VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

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

CT GROUP ……………………………..

CHEMISTRY

9729/03

Paper 3 Free Response

19 September 2023

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

2 hours

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on this cover page.
Write in dark blue or black pen.
You may use a soft 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**	**/ 24**
	2	**/ 16**
	3	**/ 20**
Section B	**4 OR 5**	**/ 20**
Total		**/ 80**

This document consists of **34** printed pages.

Section A

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

1 **(a)** Describe and explain the trend in thermal stability of the hydrogen halides. [2]

Thermal stability decreases down the group. Increase in atomic radius from F to I leading to poorer extent of overlap between the orbital of hydrogen and the orbital of the halogen. Hence H-X bond is weaker, less energy needed to break the bond.

(b) A sodium salt of the interhalogen ion, IBr_x^- is prepared. When heated, the salt evolves bromine vapour, leaving sodium iodide as the residue.

The bromine vapour evolved requires 32.0 cm^3 of 0.100 mol dm^{-3} of aqueous sodium thiosulfate for complete reaction. The balanced ionic equation for the reaction between bromine and thiosulfate is as shown below.

$$S_2O_3^{2-}(aq) + 4Br_2(g) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 8Br^-(aq) + 10H^+(aq)$$

(i) Construct a balanced equation for the thermal decomposition of $NaIBr_x$. [1]

$2NaIBr_x \rightarrow xBr_2 + 2NaI$

(ii) Calculate the amount of bromine gas evolved. [1]

Amount of thiosulfate used = 32.0 ÷ 1000 × 0.100 = 3.20×10^{-3} mol
Amount of bromine evolved = 4 × 3.20×10^{-3} = 0.0128 mol

The sodium iodide residue was completely reacted with concentrated sulfuric acid to give HI gas, which immediately further reacted with concentrated sulfuric acid to give H_2S, together with black crystals of iodine. The mass of the iodine crystals formed was found to be 1.63 g.

(iii) Calculate the amount of iodine formed and hence deduce the formula of the interhalogen ion. [2]

Amount of iodine formed = 1.63 ÷ (2 × 127) = 6.42×10^{-3} mol
Amount of sodium iodide = 6.42×10^{-3} × 2 = 0.0128 mol
Amount of bromine atom in the interhalogen ion = 2 × 0.0128 = 0.0256 mol
$x = \frac{nBr}{nI}$ = 0.0256 ÷ 0.0128 = 2
Thus, the formula of the interhalogen ion is IBr_2^-.

(c) Chloroalkanes and bromoalkanes can be made by the reaction of the corresponding halogen with alkanes. One example is given below.

$$CH_3CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CH_2Cl + HCl$$

(i) State the conditions needed for this reaction. [1]

Excess propane in the presence of UV light

(ii) Name and describe the mechanism of this reaction. [2]
Free radical substitution

Initiation:
$Cl_2 \rightarrow 2Cl\bullet$

Propagation:

$$CH_3CH_2CH_3 + Cl\cdot \longrightarrow CH_3CH_2\dot{C}H_2 + HCl$$

$$CH_3CH_2\dot{C}H_2 + Cl_2 \longrightarrow CH_3CH_2CH_2Cl + Cl$$

Termination:

$2Cl\bullet \rightarrow Cl_2$

$$CH_3CH_2\dot{C}H_2 + Cl\cdot \longrightarrow CH_3CH_2CH_2Cl$$

(iii) Suggest why it is **not** possible to make iodoalkanes by this method. [1]

As halogen atom becomes larger, the H-I and C-I bond are weaker. Thus the formation of H-I and C-I bond release insufficient energy to overcome the strong C-H.

(d) Suggest a structural formula for each of the compounds, **A** to **D**, in the following schemes shown in Figure 1.1. [4]

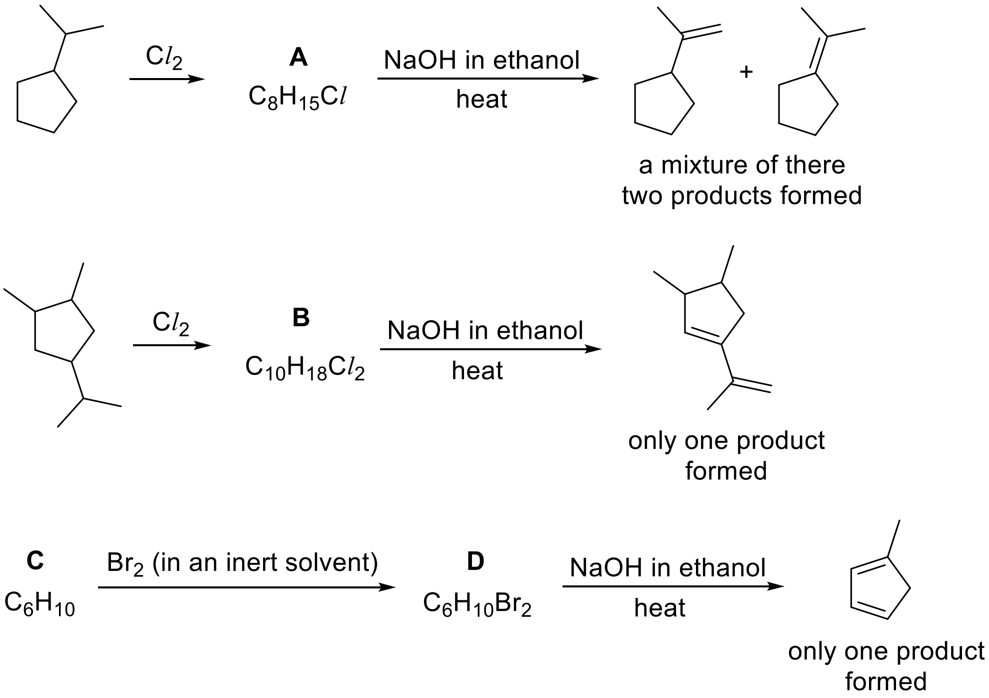
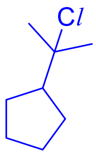
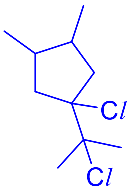


