



# RIVER VALLEY HIGH SCHOOL

## YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE  
NAME

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CLASS

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CENTRE  
NUMBER

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INDEX  
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## H2 CHEMISTRY

**9647/03**

Paper 3 Free Response

**21 September 2016**

**2 hours**

Candidates answer on separate paper.

Additional Materials: Answer Paper

Cover Page

Data Booklet

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### READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.

Write in dark blue or black pen on both sides of paper.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

Begin each question on a fresh sheet of paper.

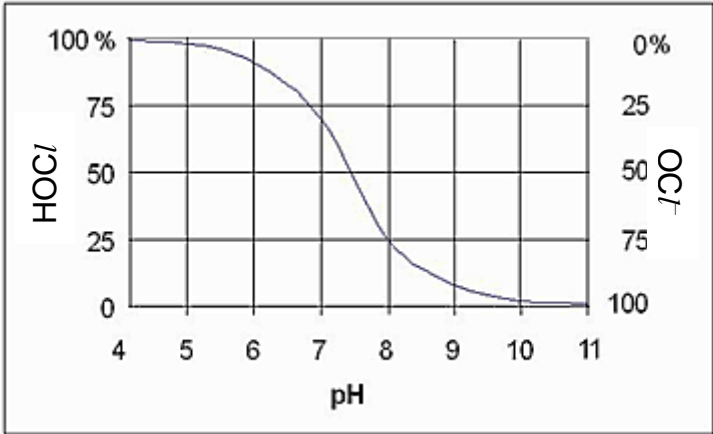
A Data Booklet is provided. Do not write anything on it.

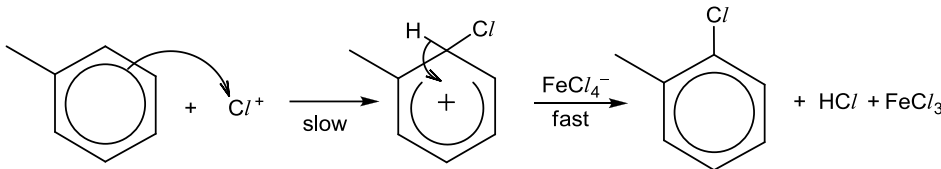
You are reminded of the need for good English and clear presentation in your answers.

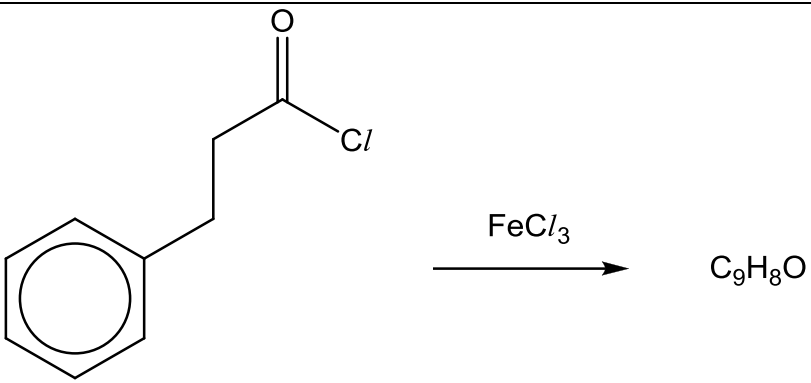
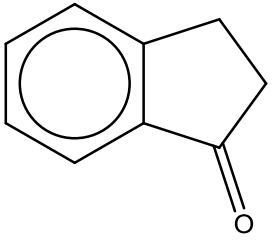
The number of marks is given in brackets [ ] at the end of each question or part question.

At the end of the examination, fasten all your work securely together, with the cover page on top.

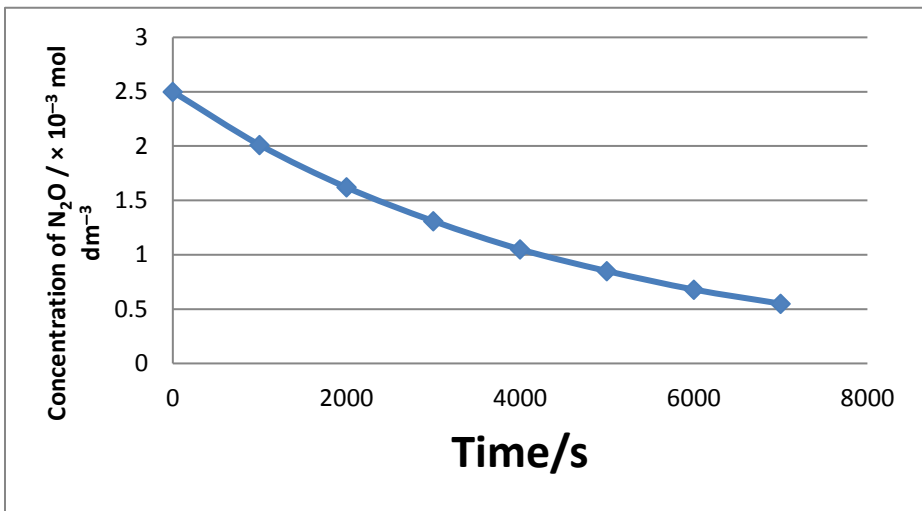
	Answer any <b>four</b> questions.			
<b>1</b>	Many compounds of chlorine are manufactured from brine, NaCl(aq). The electrolysis of brine produces Cl <sub>2</sub> (g) and NaOH(aq). In some industrial electrolytic cells, these two substances are allowed to react further. The products formed in this second reaction depends on the operating conditions used.			
	<b>(a)</b>	Write balanced equations for the reaction between Cl <sub>2</sub> (g) and		
		<b>(i)</b>	cold aqueous NaOH;	<b>[1]</b>
			Cl <sub>2</sub> + 2NaOH → NaCl + NaClO + H <sub>2</sub> O	
		<b>(ii)</b>	hot aqueous NaOH.	<b>[1]</b>
			3Cl <sub>2</sub> + 6NaOH → 5NaCl + NaClO <sub>3</sub> + 3H <sub>2</sub> O	
	<b>(b)</b>	Chlorine dioxide, ClO <sub>2</sub> , is used in the treatment of water. It is formed from ClO <sub>3</sub> <sup>-</sup> ions in an acidic solution. $\text{ClO}_3^- + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{ClO}_2 + \text{H}_2\text{O}$		
		<b>(i)</b>	Draw the dot-and-cross diagrams of ClO <sub>2</sub> and H <sub>2</sub> O <sub>2</sub> . <i>You may assume that there is no dative bond in either compound.</i>	<b>[2]</b>
			$  \begin{array}{c}  \text{xx} \quad \cdot\cdot \quad \text{xx} \\  \text{x} \text{O} \text{x} : \text{Cl} : \text{x} \text{O} \text{x} \\  \text{x} \quad \cdot \quad \text{x}  \end{array}  $ $  \begin{array}{c}  \text{xx} \quad \text{xx} \\  \text{H} \cdot \text{x} \text{O} \text{x} \text{x} \text{O} \text{x} \cdot \text{H} \\  \text{xx} \quad \text{xx}  \end{array}  $	
		<b>(ii)</b>	Construct the overall equation for the reaction of ClO <sub>3</sub> <sup>-</sup> ions with H <sub>2</sub> O <sub>2</sub> in acidic solution.	<b>[1]</b>
			2ClO <sub>3</sub> <sup>-</sup> + 2H <sup>+</sup> + H <sub>2</sub> O <sub>2</sub> → 2ClO <sub>2</sub> + 2H <sub>2</sub> O + O <sub>2</sub>	
		<b>(iii)</b>	What is the role of H <sub>2</sub> O <sub>2</sub> in the reaction?	<b>[1]</b>
			Reducing agent	

