VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ……………………………………………………………..

CT GROUP ……………………………..

CHEMISTRY 9729/03

Paper 3 Free Response **16 September 2024**

Candidates answer on the Question Paper **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section **A**
Answer **all** questions.

Section **B**
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Section A	**1**	**/ 23**
	2	**/ 19**
	3	**/ 18**
Section B	**4**	**/ 20**
	OR 5	**/ 20**
Total		**/ 80**

This document consists of **30** printed pages and **0** blank page.

Section A

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

1 **(a)** Chlorine is bubbled through 100 cm^3 of hot 4.0 mol dm^{-3} sodium hydroxide until the reaction is complete.

$$6NaOH(aq) + xCl_2(aq) \rightarrow yNaCl(aq) + zNaClO_3(aq) + 3H_2O(l)$$

(i) State the type of reaction that occurs. Explain your answer in terms of changes in oxidation numbers. [1]

- **Disproportionation reaction as Cl_2 is reduced and oxidised simultaneously. Cl_2 is reduced to Cl^-, oxidation number of Cl decreases from 0 to –1. Cl_2 is oxidised to ClO_3^-, oxidation number of Cl increases from 0 to +5.**

(ii) Determine the values of *x*, *y* and *z*. [1]

- **$x = 3$ $y = 5$ $z = 1$**

(iii) Determine the concentration of $Na^+(aq)$, in mol dm^{-3}, after the reaction. [1]

- **Concentration of $Na^+(aq)$ after the reaction = 4.0 mol dm^{-3}**

(Na^+ does not participate in the reaction thus its concentration remains the same.)

(b) Compound **A** is an ether with molecular formula $C_4H_{10}O$. When **A** is heated in a sealed container, an equilibrium mixture is produced.

$$C_4H_{10}O(g) \rightleftharpoons C_2H_6(g) + CO(g) + CH_4(g) \qquad \Delta H = -7.00 \text{ kJ mol}^{-1}$$

Table 1.1 shows the activation energy, E_a, for the reaction in the presence and absence of I_2.

Table 1.1

E_a (with I_2) / kJ mol^{-1}	E_a (without I_2) / kJ mol^{-1}
143	224

(i) State the role of I_2 in this reaction and explain what effect it has on the value of K_c. [1]

- **I_2 is a catalyst in the reaction and it has no effect on the value of K_c as it does not affect the position of equilibrium.**

(ii) Complete the energy profile diagram for this reaction in Fig. 1.1. Include labels to show the enthalpy change and the activation energy data in Table 1.1.

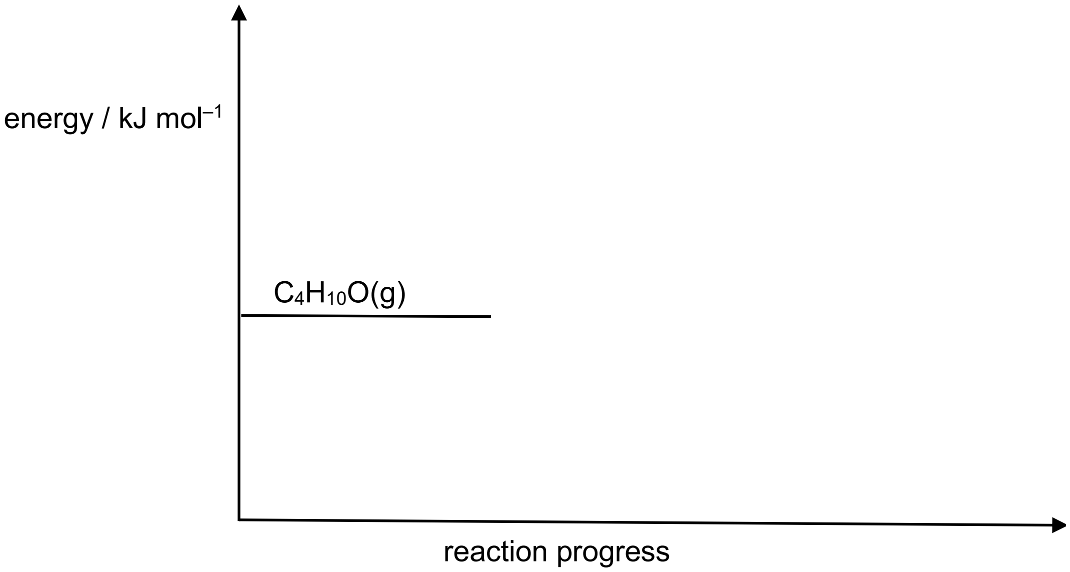
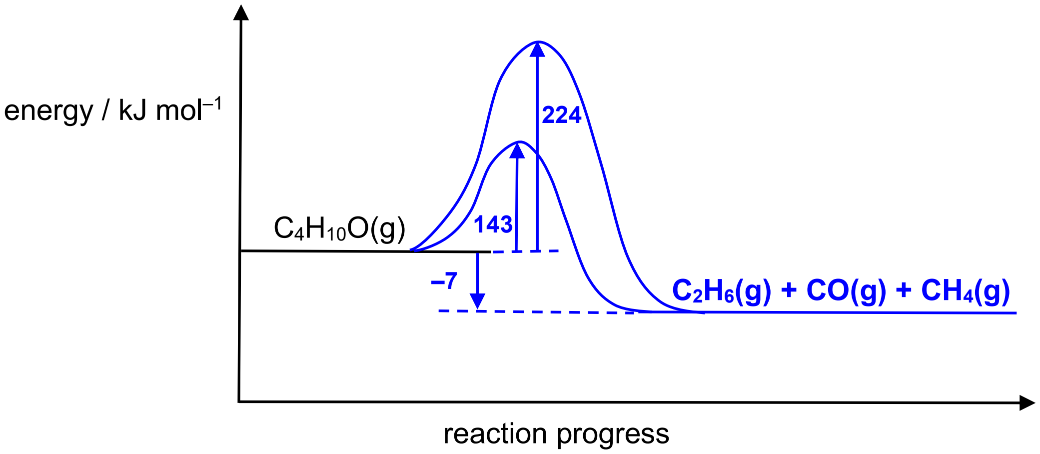