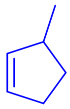
Figure 1.1



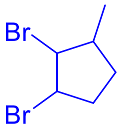
A



B



C



D

(e) 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.

(i) Suggest one reason why CFCs were originally used for these purposes. [1]

They liquefied under pressure
OR: They volatilised readily when that pressure was released
OR: They were inert and non-toxic.

(ii) Explain how CFCs destroy the ozone layer. [1]

UV radiation homolytically cleaves the C–C*l* bond in CFC molecules to generate C*l*● radicals which initiate a chain reaction leading to the destruction of ozone molecules.

(iii) Suggest one potential hazard of using alkanes instead of CFCs. [1]

Alkanes are flammable.

(f) Figure 1.2 shows two reactions involving benzene and a suitable Lewis acid as a catalyst.

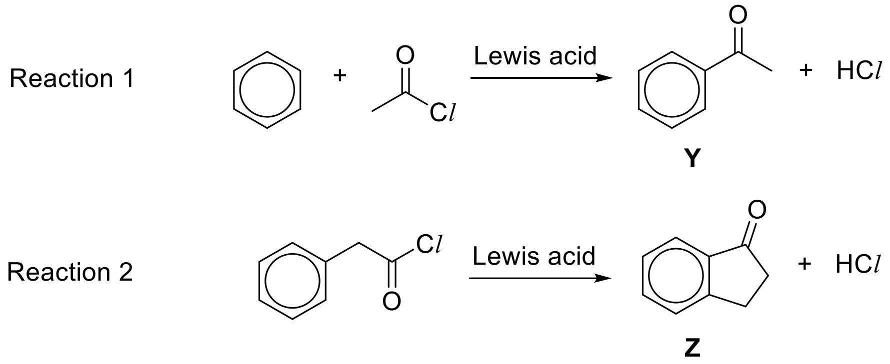


Figure 1.2

(i) Suggest the type of reaction for reaction 1. [1]

Electrophilic substitution

(ii) Suggest the reagents and conditions for a reaction that could be used to distinguish between **Y** and **Z**, and describe the observations. [2]

Reagent: Warm or heat with aqueous iodine, and NaOH(aq)
Observation: Y gives a pale yellow precipitate of CHI_3, while Z does not give any precipitate.

(g) When benzene is added to compound **Q** in the presence of $AlCl_3$, Compound **E** with the molecular formula of $C_{10}H_{12}$ is formed.

When **E** is heated with acidified $KMnO_4$, **F** is formed and effervescence is also observed,

F contains 57.8% of carbon, 3.6% of hydrogen and 38.6% of oxygen by mass. The relative molecular mass of **F** is 166. 1 mol of **F** readily reacts with 2 mol of NaOH(aq).

(i) Determine the molecular formula of **F** [1]

	C	H	O
Mass in 100 g	57.8	3.6	38.6
No. of moles	$\frac{57.8}{12} = 4.82$	$\frac{3.6}{1.0} = 3.6$	$\frac{38.6}{16} = 2.41$
Ratio	2	1.49	1
Simplest ratio	4	3	2

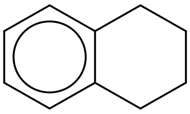
✓ Empirical formula is $C_4H_3O_2$.

Molecular formula is $(C_4H_3O_2)_n$. $(12 \times 4 + 1 \times 3 + 16 \times 2)n = 166 \Rightarrow n = 2$
Molecular formula is $C_8H_6O_4$

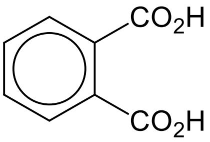
(ii) Hence, suggest the structure for **Q**, **E** and **F**. [3]

Q: $ClCH_2CH_2CH_2CH_2Cl$ or $BrCH_2CH_2CH_2CH_2Br$

E:



F:



[Total: 24]

2 **(a)** Describe what is meant by the term *nucleon number*. [1]

Nucleon number is the total number of protons and neutrons in an atom or nucleus.

(b) State two ways in which the behaviour of electrons in an electric field differs from that of protons. [1]

Electrons are deflected towards the positive potential/terminal whereas protons are deflected towards the negative potential/terminal.
Electrons have a much smaller mass than protons or are deflected more than protons.