	(c)	<p>Chlorine can also be used to disinfect water. When chlorine is added to water, it produces hypochlorous acid, <math>\text{HOCl}</math>. Hypochlorous acid is a weak acid that dissociates into hypochlorite ions, <math>\text{OCl}^-</math>, according to the following equation.</p> $\text{HOCl}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OCl}^-(\text{aq})$ <p><i>Free chlorine</i> refers to the total chlorine content in <math>\text{HOCl}</math> and <math>\text{OCl}^-</math>. The dissociation curve below illustrates the ratio of hypochlorous acid to hypochlorite at different pH values.</p>  <p>[Source: <a href="http://www.hach.com">www.hach.com</a>]</p>	
	(i)	Determine the $\text{pK}_a$ of hypochlorous acid	[1]
		<p><math>\text{pH} = \text{pK}_a</math> when <math>[\text{HA}] = [\text{A}^-]</math>. From the graph, <math>\text{pH} = 7.5</math> when <math>[\text{OCl}^-] = [\text{HOCl}]</math>. Therefore, <math>\text{pK}_a</math> is 7.4 – 7.6.</p>	
	(ii)	Hence, calculate the pH of a $0.0025 \text{ mol dm}^{-3}$ hypochlorous acid solution.	[2]
		<p><math>\text{pK}_a = 7.5</math>, <math>K_a = 10^{-7.5} = 3.16 \times 10^{-8} \text{ mol dm}^{-3}</math></p> <p><math>[\text{H}^+] = (3.16 \times 10^{-8} \times 0.0025)^{1/2} = 8.89 \times 10^{-6} \text{ mol dm}^{-3}</math></p> <p><math>\text{pH} = -\lg(8.89 \times 10^{-6}) = \underline{\underline{5.05}}</math></p>	
		<p>To determine whether the free chlorine in a sample of tap water meets the regulatory limit (4 mg <math>\text{Cl}</math> per litre), <math>\text{OCl}^-</math> is quantitatively reduced to <math>\text{Cl}^-</math> by <math>\text{I}^-</math> ions, which is in turn oxidised to <math>\text{I}_2</math>. The <math>\text{I}_2</math> is titrated with standard sodium thiosulfate. The following reaction takes place during the titration.</p> $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$	
	(iii)	Construct a balanced equation between $\text{OCl}^-(\text{aq})$ and acidified $\text{KI}(\text{aq})$	[1]
		$2\text{H}^+(\text{aq}) + 2\text{I}^-(\text{aq}) + \text{OCl}^-(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{I}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$	

		(iv)	When 2 dm <sup>3</sup> of tap water was tested, 6.0 cm <sup>3</sup> of 0.00455 mol dm <sup>-3</sup> sodium thiosulfate was required to discharge the colour of iodine. Calculate the concentration of OCl <sup>-</sup> in the sample of water.	[2]
			Amount of S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> = 2.73 × 10 <sup>-5</sup> mol Amount of iodine produced = 1.37 × 10 <sup>-5</sup> mol Amount of OCl <sup>-</sup> present = 1.37 × 10 <sup>-5</sup> mol Concentration = 6.83 × 10 <sup>-4</sup> mol dm <sup>-6</sup>	
		(v)	Suggest why the calculated concentration of OCl <sup>-</sup> has the same value as the concentration of <i>free</i> chlorine.	[2]
			In the equilibrium, HOCl(aq) ⇌ H <sup>+</sup> (aq) + OCl <sup>-</sup> (aq), as OCl <sup>-</sup> is reduced by I <sup>-</sup> , [OCl <sup>-</sup> ] decreases and the equilibrium position shifts right to favour the formation of more OCl <sup>-</sup> until all the HOCl completely dissociates.	
		(vi)	Determine if the sample of tap water is safe for consumption.	[2]
			Mass concentration of free chlorine = 6.83 × 10 <sup>-6</sup> × 35.5 = 0.242 mg per litre. The tap water is safe for consumption.	
	(d)		Chlorine is also used in organic chemistry to produce the Lewis acid catalyst, FeCl <sub>3</sub> , for the reaction between methylbenzene and chlorine.	
		(i)	Describe the mechanism of the above reaction.	[3]
			$\text{FeCl}_3 + \text{Cl}_2 \rightarrow \text{FeCl}_4^- + \text{Cl}^+$ 	
		(ii)	FeCl <sub>3</sub> reacts in a similar way with acyl chlorides. Predict the structure of the product of the following reaction.	[1]

			 <p> <chem>ClC(=O)CCc1ccccc1</chem> <math>\xrightarrow{\text{FeCl}_3}</math> <chem>C9H8O</chem> </p>	
			 <p> <chem>O=C1C=CCc2ccccc21</chem> </p>	
			[Total: 20]	