Fig. 1.1

[2]



1m: 2 curves and exothermic
1m: all correct labels include state symbols

(iii) Suggest the effect of increasing the pressure on the position of equilibrium. [1]

- **When the pressure is increased, by Le Chatelier's Principle, the position of equilibrium will shift to the left to decrease total number of moles of gas.**

(c) Potassium chloride, KCl, and magnesium chloride, $MgCl_2$, are both ionic solids.

The following data can be used to answer some parts of this question.

Table 1.2

standard enthalpy change	value / kJ mol^{-1}
standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of KCl	+15
lattice energy, $\Delta H^{\ominus}_{latt}$, of $KCl(s)$	–701
standard enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, of K^+	–322

standard enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, of Cl^-	–364
standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of $MgCl_2$	–155
lattice energy, $\Delta H^{\ominus}_{latt}$, of $MgCl_2(s)$	–2493

(i) Define the term *entropy* and state the effect on the entropy of the chemical system for the following reaction. Explain your answer. [2]

$$K^+(g) + Cl^-(g) \rightarrow KCl(s)$$

- **Entropy is a measure of the degree of disorder of a system, indicated by the physical arrangement (physical chaos) of particles and spread of energy (thermal chaos) in the particles of the system.**

- **Entropy decreases as the number of moles of gaseous particles decrease (from 2 mol to 0 mol) and there is a decrease in number of ways of arranging fewer gaseous particles.**

(ii) Potassium chloride dissolves readily in water at 25°C.

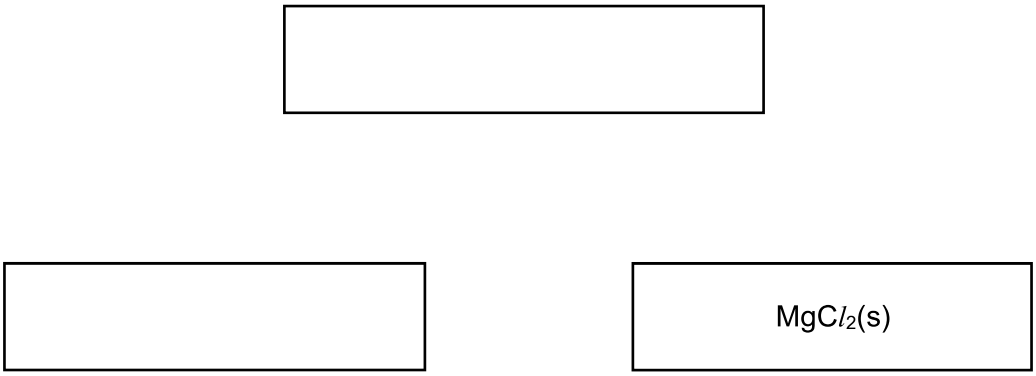
By considering the enthalpy change and Gibbs free energy change, state and explain the sign of the standard entropy change for the dissolution of potassium chloride. [1]

- **Since $\Delta G^{\ominus} < 0$, and $\Delta H^{\ominus} > 0$,**
from $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$, magnitude of $\Delta H^{\ominus}$ < magnitude of $298\Delta S^{\ominus}$ (T = 298 K under standard conditions). Thus $\Delta S^{\ominus} > 0$ under standard conditions.

(iii) Define *enthalpy change of hydration*. [1]

- **The energy change when one mole of gaseous ions is dissolved in a large amount of water.**

(iv) Complete the energy cycle involving the enthalpy change of solution (ΔH_{sol}), lattice energy (ΔH_{latt}) of magnesium chloride, and the enthalpy changes of hydration (ΔH_{hyd}). Label the enthalpy changes in your diagram. State symbols should be used.



[2]

$$\begin{tikzcd}
& \boxed{Mg^{2+}(aq) + 2Cl^-(aq) \text{ OR } MgCl_2(aq)} & \\
\boxed{Mg^{2+}(g) + 2Cl^-(g)} \arrow[ur, "\Delta H_{hyd}"] \arrow[rr, "\Delta H_{latt}"] & & \boxed{MgCl_2(s)} \arrow[ul, "\Delta H_{sol}"']
\end{tikzcd}$$

1m: correct $Mg^{2+}(aq) + 2Cl^-(aq)$ and $Mg^{2+}(g) + 2Cl^-(g)$
1m: correct directions of arrows with labels

(v) Hence, calculate the enthalpy change of hydration of magnesium ions, Mg^{2+}. Show your working. [1]

$\Delta H_{sol} = \Delta H_{hyd} - \Delta H_{latt}$
$-155 = \Delta H_{hyd}(Mg^{2+}) + 2(-364) - (-2493)$
- $\Delta H_{hyd}(Mg^{2+}) = -1920 \text{ kJ mol}^{-1}$

