



**SERANGOON JUNIOR COLLEGE**  
**General Certificate of Education Advanced Level**  
**Higher 2**

**CANDIDATE NAME**

**CLASS**

**CHEMISTRY**  
**JC2 Preliminary Examination**  
**Paper 3 Free Response**

**9647/03**  
**20 Sept 2016**  
**2 hours**

Candidates answer on separate paper.

Additional Materials: Data Booklet  
Writing Papers

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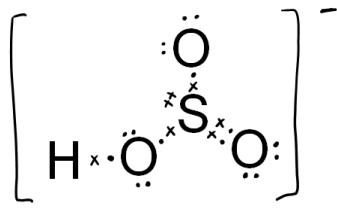
**READ THESE INSTRUCTIONS FIRST**

Write your name and class on all the work you hand in.  
Write in dark blue or black pen on both sides of the 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.  
A Data Booklet is provided.  
The use of an approved scientific calculator is expected, where appropriate.  
You are reminded of the need for good English and clear presentation in your answers.

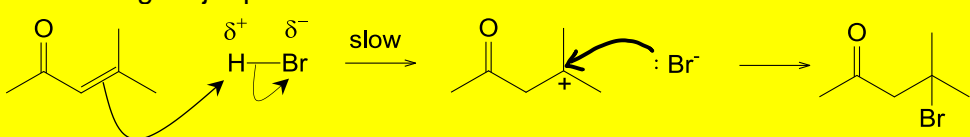
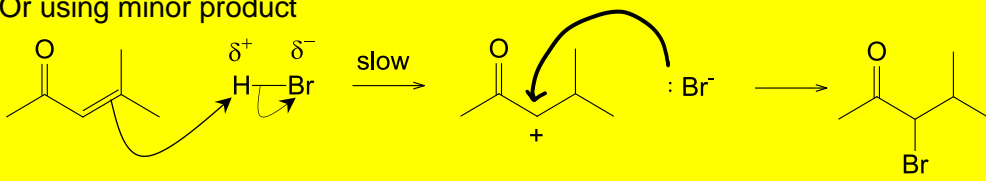
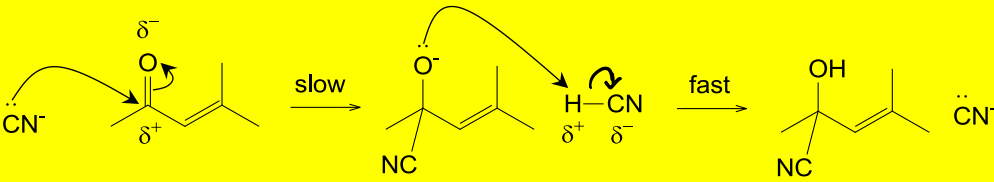
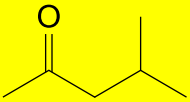
The number of marks is given in the brackets [ ] at the end of each question or part question.  
At the end of the examination, fasten all your work securely together with the cover page provided.

**SUGGESTED**  
**SOLUTIONS**

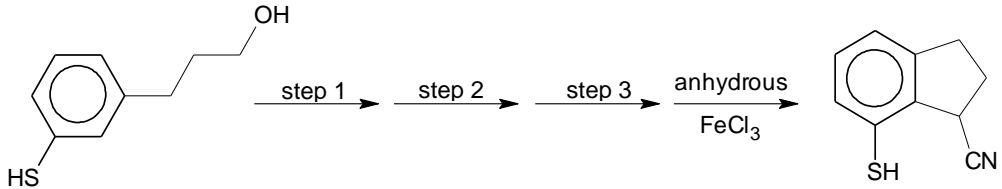
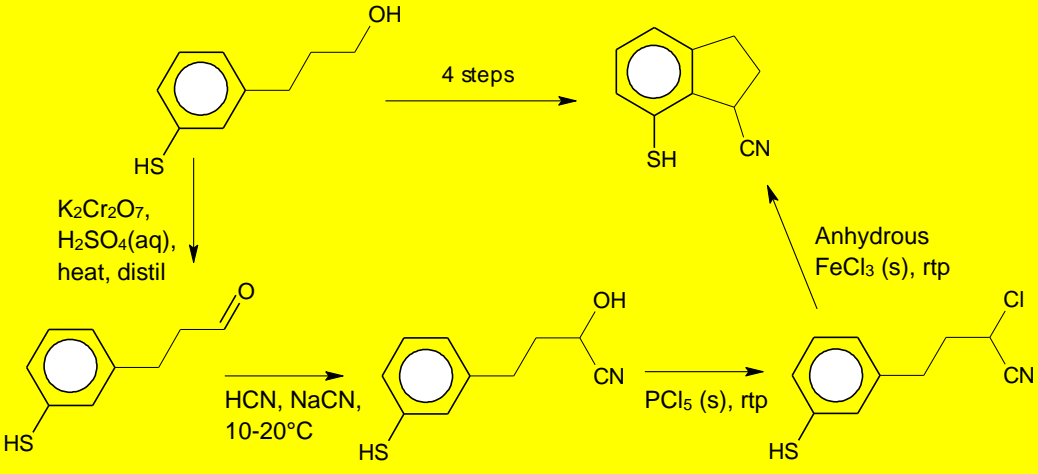
1	Sodium bisulfite ( $\text{NaHSO}_3$ ) is a useful compound to treat chemical waste after organic synthesis. It reacts with methanal, converting it into a non-toxic compound which can be disposed safely. The overall equation is shown below. <div><math display="block">\text{HSO}_3^- + \text{HCOH} \longrightarrow \text{CH}_2(\text{OH})\text{SO}_3^-</math></div>																					
(a)	Draw the dot-and-cross diagram of the bisulfite ion, $\text{HSO}_3^-$ . <div>[1]</div>																					
	<div></div>																					
(b)	<p>The initial rate of this reaction can be studied by the “clock” method, using phenolphthalein as a suitable indicator. The sudden appearance of the pink colour indicates the time to stop the stopwatch.</p> <p>A series of experiments was carried out using different concentrations of <math>\text{HSO}_3^-</math> and <math>\text{HCOH}</math>. The following results were obtained.</p> <table><tr><th>experiment number</th><th><math>[\text{HSO}_3^-]</math> / <math>\text{mol dm}^{-3}</math></th><th><math>[\text{HCOH}]</math> / <math>\text{mol dm}^{-3}</math></th><th>time for the appearance of the pink colour/ s</th></tr><tr><td>1</td><td>0.040</td><td>0.040</td><td>60</td></tr><tr><td>2</td><td>0.040</td><td>0.050</td><td>48</td></tr><tr><td>3</td><td>0.050</td><td>0.060</td><td>40</td></tr><tr><td>4</td><td>0.040</td><td>0.070</td><td>34</td></tr></table>		experiment number	$[\text{HSO}_3^-]$ / $\text{mol dm}^{-3}$	$[\text{HCOH}]$ / $\text{mol dm}^{-3}$	time for the appearance of the pink colour/ s	1	0.040	0.040	60	2	0.040	0.050	48	3	0.050	0.060	40	4	0.040	0.070	34
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4	0.040	0.070	34																			
(i)	What is the simple relationship between the time taken for the pink colour to appear and the initial rate of reaction? <div>[1]</div>																					
The <b>shorter the time</b> , the <b>faster the initial rate</b> of reaction. OR rate $\propto \frac{1}{t}$																						
(ii)	Calculate the initial rate for each of these four experiments and use the results to deduce the order of reaction with respect to the two reactants. Explain your reasoning. <div>[2]</div>																					
<p>Initial rate for experiments 1: <math>1/60 = 0.0167 \text{ s}^{-1}</math> Initial rate for experiments 2: <math>1/48 = 0.0208 \text{ s}^{-1}</math> Initial rate for experiments 3: <math>1/40 = 0.0250 \text{ s}^{-1}</math> Initial rate for experiments 4: <math>1/34 = 0.0294 \text{ s}^{-1}</math> relative rate between experiments 1 and 2: <math>\frac{0.0208}{0.0167} = 1.25</math> Using <b>experiment 1 and 2</b>, when the <b>concentration of <math>\text{HSO}_3^-</math> remains constant</b> and the <b>concentration of <math>\text{HCOH}</math> increases 1.25 times</b>, the <b>rate also increases 1.25 times</b>. Hence the order of reaction with respect to <math>\text{HCOH}</math> is <b>one</b>.</p> <p>Let the order of reaction for <math>\text{HSO}_3^-</math> be x. Using the mathematical method for experiment 2 and 3,</p>																						