2	(a)	Nitrous oxide or dinitrogen oxide, N <sub>2</sub> O, is commonly known as "laughing gas" due to the euphoric effects of inhaling it. It is used in surgery and dentistry for its anesthetic and analgesic effects. To produce N <sub>2</sub> O, ammonium nitrate is decomposed at 170 °C. Water is a by-product of this reaction.																				
	(i)	Write an equation for the production of dinitrogen oxide from ammonium nitrate.		[1]																		
		NH <sub>4</sub> NO <sub>3</sub> (s) → 2 H <sub>2</sub> O (g) + N <sub>2</sub> O (g)																				
	(ii)	In the manufacturing of N <sub>2</sub> O gas, 1 kg of N <sub>2</sub> O gas is produced for every 2.1 kg of ammonium nitrate used. Determine the percentage yield of dinitrogen oxide.		[2]																		
		Amount of NH <sub>4</sub> NO <sub>3</sub> used = $\frac{2.1 \times 1000}{14 \times 2 + 4 + 16 \times 3} = 26.3 \text{ mol}$  Theoretical amt of N <sub>2</sub> O produced = 26.3 mol  Theoretical mass of N <sub>2</sub> O produced = 26.3 × (14 × 2+ 16) = 1157g  % yield = $\frac{1000}{1157} \times 100\% = 86.4\%$																				
	(b)	At 1200 K, in the presence of gold wire, dinitrogen oxide decomposes as shown:  $2\text{N}_2\text{O}(\text{g}) \longrightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g}).$  To follow the rate of reaction, the change in concentration of a sample of N <sub>2</sub> O is measure against time. The results are shown below: <table><tr><th>Time, t / s</th><th>Concentration of N<sub>2</sub>O / × 10<sup>-3</sup> mol dm<sup>-3</sup></th></tr><tr><td>0</td><td>2.50</td></tr><tr><td>1000</td><td>2.01</td></tr><tr><td>2000</td><td>1.62</td></tr><tr><td>3000</td><td>1.31</td></tr><tr><td>4000</td><td>1.05</td></tr><tr><td>5000</td><td>0.85</td></tr><tr><td>6000</td><td>0.68</td></tr><tr><td>7000</td><td>0.55</td></tr></table>		Time, t / s	Concentration of N <sub>2</sub> O / × 10 <sup>-3</sup> mol dm <sup>-3</sup>	0	2.50	1000	2.01	2000	1.62	3000	1.31	4000	1.05	5000	0.85	6000	0.68	7000	0.55	
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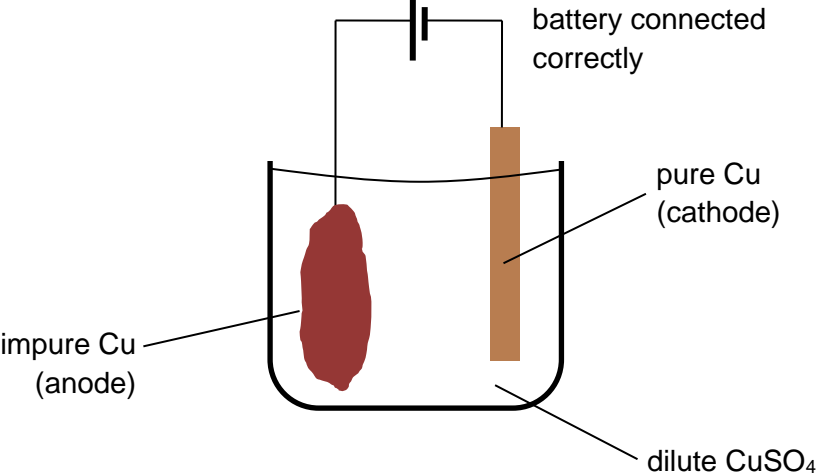
		(i)	What do you understand by the term <i>half-life</i> of $\text{N}_2\text{O}$ ?	[1]
			Half-life is time taken for the concentration of $\text{N}_2\text{O}$ to be halved.	
		(ii)	Plot the above data on a graph paper. Use the following scale: <ul style="list-style-type: none"> <li>• 2 cm to represent 1000 s on the x-axis; and</li> <li>• 2 cm to represent to represent <math>0.25 \times 10^{-3} \text{ mol dm}^{-3}</math> on the y-axis.</li> </ul>	[2]
				
		(iii)	From your graph, deduce the order of the reaction with respect to $\text{N}_2\text{O}$ .	[2]
			When concentration decreases from $2.5 \times 10^{-3}$ to $1.25 \times 10^{-3}$ , time taken is 3300 s. When concentration decreases from $1.25 \times 10^{-3}$ to $0.7 \times 10^{-3}$ , time taken is 3100 s. (to be shown on the graph) Since half-life is approximately constant, the <u>order of reaction with respect to <math>\text{N}_2\text{O}</math> is 1</u> . Show on graph that half time constant	
		(iv)	Calculate the rate constant for the reaction and state its units.	[2]
			Rate constant = $\frac{\ln 2}{t_{1/2}} = 2.17 \times 10^{-4} \text{ s}^{-1}$ Correct answer Correct units	
		(v)	The gold wire acts as a <i>heterogeneous catalyst</i> in this reaction.	[3]

			Explain the terms <i>in italics</i> and outline the mode of action of the catalyst.	
			<p>A catalyst is a substance that provides an alternative pathway with lower activation energy, remaining chemically unchanged at the end of reaction. A heterogeneous catalyst is one that is in a different phases as the reactants.</p> <p><u>Adsorption</u></p> <p>The gold wire provides active sites whereby <math>\text{N}_2\text{O}</math> molecules may be adsorbed.</p> <p>The adsorption <u>weakens N–O bonds</u> so that the <math>\text{N}_2\text{O}</math> molecules are more reactive.</p> <p><u>Reaction</u></p> <p>The <math>\text{N}_2\text{O}</math> molecules on the gold surface are in <u>close proximity and the correct orientation</u> so that they can readily react together.</p> <p><u>Desorption</u></p> <p>The products, <math>\text{N}_2</math> and <math>\text{O}_2</math>, formed diffuse away from the surface of the catalyst and the active sites become available again.</p>	
	(c)		<p>Alkenes react with carbenes <math>\text{R}_2\text{C:}</math> to yield cyclopropanes.</p> <p>One way to generate a substituted carbene is by reacting chloroform, <math>\text{CHCl}_3</math>, with a strong base.</p> <p>The mechanism to generate a carbene is described below.</p> <ol style="list-style-type: none"> <li>1. Potassium hydroxide, <math>\text{KOH}</math>, removes the proton from <math>\text{CHCl}_3</math>, leaving behind the electron pair. An anionic intermediate is formed.</li> <li>2. <math>\text{Cl}^-</math> is lost and a neutral dichlorocarbene is formed.</li> </ol>	
		(i)	<p>Based on the description above, draw a mechanism to show the generation of dichlorocarbene.</p> <p>Show relevant lone pairs and use curly arrows to indicate the movement of electron pairs.</p>	[3]



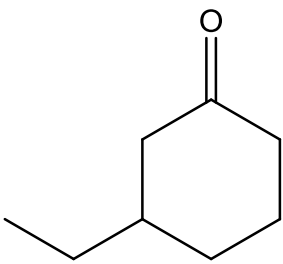
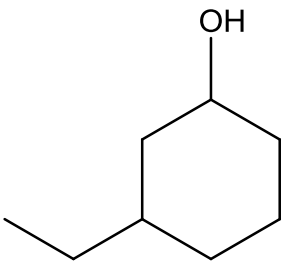
		<p>An example of a reaction between an alkene and a carbene is as shown:</p>	
	(ii)	Suggest the structure of the product formed when cyclohexene reacts with chloroform in the presence of KOH.	[1]
	(iii)	Suggest the role of carbene in its reaction with an alkene. Explain your answer.	[2]
		<p>Carbene acts as an electrophile.</p> <p>Carbon in carbene is <u>electron deficient</u> as it is bonded to two electronegative chlorine atoms/it has only 6 valence electrons, hence it acts as an electrophile.</p>	
	(iv)	Suggest the type of reaction when carbene reacts with an alkene.	[1]