(vi) Explain why the lattice energy of $MgCl_2$ is more exothermic than the lattice energy of KCl. [1]

Lattice energy $\propto \dfrac{q^+q^-}{r^+ + r^-}$

- **Mg^{2+} has a greater charge and smaller size than K^+. Hence, there is greater attraction (OR stronger ionic bonds) between Mg^{2+} and Cl^- ions, leading to more exothermic lattice energy in $MgCl_2$.**

(vii) Molten magnesium chloride is electrolysed for 15.0 minutes by a constant current. At the cathode, 4.75×10^{22} magnesium atoms are produced. Calculate the value of the current used. [2]

$Mg^{2+} + 2e^- \rightarrow Mg$

- **Amount of e^- used** $= 2\left(\dfrac{4.75 \times 10^{22}}{6.02 \times 10^{23}}\right) = 0.158$ **mol**

$Q = 0.158 \times 96500 = I \times 15.0 \times 60$
- $I = 16.9$ **A**

(d) An electrochemical cell consisting of an Fe^{3+}/Fe^{2+} half-cell and a Cl_2/Cl^- half-cell is set up. The cell reaction for the electrochemical cell is shown below.

$$Cl_2 + 2Fe^{2+} \rightarrow 2Cl^- + 2Fe^{3+}$$

In this experiment, the Fe^{2+} concentration is 0.15 mol dm^{-3}. Concentrations of all other species remain at their standard values.

The Nernst equation is shown below.

$$E = E^\ominus + \frac{0.059}{n} \lg \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

where *n* is the number of electrons transferred

(i) A salt bridge is used in an electrochemical cell. Explain the function of the salt bridge. [1]

- **A salt bridge is used to maintain electrical neutrality where ions move from the salt bridge to maintain charge balance**

  OR
  acts as an electrical connector to complete the circuit between two half-cells.

(ii) Use the Nernst equation to calculate the electrode potential, *E*, for the Fe^{3+}/Fe^{2+} half-cell in this experiment. [1]

- $E = +0.77 + \frac{0.059}{1} \lg \frac{1.00}{0.15} = +0.82\ V$

(iii) Use your answer to **(d)(ii)** to calculate E_{cell} for this electrochemical cell. [1]

- $E_{cell} = +1.36 - (+0.82) = +0.54\ V$ **(ecf)**

(e) Anodisation of aluminium is widely practiced in industry.

State why aluminium objects are anodised and explain how anodising achieves this with the aid of equations. [3]

- **Aluminium objects are anodised to thicken the layer of Al_2O_3 on aluminium objects, which helps aluminium objects resist corrosion and act as electrical insulator.**

- **During the anodising process, O_2 is produced at the anode.**
  $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

- **The O_2 produced reacts with the aluminium object at the anode to form the layer of Al_2O_3.**
  $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$
  State symbols are not required for the equations.

[Total: 23]

2 **(a)** Deoxyhaemoglobin and oxyhaemoglobin contain iron atoms in the +2 oxidation state. Each iron atom is surrounded by five nitrogen-containing ligands and one oxygen-containing ligand in an octahedral arrangement. The oxygen-containing ligand is H_2O in deoxyhaemoglobin and O_2 in oxyhaemoglobin. Each haemoglobin can bind up to four O_2 as shown below.

$$\text{deoxyhaemoglobin} + 4O_2 \rightleftharpoons \text{oxyhaemoglobin} + 4H_2O$$

(i) Explain how oxygen is transported in the body, with reference to the equilibrium above. [2]

- **At regions of high concentration of O_2 (e.g. lungs), ligand-exchange will occur as position of the above equilibrium is shifted to the right and O_2 will replace H_2O to form oxyhaemoglobin.**
- **At regions of low concentration of O_2, ligand-exchange will occur as position of the above equilibrium is shifted to the left, and O_2 is released.**
  Give credit for either ligand-exchange or POE shift

(ii) Suggest why carbon monoxide is toxic when inhaled. [1]

- **CO is toxic as it can be strongly and irreversibly bonded to Fe in haemoglobin and reduce the amount of haemoglobin available for carrying O_2, and starves the body of O_2.**

Buffer solutions are important in living systems. The buffer in blood mainly consists of carbonic acid, H_2CO_3, and bicarbonate, HCO_3^-. The buffer serves to maintain the pH of blood at 7.40 ± 0.05 to ensure proper functioning of biological enzymes.

(iii) Explain what is meant by a *buffer solution*. [1]

- **A buffer solution is a solution capable of maintaining a fairly constant pH when a small amount of acid or base is added to it.**

(iv) With the aid of equations, explain how the pH of blood is maintained. [2]

- **When the pH becomes less than 7.40, there is a large reservoir of HCO_3^- that helps to remove the small amount of H^+. Hence pH is kept relatively constant.**
  $HCO_3^- + H^+ \rightarrow H_2CO_3$
- **When the pH becomes more than 7.40, there is a large reservoir of H_2CO_3 that helps to remove the small amount of OH^-. Hence pH is kept relatively constant.**
  $H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$
  1m for explanation AND equation (for each scenario)
  OR 1m for explanations
  OR 1m for 2 equations

(v) Ringer's lactate solution is given to patients to replace fluid and electrolyte after excessive blood loss. This solution contains lactic acid, $CH_3CH(OH)CO_2H(aq)$, and lactate ions, $CH_3CH(OH)CO_2^-(aq)$, and acts as a buffer solution. The concentration of lactate ion is 0.025 mol dm^{-3} and the solution has a pH of 4.50. Calculate the concentration of lactic acid present in the solution.