(c) A mixture of $HC_2O_4^-$ and $C_2O_4^{2-}$ can act as a buffer in biochemical and molecular biology experiments.

(i) Write an expression for K_b of $C_2O_4^{2-}$, stating its units. [1]

$$K_b = \frac{[OH^-][HC_2O_4^-]}{[C_2O_4^{2-}]}$$

Units: mol dm^{-3}

(ii) The pK_b value of $C_2O_4^{2-}$ is 9.72.

Determine the amount of hydrochloric acid is needed to add to a 1.00 dm^3 solution of 0.0100 mol dm^{-3} $K_2C_2O_4$ solution so that a buffer solution with a pH of 5.0 can be prepared.
You may assume that the volume of solution remains the same with the addition of hydrochloric acid. [2]

Let the amount of HCl added to 1 dm^3 be x mol.

$[C_2O_4^{2-}] = 0.0100 - x$ mol dm^{-3}
$[HC_2O_4^-] = x$ mol dm^{-3}

pOH = 14 – 5 = 9.0

$$K_b = \frac{[OH^-][HC_2O_4^-]}{[C_2O_4^{2-}]}$$

$$10^{-9.72} = \frac{10^{-9}[HC_2O_4^-]}{[C_2O_4^{2-}]}$$

$$\frac{[HC_2O_4^-]}{[C_2O_4^{2-}]} = 0.191 = \frac{x}{0.0100-x}$$

$x = 0.00160$

The amount of HC*l* needed = 0.00160 mol

At 298 K, the K_{sp} of silver(I) ethanedioate, $Ag_2C_2O_4$ is 5.40×10^{-12} mol^3 dm^{-9}

(iii) Determine whether precipitation will be observed when 0.500 mg of $AgNO_3$ solid was added to 25.0 cm^3 of 3.50×10^{-3} mol dm^{-3} $Na_2C_2O_4$. [You can ignore hydrolysis of $C_2O_4^{2-}$ in your calculation] [2]

Amount of $AgNO_3$ = $0.500 \times 10^{-3} \div (107.9 + 14.0 + 48.0)$
$= 2.94 \times 10^{-6}$ mol

$[Ag^+] = 2.94 \times 10^{-6} \div 25.0 \times 1000$
$= 1.18 \times 10^{-4}$ mol dm^{-3}

Ionic product = $[Ag^+]^2[C_2O_4^{2-}]$
$= (1.18 \times 10^{-4})^2 \times 3.50 \times 10^{-3}$
$= 4.85 \times 10^{-11}$

Since ionic product > K_{sp}, precipitation will be observed.

(iv) Explain why the solubility of $Ag_2C_2O_4$ increases when aqueous NH_3 is added. [2]

$Ag_2C_2O_4(s) \rightleftharpoons 2Ag^+(aq) + C_2O_4^{2-}(aq)$ -- (1)

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ -- (2)

When aqueous NH_3 is added in excess, NH_3 removes Ag^+ from equilibrium (2) due to formation of complex, $[Ag(NH_3)_2]^+$. By Le Chatelier's Principle, the position of equilibrium (1) shifts right to counteract the decrease in $[Ag^+]$, causing the solubility of $Ag_2C_2O_4$ to increase.

(d) The initial rate of the reaction between persulfate and iodide ions can be studied by the clock method, using sodium thiosulfate. The equations for the reactions are as follows.

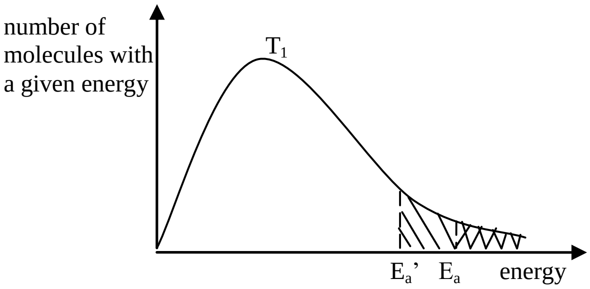
$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$ reaction 1

$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$ reaction 2

The reaction between $S_2O_8^{2-}$ and I^- ions is very slow. If a small amount of aqueous iron(II) ions is added to the mixture, the rate of reaction increases.

(i) By using the concept of activation energy and an appropriate sketch of the Boltzmann distribution, explain why the addition of iron(II) ions speeds up the reaction. [3]

A catalyst works by providing an alternative pathway with lower activation energy, E_a' so that a greater number of molecules can overcome the energy barrier for the reaction, E_a'. Hence the frequency of effective collisions increases which leads to a faster reaction rate.