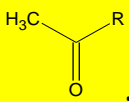
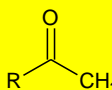
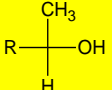
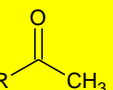
		$\frac{rate_2}{rate_3} = \frac{k[HSO_3^-]^x[HCOH]^1}{k[HSO_3^-]^x[HCOH]^1}$ $\frac{0.0208}{0.025} = \frac{k[0.04]^x[0.05]^1}{k[0.05]^x[0.06]^1}$ $\frac{0.0208}{0.025} = \left(\frac{4}{5}\right)^x \times \frac{5}{6}$ $1 = \left(\frac{4}{5}\right)^x$ $x = 0$ <p>therefore, order of reaction with respect to <math>HSO_3^-</math> is <b>zero</b>.</p>
	(iii)	Using your answer in (ii), write the rate equation for the reaction, stating the units of the rate constant. [2]
		<p>rate = <math>k[HCOH]</math></p> <p>units of rate constant = <math>\frac{mol\ dm^{-3}\ s^{-1}}{mol\ dm^{-3}} = s^{-1}</math></p>
	(iv)	Sketch the graph of concentration against time for each reactant. [2]
		<div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;"> <p><math>[HSO_3^-]/\ mol\ dm^{-3}</math></p> <p>time/s</p> </div> <div style="text-align: center;"> <p><math>[HCOH]/\ mol\ dm^{-3}</math></p> <p>time/s</p> </div> </div>
	(c)	<p>Kinetic studies suggests that the mechanism involves the following two steps:</p> <p>Step 1: Bisulfite reacts with water via an acid-base reaction, forming sulfite, <math>SO_3^{2-}</math>.</p> <p>Step 2: The resulting sulfite reacts with methanal to produce the non-toxic compound, <math>CH_2(OH)SO_3^-</math> and hydroxide ion.</p>
	(i)	Write a balanced equation each for step 1 and step 2. [2]
		<p>Step 1: <math>HSO_3^- + H_2O \rightarrow SO_3^{2-} + H_3O^+</math></p> <p>Step 2: <math>H_2O + SO_3^{2-} + HCOH \rightarrow CH_2(OH)SO_3^- + OH^-</math></p>
	(ii)	Suggest why phenolphthalein is a suitable indicator to determine the completion of the reaction. [1]
		Phenolphthalein is suitable because its <b>pH transition range</b> lies <b>within</b> the <b>region of rapid pH change</b> in the reaction mixture.

	(d)	<p>Aldol condensations are important in organic synthesis as a good way to form carbon-carbon bonds.</p> $  \begin{array}{c} \text{O} \\ \parallel \\ \text{R}_1-\text{C}-\text{CH}(\text{R}_2)-\text{H} \end{array} + \begin{array}{c} \text{O} \\ \parallel \\ \text{R}_3-\text{C}-\text{R}_4 \end{array} \longrightarrow \begin{array}{c} \text{O} \qquad \text{R}_3 \\ \parallel \qquad \diagup \\ \text{R}_1-\text{C} \qquad \text{C}-\text{R}_4 \\ \qquad \diagdown \\ \qquad \text{R}_2 \end{array} + \text{H}_2\text{O}  $ <p>(where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can be alkyl group or hydrogen atom)</p> <p>The following reaction sequence illustrate how MIBK, a solvent used on paints, could be synthesised from carbonyl compound <b>B</b>. It is known that MIBK does not undergo attack by electrophile.</p> $  \begin{array}{ccccc}  \text{Carbonyl B} & \xrightarrow{\text{aldol condensation}} & \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{CH}=\text{C}-\text{CH}_3 \\ \text{intermediate C} \end{array} & \xrightarrow{\text{reduction}} & \begin{array}{c} \text{MIBK} \\ \text{C}_6\text{H}_{12}\text{O} \end{array}  \end{array}  $
	(i)	<p>Using the information provided, draw the displayed formula carbonyl <b>B</b>.</p> $  \begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \diagup \quad \diagdown \\ \text{H} \qquad \text{H} \end{array}  $
	(ii)	<p>For each of the following reactions, describe the mechanism, showing curly arrows, dipoles and any relevant lone pairs. You are to state the condition required for reaction 2.</p> <p>Reaction 1: Intermediate <b>C</b> with dry hydrogen bromide gas.          Reaction 2: Intermediate <b>C</b> with aqueous hydrogen cyanide.</p> <p>Hence, suggest with explanation if the products formed from the two reactions could rotate plane polarised light.</p> <p style="text-align: right;">[6]</p>