The K_a of lactic acid is 1.38×10^{-4} mol dm^{-3}. [2]

Let lactic acid be HA.

$K_a = \frac{[H^+][A^-]}{[HA]}$

- $1.38 \times 10^{-4} = \frac{[10^{-4.50}] \times 0.025}{[HA]}$
- $[HA] = 5.73 \times 10^{-3}$ mol dm^{-3}

(b) The hydroxides of Group 2 are often used to neutralise acidity. For example, calcium hydroxide, $Ca(OH)_2$, is used in agriculture to neutralise acidic soil while magnesium hydroxide, $Mg(OH)_2$, is used in indigestion tablets to neutralise excess stomach acid.

(i) The solubility of calcium hydroxide, $Ca(OH)_2$, in water is 2.50×10^{-2} mol dm^{-3} at 25°C.

Calculate the pH of a saturated solution of $Ca(OH)_2$ at 25°C. [2]

pOH = –lg[OH$^-$]
= –lg[2 × 2.50 × 10^{-2}]
= 1.30

pH = 14 – 1.30 = 12.7
1m for [OH$^-$]
1m for pOH and pH

(ii) An excess of solid magnesium hydroxide, $Mg(OH)_2$, was stirred with 0.500 mol dm^{-3} magnesium nitrate, $Mg(NO_3)_2$, until equilibrium was established.

The solubility product, K_{sp}, of $Mg(OH)_2$ is 1.40×10^{-11} mol^3 dm^{-9} at 25°C. Calculate the solubility of $Mg(OH)_2$ in the 0.500 mol dm^{-3} magnesium nitrate solution. [2]

Let the solubility of $Mg(OH)_2$ in 0.500 mol dm^{-3} $Mg(NO_3)_2$ be y mol dm^{-3}

$K_{sp} = [Mg^{2+}][OH^-]^2$
$1.40 \times 10^{-11} = (0.500 + y)(2y)^2$

- $1.40 \times 10^{-11} = (0.500)(2y)^2$ **since y << 0.500 mol dm^{-3}**
- $y = 2.65 \times 10^{-6}$ mol dm^{-3}

(c) This question explores the chemistry of some transition metals.

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

- **A transition element is a d-block element which forms one or more stable ions with partially filled d subshell.**

(ii) Explain why transition metal complexes are often coloured. [2]

- **In the presence of ligands, the degenerate 3d orbitals in the octahedral complex are split into 2 different energy levels (d-d splitting).**
- **A 3d electron from the lower energy level is promoted to the upper energy level by absorbing energy from visible light (d-d transition). The complement of the colour absorbed is seen.**

(iii) Air is bubbled through an aqueous solution containing $CoCl_2$, NH_4Cl and NH_3. The resulting solution is then evaporated and crystals of a salt **B** is isolated. **B** has an empirical formula of $CoN_4H_{12}Cl_3$.

On adding an excess $AgNO_3(aq)$ to an aqueous solution containing 0.01 mol of **B**, 1.44 g of Ag*Cl*(s) is precipitated.

The cationic complex in **B** has no net dipole moment.

Deduce the formula of the cationic complex in **B** and draw its structure. Show clearly the three-dimensional arrangement of the ligands and the overall charge of the cationic complex on the structure. [2]

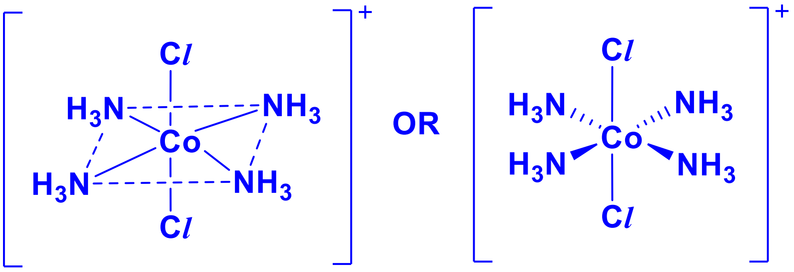
no. of moles of AgCl $= \dfrac{1.44}{107.9 + 35.5}$

$= 0.0100$ mol

- **no. of moles of B:AgCl = 1:1 (OR B has 1 mole of free Cl^- ion)**

Hence, the six ligands around the cobalt ion are four NH_3 and two Cl^- ligands.

Formula of cation in B is $[Co(NH_3)_4Cl_2]^+$.

- 

(OR the 2 Cl^- ligands placed diagonally to each other at the equatorial positions)

(iv) Hydrogen peroxide decomposes according to the following equation.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Fe^{3+} ions can be used to catalyse the decomposition.

Use the *Data Booklet* to write two equations to explain how this reaction is catalysed by Fe^{3+} ions and calculate the $E^\ominus_{cell}$ values for each step. [2]

The relevant half equations are:
$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

- **Step 1: $H_2O_2 + 2Fe^{3+} \rightarrow O_2 + 2H^+ + 2Fe^{2+}$**
  $E^\ominus_{cell} = +0.77 - (+0.68) = +0.09$ V

- **Step 2: $H_2O_2 + 2H^+ + 2Fe^{2+} \rightarrow 2H_2O + 2Fe^{3+}$**
  $E^\ominus_{cell} = +1.77 - (+0.77) = +1.00$ V
  1m for equation AND $E^\ominus_{cell}$ (for each step)
  OR 1m for 2 equations
  OR 1m for 2 $E^\ominus_{cell}$

[Total: 19]

3 **(a)** Benzoyl chloride, C_6H_5COCl, can be synthesised by the reaction of benzoic acid with either PCl_5 or $SOCl_2$.

