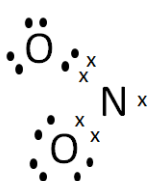
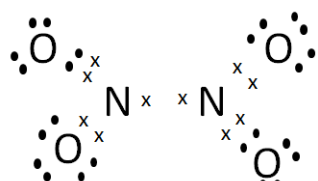
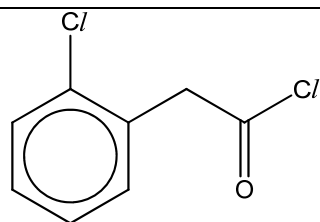


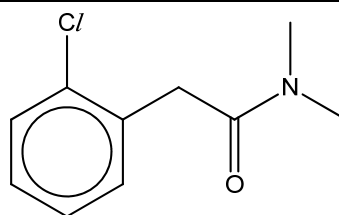
Answer any **four** questions.

1	(a)	Dinitrogen tetroxide N_2O_4 is one of the most important rocket propellants developed. N_2O_4 forms an equilibrium mixture with nitrogen dioxide NO_2 . NO_2 is favoured at higher temperatures, while at lower temperatures, N_2O_4 predominates.	
	(i)	<p>Draw dot-and-cross diagrams to show the bonding in the molecules of NO_2 and N_2O_4.</p> <div style="display: flex; justify-content: space-around; align-items: center;">   </div>	
	(ii)	<p>Suggest a value for the bond angle in each of the above two molecules.</p> <p>$120^\circ < \text{Bond angle in } \text{NO}_2 < 180^\circ$</p> <p>Bond angle in N_2O_4 is 120°</p>	[3]
	(b)	The chemistry of nitrogen oxides is very versatile.	
	(i)	<p>Given the following reactions and their standard enthalpy changes</p> <p>Reaction 1 $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_3(\text{g})$ $\Delta H^\circ_r = -39.8 \text{ kJ mol}^{-1}$</p> <p>Reaction 2 $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{N}_2\text{O}_5(\text{g})$ $\Delta H^\circ_r = -112.5 \text{ kJ mol}^{-1}$</p> <p>Reaction 3 $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$ $\Delta H^\circ_r = -57.2 \text{ kJ mol}^{-1}$</p> <p>Reaction 4 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ $\Delta H^\circ_r = -114.2 \text{ kJ mol}^{-1}$</p> <p>Reaction 5 $\text{N}_2\text{O}_5(\text{s}) \rightarrow \text{N}_2\text{O}_5(\text{g})$ $\Delta H^\circ_r = +54.1 \text{ kJ mol}^{-1}$</p> <p>Calculate the ΔH°_r for</p> <p>Reaction 6 $\text{N}_2\text{O}_3(\text{g}) + \text{N}_2\text{O}_5(\text{s}) \rightarrow 2\text{N}_2\text{O}_4(\text{g})$</p> <p>By algebraic method, $-(\text{Reaction 1}) - (\text{Reaction 2}) + 2(\text{Reaction 3}) + (\text{Reaction 4}) + (\text{Reaction 5})$ $= -(-39.8) - (-112.5) + 2(-57.2) + (-114.2) + (+54.1)$</p> <p>Answer : $-22.2 \text{ kJ mol}^{-1}$</p>	
	(ii)	<p>By considering the entropy and enthalpy change during reaction 5 and reaction 6, suggest how the standard Gibbs free energy change of the two reactions will compare in sign and in magnitude. Hence predict which reaction will be more spontaneous. Explain your reasoning.</p> <p><u>ΔS would be +ve in reaction 5 and reaction 6 owing to the increase in the number of moles of gas.</u></p> <p><u>ΔH for reaction 5 is +ve, its ΔG would only become negative at high temperatures, whereas since the ΔH for reaction 6 is -ve, the ΔG for this reaction is negative at all temperatures. Thus the reaction 6 is likely to be more spontaneous.</u></p>	[5]

	<p>(c) Compounds of elements in the second and third period of the Periodic Table show similar trends of periodicity. The Period II oxides are given as</p> <p style="text-align: center;">Li_2O BeO B_2O_3 CO_2 $\text{N}_2\text{O}_3/\text{N}_2\text{O}_5$</p>	
	<p>(i) The melting points of Li_2O and CO_2 are 1440°C and -79°C respectively. Explain for the differences in melting points.</p> <p><u>Li_2O has a giant ionic lattice structure with strong electrostatic forces of attraction between oppositely charged Li^+ and O^{2-} ions.</u></p> <p><u>CO_2 are simple covalent molecules with weak intermolecular Van der Waals forces.</u></p> <p><u>Hence more energy is needed to separate the ions in Li_2O compared to energy needed to separate the CO_2 molecules during melting process.</u></p>	
	<p>(ii) BeO is an amphoteric oxide. Write equations for the reaction between BeO with an acid and with a base.</p> <p>$\text{BeO} + 2 \text{HCl} + \text{H}_2\text{O} \rightarrow \text{BeCl}_2 + 2 \text{H}_2\text{O}$</p> <p>$\text{BeO} + 2 \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{Be}(\text{OH})_4$</p>	
	<p>(iii) B_2O_3 is weakly acidic. The oxide acidity of the Group III elements decreases down the group. Suggest a possible reason for this trend.</p> <p><u>Charge density decreases down the group OR Size of atoms/ions increase down the group while charge is constant.</u></p>	[6]
	<p>(d) Halogens are also commonly found in many organic compounds, such as an aromatic compound X with the molecular formula of $\text{C}_8\text{H}_6\text{Cl}_2\text{O}$.</p> <p>Given that one mole of X reacts with one mole of dimethylamine to form a neutral product Y and Y does not react with hot ethanolic ammonia, suggest the structures for compounds X and Y, explaining your reasoning.</p> <p>Hence, discuss the reactivities of the two chlorine atoms in compound X towards substitution.</p> <p><u>One mole of X undergoes nucleophilic substitution with one mole of dimethylamine to form an amide in Y.</u></p> <p><u>One acid chloride functional group is present in compound X.</u></p> <p><u>Absence of alkyl chloride group in both X and Y as amine (basic) functional group is not formed in Y and/or the latter does not undergo nucleophilic substitution with hot ethanolic ammonia.</u></p> <p><u>Aryl chloride must be present in both compounds.</u></p>	[6]

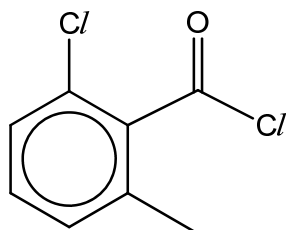


Compound X

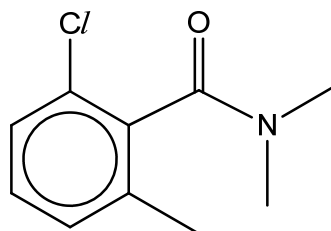


Compound Y

or



Compound X



Compound Y

Acyl chloride is reactive towards nucleophilic substitution as the C atom is highly partially positive (δ^+) as it is bonded to 2 electronegative atoms. Hence it reacts with dimethylamine to form amide at room temperature.