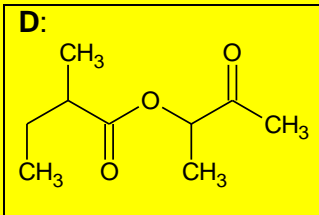
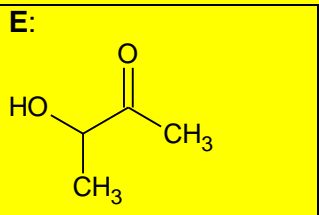
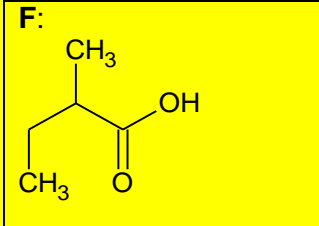
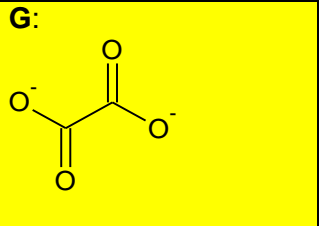
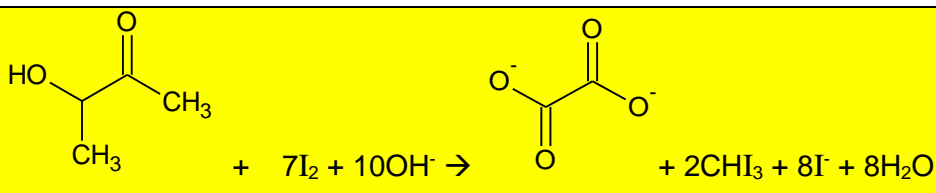
		<p>Reaction 1: Electrophilic addition Either using major product</p>  <p>Or using minor product</p>  <p>Reaction 2: Nucleophilic addition</p>  <p>Condition required for reaction 2: Presence of NaOH(aq) or NaCN, 10°C to 20°C</p> <p>Reaction 1: If use major product: No optical activity as there is absence of chiral carbon. If use minor product: No optical activity as there is presence of racemic mixture</p> <p>Reaction 2: No optical activity as there is presence of racemic mixture.</p>
	(iii)	<p>Deduce the structure of MIBK.</p> <p style="text-align: right;">[2]</p>
		<p>To deduce the structure of MIBK:</p> <p>MIBK does <u>not</u> undergo <u>electrophilic addition</u>  <math>\Rightarrow</math> <u>alkene</u> functional group absent</p>  <p>Thus MIBK looks like</p> <p>(IUPAC name is 4-methylpentan-2-one)</p>

2(a)	<p>Thiophenol is an organosulfur compound with the formula <math>C_6H_5SH</math>. The chemical structure of thiophenol is analogous to phenol, except that the oxygen atom in the hydroxyl group bonded to the aromatic ring is replaced by a sulfur atom.</p> <div data-bbox="804 331 916 528" data-label="Chemical-Block"> </div> <p style="text-align: center;">Thiophenol</p>
	<p>(i) Suggest if the C-S-H bond angle in thiophenol will be larger than the C-O-H bond angle in phenol [1]</p>
	<p><b><u>Oxygen is more electronegative than sulfur</u></b> thus the electron density around O atom will be greater. The <b><u>bond-pair electrons will be nearer to the nucleus resulting in more repulsion</u></b>. Thus the bond angle of C-O-H in phenol will be larger.</p>
	<p>(ii) Explain why thiophenol has a lower <math>pK_a</math> value than phenol. [2]</p>
	<p><b><u>Thiophenol</u></b> has a lower <math>pK_a</math>.</p> <p>The sulfur atom is <b><u>less electronegative</u></b> and the lone pair of electrons on the conjugate base is able to <b><u>delocalise</u></b> into the benzene ring <b><u>more readily</u></b> as compared to phenol, thus <b><u>stabilising its conjugate base</u></b> more than the phenoxide ion.</p>

	<p>(iii) The reaction scheme below shows how one thiophenol derivative could be synthesised into another organic compound in <b>four</b> steps using inorganic reagents. Draw the structure of the intermediate compounds and state the reagents and conditions for each step 1, 2 and 3.</p>  <p style="text-align: right;">[4]</p>
	
(b)	<p>The use of <i>Data Booklet</i> is relevant in this question.</p> <p>In an experiment to determine the enthalpy change of combustion of thiophenol, 2.00 cm<sup>3</sup> of thiophenol with density of 1.08 g cm<sup>-3</sup> was burnt as fuel to bring a calorimeter containing 170 cm<sup>3</sup> of water at 30°C to boil.</p>
(i)	<p>Define standard enthalpy change of combustion.</p> <p style="text-align: right;">[1]</p>
	<p>Standard enthalpy change of combustion is the energy <b>evolved</b> when <b>one mole</b> of substance is <b>completely burnt in oxygen</b> under <b>standard conditions</b>.</p>
(ii)	<p>Calculate the enthalpy change of combustion of thiophenol, <math>\Delta H_c</math>, given that the process is 80% efficient.</p> <p style="text-align: right;">[2]</p>
	$Q' = mc\Delta T = 170 \times 4.18 \times (100 - 30) = 49742 \text{ J}$ $Q' = \frac{80}{100} Q$ $Q = \frac{100}{80} \times 49742 = 62177.5 \text{ J}$ $n_{\text{thiophenol}} = \frac{1.08 \times 2.00}{110.1} = 0.01962 \text{ mol}$ $\Delta H_c = - \frac{62177.5}{0.01962} = \underline{\underline{-3169 \text{ kJ mol}^{-1}}}$