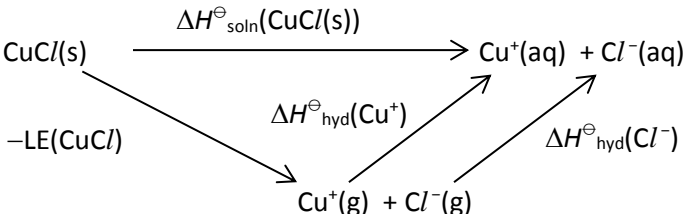
			Addition	
			<b>[Total: 20]</b>	

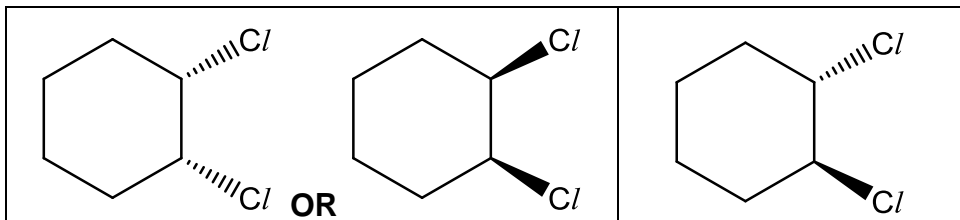
3	Copper is a rare element, constituting only $6.8 \times 10^{-3}$ percent of the Earth's crust by mass. However, it has a wide range of uses such as in alloys, plumbing and in electrical cables. The common oxidation states of copper are +2 and +1.	
	(a) Copper can be obtained by roasting a copper ore, $\text{CuFeS}_2$ , to give $\text{Cu}_2\text{S}$ , which is further oxidised to form metallic copper. This impure copper can be purified by electrolysis.	
	(i) Draw a diagram to illustrate the electrolytic cell used in the purification of copper, using $\text{CuSO}_4(\text{aq})$ as the electrolyte.	[2]
		
	(ii) If a current of 0.8 A was passed through the cell, calculate the time required for 0.25 g of pure copper to be collected.	[2]
	<p>Amt of Cu = <math>0.25 / 63.5 = 3.94 \times 10^{-3}</math> mol</p> <p><math>\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})</math></p> <p>Amt of <math>\text{e}^-</math> required = <math>2(3.94 \times 10^{-3}) = 7.88 \times 10^{-3}</math> mol</p> <p>Quantity of charge required = <math>nF = 7.88 \times 10^{-3} \times 96500 = 760 \text{ C}</math></p> <p>Time required = <math>Q / I = 760 / 0.8 = \underline{\underline{950 \text{ s}}}</math> (or 15.8 min)</p>	
	(b) Anhydrous copper(II) sulfate, $\text{CuSO}_4(\text{s})$ , is a white powder. It dissolves in water to form a pale blue solution.	
	(i) State the species responsible for the pale blue colour of the solution.	[1]
	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	
	(ii) Explain why the solution is pale blue in colour.	[3]
	$\text{Cu}^{2+}$ has a <u>partially filled 3d subshell</u> (electronic configuration $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^9$ ). In the presence of $\text{H}_2\text{O}$ ligands in	

			[Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> , the <u>3d orbitals</u> of Cu <sup>2+</sup> <u>are split into 2 sets of orbitals with different energies/become non-degenerate</u> . The <u>difference in energies (<math>\Delta E</math>)</u> between these 2 sets of non-degenerate 3d orbitals is <u>small</u> and <u>radiation from the visible region of the electromagnetic spectrum is absorbed</u> when an electron is promoted from a <u>lower energy d-orbital to another unfilled/partially-filled d orbital of higher energy</u> . The (blue) <u>colour</u> observed corresponds to the <u>complement of the (orange) light</u> absorbed.	
		(iii)	Describe the colour changes observed when the following solutions are added to the pale blue solution, giving the formulae of all relevant species.  I. Dilute NH <sub>3</sub> (aq), until in excess; II. KI(aq).	[4]
			I. A <b>(pale) blue precipitate</b> of <b>Cu(OH)<sub>2</sub></b> is formed, which is soluble in excess NH <sub>3</sub> (aq) to form a <b>dark blue solution</b> of <b>[Cu(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup></b> . II. An <b>off-white/cream precipitate</b> of <b>CuI</b> (Accept: Cu <sub>2</sub> I <sub>2</sub> ) is formed in a <b>brown solution</b> of <b>I<sub>2</sub></b> .	
	(c)		When Na <sub>2</sub> CO <sub>3</sub> is added to a solution of CuSO <sub>4</sub> and the resultant mixture is filtered, a green solid, cupric carbonate, is obtained. The formula of this solid is Cu <sub>2</sub> (OH) <sub>a</sub> (CO <sub>3</sub> ) <sub>b</sub> .  0.10 mol of Cu <sub>2</sub> (OH) <sub>a</sub> (CO <sub>3</sub> ) <sub>b</sub> required 0.40 mol of hydrochloric acid for complete reaction. The products of this reaction include copper(II) chloride, carbon dioxide and water.	
		(i)	Given that 2.4 dm <sup>3</sup> of CO <sub>2</sub> was formed at room temperature and pressure, determine the values of <b>a</b> and <b>b</b> .	[2]
			Cu <sub>2</sub> (OH) <sub>a</sub> (CO <sub>3</sub> ) <sub>b</sub> + (a + 2b)H <sup>+</sup> → 2Cu <sup>2+</sup> + bCO <sub>2</sub> + (a + b)H <sub>2</sub> O Amt of CO <sub>2</sub> formed = 2.4 / 24 = 0.10 mol  $\frac{1}{b} = \frac{0.10}{0.10} \Rightarrow \mathbf{b = 1}$  $\frac{1}{a + 2b} = \frac{0.10}{0.40} \Rightarrow \mathbf{a + 2b = 4} \Rightarrow \mathbf{a = 2}$	
		(ii)	Hence, write an equation for the reaction of cupric carbonate with	[1]