Whereas the C-Cl of the aryl chloride is strengthened by overlapping of the p-orbital of Cl with the π orbitals of the benzene ring which results in the delocalisation of electrons (partial double bond character), hence making aryl chloride very much less reactive and the substitution of the halogen atom very difficult. Thus there is no reaction with both dimethylamine and hot dilute NaOH.

Or

Aryl chloride is very much less reactive as the high electron density of the aromatic ring hinders the nucleophilic attack, due to electrostatic repulsion between like charges.

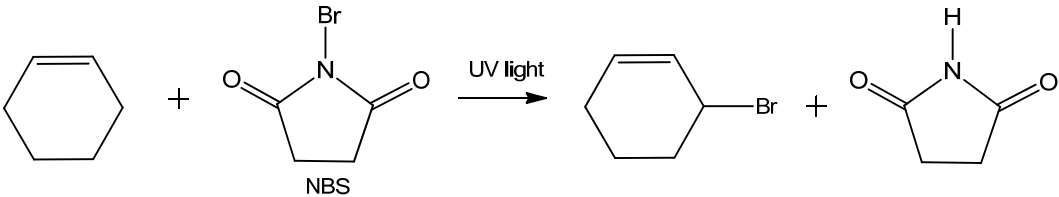
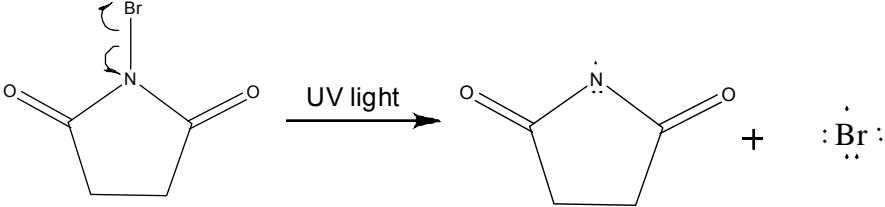
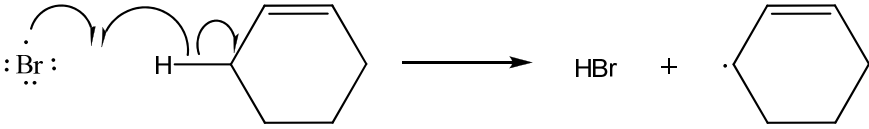
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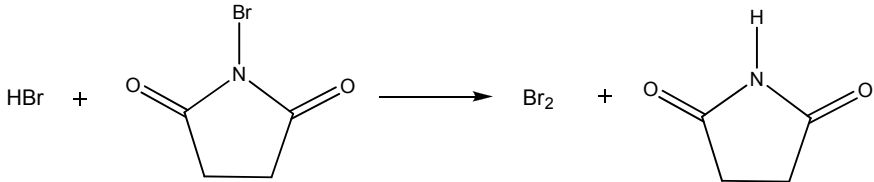
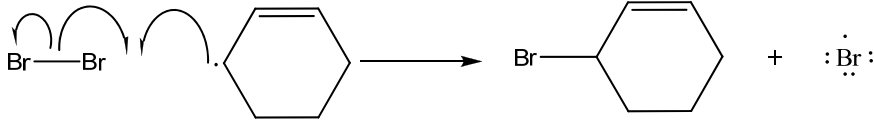
2	(a)	<p>Sodium chloride and silver chloride are two simple salts and their solubilities in water are being considered in this question.</p> <table><tr><td>Salt</td><td>$\Delta H_{\text{soln}}^{\ominus} / \text{kJ mol}^{-1}$</td><td>$\Delta S_{\text{soln}}^{\ominus} / \text{J mol}^{-1} \text{K}^{-1}$</td></tr><tr><td>NaCl/</td><td>+3.6</td><td>+43.2</td></tr><tr><td>AgCl/</td><td>+65.7</td><td>+34.3</td></tr></table>	Salt	$\Delta H_{\text{soln}}^{\ominus} / \text{kJ mol}^{-1}$	$\Delta S_{\text{soln}}^{\ominus} / \text{J mol}^{-1} \text{K}^{-1}$	NaCl/	+3.6	+43.2	AgCl/	+65.7	+34.3	
Salt	$\Delta H_{\text{soln}}^{\ominus} / \text{kJ mol}^{-1}$	$\Delta S_{\text{soln}}^{\ominus} / \text{J mol}^{-1} \text{K}^{-1}$										
NaCl/	+3.6	+43.2										
AgCl/	+65.7	+34.3										
	(i)	<p>Use the values given in the table to calculate $\Delta G_{\text{soln}}^{\ominus}$ for each of the salts and hence deduce its solubility in water.</p> <p>$\Delta G_{\text{soln}}^{\ominus}(\text{NaCl}) = \Delta H_{\text{soln}}^{\ominus} - T\Delta S_{\text{soln}}^{\ominus}$ $= +3.6 - 298(43.2/1000) = -9.27 \text{ kJ mol}^{-1} < 0$ (feasible reaction, NaCl is soluble in water)</p> <p>$\Delta G_{\text{soln}}^{\ominus}(\text{AgCl}) = \Delta H_{\text{soln}}^{\ominus} - T\Delta S_{\text{soln}}^{\ominus}$ $= +65.7 - 298(34.3/1000) = +55.5 \text{ kJ mol}^{-1} > 0$ (reaction is not feasible, AgCl is not soluble in water)</p>										
	(ii)	<p>The solubility product, K_{sp}, of AgCl is related to $\Delta G_{\text{soln}}^{\ominus}(\text{AgCl})$ by the following equation, $\Delta G_{\text{soln}}^{\ominus} = -2.303RT \lg K_{\text{sp}}$ where R is $8.31 \text{ J mol}^{-1} \text{K}^{-1}$ and T is the temperature in K.</p> <p>Use the equation given above to calculate the value of K_{sp} of AgCl at 298K.</p> <p>$\lg K_{\text{sp}} = -(55.5 \times 10^3)/(2.303 \times 8.31 \times 298) = -9.73$ $K_{\text{sp}} = 10^{-9.73} = 1.86 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$</p>										
	(iii)	<p>Explain how solubility of AgCl will change with increasing temperature?</p> <ul style="list-style-type: none">As T increases, $-T\Delta S_{\text{soln}}^{\ominus}$ gets more negativeIt is assumed that $\Delta H_{\text{soln}}^{\ominus}$ and $\Delta S_{\text{soln}}^{\ominus}$ do not change much with T \Rightarrow an increase in T will cause $\Delta G_{\text{soln}}^{\ominus}$ to be more negative <p>Hence solubility of AgCl will increase with T.</p> <p>OR</p> <p>$\text{AgCl(s)} + \text{aq} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \quad \Delta H_{\text{soln}}^{\ominus} = +65.7 \text{ kJ mol}^{-1}$</p> <p>As T increases, position of equilibrium shifts to the right in favour of the endothermic reaction,</p> <p>hence solubility of AgCl increases with T</p>										
			[5]									
	(b)	(i)	<p>Draw a fully labelled diagram of the electrochemical cell you would use to determine the standard electrode potential of the $\text{Ag}^+(\text{aq}) \text{Ag(s)}$ electrode system and show the direction of electron flow .</p>									