(c)	<p>The use of <i>Data Booklet</i> is relevant in this question.</p> <p>In nuclear magnetic resonance (NMR) spectroscopy, the proton chemical shift can be used to diagnose the structure of an organic molecule.</p> <p>Compound <b>D</b> has a molecular formula of <math>C_9H_{16}O_3</math>. When heated with hydrochloric acid, compound <b>E</b> and <b>F</b> are produced.</p> <p>Compound <b>E</b> has a proton chemical shift of 2.1ppm. When 1 mole of <b>E</b> is warmed with alkaline aqueous iodine, 2 mole of yellow precipitates are formed, along with compound <b>G</b>. White fumes were also observed when <b>E</b> is reacted with thionyl chloride.</p> <p>Compound <b>F</b>, <math>C_5H_xO_2</math>, rotates plane polarised light and has a proton chemical shift of 13.0ppm. Compound <b>F</b>, however, do not exhibit cis-trans isomerism and will not decolourise oxidising agents.</p>
(i)	<p>Suggest the structures of <b>D</b> to <b>F</b>, and explain the observations described above.</p> <p style="text-align: right;">[9]</p>
	<p><b>D</b> undergoes <u>acidic hydrolysis</u> to form <b>E</b> and <b>F</b>.  <math>\Rightarrow</math> <b>D</b> is an <u>ester</u>.  <math>\Rightarrow</math> <b>E</b> and <b>F</b> are alcohol and carboxylic acid.</p> <p><b>E</b> has a proton chemical shift of 2.1ppm.</p> <p><math>\Rightarrow</math> <b>E</b> contains <b>ketone with this structure</b> .</p> <p><b>E</b> undergoes mild <u>oxidation</u> with alkaline aqueous iodine to form 2 mol of yellow ppt and <b>G</b>.</p> <p><math>\Rightarrow</math> <b>E</b> has  and either  <b>or</b> .</p> <p><math>\Rightarrow</math> <b>G</b> contains carboxylate ion.</p> <p><b>E</b> undergoes <u>nucleophilic substitution</u> with <math>SOCl_2</math>.  <math>\Rightarrow</math> <b>E</b> has alcohol or carboxylic acid</p> <p><b>F</b> is <u>chiral</u> and has a proton chemical shift of 13.0ppm.  <math>\Rightarrow</math> <b>C</b> has <u>4 different groups attached and is a carboxylic acid</u>.</p> <p><b>F</b> does not contain alkene as it does not undergo oxidation</p>



		<div style="display: flex; flex-wrap: wrap;"> <div style="width: 50%; padding: 5px;"> <b>D:</b>   </div> <div style="width: 50%; padding: 5px;"> <b>E:</b>   </div> </div> <div style="display: flex; flex-wrap: wrap; margin-top: 10px;"> <div style="width: 50%; padding: 5px;"> <b>F:</b>   </div> <div style="width: 50%; padding: 5px;"> <b>G:</b>   </div> </div>
	(ii)	Construct a balanced chemical equation of the reaction between <b>E</b> and alkaline aqueous iodine. <span style="float: right;">[1]</span>
		

3	(a)	<p>Haemoglobin is the iron-containing oxygen transport protein found in the red blood cells.</p> <p>In general, haemoglobin can be saturated with oxygen molecules (oxyhaemoglobin) or desaturated with oxygen molecules (deoxyhaemoglobin).</p> <p>The absorption spectra of oxyhaemoglobin and deoxyhaemoglobin differ. The oxyhaemoglobin has significantly lower absorption of the 660 nm wavelength as compared with deoxyhaemoglobin which is valued at 940 nm wavelength. This difference is used for the measurement of the amount of oxygen in a patient's blood by an instrument called a pulse oximeter.</p>
	(i)	<p>With reference to the haemoglobin molecule, describe and explain what is meant by the term <i>quaternary structure</i> of proteins. In your answer, you should state the type of bonding or interaction involved.</p> <p style="text-align: right;">[2]</p>
		<p>Quaternary structure consists of <b>more than one polypeptide chain</b> coming together to form the <b>complete protein</b> held together by <b>ionic bonds</b>, <b>hydrogen bonds</b>, <b>Van der Waals' interaction</b> and <b>disulfide linkages</b> between the <b>R groups</b> of the polypeptides.</p> <p>The haemoglobin molecule consists of <b>4 polypeptide chains</b>: <b>2 <math>\alpha</math>-sub-units</b> and <b>2 <math>\beta</math>-sub-units</b>, with each sub-unit being <b>non-covalently</b> bonded to a <b>heme</b> (iron) group.</p> <p>Each heme group consists of a central <math>\text{Fe}^{2+}</math> ion that can bond to one <math>\text{O}_2</math> oxygen. <b>All four components</b> (4 sub-units and 4 haem groups) <b>must be present</b> to form haemoglobin.</p>
	(ii)	<p>Haemoglobin is typically an all alpha-protein consisting of four subunits. However, some of the connecting loops between the helices can sometimes exist in a very short beta-stranded conformation.</p> <p>With the aid of a diagram, describe how a polypeptide chain is held in the shape of a beta-stranded conformation.</p> <p style="text-align: right;">[2]</p>
		<div data-bbox="395 1417 1058 1798" data-label="Chemical-Block"> </div> <ul style="list-style-type: none"> <li>• All peptide linkages are involved in intra-chain hydrogen bonding.</li> <li>• It is stabilized by hydrogen bonds between the <math>\text{C}=\text{O}</math> group of a peptide in one strand and the <math>\text{N}-\text{H}</math> group of another peptide in the adjacent strand.</li> </ul> <p>R groups (side chains) project above and below the sheet and are <math>90^\circ</math> to the plane of the pleated sheet.</p>

		(iii)	Using the information from the question, explain if oxyhaemoglobin or deoxyhaemoglobin contain the larger energy gap, E, between its d-orbital. [2]
			<p><b><u>Wavelength</u></b> of light absorbed: oxyhaemoglobin (660nm) &lt; deoxyhaemoglobin (940nm)</p> <p>Since E is inversely proportional to wavelength of light</p> <p><b><u>Energy</u></b> required for d-d transition: oxyhaemoglobin &gt; deoxyhaemoglobin</p> <p>Thus, oxyhaemoglobin has a larger energy gap E.</p>