(i) Complete the equation for reaction 1.

reaction 1 $C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl$ + ………………. + ……………….

reaction 2 $C_6H_5COOH + SOCl_2 \rightarrow C_6H_5COCl + SO_2 + HCl$

[1]

- **$POCl_3$ and HCl**

(ii) Use your answer to **(a)(i)** to suggest why it is easier to isolate the C_6H_5COCl, in pure form, from reaction 2 compared to reaction 1. [1]

- **In reaction 2, all the by-products, SO_2 and HCl are gaseous (OR no liquid by-products are formed), which can be easily removed.**

(iii) C_6H_5COCl contains a benzene ring in its structure.

Describe and explain the shape of benzene.

In your answer, include:

- the shape and bond angle around each carbon atom
- the hybridisation of the carbon atoms
- how orbital overlap forms σ and π bonds between the carbon atoms

[3]

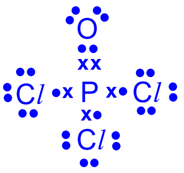
- **The bond angle is 120° and shape is trigonal planar around each C (OR hexangonal ring planar).**
- **Each carbon atom is sp^2 hybridised and uses two of the three sp^2 hybrid orbitals to overlap head-on with the sp^2 hybrid orbitals of the adjacent carbon atoms to form C–C σ bond.**
- **Each carbon atom has an unhybridised 2p orbital that overlaps sideways with the adjacent two 2p orbitals to form π bonds. This results in delocalised electrons in the π system.**

(b) Phosphorus oxychloride, $POCl_3$, shows similar chemical properties to PCl_5. $POCl_3$ has a melting point of 1°C and a boiling point of 106°C. $POCl_3$ reacts vigorously with water, forming misty fumes and an acidic solution.

(i) With the aid of an equation, explain the reaction of $POCl_3$ with water. [1]

- **In water, $POCl_3$ undergoes complete hydrolysis to give off misty fumes of HCl and an acidic H_3PO_4 solution.**
  $POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$

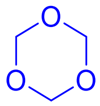
(ii) Draw a dot-and-cross diagram to show the bonding in $POCl_3$. [1]

- 

(c) Trioxanes are structures made up of three carbon atoms and three oxygen atoms in a six-membered ring.

Compound **C**, of molecular formula $C_3H_6O_3$, can form only **one** mono-chloro derivative when reacted with Cl_2 under light.

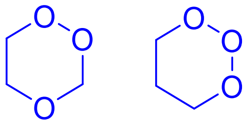
(i) Draw the structural formula of trioxane, **C**. [1]

• 

There are three possible structural isomers of trioxane.

The other two trioxane structural isomers are known to be hypothetical structures and cannot be isolated.

(ii) Draw the structural formulae of the other two trioxane isomers. [1]

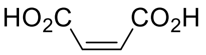
• 

(d) Dicarboxylic acids ionise in 2 stages.

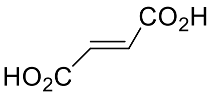
$$HO_2CRCO_2H \rightleftharpoons HO_2CRCO_2^- + H^+ \qquad K_{a1}$$

$$HO_2CRCO_2^- \rightleftharpoons {}^-O_2CRCO_2^- + H^+ \qquad K_{a2}$$

A hydrogen bond can form within a monoanion of *cis*-butenedioic acid. This intramolecular hydrogen bond stabilises the ion.

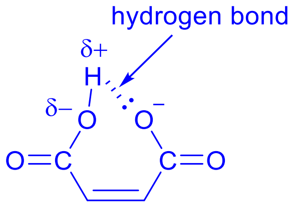


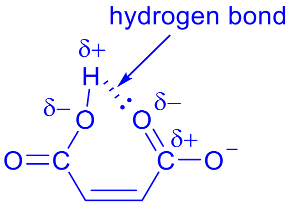
cis-butenedioic acid



trans-butenedioic acid

(i) Draw a diagram of the monoanion of *cis*-butenedioic acid showing the intramolecular hydrogen bond formed. [1]



(Accept 

)

Labelled diagram showing dipoles, lone pair on O⁻ and labelling of hydrogen bond

•

(ii) Explain why a monoanion of *trans*-butenedioic acid is unable to form intramolecular hydrogen bonds. [2]

- **There is restricted rotation about C=C,**
- **and the $-CO_2H$ and $-CO_2^-$ groups of the trans monoanion are too far apart for intramolecular hydrogen bond to be formed. (allow similar ideas, such as pointing away from each other or not in the correct orientation.)**

(iii) Suggest how the ability of these acids to form intramolecular hydrogen bonds affects the acid strength, and the value of K_{a1} for *cis*-butenedioic acid compared to *trans*-butenedioic acid. [1]

- **The intramolecular hydrogen bond formed increased the stability of the *cis*-monoanion and made it is more likely to be formed so *cis*-butenedioic acid is a stronger acid with larger K_{a1} than *trans*-butenedioic acid since.**

(e) The compound **D** has the molecular formula $C_9H_8O_2$. **D** does not liberate carbon dioxide with sodium hydrogencarbonate. **D** reacts with Tollens' reagent to give an organic species **E** and a grey precipitate. Upon acidification of **E**, a white precipitate with a molecular formula of $C_9H_8O_3$ is formed.