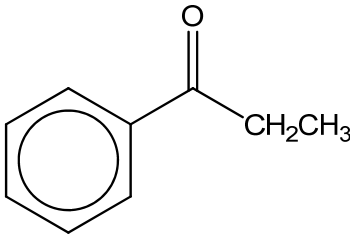
	(ii)	<p>When aqueous sodium chloride is added to the $\text{Ag}^+(\text{aq}) \text{Ag}(\text{s})$ electrode system in the above electrochemical cell in (b)(i), explain qualitatively how the E_{cell} will change as a result.</p> <p>On addition of NaCl,</p> <ul style="list-style-type: none"> • $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(\text{s})$ • $\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) \quad E^\theta = +0.80\text{V}$ • POE shifts left to increase $[\text{Ag}^+]$ \Rightarrow Electrode potential becomes less positive • $E_{\text{cell}} = E_{\text{Ag}^+/\text{Ag}} - E_{\text{H}_2/\text{H}^+}$ will decrease 	
	(iii)	<p>At 298K, the equation below relate the concentration of silver ions in solution with the electrode potential under non-standard conditions.</p> $E = E^\theta + 0.060 \lg [\text{Ag}^+(\text{aq})] \quad \text{where}$ <p>E = electrode potential of silver under non-standard conditions E^θ = standard electrode potential of silver</p> <p>The addition of excess aqueous sodium chloride, $\text{NaCl}(\text{aq})$, to the $\text{Ag}^+(\text{aq}) \text{Ag}(\text{s})$ half-cell results in a chloride ion concentration of 2.1 mol dm^{-3}.</p> <p>Using the value of the K_{sp} of AgCl calculated in (a)(ii), calculate the value of E, the electrode potential of the $\text{Ag}^+(\text{aq}) \text{Ag}(\text{s})$ electrode system, after the addition of excess aqueous sodium chloride to the $\text{Ag}^+(\text{aq}) \text{Ag}(\text{s})$ half-cell.</p> <p>[You may use this value of K_{sp} of $\text{AgCl} = 2.00 \times 10^{-10}$ for this calculation if you did not get an answer for (a)(ii)]</p> <p>$[\text{Ag}^+][\text{Cl}^-] = K_{\text{sp}} = 1.86 \times 10^{-10}$ $[\text{Ag}^+](2.1) = 1.86 \times 10^{-10}$ $[\text{Ag}^+] = 1.86 \times 10^{-10} / 2.1 = 8.86 \times 10^{-11}$</p> <p>$E = 0.80 + 0.060 \lg (8.86 \times 10^{-11}) = +0.197 \text{ V}$</p> <p>Or</p> <p>$[\text{Ag}^+][\text{Cl}^-] = K_{\text{sp}} = 2.00 \times 10^{-10}$ $[\text{Ag}^+](2.1) = 2.00 \times 10^{-10}$</p>	

			$[Ag^+] = 2.00 \times 10^{-10} / 2.1 = 9.52 \times 10^{-11}$ $E = 0.80 + 0.060 \lg (9.52 \times 10^{-11}) = +0.199 \text{ V}$	
				[7]
	(c)	Silver-oxide primary batteries account for over 20% of all primary battery sales in Japan. It is available in small sizes as button cells and are used in watches, cameras, heart pacemakers and hearing aids due to its very steady output. A silver-oxide battery uses silver oxide as the positive electrode and zinc as the negative electrode and an alkaline electrolyte such as sodium hydroxide. The chemical reaction that takes place inside the battery is as follows: $Zn + Ag_2O \rightarrow ZnO + 2Ag \quad E_{\text{cell}} = +1.6V$		[3]
	(i)	Write the two half-equations that occur at the anode and cathode respectively. Cathode: $Ag_2O + H_2O + 2e \rightarrow 2Ag + 2OH^-$ Anode: $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e$		
	(ii)	Suggest a reason why this button battery is often used as stated in the question. <ul style="list-style-type: none">• Very small and light• Relatively long life• Constant output voltage• Non-toxic nature has allowed for use inside the body		
	(d)	Electrodes used in electrocardiography are disposable and many incorporate silver. The silver metal is deposited in a thin layer on a small plastic “button” and then some is converted to AgCl. $Ag(s) + Cl^-(aq) \rightleftharpoons AgCl(s) + e^-$ The volume of silver used in plating one electrode is $1.5 \times 10^{-2} \text{ cm}^3$. The density of silver metal is 10.5 g cm^{-3} .		
	(i)	What is the mass of Ag used for plating one electrode? Mass of Ag = $1.5 \times 10^{-2} \times 10.5 = 0.158 \text{ g}$		

		<p>(ii) If Ag is plated on the “button” from an Ag^+ solution with a current of 12.0 mA, how long does the plating take?</p> <p>$\text{Ag}^+ + \text{e} \rightarrow \text{Ag}$</p> <p>No of moles of Ag = $0.158/108 = 1.46 \times 10^{-3}$ No of moles of e = 1.46×10^{-3} Quantity of charge = $1.46 \times 10^{-3} \times 96500 = 141 \text{ C}$</p> <p>It = 141 $(12 \times 10^{-3}) \times \text{time} = 141$</p> <p>Time = 196 mins or 3.27 hours or $11.8 \times 10^3 \text{ s}$</p>	
			[3]
	(e)	<p>Diammine silver (I) has the formula $[\text{Ag}(\text{NH}_3)_2]^+$ and is the active ion in Tollens' reagent. It produces a characteristic silver mirror on the side of the test-tube and this is used as the basis of the test for aldehydes.</p> <p>Tollens' reagent also gives a positive result with methanoic acid which is fully oxidised to water and carbon dioxide.</p> <p>Write two half-equations showing the reduction of Tollens' reagent and the oxidation of methanoic acid, followed by the balanced equation for the reaction between Tollens' reagent and methanoic acid.</p> <p>$[\text{Ag}(\text{NH}_3)_2]^+ + \text{e} \rightarrow \text{Ag(s)} + 2\text{NH}_3$</p> <p>$\text{HCOO}^- + \text{OH}^- \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2\text{e}$</p> <p>$\text{HCOO}^- + 2[\text{Ag}(\text{NH}_3)_2]^+ + \text{OH}^- \rightarrow 2\text{Ag} + 4\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$</p>	[2]
[Total: 20 marks]			