	(b)	<p>Carbon monoxide mainly causes adverse effects in humans by combining with haemoglobin in the blood.</p> <p>Human <i>cytochrome c oxidase</i> is composed of several subunits. Some of the amino acids found in <i>cytochrome c oxidase</i> are listed below.</p> <table><tr><th>Amino acid</th><th>Formula of side chain (R in RCH(NH<sub>2</sub>)CO<sub>2</sub>H)</th></tr><tr><td>valine (val)</td><td>-CH(CH<sub>3</sub>)<sub>2</sub></td></tr><tr><td>aspartic acid (asp)</td><td>-CH<sub>2</sub>COOH</td></tr><tr><td>lysine (lys)</td><td>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub></td></tr><tr><td>cysteine (cys)</td><td>-CH<sub>2</sub>SH</td></tr><tr><td>asparagine (asp)</td><td>-CH<sub>2</sub>CONH<sub>2</sub></td></tr><tr><td>threonine (thr)</td><td>-CH(OH)CH<sub>3</sub></td></tr></table>	Amino acid	Formula of side chain (R in RCH(NH <sub>2</sub> )CO <sub>2</sub> H)	valine (val)	-CH(CH <sub>3</sub> ) <sub>2</sub>	aspartic acid (asp)	-CH <sub>2</sub> COOH	lysine (lys)	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	cysteine (cys)	-CH <sub>2</sub> SH	asparagine (asp)	-CH <sub>2</sub> CONH <sub>2</sub>	threonine (thr)	-CH(OH)CH <sub>3</sub>
Amino acid	Formula of side chain (R in RCH(NH <sub>2</sub> )CO <sub>2</sub> H)															
valine (val)	-CH(CH <sub>3</sub> ) <sub>2</sub>															
aspartic acid (asp)	-CH <sub>2</sub> COOH															
lysine (lys)	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>															
cysteine (cys)	-CH <sub>2</sub> SH															
asparagine (asp)	-CH <sub>2</sub> CONH <sub>2</sub>															
threonine (thr)	-CH(OH)CH <sub>3</sub>															
	(i)	<p>Explain how carbon monoxide affects the normal functioning of haemoglobin. [2]</p> <p><b><u>CO is a stronger ligand</u></b> than O<sub>2</sub></p> <p>CO <b><u>bonds irreversibly</u></b> with haemoglobin forming a stable carboxyhaemoglobin complex, thus <b><u>preventing the haemoglobin from carrying oxygen</u></b>.</p> <p>This results in carbon monoxide poisoning due to oxygen starvation.</p>														
	(ii)	<p>Using the dipeptide segment of <b>lys-thr</b> in <i>cytochrome c oxidase</i>, give the structural formulae of the products obtained when hot hydrochloric acid is added. [2]</p> <div><div><math display="block">\begin{array}{c} \text{H} \\   \\ \text{H}_3\text{N}^+ - \text{C} - \text{COOH} \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{NH}_3^+ \end{array}</math></div><div><math display="block">\begin{array}{c} \text{H} \\   \\ \text{H}_3\text{N}^+ - \text{C} - \text{COOH} \\   \\ \text{HO} - \text{CH} \\   \\ \text{CH}_3 \end{array}</math></div></div>														

		(iii)	<p><i>Cytochrome c oxidase</i> can undergo denaturation due to various factors, resulting in loss of its biological function.</p> <p>Identify the site whereby the R group interactions are broken under the following conditions and explain how these interactions are affected in each cases:</p>
			1) The addition of a reducing agent.
			Reducing agents <b>break disulfide linkages</b> and thus R group interaction at <b>cysteine</b> will be affected
			2) The addition of a base. [2]
			The base <b>will disrupt</b> the <b>ionic bonds at asp or lys</b> holding the <b>tertiary</b> and <b>quaternary</b> structures.
		(c)	<p>In cyanide poisoning, the enzyme <i>cytochrome c oxidase</i> which aid in respiration in human are thought to be adversely affected.</p> <p>To treat this cases of poisoning, the United State standard cyanide antidote kit was developed and it comprises of a three step process.</p> <p>Step 1: Inhale small dosage of amyl nitrite.  Step 2: Intravenous of sodium nitrite, <math>\text{NaNO}_2</math>.  Step 3: Intravenous of sodium thiosulfate.</p>
		(i)	<p>Sodium nitrite is part of the cyanide antidote kit. It decomposes to form an acidic brown gas, a solid residue and a free radical.</p> <p>When the residual solid was placed in water, it forms a solution of pH 13.</p> <p>Using the information provided, construct a balanced chemical equation for the decomposition of sodium nitrite. [1]</p>
			<b><math>2\text{NaNO}_2 \rightarrow \text{NO}_2 + \text{Na}_2\text{O} + \text{NO}</math></b>
		(ii)	<p>Thiosulfate reacts differently with chlorine and iodine. Using equations only suggest an explanation for this difference. [2]</p>
			$\text{S}_2\text{O}_3^{2-}(\text{aq}) + 4\text{Cl}_2(\text{aq}) + 5\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + 10\text{H}^+(\text{aq}) + 8\text{Cl}^-(\text{aq})$ $2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$ <p><b><math>\text{Cl}_2</math> is a stronger oxidising agent compared to iodine.</b> Hence, it oxidises S in <math>\text{S}_2\text{O}_3^{2-}</math> from +2 to +6 while iodine oxidises S in <math>\text{S}_2\text{O}_3^{2-}</math> from +2 to +2.5.</p>

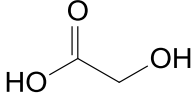
	<p><b>(d)</b> The Maillard reaction is a chemical reaction between amino acid and reducing sugar that gives browned food its desirable flavour. Pan-fried dumplings, french fries and toasted marshmallows undergo this reaction when heated at high temperature.</p> <div style="text-align: center;"> <p>Amino acid + Dicarbonyl <math>\xrightarrow{\text{Step I}}</math> Schiff Base</p> <p>Schiff Base <math>\xrightarrow{\text{Step II}}</math> Intermediate</p> <p>Intermediate + Dicarbonyl <math>\xrightarrow{\text{Step III}}</math> Acrylamide + <math>\text{NH}_3</math></p> </div> <p>Acrylamide, <math>\text{C}_3\text{H}_5\text{NO}</math>, a possible human carcinogen, can be generated as a by-product of Maillard reaction between reducing sugars and amino acid.</p>
	<p><b>(i)</b> Using the table from <b>(b)</b>, state the amino acid that is required in the synthesis of acrylamide. [1]</p>
	<p>Asparagine</p>
	<p><b>(ii)</b> Suggest the gas that was produced in Step II and propose how this gas can be identified. [1]</p>
	<p><math>\text{CO}_2</math> Pass the gas into <math>\text{Ca}(\text{OH})_2</math>, white ppt of <math>\text{CaCO}_3</math> will be observed.</p>
	<p><b>(iii)</b> Suggest the structural formula of acrylamide. [1]</p>
	<p></p>
	<p><b>(iv)</b> Propose an isomer of acrylamide which does not evolve ammonia gas on heating with aqueous sodium hydroxide. Hence, state the type of isomerism involved. [2]</p>
	<p></p> <p>Functional group isomerism</p>
<p style="text-align: right;"><b>[Total: 20m]</b></p>	