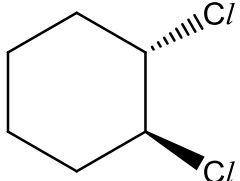
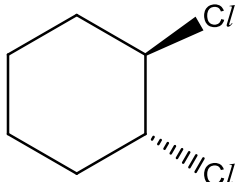
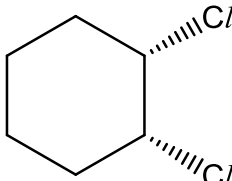
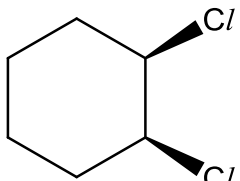
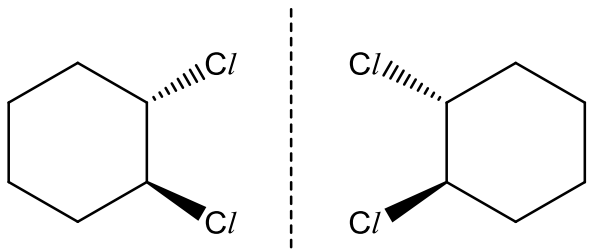
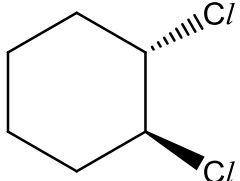
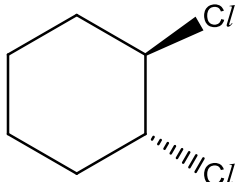
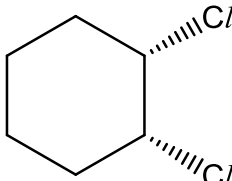
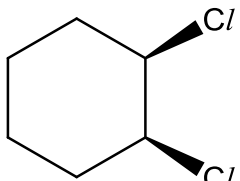
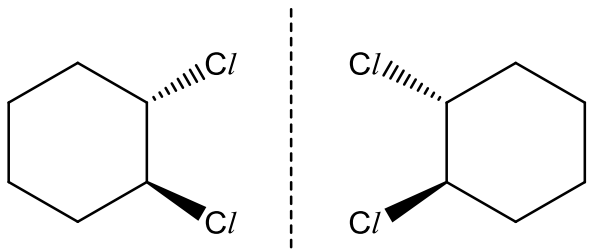
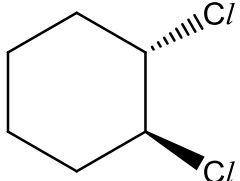
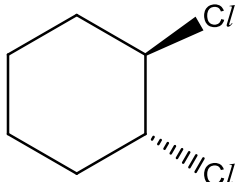
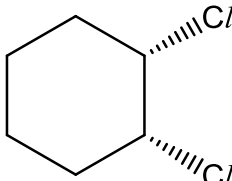
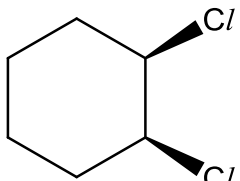
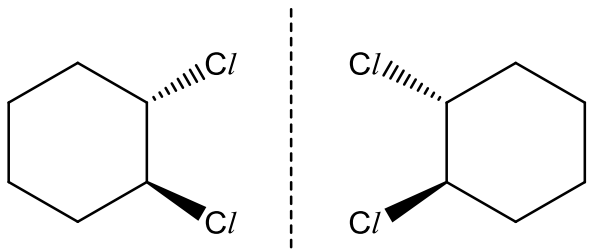
		hydrochloric acid.	
		$\text{Cu}_2(\text{OH})_2\text{CO}_3 + 4\text{HCl} \rightarrow 2\text{CuCl}_2 + \text{CO}_2 + 3\text{H}_2\text{O}$	
	(d)	$\text{Cu}_2\text{O}$ , a brick red solid, is a compound where copper is in the oxidation state of +1. It can be formed by reacting an alkaline solution of complexed $\text{Cu}^{2+}$ with a particular organic functional group.	
	(i)	State the functional group that will produce $\text{Cu}_2\text{O}$ with the alkaline solution of complexed $\text{Cu}^{2+}$ .	[1]
		<b>Aliphatic/Non-aromatic aldehyde</b>	
	(ii)	Name the type of reaction undergone by the functional group in (i).	[1]
		<b>Oxidation</b>	
	(e)	<p>Organocopper compounds are useful reagents in organic synthesis. One such class of compounds is the Gilman reagents, with the general formula <math>\text{R}_2\text{CuLi}</math>, where R represents an alkyl group.</p> <p>Gilman reagents are effective nucleophiles used in conjugate addition reactions. Conjugate addition involves the addition of a nucleophile across a <math>\text{C}=\text{C}</math> bond instead of across a <math>\text{C}=\text{O}</math> bond. This is illustrated in the example below:</p> <div style="text-align: center;"> <p>Reaction scheme: Methyl vinyl ketone <math>\xrightarrow[2. \text{HCl}]{1. \text{R}_2\text{CuLi, ether}}</math> 4-methyl-2-pentanone + <math>\text{RCu} + \text{LiCl}</math></p> </div> <p>The Gilman reagent can be seen as providing the “R-” nucleophile while a mineral acid (e.g. <math>\text{HCl}</math>) provides the proton that is added to one of the carbon atoms in the <math>\text{C}=\text{C}</math> bond.</p>	
		<p>The following synthesis involves a Gilman reagent for one of the steps:</p> <div style="text-align: center;"> <p>Reaction scheme: Cyclohex-2-en-1-ol (I) <math>\rightarrow</math> Cyclohex-2-en-1-one <math>\xrightarrow[2. \text{HCl}]{1. (\text{CH}_3\text{CH}_2)_2\text{CuLi, ether}}</math> A <math>\xrightarrow[\text{III}]{\text{NaBH}_4}</math> B</p> </div> <p>Suggest the reagent and conditions for Step I and the structures of compounds A and B.</p>	[3]
		<b>Reagents and conditions for Step I:</b>	

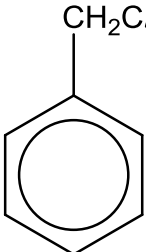
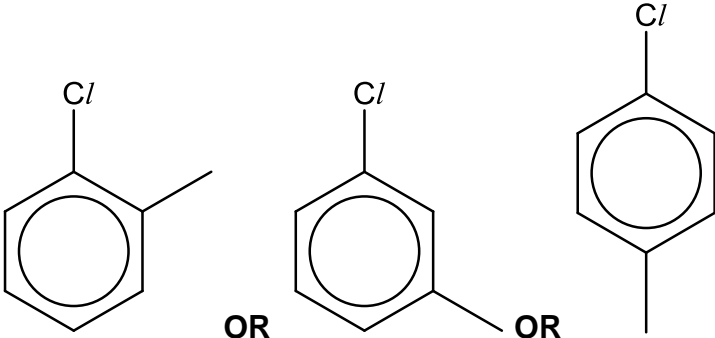
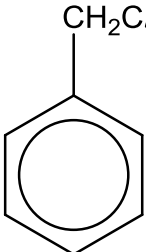
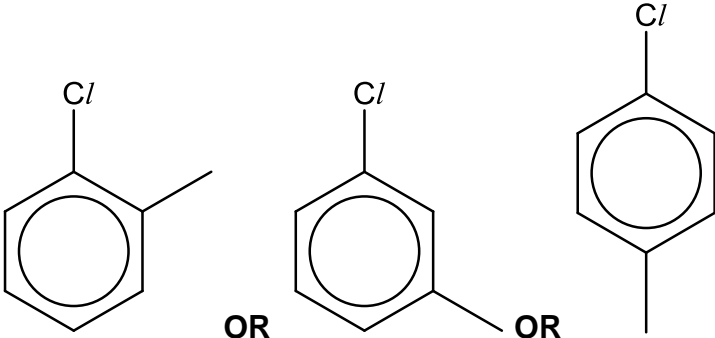
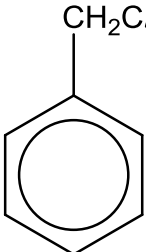
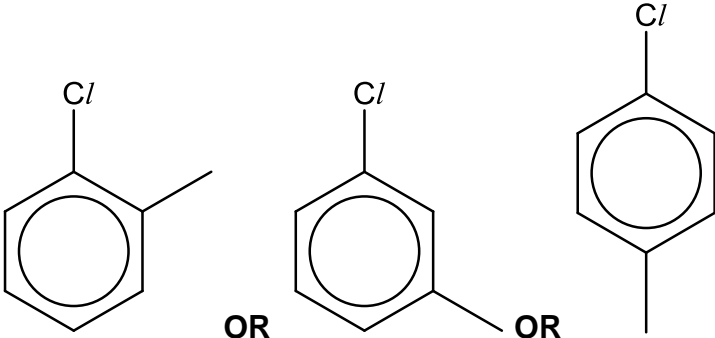
		acidified $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ , heat (under reflux)		
		<b>Structures:</b>		
				