3	This question is about halogens and halogenated organic compounds.	
	<p>(a) One way to prepare brominated products is described as below:</p> <p>Cyclohexene reacts with N-bromosuccinimide (NBS) in the presence of UV light to give 3-bromocyclohexene resulting from the substitution of hydrogen by bromine at the allylic position – the position next to the double bond.</p> <p>The overall equation is shown below.</p>  <p>The allylic bromination with NBS works in a similar manner as free radical substitution. The steps in the mechanism are shown below.</p> <p>Step 1: Homolytic cleavage of the N-Br bond of NBS generates a Br radical.</p> <p>Step 2: The Br radical abstracts an allylic hydrogen from the cyclohexene to form an allylic radical.</p> <p>Step 3: The HBr formed reacts with NBS to produce a Br₂ molecule.</p> <p>Step 4: This Br₂ molecule reacts with the allylic radical formed in step 2, regenerating a new bromine radical that can begin the cycle again.</p>	
	<p>(i) Describe the mechanism, using curly arrows to represent the flow of electrons, of the reaction between cyclohexene and NBS. (You need not show arrows for step 3)</p> <p>Step 1:</p>  <p>Step 2:</p> 	

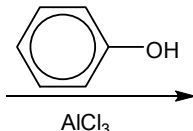
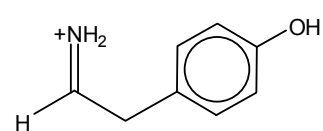
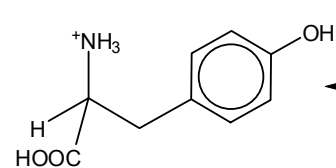
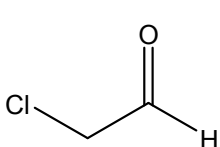
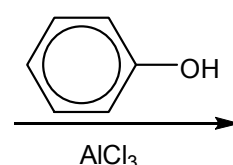
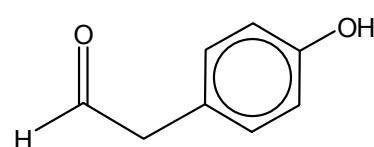
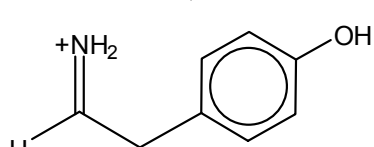
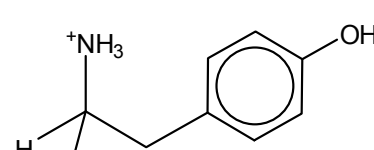
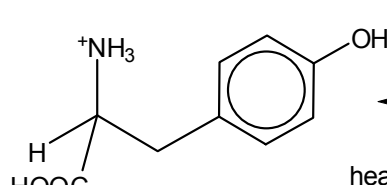
		<p>Step 3:</p>  <p>Step 4:</p> 	
	(ii)	<p>Suggest why NBS is used as the bromine source instead of adding Br₂ directly?</p> <p>This is to keep the <u>concentration of bromine low</u> so as to <u>reduce competition by electrophilic addition</u> of bromine to give 1,2-dibromocyclohexane.</p>	
	(iii)	<p>The enthalpy change of reaction in step 2 is -6 kJ mol⁻¹. Using the Data Booklet, calculate the bond energy of the allylic C-H bond.</p> $\Delta H_{\text{reaction}} = \text{Bond breaking} - \text{Bond forming}$ $-6 = \text{BE(allylic C-H)} - \text{BE(H-Br)}$ $\text{BE(allylic C-H)} = -6 + 366$ $= \underline{\underline{360 \text{ kJmol}^{-1}}}$	
	(iv)	<p>By quoting relevant information from the Data Booklet, and using your answer from part (iii), explain why bromination using NBS occurs exclusively at an allylic position rather than any position in cyclohexene?</p> <p>Your answer should also include the discussion of the stability of the allylic radical.</p> <p>The bond dissociation energies of the different C-H bonds found in cyclohexene can help to explain the relative stabilities of the radicals formed.</p> <p>By comparing the bond strength of the allylic C-H bond and that of the alkyl C-H bond, the <u>bond energy of allylic C-H bond is 360 kJ/mol while the bond energy of alkyl C-H bond is 410 kJ/mol</u>. This means that the <u>allylic C-H bond is weaker and easier to break</u>.</p> <p><u>This also shows that the allylic radical is more stable. The allylic radical is more stable as the π system of a double bond can stabilize the radical through resonance / the unpaired electron is delocalized over an extended π network.</u></p>	[7]
	(b)	<p>Alkyl halides are used in the synthesis of Gilman reagents, which are very useful in organic synthesis because they make it possible to prepare larger molecules from smaller ones.</p>	