4	(a)	Limestone is mainly composed of calcite, $\text{CaCO}_3$ , and is usually white or transparent, shimmering crystals depending on how it is formed. It takes on a different colour when exposed to different impurities such as siderite, $\text{FeCO}_3$ .	
		(i)	Using information from the <i>Data Booklet</i> , suggest if calcite or siderite has a lower decomposition temperature.  [2]
			<p><b>Cationic radius: <math>\text{Fe}^{2+}</math> (0.076nm) &lt; <math>\text{Ca}^{2+}</math> (0.099nm)</b></p> <p><b>Charge density: <math>\text{Fe}^{2+}</math> &gt; <math>\text{Ca}^{2+}</math></b></p> <p><b>Polarising effect</b> on the anion: <b><math>\text{Fe}^{2+}</math> &gt; <math>\text{Ca}^{2+}</math></b></p> <p>Or</p> <p><b>Anion electron cloud distortion: <math>\text{Fe}^{2+}</math> &gt; <math>\text{Ca}^{2+}</math></b></p> <p><b>Less energy</b> is required to overcome the <b>C–O</b> for <b>siderite hence lower temperature</b> is required to decompose the compound.</p>
		(ii)	<p>Dolomitization is a process by which dolomite, <math>\text{CaMg}(\text{CO}_3)_2</math>, is formed when magnesium ions replaces calcium ions in calcite.</p> <p>When 1.000 g of an impure sample of dolomite was completely dissolved in excess hydrochloric acid, the carbon dioxide evolved was bubbled into aqueous calcium hydroxide where 0.80 g of white insoluble solid was isolated. Calculate the percentage purity of the dolomite.</p> <p>[2]</p>
			<p><math>\text{CaMg}(\text{CO}_3)_2 + 4\text{HCl} \rightarrow \text{CaCl}_2 + \text{MgCl}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O}</math></p> <p><math>\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}</math></p> <p>Amt of ppt = <math>0.80 / 100.1 = 0.007992</math> mol</p> <p>Amt of <math>\text{CO}_2</math> produced = 0.007992 mol</p> <p>Amt of dolomite = <math>0.007992 \div 2 = 0.003996</math> mol</p> <p>Mass of dolomite = <math>0.003996 \times 184.4 = 0.7369</math> g</p> <p>Percentage purity = <math>(0.7369/1) \times 100 = 73.7\%</math></p>
	(b)	<p>Stalagmites and stalactites in limestone caves are created when the calcite is dissolved in rain water and subsequently precipitated when the water drips off the ceiling of the cave to the cave floor.</p> <p>Dissolution of calcite occurs mainly via the following equilibrium:</p> $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \text{ ---- (1)}$ <p>However, it is also affected by the amount of atmospheric carbon dioxide present, and it can be represented via these four additional equilibria:</p> $\text{CO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) \text{ ---- (2)}$ $\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) \text{ ---- (3)}$ $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{aq}) \text{ ---- (4)}$ $\text{CO}_2(\text{aq}) \rightleftharpoons \text{CO}_2(\text{g}) \text{ ---- (5)}$	

		(i)	<p>Calculate the enthalpy change of solution of calcite using the information given below.</p> <table><tr><td></td><td><math>\Delta H^\circ_f / \text{kJ mol}^{-1}</math></td></tr><tr><td><math>\text{CaCO}_3 (\text{s})</math></td><td>-1206.9</td></tr><tr><td><math>\text{Ca}^{2+} (\text{aq})</math></td><td>-542.8</td></tr><tr><td><math>\text{CO}_3^{2-} (\text{aq})</math></td><td>-677.1</td></tr></table> <p>[1]</p>		$\Delta H^\circ_f / \text{kJ mol}^{-1}$	$\text{CaCO}_3 (\text{s})$	-1206.9	$\text{Ca}^{2+} (\text{aq})$	-542.8	$\text{CO}_3^{2-} (\text{aq})$	-677.1
	$\Delta H^\circ_f / \text{kJ mol}^{-1}$										
$\text{CaCO}_3 (\text{s})$	-1206.9										
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$\text{CO}_3^{2-} (\text{aq})$	-677.1										
			$\Delta H_{\text{sol}} = -542.8 - 677.1 - (-1206.9)$ $= \underline{\underline{-13.0 \text{ kJ mol}^{-1}}}$								
		(ii)	<p>Explain how the enthalpy change of solution of calcite would differ from siderite.</p> <p>[3]</p>								
			<p><b><u>Charge of <math>\text{Fe}^{2+}</math> and <math>\text{Ca}^{2+}</math> is the same</u></b> <b><u>Radii: <math>\text{Ca}^{2+} &gt; \text{Fe}^{2+}</math></u></b></p> <p><b><u><math> \Delta H_{\text{latt}} </math>: <math>\text{CaCO}_3 &lt; \text{FeCO}_3</math></u></b> <b><u>and <math> \Delta H_{\text{hyd}}(\text{cation}) </math>: <math>\text{Ca}^{2+} &lt; \text{Fe}^{2+}</math></u></b></p> <p>Due to the <b><u>large anionic radius</u></b>, the decrease in <math> \Delta H_{\text{latt}} </math> is <b><u>less significant</u></b> than the decrease in <math> \Delta H_{\text{hyd}}(\text{cation}) </math>.</p> <p><math>\Delta H_{\text{soln}}</math> of siderite would be <b><u>more exothermic</u></b>.</p>								
		(iii)	<p>Given that the enthalpy change of atomisation of calcium is <math>178.2 \text{ kJ mol}^{-1}</math>, and the lattice energy of calcite is <math>-2804 \text{ kJ mol}^{-1}</math>, calculate the enthalpy change of formation of gaseous carbonate ions using an energy level diagram and other relevant information from the <i>Data Booklet</i>.</p> <p>[3]</p>								



			<p>Energy / kJ mol<sup>-1</sup></p> <p>Ca<sup>2+</sup> (g) + C (s) + <math>\frac{3}{2}</math>O<sub>2</sub> (g) + 2e</p> <p>Ca<sup>2+</sup> (g) + CO<sub>3</sub><sup>2-</sup> (g)</p> <p>1<sup>st</sup> and 2<sup>nd</sup> I.E = 1740</p> <p>Ca (g) + C (s) + <math>\frac{3}{2}</math>O<sub>2</sub> (g)</p> <p>ΔH<sub>a</sub> = 178.2</p> <p>0</p> <p>Ca (s) + C (s) + <math>\frac{3}{2}</math>O<sub>2</sub> (g)</p> <p>L.E. = -2804</p> <p>CaCO<sub>3</sub> (s)</p> <p>ΔH<sub>f</sub> = -1206.9</p> <p>ΔH<sub>f</sub> = -1740 - 178.2 + (-1206.9) - (-2804)  = <b><u>-321.1 kJ mol<sup>-1</sup></u></b></p>
		(iv)	<p>With reference to the equilibria given, suggest what would happen to the calcite formations in limestone caves when the acidity of rain and river water increases due to pollutants.</p> <p style="text-align: right;">[3]</p>
			<p>The calcite formations will be <b><u>dissolved/destroyed</u></b>.</p> <p>By <b><u>LCP</u></b>, an <b><u>increase in [H<sup>+</sup>]</u></b> would cause the <b><u>position of equilibria of equilibria (2) to shift right</u></b> to <b><u>reduce [H<sup>+</sup>]</u></b>, favouring the production of HCO<sub>3</sub><sup>-</sup>.</p> <p>This then <b><u>causes [CO<sub>3</sub><sup>2-</sup>] in equilibrium 2 to decrease</u></b> and thus by <b><u>LCP</u></b>, the <b><u>position of equilibrium (1) would then shift right</u></b> to <b><u>increase [CO<sub>3</sub><sup>2-</sup>]</u></b>, <b><u>increasing the solubility of CaCO<sub>3</sub></u></b>.</p>