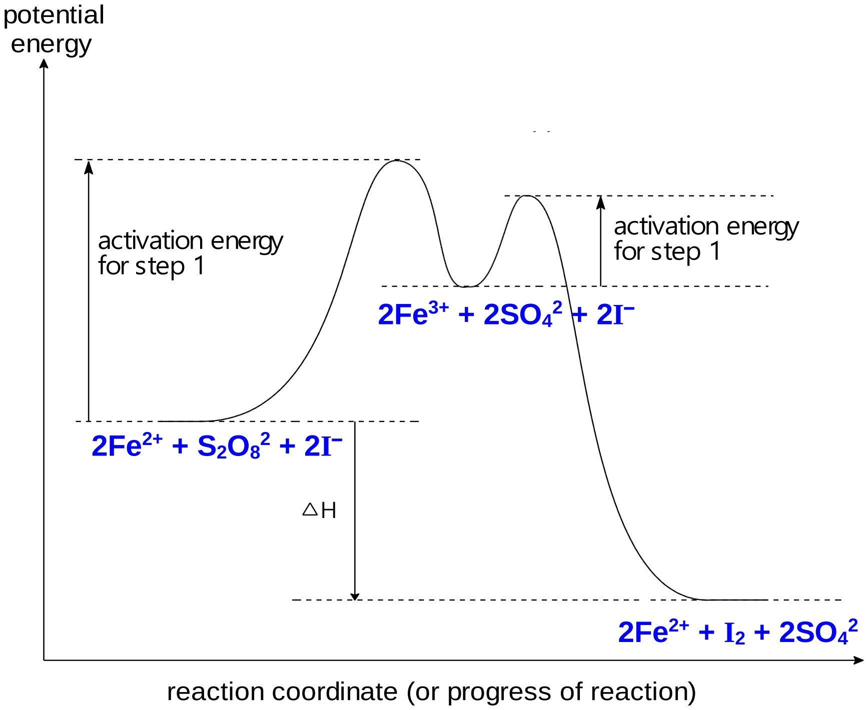


(ii) Write equations to show how iron(II) ions is used as catalyst. [2]

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

(iii) Sketch an energy profile diagram for the catalysed reaction. Label the activation energies, enthalpy change of reaction, and identity of the species present as reactants, intermediates and products clearly on the diagram. [2]



Graph showing E_{a1} and E_{a2} for steps 1 and 2 (can be either endo / exo reaction)
Reactants, intermediates and products are correctly shown

[Total: 16]

3 **(a)** **(i)** Iodine and chlorine react together to form iodine monochloride.

$$I_2(s) + Cl_2(g) \rightarrow 2ICl(s)$$

Explain the term, *bond energy*, with reference to I-C*l* bond. [1]

Bond energy is the energy <u>absorbed</u> to break <u>1 mole of I</u>-<u>C*l* covalent bonds</u> from <u>gaseous IC*l* molecules to form gaseous I and C*l* atoms</u>.

(ii) Construct a fully labelled energy cycle to calculate the bond energy of the I-C*l* bond in IC*l*.

Your cycle should include relevant data from the *Data Booklet* together with the following data:

standard enthalpy change of formation, ($\Delta H_f^\ominus$) of IC*l*(s) = –35.5 kJ mol^{-1}
enthalpy change of sublimation of $I_2(s) \rightarrow I_2(g)$ = +62.4 kJ mol^{-1}
enthalpy change of sublimation of $ICl(s) \rightarrow ICl(g)$ = +52.9 kJ mol^{-1} [3]

Bond energy is the amount of energy <u>absorbed</u> to break <u>1 mole of I</u>-<u>C*l* covalent bonds</u> from <u>gaseous IC*l* molecules</u>. [1]

$$\begin{tikzcd}
I_2(s) + Cl_2(g) \arrow[rr, "2\,(-35.5)"] \arrow[d, "+62.4"] & & 2ICl(s) \arrow[dd, "+2(52.9)"] \\
I_2(g) + Cl_2(g) \arrow[d, "\text{BE (I–I)} = 151"] & & \\
2I(g) + Cl_2(g) \arrow[d, "\text{BE (Cl–Cl)} = 244"] & & 2ICl(g) \arrow[dll, "2 \times \text{BE (I–Cl)}"] \\
2I(g) + 2Cl(g) & &
\end{tikzcd}$$

2 (–35.5) = 62.4 + 151 + 244 – 2 × BE (I–C*l*) – 2(52.9)
BE (I–C*l*) = 211 kJ mol^{-1}

(iii) The standard Gibbs free energy of formation, $\Delta G_f^\ominus$, of IC*l*(s) is +7.19 kJ mol^{-1}.

Calculate $\Delta S_f^\ominus$ and comment on its sign with respect to the reaction. [2]

$\Delta G = \Delta H - T\Delta S$
$+7.19 = -35.5 - 298\,\Delta S_f^\ominus$
$\Delta S_f^\ominus = -0.143$ kJ mol^{-1} K^{-1}

$\Delta S_f^\ominus$ is <u>negative</u> which indicates a decrease in entropy. This is expected since the reaction causes a <u>decrease in the moles of gas</u> [from ½ to 0 mol for the equation $\frac{1}{2} I_2(s) + \frac{1}{2} Cl_2(g) \rightarrow ICl(s)$]

(b) Figure 3.1 shows a synthesis scheme involving iodine monochloride in one of the steps.