		<b>A</b>	<b>B</b>	
			<b>[Total: 20]</b>	

4	(a)	Copper(I) chloride is used as a precursor of a fungicide and a catalyst for a variety of organic reactions. It is sparingly soluble in water.								
	(i)	Define the standard enthalpy change of hydration of an ion.		[1]						
		The standard enthalpy change of hydration of an ion is the enthalpy change when <b>one mole of gaseous ions is hydrated</b> under standard conditions.								
	(ii)	Using the data given in the following table, draw an appropriate energy cycle and calculate the standard enthalpy change of solution for copper(I) chloride. <table border="1"><tr><td><math>\Delta H^{\ominus}_{\text{hyd}}(\text{Cu}^+)</math></td><td><math>-593 \text{ kJ mol}^{-1}</math></td></tr><tr><td><math>\Delta H^{\ominus}_{\text{hyd}}(\text{Cl}^-)</math></td><td><math>-378 \text{ kJ mol}^{-1}</math></td></tr><tr><td>Lattice Energy of CuCl</td><td><math>-979 \text{ kJ mol}^{-1}</math></td></tr></table>		$\Delta H^{\ominus}_{\text{hyd}}(\text{Cu}^+)$	$-593 \text{ kJ mol}^{-1}$	$\Delta H^{\ominus}_{\text{hyd}}(\text{Cl}^-)$	$-378 \text{ kJ mol}^{-1}$	Lattice Energy of CuCl	$-979 \text{ kJ mol}^{-1}$	[3]
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Lattice Energy of CuCl	$-979 \text{ kJ mol}^{-1}$									
		$\Delta H^{\ominus}_{\text{soln}}(\text{CuCl(s)}) = \Delta H^{\ominus}_{\text{hyd}}(\text{Cu}^+) + \Delta H^{\ominus}_{\text{hyd}}(\text{Cl}^-) - \text{LE}(\text{CuCl})$ $= (-593) + (-378) - (-979) = +8 \text{ kJ mol}^{-1}$ 								
	(b) (i)	Explain what is meant by the term <i>entropy</i> of a chemical system.		[1]						
		Entropy is a measure of the <b>disorder</b> in a system. (The more disordered a system, the greater the number of ways for particles and energy to be dispersed, therefore the larger its entropy.)								
		Describe and explain how the entropy of the following systems will change during the stated process. Assume the pressure of each system remains at 1 atm throughout.								
	(ii)	1 mol of Cl <sub>2</sub> (g) at 298 K is heated to 500 K.		[1]						
		<b>Entropy increases/ΔS &gt; 0.</b> There is an increase in disorder as the particles have <b>more kinetic energy on average</b> and there are <b>more ways to distribute</b> the <b>larger number of quanta</b> of energy.								
	(iii)	1 mol of Cl <sub>2</sub> (g) at 298 K is reacted with copper according to the following equation.		[1]						

			$\text{Cu(s)} + \text{Cl}_2\text{(g)} \rightarrow \text{CuCl}_2\text{(s)}$								
			<b>Entropy decreases/<math>\Delta S &lt; 0</math>.</b> There is an decrease in disorder as the <b><u>number of gaseous molecules decreases</u></b> from 1 to 0.								
	(c)	Copper(II) ions are pollutants found in water. One method of purification is via precipitation of $\text{Cu(OH)}_2$ and $\text{CuS}$ . <table border="1" style="margin: 10px auto; width: 60%;"><thead><tr><th></th><th><math>K_{\text{sp}}</math> (298 K)</th></tr></thead><tbody><tr><td><math>\text{CuS}</math></td><td><math>6.3 \times 10^{-36}</math></td></tr><tr><td><math>\text{Cu(OH)}_2</math></td><td><math>2.0 \times 10^{-19}</math></td></tr></tbody></table> Using the above data, calculate:				$K_{\text{sp}}$ (298 K)	$\text{CuS}$	$6.3 \times 10^{-36}$	$\text{Cu(OH)}_2$	$2.0 \times 10^{-19}$	
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$\text{CuS}$	$6.3 \times 10^{-36}$										
$\text{Cu(OH)}_2$	$2.0 \times 10^{-19}$										
	(i)	the minimum concentration of $\text{Cu}^{2+}$ for a precipitate of $\text{CuS}$ to form in 10 ppm $\text{S}^{2-}$ solution; <i>(1 ppm = 1 mg dm<sup>-3</sup>)</i>			[2]						
		$[\text{S}^{2-}] = (0.01 / 32.1) = 3.12 \times 10^{-4} \text{ mol dm}^{-3}$ $[\text{Cu}^{2+}] = (6.3 \times 10^{-36}) / (3.12 \times 10^{-4}) = \underline{\underline{2.02 \times 10^{-32} \text{ mol dm}^{-3}}}$									
	(ii)	the maximum pH of a solution containing $0.100 \text{ mol dm}^{-3} \text{ Cu}^{2+}$ ions.			[3]						
		$K_{\text{sp}}(\text{Cu(OH)}_2) = [\text{Cu}^{2+}][\text{OH}^-]^2$ $2.0 \times 10^{-19} = (0.1)(x)^2$ $[\text{OH}^-] = 1.41 \times 10^{-9} \text{ mol dm}^{-3}$  $\text{pOH} = -\lg(1.41 \times 10^{-9}) = 8.85$ $\text{pH} = 14 - \text{pOH} = 14 - 8.85 = \underline{\underline{5.15}}$									
	(d)	Many organic compounds also contain chlorine. An example would be 1,2-dichlorocyclohexane, which exhibits both geometrical and optical isomerism.									
	(i)	Explain why 1,2-dichlorocyclohexane can exhibit geometrical isomerism.			[1]						
		There is <b><u>restricted rotation</u></b> about the carbon-carbon bond in the ring structure, resulting in cis- and trans-1,2-dichlorocyclohexane [1]. <div style="text-align: center; margin-top: 10px;"></div>									

