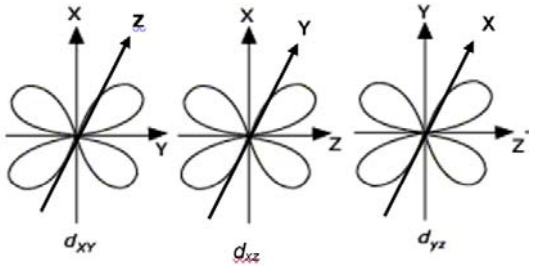
(ii) In both oxyhaemoglobin and deoxyhaemoglobin, the 3d orbitals are no longer degenerate as they are split into two different energy levels.

Explain this observation. Using the Cartesian axes like those shown below, draw a fully labelled diagram of one of the 3d orbitals which has a lower energy level.



[3]

In octahedral complexes, the lone pair of electrons on the 6 ligands **approach Fe^{2+} along the axes**. This results in **electronic repulsion**, which causes the energy level of $3d_{x^2-y^2}$ and $3d_{z^2}$ to be higher.



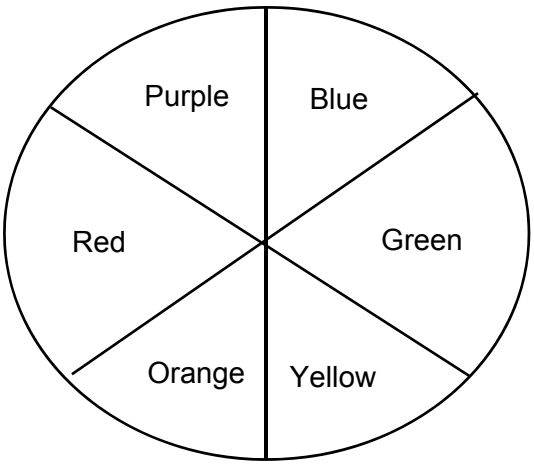
Either one:

(iii) Explain why oxyhaemoglobin is red. **[2]**

When a **d electron from the lower energy d orbital absorbs light energy (visible light with wavelength corresponding to this energy gap)**, it is **promoted to the higher energy d orbital** and this is d-d transition.

The **red colour seen is complementary to the colour absorbed / red colour is not absorbed**.

(iv) The complementary colours are shown using the following colour wheel.



The wavelength of each colour component in visible light is as provided.

Colour	**Purple**	**Blue**	**Green**	**Yellow**	**Orange**	**Red**
Wavelength / nm	380 - 450	450 - 495	495 - 570	570 - 590	590 - 620	620 – 750

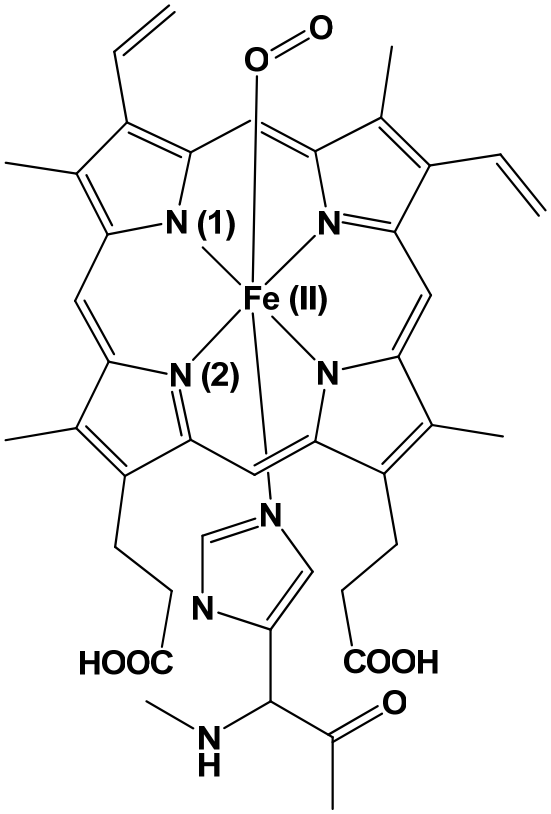
Oxyhaemoglobin is bright red while deoxyhaemoglobin is blue. Given that the wavelength of light is inversely proportional to energy, state and explain if water or oxygen causes a larger energy gap between the 3d orbitals.

[2]

O_2 causes a larger energy gap between the 3d orbitals.

Oxyhaemoglobin absorbs **green colour which is of lower wavelength / higher energy than the orange colour** that deoxyhaemoglobin absorbs.

(v) Fe^{2+} complex in oxyhaemoglobin does not have an overall charge. The structure is as shown.



State the charge around the N atom labelled **(1)** and the bond angle around the N atom labelled **(2)**.

[2]

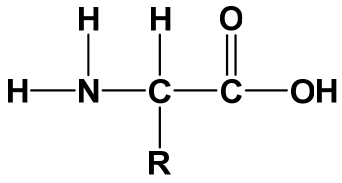
Charge around N(1): 1−

Bond angle around N(2): 120□

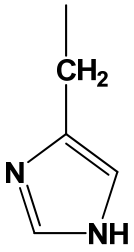
(vi) Besides Fe^{2+}, Fe^{3+} may also exist in haemoglobin. Explain why Fe can have variable oxidation states in haemoglobin. **[1]**

The **energy of 3d and 4s electrons are close in proximity**. Hence, the electrons in 3d and 4s orbitals may be shared or lost to give variable oxidation states.