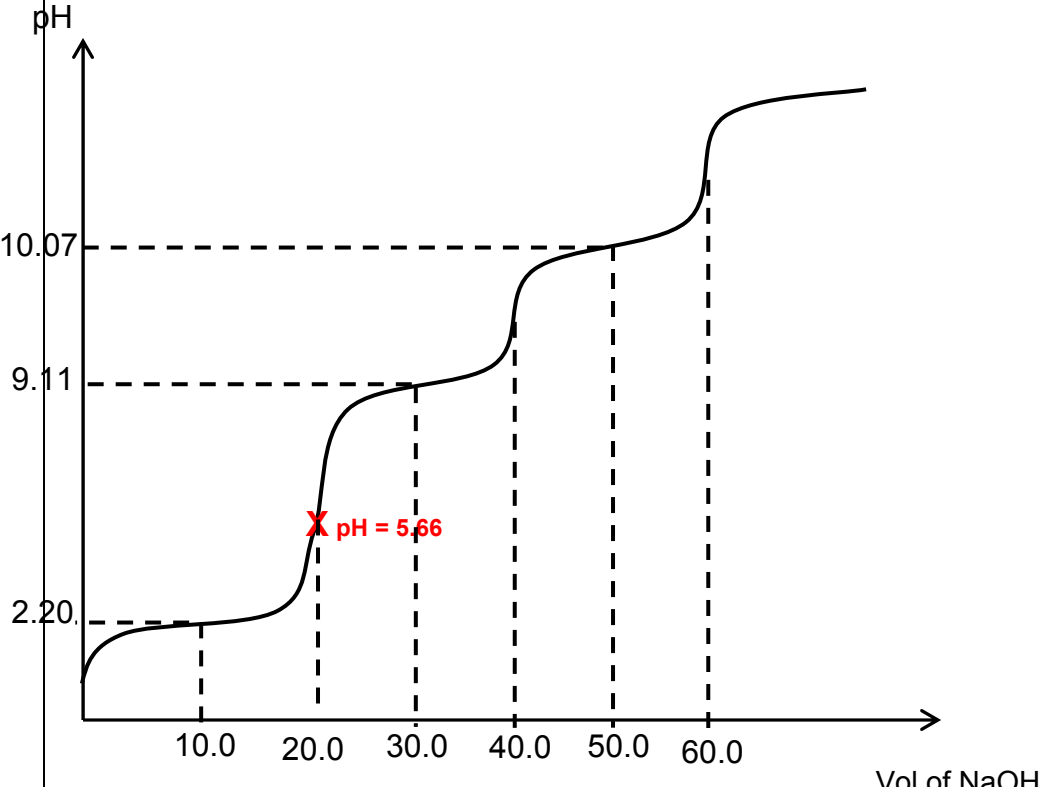
		<p>In the preparation of Gilman reagent, the following two steps take place:</p> $\text{RBr} + 2 \text{Li} \rightarrow \text{RLi} + \text{LiBr}$ $2 \text{RLi} + \text{CuI} \rightarrow \text{R}_2\text{Cu}^-\text{Li}^+ + \text{LiI}$ <p style="text-align: center;">Gilman reagent</p> <p>This Gilman reagent can be used to synthesize bigger molecules from alkyl halides. For example, lithium dimethylcopper reacts with 1-iododecane to give undecane as below:</p> $(\text{CH}_3)_2\text{CuLi} + \text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{I} \rightarrow \text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{CH}_3 + \text{LiI} + (\text{CH}_3)_2\text{Cu}$ <p>The above reaction is called organometallic coupling reaction.</p>	
		<p>Similarly, ketones can be formed in organometallic coupling reactions between suitable Gilman reagents and acid chlorides.</p> <p>Hence, suggest a suitable Gilman reagent and an acid chloride that can be used to synthesize 1-phenylpropan-1-one.</p> <div style="text-align: center;">  </div> <p>$\text{C}_6\text{H}_5\text{COCl}$ and $(\text{CH}_3\text{CH}_2)_2\text{CuLi}$ Or $\text{CH}_3\text{CH}_2\text{COCl}$ and $(\text{C}_6\text{H}_5)_2\text{CuLi}$</p>	[2]
	(c)	It is known that halogens can form many compounds with different oxidation states under different conditions.	
	(i)	<p>With the aid of balanced equations, explain how different chlorine containing products are obtained when chlorine reacts with sodium hydroxide under different conditions. State the type of reaction that happens clearly.</p> <p>With cold aqueous NaOH, Cl_2 undergoes <u>disproportionation</u> to give a mixture of chloride and chlorate (I) ions.</p> $2\text{NaOH (aq)} + \text{Cl}_2 \text{ (aq)} \rightarrow \text{NaCl (aq)} + \text{NaClO (aq)} + \text{H}_2\text{O (l)}$ <p>With hot aqueous NaOH, ClO^- undergoes further disproportionation to give a mixture of chloride and chlorate (V) ions.</p> $6\text{NaOH (aq)} + 3\text{Cl}_2 \text{ (aq)} \rightarrow 5\text{NaCl (aq)} + \text{NaClO}_3 \text{ (aq)} + 3\text{H}_2\text{O (l)}$	

	(ii)	<p>It is given that 0.240 mol of chlorine was made to react with NaOH at a certain temperature that allowed two different reactions to occur. After all of the chlorine had reacted, it was found that the solution contained 0.320 mol of NaCl.</p> <p>Calculate the amount of NaClO₃ produced.</p> $\begin{array}{ccccccc} \text{Cl}_2 & + & 2\text{NaOH} & \rightarrow & \text{NaOCl} & + & \text{H}_2\text{O} + \text{NaCl} \\ \text{Amount} & & 0.240 - x & & & & 0.240 - x \end{array}$ $\begin{array}{ccccccc} 3\text{Cl}_2 & + & 6\text{NaOH} & \rightarrow & \text{NaClO}_3 & + & 3\text{H}_2\text{O} + 5\text{NaCl} \\ \text{Amount} & & x & & x/3 & & 5x/3 \end{array}$ <p>Total amount of NaCl = 0.240 - x + 5x/3 = 0.320 $x = 0.120$</p> <p>Amount of NaClO₃ = 0.120/3 = 0.0400 mol</p>	[5]
(d)	(i)	<p>The yellow gas chlorine dioxide, ClO₂ has been used for many years as a flour-improving agent in bread-making. It can be made in the laboratory by the following reaction.</p> $2\text{AgClO}_3(\text{s}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{AgCl}(\text{s}) + 2\text{ClO}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta H = \text{zero}$ <p>Calculate and comment on the value of ΔH°_f ClO₂ of given the following data:</p> $\Delta H^\circ_f \text{AgClO}_3 = -25 \text{ kJ mol}^{-1}$ $\Delta H^\circ_f \text{AgCl} = -127 \text{ kJ mol}^{-1}$ <p>$\Delta H^\circ_f \text{ClO}_2 = [2(-25) + 2(-127)] \div 2 = +102 \text{ kJ mol}^{-1}$ The endothermic heat of formation is related to the likely instability of ClO₂</p>	
	(ii)	<p>Assuming that ΔH remains constant upon temperature change, suggest how the position of equilibrium will change when the temperature is increased. Explain your answer.</p> <p>The position of equilibrium remains the same because neither the forward or backward reaction can be favoured to absorb the excess heat.</p>	[4]
(e)		<p>The compound FO₂ does not exist but OF₂ does. By considering the possible types of bonding in the two compounds, suggest reasons for this difference.</p> <p>(Assume that the fluorine and oxygen atom occupies the central position in FO₂ and OF₂ molecules respectively)</p> <p>Being the central atom in FO₂, fluorine <u>cannot expand its octet</u>, the only alternative would be for fluorine to provide two dative bonds. However <u>fluorine does not do this because it is too electronegative for dative bonding</u>.</p> <p>The central atom O in OF₂ would achieve its octet configuration by forming <u>2 single covalent bonds with fluorine (similar to H₂O)</u></p>	[2]

				[Total: 20]	
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4	<p>Tyrosine (Tyr) is synthesised from the essential amino acid phenylalanine (phe), which is derived from food products such as milk, peanuts, almonds, soy products, and bananas. The conversion of phe to tyr is catalyzed by the enzyme phenylalanine hydroxylase. This enzyme catalyzes the reaction causing the addition of a hydroxyl group to the end of the 6-carbon aromatic ring of phenylalanine, such that it becomes tyrosine.</p> <div data-bbox="497 495 1059 696" data-label="Chemical-Block"> <p style="text-align: center;"><i>Tyrosine</i></p> </div>	
(a)	<p>In the laboratory, amino acids can be formed from aldehydes using the Strecker amino acid synthesis. This is a sequence of chemical reactions that produces amino acids from aldehydes. The steps for the conversion are shown below.</p> <div data-bbox="475 913 1166 1464" data-label="Chemical-Block"> <p style="text-align: center;"><i>Strecker amino acid synthesis</i></p> </div>	
(i)	<p>The following synthesis was proposed for the synthesis of tyrosine from phenol.</p>	