Upon oxidation with excess hot acidified potassium manganate(VII), 1 mol of **D** gives 1 mol of carbon dioxide and 1 mol of a compound, $C_8H_6O_5$. **D** reacts with aqueous bromine to form a white precipitate **F**, $C_9H_6O_3Br_4$.

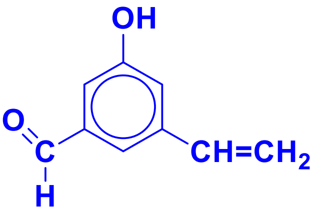
Suggest possible structures for **D, E** and **F**. For each reaction, state the *type of reaction* described and explain what the information tells you about the functional groups present in each structure. [5]

D contains a benzene ring due to the relatively high carbon to hydrogen ratio as seen from the molecular formula.

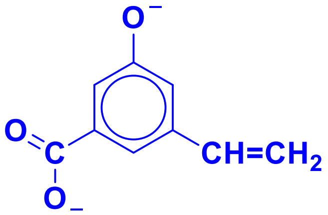
- **D does not undergo acid-base reaction with $NaHCO_3$ and is not a carboxylic acid.**
- **D undergoes oxidation with Tollens' reagent to give a grey precipitate of Ag and E, a carboxylate salt. D is an aldehyde.**
- **Oxidative cleavage / oxidation of alkene in D occurs with acidified $KMnO_4$. The $C=CH_2$ structural unit (or terminal alkene) is oxidised to give 1 mol CO_2.**
- **Oxidation of aldehyde in D also occurs. The oxidation product, $C_8H_6O_5$ contains 2 –COOH groups. With a molecular formula of $C_8H_6O_5$, the oxidation product must also contain a phenolic –OH group. Hence the oxidation product contains a benzene ring with 3 substituents i.e. 2 –COOH groups and 1 –OH group.**
- **D contains a benzene ring with 3 substituents i.e. –CHO, $–CH=CH_2$ and –OH groups.**
- **D undergoes electrophilic addition with aqueous Br_2. Hence, D is an alkene.**
- **D undergoes electrophilic substitution with aqueous Br_2. Hence, D is a phenol, and its two substituents are at positions 3 and 5.**

max 3m for explanation

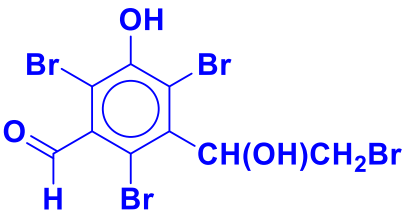
D:



E:



F:



3m for structures
overall max 5m

[Total: 18]

Section B

Answer **one** question from this section.

4 **(a)** Describe what is meant by the term *enhanced greenhouse effect*. [1]

- **Enhanced greenhouse effect is primarily driven by increased human activities that release excessive amounts of greenhouse gases into the atmosphere, leading to an intensified trapping of heat and subsequent global warming.**

(b) Compound **K** has the structural formula $CH_2{=}CHCH(NH_2)CO_2H$ and it exhibits stereoisomerism.

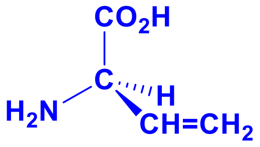
(i) Define the term *stereoisomerism*. [1]

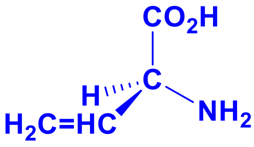
- **Stereoisomerism is a form of isomerism in which molecules have the same structural (constitutional) formula but differ in the three-dimensional orientation of their atoms in space.**

(ii) Name all the functional groups in **K**. [1]

- **Alkene, primary amine and carboxylic acid**

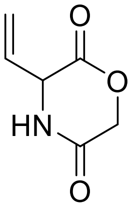
(iii) Draw three-dimensional structures for the two stereoisomers of **K** and name this type of stereoisomerism. [2]

- 



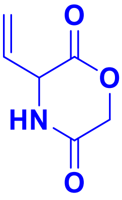
- **Enantiomerism**

Compound **K** can be prepared from the reaction of **L** with a controlled amount of hot aqueous acid.



compound **L**

(iv) Write the equation for the reaction between **L** and a hot aqueous acid to form **K**. [1]

- 

$+ 2H_2O \rightarrow CH_2{=}CHCH(NH_2)CO_2H + CH_2(OH)CO_2H$

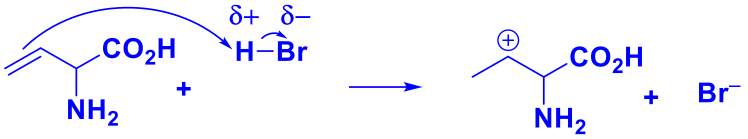
(v) Suggest which compound, **K** or **L**, is a stronger base. Explain your reasoning. [2]

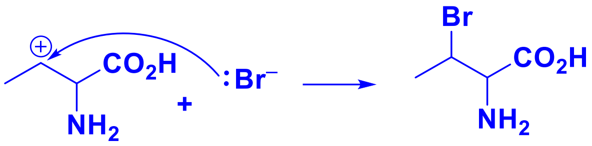
- **K is a stronger base.**
-

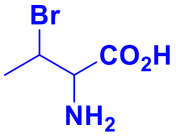
There is a primary amine in K which <u>can donate its lone pair on nitrogen</u>. In L, the lone pair electrons on nitrogen is <u>delocalised in the C=O bond and is not available for donation</u>, so it is not basic.