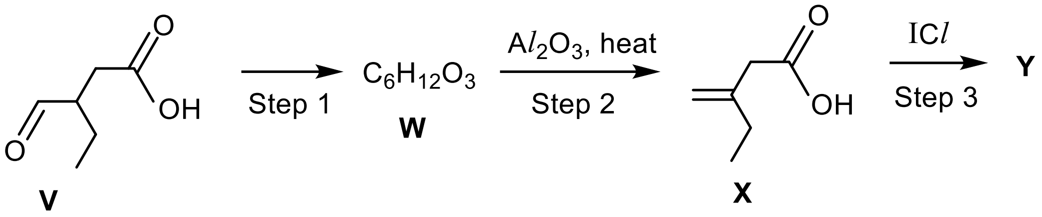
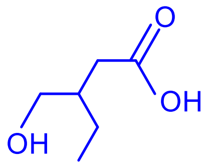


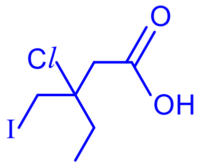
Figure 3.1

(i) Draw the structure of **W** and state the reagents and conditions for Step 1. [2]



Reagents and conditions:
H_2 with Pt catalyst
OR H_2 with Ni catalyst, heat
OR $NaBH_4$ in ethanol

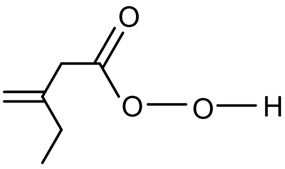
(ii) **Y** is the major product of the reaction in Step 3.
Suggest the structure of **Y**. [1]



(iii) When I_2 is used as the reagent instead of ICl in Step 3, the reaction occurs less readily. Suggest an explanation for this observation. [1]

Iodine in ICl carries a partial positive charge hence will be a better electrophile.
OR
I_2 is non–polar whereas ICl is polar. Hence, I_2 is expected to be a weaker electrophile and hence attacks the alkene group less readily.

(c) Peroxyacids are compounds containing the $–CO_3H$ group. The structure of **Z**, which contains the $–CO_3H$ group, is shown below.



Z

Suggest why **Z** has a higher pK_a value than **X**. [2]

X dissociates to form the carboxylate anion: $RCO_2H \rightleftharpoons RCO_2^- + H^+$

In the carboxylate anion, the p–orbitals in the $–CO_2^-$ group overlap, leading to delocalisation of the lone pair on the O^- atom. This causes the negative charge to be dispersed, thus stabilising the ion by resonance.

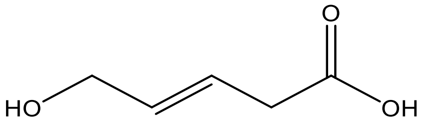
However, for Z, the O^- is separated from the C=O bond by an extra oxygen in the $–CO_3^-$ group. Hence, its p-orbital cannot overlap with those of the C=O group (OR there is no resonance OR lone pair on O^- cannot be delocalised).

The anion is not stabilised, which causes Z to be a weaker acid with a higher pK_a value.

(d) **B** and **C** are isomers with the molecular formula $C_5H_6O_2$.

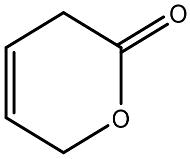
B forms a brick-red precipitate with Fehling's solution but does not give effervescence with sodium.

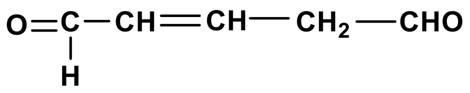
C reacts with hot aqueous sodium hydroxide. Upon acidification, it forms the product shown below.



When **B** and **C** are separately reacted with hot acidified $KMnO_4$, they form the same mixture of organic products, **D** ($C_3H_4O_4$) and **E** ($C_2H_2O_4$). **E** undergoes further oxidation to give effervescence.

Deduce the structures of **B** to **E**, and explain the chemistry involved. [8]

Reactions	**Reaction type**	**Structural feature**
B + Fehling's solution	**Oxidation**	**B contains aldehyde group.** **Brick red ppt is Cu_2O.**
B + sodium	**Redox**	**B does not contain -OH group.**
C + hot sodium hydroxide	**Hydrolysis**	**Since C contains 2 oxygen atoms, ester group is present.** **Based on the hydrolysis product, C is a cyclic ester with the structure:** 
C + hot acidified $KMnO_4$	**Hydrolysis (of ester) and oxidation**	**C reacts to give D, $HO_2C–CH_2–CO_2H$, and E, $HO_2C–CO_2H$.** **E is further oxidised to give CO_2 effervescence.**
B + hot acidified $KMnO_4$	**Oxidation**	**Since B undergoes cleavage, it contains an alkene.** **$–CO_2H$ groups in oxidation products D and E are formed from either RCH= or –CHO in B.** **Structure of B is**

		 $O=C(H)-CH=CH-CH_2-CHO$

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Chromium is the Earth's 21st most abundant element and the 6th most abundant transition metal.

The most common oxidation state of chromium is +3.

(i) Write an equation, with state symbols, to show a possible way of converting chromium metal to a compound with chromium in its +3 oxidation state. [1]

$4Cr(s) + 3O_2(g) \rightarrow 2Cr_2O_3(s)$

(ii) Hydrated chromium(III) chloride exists as isomers, with the general formula of $CrCl_3 \bullet 6H_2O$. Each of the isomers is of a different colour. One such isomer is the hydrated dark green compound $[CrCl_2(H_2O)_4]Cl \bullet 2H_2O$.