		<div style="display: flex; align-items: center; justify-content: center;"><div style="border: 1px solid black; width: 150px; height: 80px; margin-right: 10px; text-align: center; line-height: 80px;">X</div><div style="text-align: center; margin-right: 10px;"> $\xrightarrow[\text{AlCl}_3]{\text{C}_6\text{H}_5\text{OH}}$</div><div style="border: 1px solid black; width: 250px; height: 80px; margin-right: 10px; text-align: center; line-height: 80px;">Y</div><div style="text-align: center; margin-right: 10px;">$\downarrow \text{NH}_4\text{Cl}$</div><div style="text-align: center; margin-right: 10px;"></div><div style="text-align: center; margin-right: 10px;">$\downarrow \begin{matrix} \text{HCN} \\ \text{NaCN} \end{matrix}$</div><div style="border: 1px solid black; width: 250px; height: 80px; margin-right: 10px; text-align: center; line-height: 80px;">Z</div><div style="text-align: center;">$\xleftarrow{\text{Step IV}}$</div><div style="text-align: center;"></div></div>		
	(i)	In light of the Strecker amino acid synthesis method, identify the structures of X , Y and Z .		
	(ii)	Name the reagents and conditions for Step IV .		
				[4]
		<div>ANSWER:<div style="display: flex; align-items: center; justify-content: center; margin-top: 20px;"><div style="text-align: center; margin-right: 10px;"> $\text{ClCH}_2\text{CH}_2\text{CHO}$</div><div style="text-align: center; margin-right: 10px;"> $\xrightarrow[\text{AlCl}_3]{\text{C}_6\text{H}_5\text{OH}}$</div><div style="text-align: center; margin-right: 10px;"> $\text{HCHOCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OH}$</div><div style="text-align: center; margin-right: 10px;">$\downarrow \text{NH}_4\text{Cl}$</div><div style="text-align: center; margin-right: 10px;"></div><div style="text-align: center; margin-right: 10px;">$\downarrow \begin{matrix} \text{HCN} \\ \text{NaCN} \end{matrix}$</div><div style="text-align: center; margin-right: 10px;"> $\text{HNC(CH}_3\text{)CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OH}$</div><div style="text-align: center;">$\xleftarrow[\text{heat under reflux}]{\text{H}^+ (\text{aq})}$</div><div style="text-align: center;"> $\text{H}^+\text{NH}_3^+\text{CH(CH}_3\text{)CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OH}$</div></div></div>		

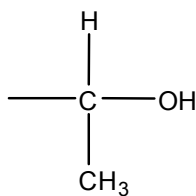
(b)	(i)	<p>Tyrosine has three pK_a values.</p> <p>pK_a of α-carboxyl = 2.20 pK_a of α-amino = 9.11 pK_a of R-group = 10.07</p> <p>By referring to the pK_a values of tyrosine, sketch the graph of pH against volume of NaOH (cm^3) when excess 0.1 mol dm^{-3} NaOH (aq) is used to titrate 20.0 cm^3 of 0.1 mol dm^{-3} of aqueous tyrosine. In your answer, indicate where the equivalence points and maximum buffer capacities of the solution occur.</p>	
			
	(ii)	<p>On your graph in (b)(i), use 'X' to label the point where the zwitterion is present in the highest concentration. Calculate the pH of this point.</p> <p>$pI = (9.11 + 2.20) / 2 = 5.66$</p>	
	(iii)	<p>0.05g of solid NaOH is added to a 20 cm^3 solution containing 0.1 mol dm^{-3} of the tyrosine zwitterion. Calculate the pH of the resulting solution when the solid is completely dissolved.</p> <p>You might find it useful to represent the zwitterion with HA.</p>	
		<p>$n(\text{NaOH}) = 0.05 / (23 + 16 + 1) = 0.00125 \text{ mol}$ Initial $n(\text{HA}) = 20 / 1000 \times 0.10 = 0.002 \text{ mol}$</p>	

		<p> $n(\text{HA})$ after acid-base reaction = $0.002 - 0.00125 = 7.50 \times 10^{-4} \text{ mol}$ $n(\text{A}^-)$ after acid-base reaction = 0.00125 mol both no of moles </p> <p> $\text{pH} = \text{pK}_a + \log (0.00125 / 0.000075)$ $= 9.11 + 0.2218$ $= 9.33$ </p>	
	(iv)	<p>With the help of equations, explain how the solution from (b)(iii) can act as a buffer.</p> <div style="text-align: center;"> </div>	
			[8]
(c)	<p>Compound A is an isomer of tyrosine. 1 mol of compound A reacts with Na to form 0.5 mol of hydrogen gas at room temperature and pressure. Compound A decolourises excess aqueous Br_2 to form B, $\text{C}_9\text{H}_9\text{O}_3\text{NBr}_2$. A does not decolourise cold alkaline KMnO_4. When A was heated with aqueous NaOH and distilled, compound C and a distillate D were formed. Compound D produced a yellow precipitate when warmed with alkaline aqueous iodine. Upon crystallisation, C is found to have a molar mass of 197 g mol^{-1}.</p> <p>Suggest the structures of compounds A to D, giving reasons for your answer.</p>		[8]
	<p>Since 1 mol of A reacts with 1 mole of Na to form 0.5 mol of H_2, A has only 1 hydroxyl or carboxyl group.</p>		

A is not an alkene or alcohol as it does not oxidise in the presence of cold alkaline KMnO_4 .

A is a phenylamine or phenol as it undergoes electrophilic substitution with aqueous Br_2 .