	(c)	<p>Limescale, which is primarily calcium carbonate is the off-white deposit that is commonly found in kettles. In addition to being unsightly and hard to clean, limescale impairs the operation of medical equipment.</p> <p>Ethanoic acid and glycolic acid can serve as good descaling agent and are used to remove the limescale.</p> <div style="text-align: center;">  <p>Glycolic acid</p> </div> <p>Both organic acids can be treated using the following steps to recover a carbonyl containing compound from limescale.</p> <p>Step 1: Heat the limescale with the organic acid to ensure all the limescale has reacted.</p> <p>Step 2: Evaporate the sample and collect the salt.</p> <p>Step 3: Heat the salt in a test-tube and allow to cool to room temperature. Calcium carbonate will be formed together with a liquid carbonyl containing compound.</p> <p>Step 4: Separate the calcium carbonate residue from the liquid carbonyl containing compound using vacuum filtration.</p>
	(i)	<p>Propose chemical test to differentiate ethanoic acid and glycolic acid in the school laboratory. You are to state clearly the reagents and condition used and the expected observation to be made. [2]</p>
		<p>Test: Add <math>\text{KMnO}_4</math> in dilute <math>\text{H}_2\text{SO}_4</math>, heat          Observation: Purple <math>\text{KMnO}_4</math> decolourised in glycolic acid but not ethanoic acid (Note: Glycolic acid will form <math>\text{CO}_2</math> and <math>\text{H}_2\text{O}</math> upon reaction with acidified <math>\text{KMnO}_4</math>, heat.)</p>
	(ii)	<p>Write a balanced equation, for the reaction of limescale and ethanoic acid. Include state symbols in your answer. [1]</p>
		<p><math>\text{CaCO}_3 (\text{s}) + 2\text{CH}_3\text{COOH} (\text{aq}) \rightarrow 2(\text{CH}_3\text{COO}^-)_2\text{Ca}^{2+}(\text{aq}) + \text{CO}_2 (\text{g}) + \text{H}_2\text{O}(\text{l})</math></p>
	(iii)	<p>With reference to structure and bonding, suggest why it is possible to isolate the salt via evaporation. [1]</p>
		<p>Evaporation technique is appropriate as the salt has a <b><u>much higher boiling point</u></b> than the water.</p> <p><i>The salt has a giant ionic structure with stronger electrostatic forces of attraction between the oppositely charged ions while water is a simple molecular structure with weaker intermolecular hydrogen bonding. Thus by heating the sample, only sufficient energy is supplied to cause the water molecule to evaporate leaving behind the salt.</i></p>

		(iv)	With reference to Step 3, suggest the structural formulae of the organic products formed when calcium ethanoate and calcium glycolate is heated in separate test-tubes. <span style="float: right;">[2]</span>
			<p>From calcium ethanoate:</p> $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{CH}_3 \end{array}$ <p>From calcium glycolate:</p> $\begin{array}{c} \text{OH} \quad \text{O} \quad \text{OH} \\   \quad \parallel \quad   \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \\   \quad \quad   \\ \text{H} \quad \quad \text{H} \end{array}$
			[Total: 20]

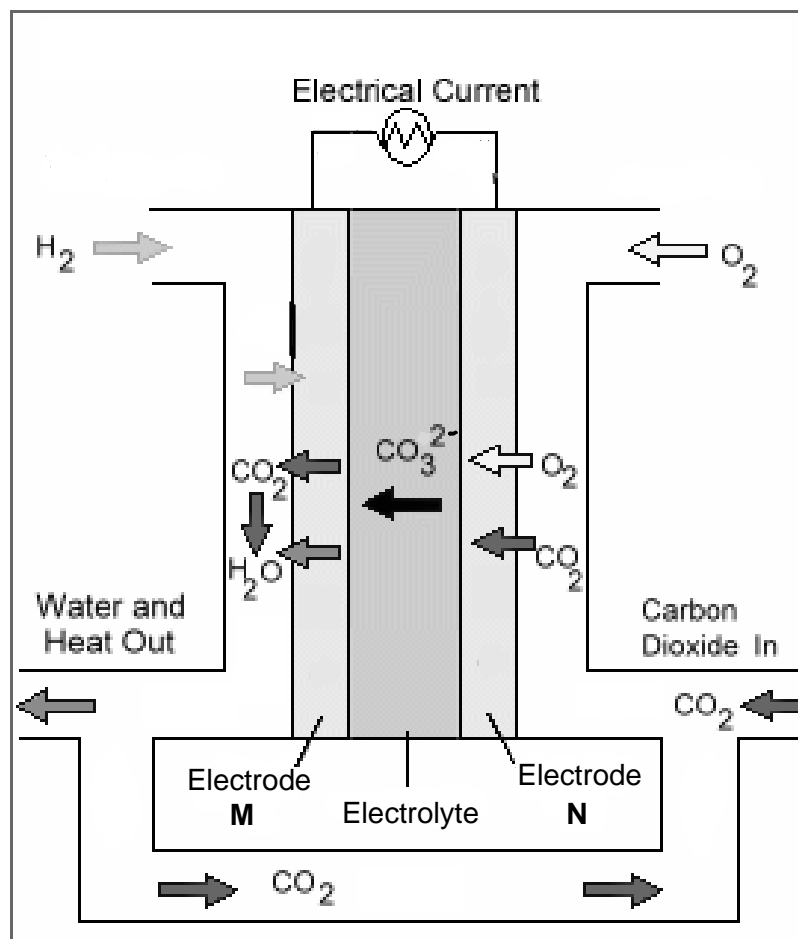
5	(a)	The following table shows some common oxidation numbers of selected metals.																														
		<table><tr><th>Metals</th><th colspan="3">Oxidation Numbers</th></tr><tr><td>Sc</td><td></td><td></td><td>+3</td></tr><tr><td>Ti</td><td></td><td></td><td>+3</td></tr><tr><td>V</td><td></td><td>+2</td><td>+3</td></tr><tr><td>Fe</td><td></td><td>+2</td><td>+3</td></tr><tr><td>Cu</td><td>+1</td><td>+2</td><td></td></tr><tr><td>Zn</td><td></td><td>+2</td><td></td></tr></table>			Metals	Oxidation Numbers			Sc			+3	Ti			+3	V		+2	+3	Fe		+2	+3	Cu	+1	+2		Zn		+2	
Metals	Oxidation Numbers																															
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		<b>Table 1</b>																														
	(i)	From <b>Table 1</b> , state all the ions that are colored. <span style="float:right">[1]</span>																														
		Ti <sup>3+</sup> , V <sup>2+</sup> , V <sup>3+</sup> , Fe <sup>2+</sup> , Fe <sup>3+</sup> , Cu <sup>2+</sup>																														
	(ii)	Using one of the ions stated in <b>(a)(i)</b> , explain why it is colored. <span style="float:right">[3]</span>																														
		Using Cu <sup>2+</sup> as example: <ul style="list-style-type: none"><li>▪ The <b>d orbitals</b> of Cu<sup>2+</sup> are <b>split into two levels by ligands</b>.</li><li>▪ The <b>d electron</b> undergoes <b>d-d transition</b> and is <b>promoted to a higher energy d orbital</b></li><li>▪ In the process, the d electron <b>absorbs certain wavelength of light energy</b> from the visible region of the electromagnetic spectrum and <b>transmits the remaining wavelength</b> which appears as the colour observed</li></ul>																														
	(iii)	When dilute aqueous ammonia is added to a solution that contains copper(II) ions, a pale blue precipitate is obtained. This precipitate dissolves to form a deep blue solution when excess ammonia is added.  Give an explanation for these observations using relevant equations. <span style="float:right">[3]</span>																														
		$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ $\text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightleftharpoons \text{Cu}(\text{OH})_2(\text{s}) \quad \text{Eqn (1)}$ <ul style="list-style-type: none"><li>○ When <b>dilute NH<sub>3</sub> is added</b> gradually, <b>[OH<sup>-</sup>] increases</b>.</li><li>○ <b>Ionic product of Cu(OH)<sub>2</sub> &gt; K<sub>sp</sub> of Cu(OH)<sub>2</sub></b> or</li><li>○ Pale blue precipitate of Cu(OH)<sub>2</sub> is formed.</li></ul> $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \quad \text{Eqn (2)}$ <p style="text-align: center;">deep blue</p> <ul style="list-style-type: none"><li>○ When excess NH<sub>3</sub> is added, <b>NH<sub>3</sub> ligands replace H<sub>2</sub>O ligands</b> to form the <b>more stable deep blue [Cu(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> complex</b>.</li><li>○ <b>[Cu<sup>2+</sup>] decreases</b> as it is used to form the complex.</li></ul>																														