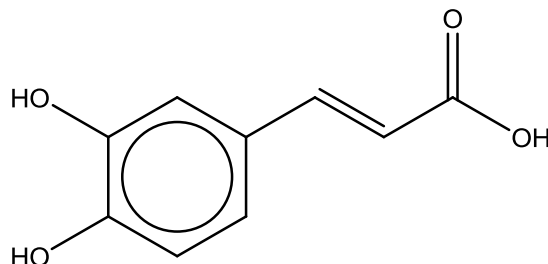
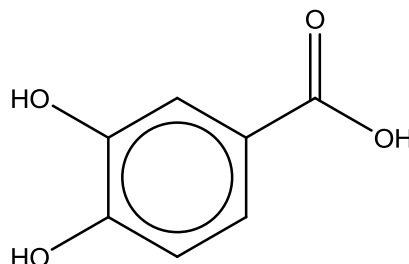
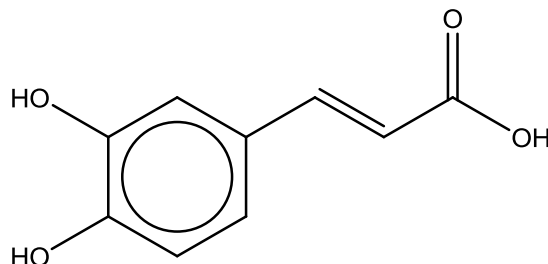
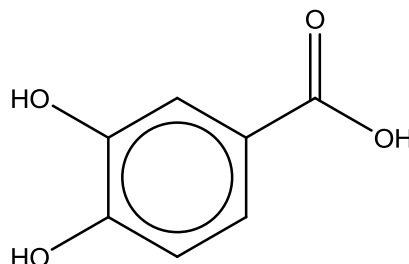
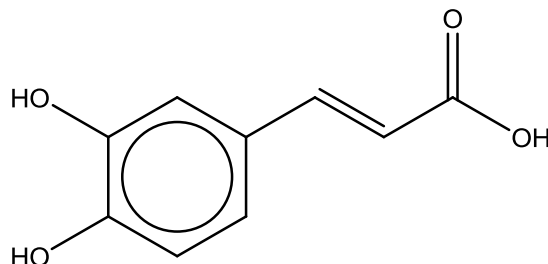
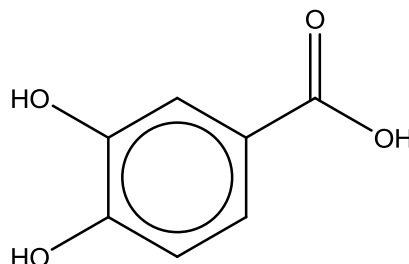


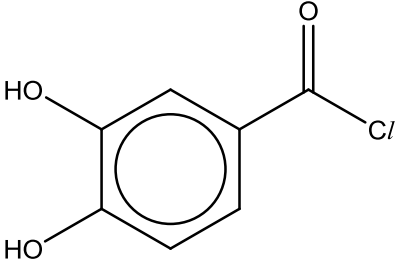
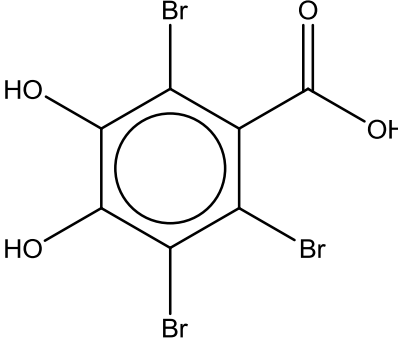
			cis isomer	trans isomer																						
		(ii)	<p>The effect of plane polarised light on 1,2-dichlorocyclohexane was investigated. Three different types of 1,2-dichlorocyclohexane was identified:</p> <ul style="list-style-type: none"><li>• Molecule <b>X</b> rotated plane polarised light to the left</li><li>• Molecule <b>Y</b> rotated plane polarised light to the right</li><li>• Molecule <b>Z</b> had no effect on plane polarised light</li></ul> <p>Suggest an explanation for these observations.</p>			[3]																				
			<table><tr><th>Molecule</th><th colspan="2">Explanation</th></tr><tr><td><b>X</b></td><td></td><td rowspan="2"><p>Molecules possess <b>two chiral carbons</b> and <b>no plane of symmetry</b>. Hence, they are mirror images of each other that are non-superimposable (i.e. enantiomers of each other)</p><p>Structure of <b>X</b> and <b>Y</b> can be interchanged.</p></td></tr><tr><td><b>Y</b></td><td></td></tr><tr><td><b>Z</b></td><td> <b>OR</b> </td><td><p>Although the molecule has two chiral carbons, there is a <b>plane of symmetry present</b>. Hence, the mirror images are <b>superimposable</b>.</p></td></tr><tr><td colspan="3"></td><td colspan="2"></td></tr><tr><td colspan="3"><div style="display: flex; justify-content: space-around; width: 100%;"><span><b>X</b></span><span><b>Y</b></span></div></td><td colspan="2"></td></tr></table>			Molecule	Explanation		<b>X</b>		<p>Molecules possess <b>two chiral carbons</b> and <b>no plane of symmetry</b>. Hence, they are mirror images of each other that are non-superimposable (i.e. enantiomers of each other)</p> <p>Structure of <b>X</b> and <b>Y</b> can be interchanged.</p>	<b>Y</b>		<b>Z</b>	 <b>OR</b> 	<p>Although the molecule has two chiral carbons, there is a <b>plane of symmetry present</b>. Hence, the mirror images are <b>superimposable</b>.</p>						<div style="display: flex; justify-content: space-around; width: 100%;"><span><b>X</b></span><span><b>Y</b></span></div>				
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<p>(e) Compounds <b>C</b> and <b>D</b> both have the molecular formula <math>C_7H_7Cl</math>. In an experiment, both compounds are separately heated under reflux for some time with aqueous sodium hydroxide. The resulting solutions are cooled and acidified with dilute nitric acid. When aqueous silver nitrate is added subsequently, a white precipitate is formed with <b>C</b> while no precipitate is formed with <b>D</b>.</p> <p>Suggest the structures of <b>C</b> and <b>D</b>. Explain your reasoning for <b>each</b> compound.</p>	<b>[4]</b>								
<table border="1" style="width: 100%; border-collapse: collapse;"><tr><td style="width: 10%; text-align: center; vertical-align: top;"><b>C</b></td><td style="text-align: center; vertical-align: middle;"></td></tr><tr><td></td><td><p><b>C</b> undergoes <u>nucleophilic substitution</u> when heated with NaOH. <u>Free chloride ion then combines with <math>Ag^+</math></u> to form white precipitate of AgCl.</p></td></tr><tr><td style="text-align: center; vertical-align: top;"><b>D</b></td><td style="text-align: center; vertical-align: middle;"></td></tr><tr><td></td><td><p>C–Cl bond in <b>D</b> has <u>partial double bond character</u> due to the <u>delocalisation of a lone pair of electrons of chlorine into the benzene ring</u>. Hence, <b>D</b> does not undergo nucleophilic substitution with NaOH.</p></td></tr></table>	<b>C</b>			<p><b>C</b> undergoes <u>nucleophilic substitution</u> when heated with NaOH. <u>Free chloride ion then combines with <math>Ag^+</math></u> to form white precipitate of AgCl.</p>	<b>D</b>			<p>C–Cl bond in <b>D</b> has <u>partial double bond character</u> due to the <u>delocalisation of a lone pair of electrons of chlorine into the benzene ring</u>. Hence, <b>D</b> does not undergo nucleophilic substitution with NaOH.</p>	
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<b>[Total: 20]</b>									