Give the formula of two other isomers of hydrated chromium(III) chloride with a coordination number of 6. [1]

$[CrCl(H_2O)_5]Cl_2 \bullet H_2O$, $[Cr(H_2O)_6]Cl_3$, $[CrCl_3(H_2O)_3] \bullet 3H_2O$

Figure 4.1 shows some reactions of chromium(III) chloride.

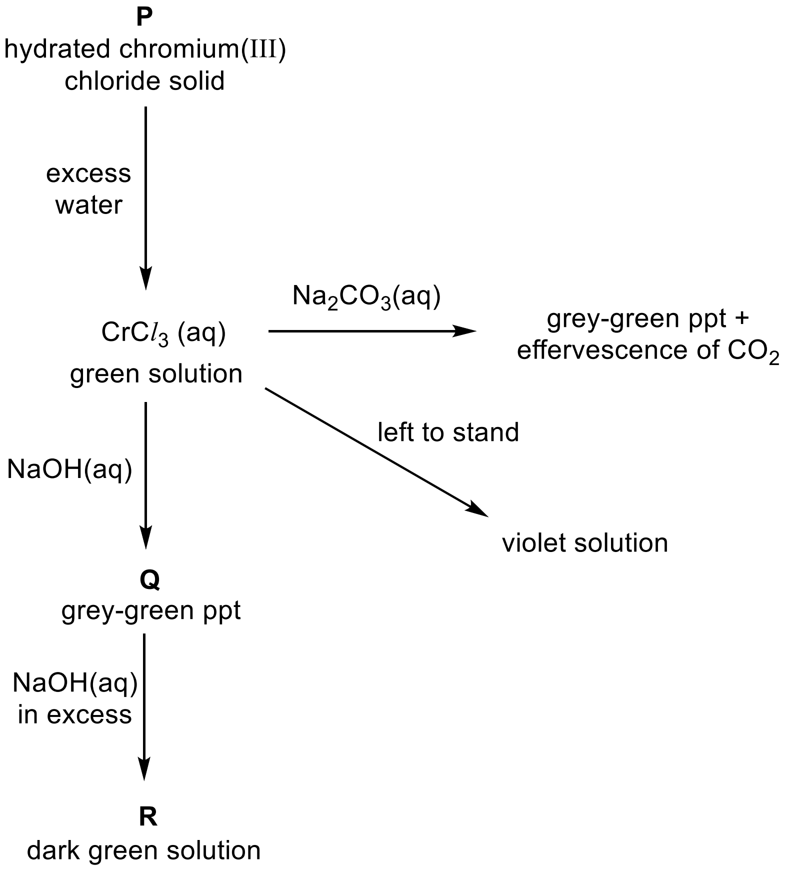


Figure 4.1

(iii) Explain why carbon dioxide is evolved when $Na_2CO_3(aq)$ is added to aqueous chromium(III) chloride. Include any relevant equations in your answer. [1]

A solution containing Cr^{3+} is acidic in nature due to the high charge density of the cation.
$[Cr(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Cr(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$

(iv) Identify the grey-green precipitate **Q**. [1]

Chromium(III) hydroxide or $Cr(OH)_3$ or $[Cr(OH)_3(H_2O)_3]$

(v) Suggest a formula for the complex ion present in **R**. [1]

$[Cr(OH)_6]^{3-}$

(vi) A student conducted an experiment where he reacted zinc metal with a solution of acidified dichromate(VI) ions. He observed several changes in colour: the orange solution first turned green then bright blue.

Use $E^\ominus$ values from the *Data Booklet* to explain all the colour changes that are taking place. Write equations for the reactions that occurred. [3]

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $E^\ominus = +1.33$ V
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$ $E^\ominus = -0.41$ V
$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76$ V

1st colour change:
$Cr_2O_7^{2-}$ (orange) → Cr^{3+} (green)
$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox} = +1.33 - (-0.76) = +2.09$ V

$3Zn + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Zn^{2+} + 2Cr^{3+} + 7H_2O$

2nd colour change:
Cr^{3+} (green) → Cr^{2+} (blue)
$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox} = -0.41 - (-0.76) = +0.35$ V

$Zn + 2Cr^{3+} \rightarrow Zn^{2+} + 2Cr^{2+}$

(vii) Explain why a solution of chromium(III) chloride is coloured. [2]

The degenerate 3d orbitals of the Cr^{3+} ion in the octahedral complex is split into 2 different energy levels due to the presence of ligands (d-d splitting).

d-d transition took place whereby a 3d electron from the lower energy level is promoted to the upper energy level by absorbing energy from the visible region of the electromagnetic spectrum. The colour seen is the complement of the colour absorbed.

(b) The oxides of phosphorus and sulfur react with water.

Write equations for reaction between oxides of phosphorus and sulfur with water. Describe the effect of the resulting solutions on Universal Indicator solution. [3]

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

Both dissociate in water to give H^+ ions to form acidic solutions, thus turning the Universal Indicator solution red.