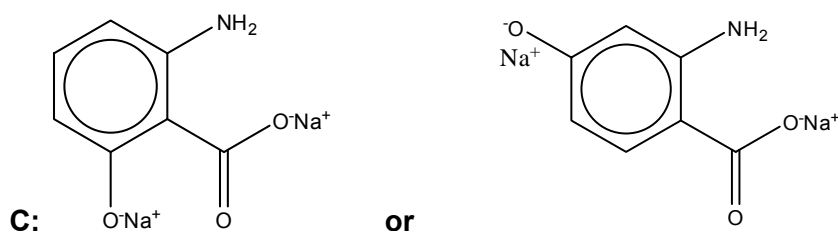
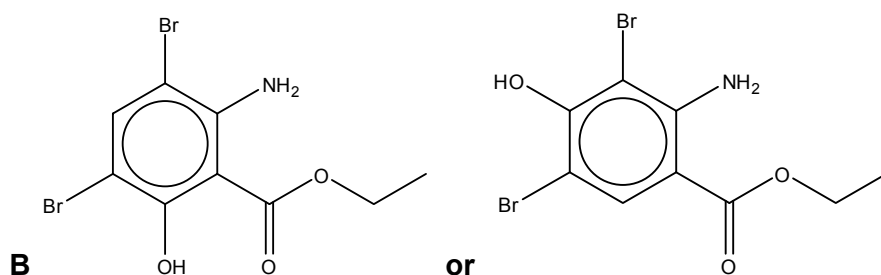
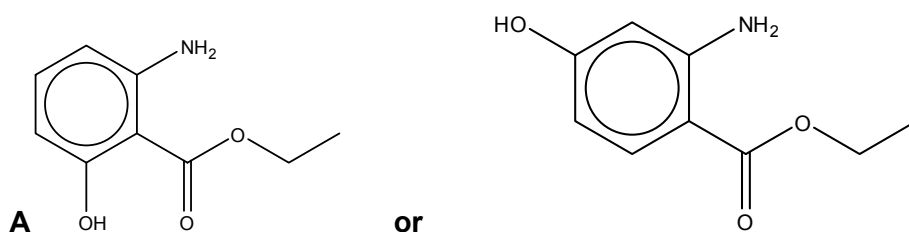
Compound A has an ester or amide group that undergoes alkaline hydrolysis to form a compound C and distillate D.



Distillate D has the structure of CH_3 as it forms CHI_3 in the presence aqueous alkaline iodine OR undergoes oxidation in warm aqueous alkaline iodine.

Since D is an alcohol, A has an ester group.

Since A is substituted with Br atoms at only two positions, the phenol / phenylamine has one side chain at position 2 / 4 / 6.



D: $\text{CH}_3\text{CH}_2\text{OH}$

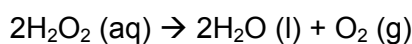
			[Total: 20]	

5	Transition metal ions are often brightly coloured and can exist in a wide range of oxidation states. Vanadium was named after the Scandinavian goddess of beauty and fertility, Vanadis because of the wide range of colours found in vanadium compounds. The colours of the various vanadium ions are given in the table below.													
		<table><tr><td>Vanadium Species</td><td>VO_2^+</td><td>VO^{2+}</td><td>V^{3+}</td><td>V^{2+}</td></tr><tr><td>Colour</td><td>Yellow</td><td>Blue</td><td>Green</td><td>Violet</td></tr></table>			Vanadium Species	VO_2^+	VO^{2+}	V^{3+}	V^{2+}	Colour	Yellow	Blue	Green	Violet
Vanadium Species	VO_2^+	VO^{2+}	V^{3+}	V^{2+}										
Colour	Yellow	Blue	Green	Violet										
(a)	V^{2+} ions are used in a redox titration to determine the concentration of Fe^{3+} ions in an unknown solution. Fe^{3+} is reduced to Fe^{2+} and the solution is acidic throughout the entire process. The indicator used in the titration is potassium thiocyanate, KSCN. The thiocyanate ions, SCN^- , form an intense blood red complex ion with Fe^{3+} in solution while it appears colourless when complexed with Fe^{2+} . It was found that V^{2+} reacts in a 1 : 1 ratio with Fe^{3+} .													
(i)	State the electronic configuration of the V^{2+} ion and hence explain why a solution containing V^{2+} ions is coloured. V^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$ In the presence of water ligands, the 3d subshells of V are split into 2 groups of different energy levels. d electrons in the lower energy level absorb a certain wavelength of light from the visible region of the electromagnetic spectrum and are promoted to the higher energy level. The wavelengths that are not absorbed are then transmitted and hence the colour observed is the complement to the colour absorbed.													
(ii)	Write the two half equations as well as the balanced equation for the titration reaction. $\text{V}^{2+} \rightarrow \text{V}^{3+} + e^-$ $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ Overall: $\text{V}^{2+} + \text{Fe}^{3+} \rightarrow \text{V}^{3+} + \text{Fe}^{2+}$													
(iii)	State the colour change observed at the end point of the titration. <u>Blood red</u> (Fe^{3+}-SCN complex) to <u>green</u> (V^{3+} and Fe^{2+})													
(b)	During his preparation of a $0.500 \text{ mol dm}^{-3}$ solution of VSO_4 , a student weighed out a certain mass of hydrated vanadyl sulfate ($\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$) and added a zinc to form V^{2+} . As it was getting late, the student decided to filter the solution and perform the titration the next day. He left the pale violet solution out on the bench uncovered and left. The next day, the student returned to find that his pale violet solution had taken on a slightly green tinge.													
(i)	Write out the equation for the reaction of V^{2+} with air and calculate the E_{cell}^\ominus to show that it is feasible. $4\text{V}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{V}^{3+} + 2\text{H}_2\text{O}$ $E_{\text{cell}} = +1.23 - (-0.23) = +1.46\text{V} > 0$ $E_{\text{cell}} > 0 \rightarrow \text{feasible}.$													