(vi) Compound **K** undergoes an addition reaction with hydrogen bromide. Suggest a mechanism for this reaction and use it to predict the major product. Explain your reasoning. [3]

Electrophilic Addition

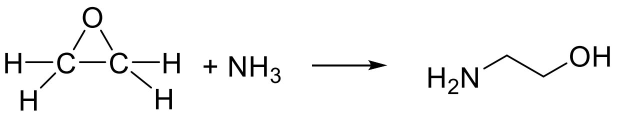
- 

- 

- 

is the major product since the <u>carbocation intermediate formed is more stable</u> as there are <u>greater number of electron-donating alkyl groups</u> that helps to <u>disperse the positive charge</u>.

(c) 2-aminoethanol can be synthesised from oxirane as shown below.

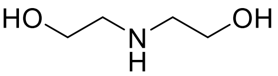


oxirane 2-aminoethanol

(i) State the type of reaction undergone by oxirane to form 2-aminoethanol. [1]

- **Nucleophilic substitution**

(ii) A small amount of by-product **M** is produced during this reaction.



compound **M**

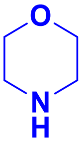
Explain how the by-product **M** is produced and hence suggest how the formation of by-product **M** can be minimised. [2]

- **The nitrogen in the 2-aminoethanol <u>contains a lone pair of electrons and it can act as a nucleophile</u> to further react with oxirane to form compound M.**
- **Use <u>NH_3</u> in large <u>excess</u> to minimise the formation of by-product M.**

(iii) Compound **P**, C_4H_9NO can be formed from the reaction of by-product **M**, $C_4H_{11}NO_2$, with concentrated H_2SO_4.

Compound **P** is a saturated and basic organic compound.

Suggest a structure for compound **P**. [1]

- 

(iv) Suggest a simple chemical test to confirm that **M** has been completely removed from the reaction mixture by the concentrated H_2SO_4. [2]

- **Heat with $KMnO_4(aq)$ and $H_2SO_4(aq)$.**
- **If M has been completely removed, the solution will remain purple. Otherwise, purple solution will turn colourless.**
  (OR Heat with $K_2Cr_2O_7(aq)$ and $H_2SO_4(aq)$. If M has been completely removed, the solution will remain orange. Otherwise, orange solution will turn colourless.)
  (allow Na for BOD)

(d) In aqueous solution, iodide ions react with acidified hydrogen peroxide as shown below.

$$2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2H_2O$$

The initial rate of the above reaction is found to be first order with respect to I^-, first order with respect to H_2O_2 and first order with respect to H^+.

A possible four-step mechanism for this reaction is proposed below.

step 1 $H_2O_2 + I^- \rightarrow IO^- + H_2O$
step 2 $H^+ + IO^- \rightarrow HIO$
step 3 $HIO + I^- \rightarrow I_2 + OH^-$
step 4 $OH^- + H^+ \rightarrow H_2O$

(i) Suggest which of the steps, 1, 2, 3 or 4, in this mechanism is the rate-determining step. Explain your answer. [1]

- **Step 2.**
  When Step 2 is the slow step, based on the coefficient of the reactant in step 2, there is one H^+ and one IO^-, rate = $k'[H^+][IO^-]$. Since IO^- is an intermediate, from the first step, $[IO^-]$ is directly proportional to $[H_2O_2][I^-]$.
  Hence, the rate equation = $k[H^+][H_2O_2][I^-]$. That is consistent with the observed order of reaction.

(ii) Suggest the role of HIO in this mechanism. Explain your reasoning. [1]

- **Intermediate as it is formed in step 2 and then consumed in step 3.**

(iii) This reaction is repeated in two separate experiments. The experiments are carried out at the same temperature and with the same concentrations of I^- and H_2O_2.

One experiment takes place at pH 1.0 and the other experiment takes place at pH 2.0.

Suggest the value of $\dfrac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$. [1]

- **10. Since at pH 1.0, $[H^+]$ is 10 times of that at pH 2.0, and this reaction is first order with respect to $[H^+]$, so the rate of reaction at pH 1.0 is 10 times that at pH 2.0.**

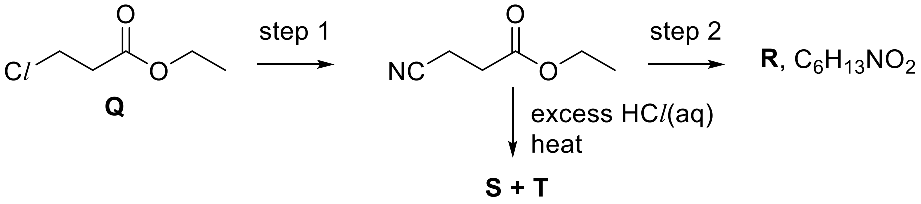
[Total: 20]

5 **(a)** Chlorofluorocarbons (CFCs) were commonly used as a refrigerant. In recent years, it has slowly been replaced by other organic substances.

Outline the environmental consequence of releasing CFC into the atmosphere. [1]

- **When CFC is released into the atmosphere, the C–C*l* bond can break to give C*l*• radicals which catalyse the decomposition of ozone. This leads to depletion of ozone layer which is important for removing UV radiation from the Sun.**

(b) A reaction scheme is shown below.