		<ul style="list-style-type: none"> <li>○ The equilibrium position in Eqn (1) shifts to the <b>left</b> to <b>increase [Cu<sup>2+</sup>]</b>.</li> <li>○ Thus, the pale blue precipitate dissolves.</li> </ul>
	<b>(b)</b>	Iron by mass, is the most common element on Earth, forming much of Earth's outer and inner core. It forms compounds mainly in the +2 and +3 oxidation states. Iron and its compounds are widely used as catalyst.
	<b>(i)</b>	Suggest why iron has the ability to exist in variable oxidation states. [1]
		Iron which is a transition metals possess variable oxidation states due to the <b><u>small energy level difference between the 3d and 4s electrons</u></b> . This results in different numbers of 3d and 4s electrons lost to form stable ions and compounds of different oxidation states.
	<b>(ii)</b>	<p>Hydrogen peroxide decompose according to the following equation:</p> $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ <p>Iron(III) ions can be used to catalyse this decomposition. Using relevant data from the <i>Data Booklet</i>, suggest a mechanism for this catalysis, calculating the E<sup>θ</sup> values for each step. [3]</p>
		<p>The relevant half equations are :</p> $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$ $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$ <p>Step 1: <math>\text{H}_2\text{O}_2 + 2\text{Fe}^{3+} \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{Fe}^{2+}</math></p> $E^\theta_{\text{cell}} = 0.77 - 0.68 = +0.09 \text{ V}$ <p>Step II: <math>\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{Fe}^{2+} \rightarrow 2\text{H}_2\text{O} + 2\text{Fe}^{3+}</math></p> $E^\theta_{\text{cell}} = 1.77 - 0.77 = +1.00 \text{ V}$

		(iii)	<p>The following diagram shows the reactions of some iron compounds.</p> <pre> graph TD     A[Fe<sup>2+</sup>(aq) green] -- "Step I Cl<sub>2</sub>" --&gt; B[Yellow solution]     A -- "Step II" --&gt; C[[Fe(CN)<sub>6</sub>]<sup>4-</sup>(aq)]     B -- Mg --&gt; D[gas J]     C -- Fe<sup>3+</sup> --&gt; E[Deep blue precipitate, K]           </pre>
			<p>Name the type of reaction in <b>Step II</b> and identify gas <b>J</b> and precipitate <b>K</b>. [3]</p>
			<p><b>Step II:</b> ligand exchange  <b>J:</b> H<sub>2</sub>  <b>K:</b> Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub> (note cation: Fe<sup>3+</sup>, anion: [Fe(CN)<sub>6</sub>]<sup>4-</sup>)</p>

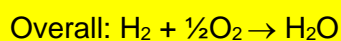
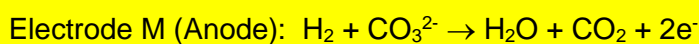
- (c) Molten carbonate fuel cells (MCFCs) are high-temperature fuel cells that use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic matrix.

The following diagram show a MCFC:



At the electrode **N**, carbon dioxide is reacted with oxygen to form carbonate as the only product. The carbonate ions move towards electrode **M** and react with hydrogen to form carbon dioxide and water.

- (i) Write half-equations for the reactions taking place at the electrodes of the fuel cell and hence, construct the overall equation for the fuel cell reaction. [3]



		(ii)	State the direction of the electron flow with respect to the electrode. [1]
			Electrons flow from electrode <b>M</b> to <b>N</b> .
		(iii)	Besides being high in efficiency and high operating cost, suggest one advantage and disadvantage of the molten carbonate fuel cell. [2]
			<p>Advantage: The <u>product is clean</u> and it <u>does not generate greenhouse gas</u>.</p> <p>Disadvantage: <u>High temperatures</u> at which these cells operate and the <u>corrosive electrolyte</u> used accelerate component breakdown and corrosion, <u>decreasing cell life</u>.</p>
			[Total: 20]

END