5	(a)	The electrical conductivities of some Period 3 elements are shown below.						
		Element	Na	Mg	Al	P	S	Cl
		Electrical conductivity at 298 K / $\times 10^7 \text{ S m}^{-1}$	2.1	2.3	3.5	Non-conductors		

		(i)	With reference to the data above, describe and explain the difference in electrical conductivities of the elements above.	[3]
			<u>Na, Mg &amp; Al</u> They are metals / have giant metallic structure. Presence of delocalised valence electrons which act as mobile charge carriers thus making them good conductors. Electrical conductivity increases from Na ( $2.1 \times 10^7 \text{ S m}^{-1}$ ) to Mg ( $2.3 \times 10^7 \text{ S m}^{-1}$ ) to Al ( $3.5 \times 10^7 \text{ S m}^{-1}$ ) as the number of valence electrons increases.  <u>P<sub>4</sub>, S<sub>8</sub> &amp; Cl<sub>2</sub></u> They are non-metals / have simple covalent structure. Absence of mobile charge carriers thus they are non-conductors.	
		(ii)	Silicon carbide (SiC), also known as carborundum and moissanite, is used in abrasive and cutting tools. Suggest the structure and bonding of SiC.	[2]
			Giant covalent structure with strong electrostatic forces of attraction between the Si and C nuclei and the shared pair of electrons.	
	(b)		Chlorides of Period 3 elements dissolve in water to give solutions of varying pH. Explain the following pH values and write the chemical equations for any reactions that occur:	
		(i)	AlCl <sub>3</sub> dissolves readily in water to form an acidic solution (pH = 3).	[3]
			Both hydration of ions and substantial hydrolysis of Al <sup>3+</sup> (aq) occurs. Due to its high charge density, Al <sup>3+</sup> is <b>highly polarising</b> and <b>weakens the O–H bonds</b> in the water molecules of the complex, causing the O–H bonds to break and hence release the hydrogen ions. $\text{AlCl}_3(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow [\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 3\text{Cl}^{-}(\text{aq})$ $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}(\text{aq}) + \text{H}_3\text{O}^{+}(\text{aq})$	
		(ii)	SiCl <sub>4</sub> (l) dissolves in water to form a strongly acidic solution (pH = 2)	[2]
			SiCl <sub>4</sub> undergoes hydrolysis in water. This is because Si atom in SiCl <sub>4</sub> has <b>energetically accessible vacant 3d orbital for dative bonding</b> with water molecules.	

		$\text{SiCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{SiO}_2(\text{s}) + 4\text{HCl}(\text{aq})$				
(c)	<p>Caffeic acid is an organic compound found in all plants as it is a key intermediate in the biosynthesis of lignin, one of the principal components of plant biomass.</p> <p>Caffeic acid has the molecular formula <math>\text{C}_9\text{H}_8\text{O}_4</math>. Caffeic acid reacts with <math>\text{Br}_2(\text{l})</math> to give <math>\text{C}_9\text{H}_8\text{O}_4\text{Br}_2</math>. When treated with hot <math>\text{KMnO}_4</math> and <math>\text{H}_2\text{SO}_4</math>, caffeic acid reacts to give <b>F</b>, <math>\text{C}_7\text{H}_6\text{O}_4</math>, and a colourless gas that produces a white solid with <math>\text{Ca}(\text{OH})_2(\text{aq})</math>. <b>F</b> reacts with <math>\text{PCl}_5</math> to give <b>G</b>, <math>\text{C}_7\text{H}_5\text{O}_3\text{Cl}</math>, with the production of steamy white fumes. <b>G</b> reacts with water to form an acidic solution. When added to neutral <math>\text{FeCl}_3(\text{aq})</math>, <b>G</b> also forms a violet colouration. <b>G</b> reacts with <math>\text{Br}_2(\text{aq})</math> to give <b>H</b>, <math>\text{C}_7\text{H}_3\text{O}_4\text{Br}_3</math>.</p> <p>Use the information above to deduce the structures of caffeic acid and compounds <b>F</b> to <b>H</b>, explaining all the reactions involved.</p>	[10]				
	<p>Caffeic acid <u>C:H ratio <math>\approx 1:1</math></u> which suggests <u>presence of benzene ring</u>.</p> <p>Caffeic acid <u>has a C=C double bond/has an alkene group</u> as it undergoes <u>electrophilic addition</u> with <math>\text{Br}_2</math>.</p> <p>Caffeic acid undergoes <u>oxidation/oxidative cleavage</u> with hot <math>\text{KMnO}_4</math> to give <u>carbon dioxide gas</u>. Loss of 2 carbons as <math>\text{CO}_2</math> suggests formation of <u>ethanedioic acid/<math>\text{HO}_2\text{CCO}_2\text{H}</math></u> after oxidative cleavage.</p> <p><b>F</b> contains a <u>carboxylic functional group</u> as it undergoes (nucleophilic) <u>substitution</u> with <math>\text{PCl}_5</math> to give <b>G</b>, an acid chloride that hydrolyses in water, and fumes of <u><math>\text{HCl}</math></u>.</p> <p><b>G</b> contains <u>phenol functional group</u> as it forms a <u>complex</u> with <math>\text{FeCl}_3(\text{aq})</math>.</p> <p><b>G</b> undergoes <u>electrophilic substitution</u> with <math>\text{Br}_2(\text{aq})</math>. Substitution of 3 Br atoms suggests 3 positions on benzene ring that are available for substitution.</p>					
	<table><tr><td><b>Caffeic acid</b></td><td></td></tr><tr><td><b>F</b></td><td></td></tr></table>	<b>Caffeic acid</b>		<b>F</b>		
<b>Caffeic acid</b>						
<b>F</b>						

		<b>G</b>		
		<b>H</b>		
		<b>[Total: 20]</b>		

– End of Paper –