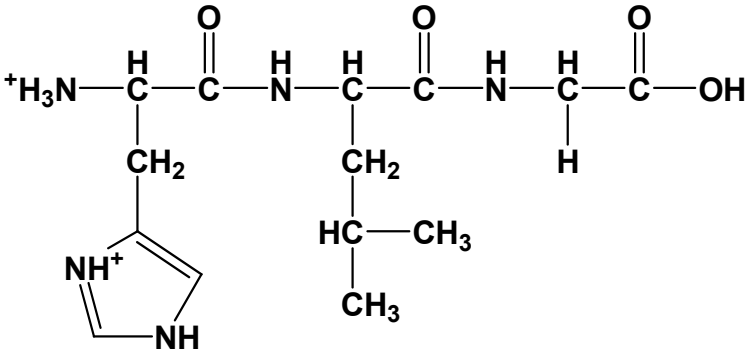
(vii) Each polypeptide chain in haemoglobin is made up of more than 100 amino acid residues. The general structure of an amino acid is as shown below.



In each chain, histidine, leucine and glycine amino acids can be found.

Amino acid	R group
Histidine	
Leucine	$-CH_2CH(CH_3)_2$
Glycine	-H

Draw the structural formula of a tripeptide with the sequence histidine-leucine-glycine at pH 2. **[2]**

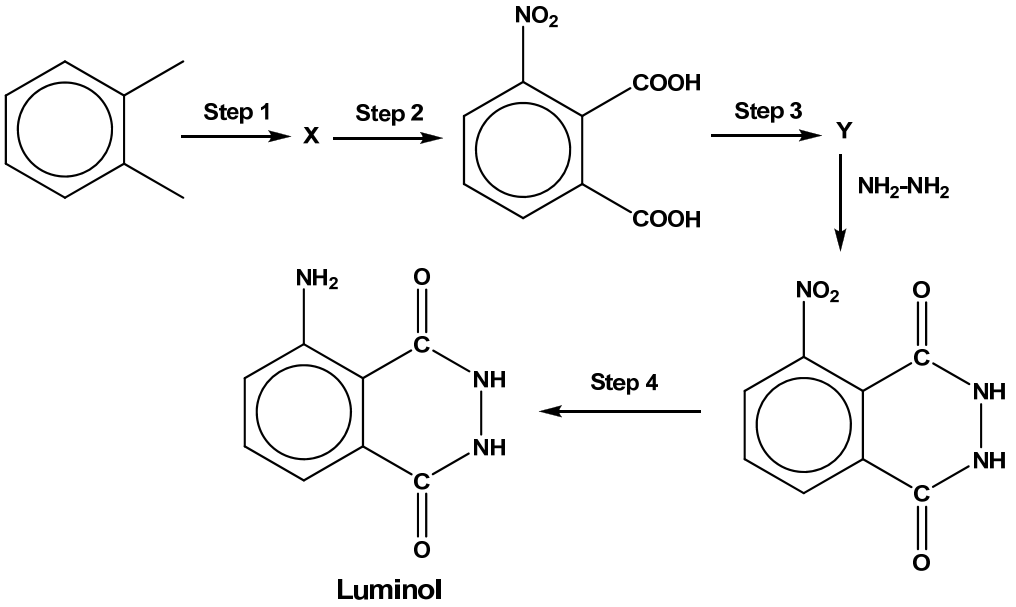


(viii) Haemoglobin can undergo complete hydrolysis non-enzymatically. State the reagents and condition for this to occur. **[1]**

(6 mol dm^{-3}) **concentrated** HCl (Any mineral acid), **prolonged heating** / several hours (for 24h)

(b) To detect for the presence of blood in a crime scene, an organic compound named luminol may be used. Luminol uses iron in haemoglobin to catalyse the decomposition of hydrogen peroxide, which eventually leads to a blue glow to indicate the presence of blood.

The synthetic route for luminol is as shown.



(i) State the reagents and conditions for **steps 1** to **3**. **[3]**

Step 1: Concentrated sulfuric acid, concentrated nitric acid, < 55 °C

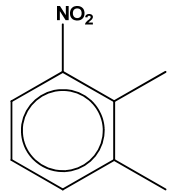
Step 2: $KMnO_4$, H_2SO_4 (aq), heat

Step 3: PCl_5 or $SOCl_2$

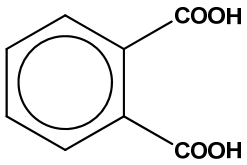
Note: Steps 1 and 2 can be interchangable but temperature > 55°C

(ii) Draw the structures for intermediate products **X** and **Y**. **[2]**

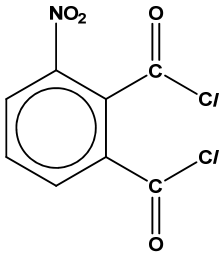
X:



or



Y:



(iii) For **Step 4**, $Na_2S_2O_4$ is commonly used as the reagent.

State the role of $Na_2S_2O_4$. **[1]**

Reducing agent

[Total: 20]