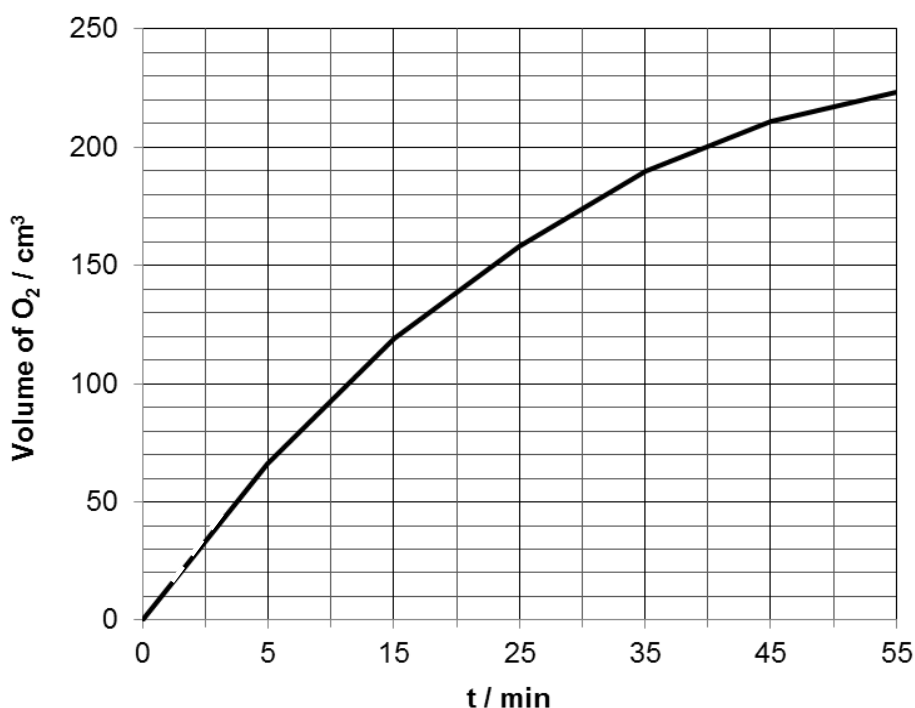
		(ii)	<p>The student also discovered the possibility of the following reaction between the V^{2+} ions and H^{+} ions in solution:</p> $2V^{2+} (aq) + 2H^{+} (aq) \rightarrow 2V^{3+} (aq) + H_2(g)$ <p>Fortunately for him, this reaction is very slow under normal conditions.</p> <p>Explain why this reaction is very slow.</p> <p>The reaction <u>occurs between two positively charged ions</u> and hence <u>experiences electronic repulsion</u> leading to a slow reaction.</p>	[3]																
	(c)	<p>25.0 cm³ samples of an iron (III) solution of unknown concentration were titrated against another freshly prepared 0.500 moldm⁻³ V^{2+} solution. The titration results obtained are in the table below.</p> <table><tr><td></td><td>1</td><td>2</td><td>3</td></tr><tr><td>Final burette reading /cm³</td><td>22.10</td><td>44.70</td><td>22.50</td></tr><tr><td>Initial burette reading /cm³</td><td>0.00</td><td>22.10</td><td>0.30</td></tr><tr><td>Volume of V^{2+} solution used /cm³</td><td>22.10</td><td>22.60</td><td>22.20</td></tr></table>				1	2	3	Final burette reading /cm ³	22.10	44.70	22.50	Initial burette reading /cm ³	0.00	22.10	0.30	Volume of V^{2+} solution used /cm ³	22.10	22.60	22.20
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Final burette reading /cm ³	22.10	44.70	22.50																	
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Volume of V^{2+} solution used /cm ³	22.10	22.60	22.20																	
	(i)	<p>Calculate the mass of $VOSO_4 \cdot 2H_2O$ required to prepare 250cm³ of the V^{2+} standard solution.</p> <p>Amt of V^{2+} in solution = 250/1000 x 0.500 = 0.125 mol</p> <p>Amt of $VOSO_4 \cdot 2H_2O$ required = Amt of V^{2+} = 0.125 mol</p> <p>Mass of $VOSO_4 \cdot 2H_2O$ required = 0.125 x (50.9 + 7x16.0 + 32.1 + 4x1.0) = 24.9 g</p>																		
	(ii)	<p>Calculate the mean titre from the titration results above and hence calculate the concentration of Fe^{3+} ions in the unknown solution.</p> <p>Mean titre = (22.10 + 22.20)/2 = 22.15 cm³</p> <p>Amt of V^{2+} reacted = 22.15/1000 x 0.500 = 0.011075 mol</p> <p>Amt of V^{2+} = Amt of Fe^{3+}</p> <p>Concentration of Fe^{3+} = 0.011075 / (25/1000) = 0.443 moldm⁻³</p>			[3]															
	(d)	<p>Another feature of transition metals is their ability to act as catalysts for reactions.</p> <p>For example, Mn^{2+} (aq) acts as a <i>homogeneous catalyst</i> for the decomposition of hydrogen peroxide.</p>																		
	(i)	<p>What do you understand by the term <i>homogeneous catalyst</i>?</p> <p>It means that the catalyst and the reactants are in the <u>same phase</u>.</p>																		
	The decomposition of hydrogen peroxide takes place more slowly in the absence																			

of $\text{Mn}^{2+}(\text{aq})$.

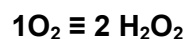
40.0 cm^3 of 0.50 mol dm^{-3} of acidified hydrogen peroxide solution was connected to a gas syringe in an air tight setup. The kinetics for the decomposition of hydrogen peroxide at room temperature was studied by measuring the volume of oxygen as it changes with time, t .



Time, t / min	0	5	15	25	35	45	55
Volume of O_2 / cm^3	0	66	119	158	190	211	223



- (ii) Determine the volume of $\text{O}_2(\text{g})$ formed at room temperature and pressure upon the completion of the reaction.



$$n(\text{O}_2) = 0.5 \times 0.040 \div 2 = 0.01 \text{ mol}$$

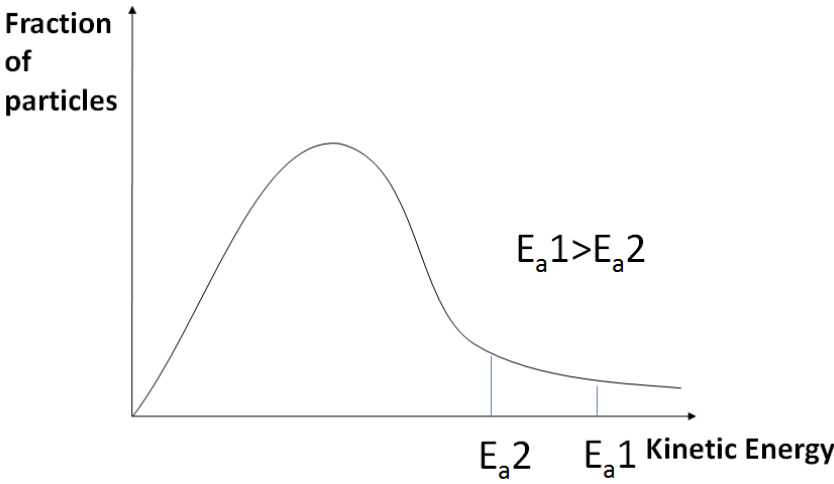
$$\text{Volume of } \text{O}_2 \text{ formed at the end of the reaction} \\ = 0.01 \times 24000 = \underline{240 \text{ cm}^3}$$

- (iii) Using the graph provided above, determine the order of reaction with respect to $\text{H}_2\text{O}_2(\text{aq})$.

Hence write the rate equation for the decomposition of H_2O_2 .

$$\text{Volume when 50\% of the total amount of oxygen is formed} = 120 \text{ cm}^3 \\ 1^{\text{st}} t_{1/2} = 15 \text{ min}$$

$$\text{Volume when 75\% of the total amount of oxygen is formed} = 180 \text{ cm}^3 \\ 2^{\text{nd}} t_{1/2} = 31 - 15 = 16 \text{ min}$$

		<p>Since $t_{1/2}$ is approximately constant, reaction is first order with respect to H_2O_2.</p> <p>Rate = $k [\text{H}_2\text{O}_2]$</p>	
	(iv)	<p>With the aid of a Maxwell-Boltzmann Curve, explain how using Mn^{2+} helps to speed up the decomposition of H_2O_2.</p>  <p>When Mn^{2+} is used, it provides an <u>alternative pathway of lower activation energy (E_{a2})</u>. As a result, <u>a larger number of particles have energy $\geq E_a$ and the frequency of effective collisions increase</u>. As a result, the rate of reaction increases.</p>	[7]
[Total: 20 marks]			

End of Paper