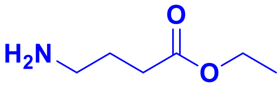
(i) Give the systematic name for **Q**. [1]

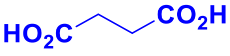
- **ethyl 3-chloropropanoate**

(ii) Suggest the reagents and conditions used for steps 1 and 2. [2]

- **step 1: KCN in ethanol and heat**
- **step 2: H_2(g), Ni catalyst and heat OR H_2(g), Pt/Pd catalyst**

(iii) Suggest the structures of compounds **R**, **S** and **T**. [2]

- **R:** 

- **S and T:**  **and CH_3CH_2OH**

When compound **Q** undergoes hydrolysis under different reaction conditions, it gives $CH_2ClCH_2CO_2H$ or $CH_2(OH)CH_2CO_2H$.

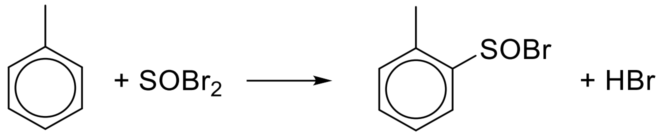
(iv) Suggest which organic acid, $CH_2ClCH_2CO_2H$ or $CH_3CH_2CO_2H$ is a stronger acid. Explain your reasoning. [1]

- **$CH_2ClCH_2CO_2H$ is a stronger acid as C*l* exerts electron-withdrawing inductive effect that helps to disperse the negative charge of the anions formed when the acid dissociates in water.**

(v) Write an equation to show how $CH_2(OH)CH_2CO_2^-$ is formed from **Q**. [1]

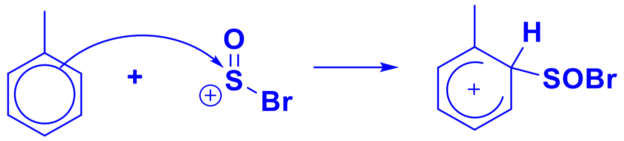
- **$CH_2ClCH_2CO_2CH_2CH_3 + 2OH^- \rightarrow CH_2(OH)CH_2CO_2^- + CH_3CH_2OH + Cl^-$**

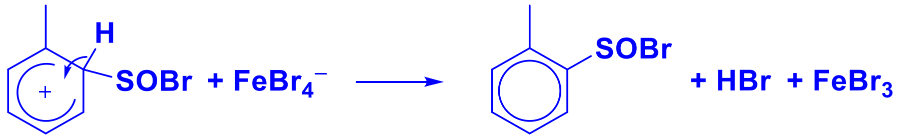
(c) The reaction of methylbenzene with thionyl bromide, $SOBr_2$, in the presence of an iron(III) bromide catalyst, $FeBr_3$, is shown below.



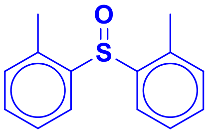
The mechanism of this reaction is similar to that of bromination of benzene.

(i) Suggest the mechanism for this reaction. Include relevant curly arrows and charges. [3]

- **Electrophilic Substitution**
  $SOBr_2 + FeBr_3 \rightarrow {}^{+}SOBr + FeBr_4^-$
- 

- 

(ii) This reaction produces a small amount of a by-product, **U**, $C_{14}H_{14}OS$. Suggest a structure for by-product **U**. [1]

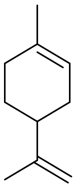
- 

  Allow other 2,4-directing products

(iii) Suggest which compound, methylbenzene or nitrobenzene, reacts with thionyl bromide at a higher rate. Explain your reasoning. [1]

- **Methylbenzene reacts at a higher rate than nitrobenzene as methyl group exerts electron-donating inductive effect which makes the electron density in benzene greater so that it is more susceptible to electrophilic attack (OR Nitro group exerts electron-withdrawing inductive/resonance effect, and it makes the electron density in the benzene lower so that it is less susceptible to electrophilic attack).**

(d) Limonene, $C_{10}H_{16}$, occurs naturally in the pith oil of citrus fruits. It has been used as a biofuel in diesel engines.



limonene

(i) Use the molecular formula of limonene to write a balanced equation for its complete combustion in air. [1]

- **$C_{10}H_{16} + 14O_2 \rightarrow 10CO_2 + 8H_2O$**

(ii) Use bond energy values from the *Data Booklet* to calculate the enthalpy change of combustion of limonene. [2]

- **Bond breaking: 8 × C–C, 2 × C=C, 16 × C–H, 14 O=O**

Bond formed: 20 × C=O, and 16 × O–H

- **Enthalpy change of combustion**
  = 8(350) + 2(610) + 16(410) + 14(496) – [20(805) + 16(460)]
  = –5940 kJ mol^{-1}

(iii) The enthalpy change of combustion of diesel fuel is about –45 kJ g^{-1}. How does the enthalpy change of combustion of limonene per gram compare to this value? Show your working. [2]

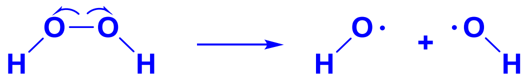
Molar mass of $C_{10}H_{16}$ = 10 × 12 + 16 = 136 g mol^{-1}

- **enthalpy change of combustion of limonene per gram = –5936 ÷ 136**
  = –43.6 kJ g^{-1}

- **The enthalpy change of combustion of limonene per gram is <u>slightly less exothermic than (or comparable to)</u> diesel.**

(e) Define the term *free radical* and explain with the aid of an equation with curly arrows how the bond in hydrogen peroxide, H_2O_2, breaks to form •OH free radical. [2]

- **A free radical is a particle (OR atom, molecule or ion) that has at least one unpaired electron.**

- 

[Total: 20]