(c) Sulfuric acid is manufactured in a series of steps, starting with sulfur. In one of these steps, sulfur dioxide is oxidised in a reversible reaction.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(i) The initial partial pressures of $SO_2(g)$ and $O_2(g)$ are 100 kPa and 50 kPa respectively at a fixed temperature in a closed vessel having a fixed volume. Given that the total pressure at equilibrium is 110 kPa, calculate K_p for this equilibrium. Include the units of K_p in your answer. [2]

	$2SO_2(g)$ +	**$O_2(g)$ $\rightleftharpoons$**	**$2SO_3(g)$**
Initial / kPa	**100**	**50**	**0**
Change / kPa	**$-2x$**	**$-x$**	**$+2x$**
Equilibrium / kPa	**$100-2x$**	**$50-x$**	**$2x$**

Sum of partial pressures at eqm =150 − x = 110
x = 40 kPa

$$K_p = \frac{P^2_{SO_3}}{P^2_{SO_2} \times P_{O_2}} = \frac{(80)^2}{(20)^2 \times (10)} = 1.60\ \ (\text{kPa})^{-1}$$

(ii) The above reaction is catalysed by vanadium(V) oxide, V_2O_5. Explain the mode of action of V_2O_5 in the reaction. [2]

Transition metal atoms (V in this case) can use their partially filled 3d subshell to form weak bonds with reactant molecules (SO_2 and O_2). Adsorption of reactant molecules on the catalyst's surface increases rate of reaction as adsorption weakens the covalent bonds within the reactant molecules, thereby reducing the activation energy for the reaction.

Adsorption also increases the concentration of reactant molecules at the catalyst surface allowing reactant molecules to come into close contact with proper orientation for reaction. In the final stage, products (SO_3) formed desorb from the catalyst surface.

(d) Copper(II) oxide is produced on a large scale in the process of extracting copper from its ores.

When concentrated hydrochloric acid is added to solid copper(II) oxide, the black CuO dissolves to form a dark yellow solution. When water is subsequently added in excess, a blue solution is formed.

Suggest an explanation for the observations described. Include relevant equations in your answer.

[3]

Black CuO dissolves in concentrated HC*l* to form the yellow-coloured complex $[CuCl_4]^{2-}$.

$CuO + 4HCl \rightarrow [CuCl_4]^{2-} + H_2O + 2H^+$

When water is added in excess, a ligand exchange reaction occurs as the H₂O ligands replace the Cl⁻ ligands to form the blue-coloured complex $[Cu(H_2O)_6]^{2+}$.

$[CuCl_4]^{2-}(aq) + 6H_2O(l) \rightleftharpoons [Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq)$

[Total: 20]

5 *Use of the Data Booklet is relevant for this question.*

This question explores the chemistry of various transition elements.

(a) The stability constant of a transition metal complex, K_{stab}, is an equilibrium constant associated with the following reaction.

$$M(H_2O)_6{}^{n+}(aq) + mL(aq) \rightleftharpoons ML_m(H_2O)_{6-m}{}^{n+}(aq) + mH_2O(l) \quad \text{where L is a ligand.}$$

For example, the stability constant of the complex formed when excess NH_3 is added to $Cu^{2+}(aq)$ is as shown:

$$K_{stab} = \frac{[[Cu(NH_3)_4(H_2O)_2]^{2+}]}{[[Cu(H_2O)_6]^{2+}][NH_3]^4}$$

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

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

The following table lists some iron complexes together with their colours and their stability constants.

complex	**colour**	**K_{stab}**
$[Fe(SCN)(H_2O)_5]^{2+}(aq)$	deep red	1×10^2
$[FeF_6]^{3-}(aq)$	colourless	2×10^{15}
$[Fe(CN)_6]^{4-}(aq)$	pale yellow	1×10^{24}
$[Fe(CN)_6]^{3-}(aq)$	orange-yellow	1×10^{31}
$[Fe(H_2O)_6]^{3+}(aq)$	yellow	-

(ii) Use the data in the table to predict and explain what will be observed when a solution of $Fe^{3+}(aq)$ is treated with excess KSCN(aq). Include relevant equation(s) where appropriate. [1]

Solution turns from yellow to deep red on addition of KSCN.
Ligand exchange occurs. H_2O ligand replaced by SCN^- due to high K_{stab} value of $[Fe(SCN)(H_2O)_5]^{2+}$.

(iii) As shown by their $E^\ominus$ values, $Fe(CN)_6{}^{3-}(aq)$ is a weaker oxidising agent than $Fe^{3+}(aq)$. Use the data in the table above to explain why this is the case. [2]

K_{stab} of $Fe(CN)_6{}^{3-}$ is very large, equilibrium position lies very far to the right and this complex is very stable as compared to $Fe(H_2O)_6{}^{3+}$.

Fe^{3+} in $Fe(CN)_6{}^{3-}$ has a lower tendency to gain electrons and be reduced as compared to $Fe(H_2O)_6{}^{3+}$.

(iv) FeF_6^{3-}(aq) is unusual in that it is colourless despite the occurrence of d-d transition just as in typical Fe(III) species. Suggest a reason for this observation. [1]

The energy gap between the lower and higher energy d orbitals is too large and falls outside the visible region of the electromagnetic spectrum.

(b) **(i)** Describe the electrolytic purification of copper, which contains the impurities silver and nickel. In your answer you should discuss about the nature of the electrodes, the electrolyte used and the reactions occurring at the anode and cathode with reference to relevant $E^\ominus$ values from the *Data Booklet*. [3]

Anode (+): impure Cu (containing Ni and Ag impurities)
Cathode (–): pure Cu
Electrolyte: Copper(II) sulfate solution, $CuSO_4$(aq).

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	$E^\ominus = +0.80$ V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	$E^\ominus = +0.34$ V
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	$E^\ominus = -0.25$ V
$2H_2O(l) + 2e^- \rightleftharpoons H_2 + 2OH^-(aq)$	$E^\ominus = -0.83$ V

Reactive metals on the anode can be oxidised. Ni(s), followed by Cu(s), will undergo oxidation preferentially due to them having the most negative (least positive) $E^\ominus$.

Impurities such as Ag has $E^\ominus$ value which is more positive than $E^\ominus(Cu^{2+}|Cu)$ = +0.34 V. Hence, silver is not oxidised at the anode and silver will remain undissolved (in reduced (metal) form). It drops to the base as anode sludge.

Cu^{2+}(aq) will undergo reduction preferentially due to the most positive (least negative) $E^\ominus$.

Adding KI(aq) to a solution containing Cu^{2+}(aq) causes a reaction to take place, which produces brown solution and a white precipitate. Upon adding $Na_2S_2O_3$, the brown solution turns colourless.

(ii) Construct a balanced equation for the reaction between Cu^{2+}(aq) and I^-(aq). [1]

$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$

(iii) By selecting appropriate $E^\ominus$ values from the *Data Booklet,* explain why it would be expected that this redox reaction would not occur. [2]

$Cu^{2+} + e^- \rightleftharpoons Cu^+$ $E^\theta = +0.15$ V
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\theta = +0.54$ V

$E^\ominus_{cell} = 0.15 - 0.54 = -0.39 \text{ V} < 0$

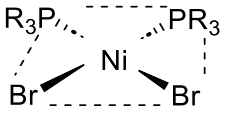
$E^\ominus_{cell}$ obtained is negative and hence the reaction is predicted to be non-feasible.

(iv) Suggest a possible reason for why it does in fact occur. [1]

Since CuI is insoluble in aqueous solutions, the precipitate would extract Cu^{2+}(aq) ions from the solution, leaving only a low concentration. Equilibrium position of $Cu^{2+} + e^- \rightleftharpoons Cu^+$ shifts right so that its *electrode potential exceeds* +0.15 V such that $E_{cell} > 0$. Hence, the reaction does in fact occur.

(c) Molecules **D** and **E** with the structural formula $NiBr_2(PR_3)_2$ (where R = phenyl) are *cis-trans* isomers. The molecules differ in the spatial arrangements of the ligands around the central metal ion.

Both isomers are planar and the ligand-metal-ligand bond angle in the plane of the molecule is 90°. The structure of molecule **D**, the *cis* isomer is shown in Figure 5.1.



Molecule **D**

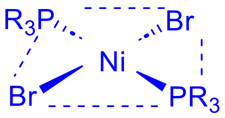
Figure 5.1

(i) State the coordination number of Ni in molecule **D**. [1]

4

(ii) Draw the 3-dimensional structure of molecule **E** which exist in the *trans* isomer. [1]

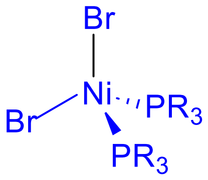
E:



(iii) Molecule **F**, is another isomer of **D**. It has a dipole moment just like **D**. The coordination number of Ni in molecule **F** is the same as that in **D**.

Suggest and draw a possible structure of **F**. [1]

F:



(d) A hot solution of sodium tartrate reacts with hydrogen peroxide giving a very slow stream of carbon dioxide.

When a few drops of an aqueous cobalt(II) salt is added to the mixture, a pink colour is seen. Soon the colour of the solution turns green and a vigorous effervescence of carbon dioxide takes place. When the reaction stops the pink colour is restored.

(i) What is the role of the cobalt(II) salt in the reaction? [1]

Homogenous catalyst

(ii) With reference to the observations above, give reasons which support your answer in **(d)(i)**. [2]

Same physical state as the reactants (aqueous), undergoes a change in oxidation state during the reaction but does not undergo permanent chemical change as colour changes from pink to green and back to pink.

Rate of reaction increases as seen by the vigorous effervescence of carbon dioxide.

Reaction occurs via an alternative pathway as seen by the presence of different coloured species of Co.

(e) $CoCO_3$ decomposes at approximately 295°C whereas $CuCO_3$ decomposes at approximately 335°C.

By quoting relevant data from the *Data Booklet*, explain the difference in decomposition temperature of these two compounds. [2]

Ionic radii: Co^{2+}(0.065 nm), Cu^{2+}(0.073 nm),
As Cu^{2+} ion is larger, charge density of Cu^{2+} is lower and polarises the carbonate anion to a lesser extent. The carbonate becomes more thermally stable and decomposes at higher temperature.

[Total: 20]