



SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 1

CHEMISTRY
Preliminary Examination
Paper 2

8872/02
19 September 2016
2 hours

Additional Materials: Data Booklet
Writing papers

READ THESE INSTRUCTIONS FIRST

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

The use of an approved scientific calculator is expected, where appropriate.

Section A

Answer **all** the questions.

Section B

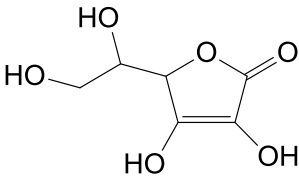
Answer **two** questions on separate answer paper.

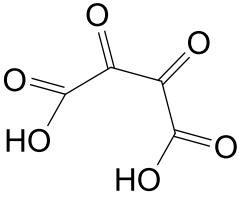
At the end of the examination, fasten all your work securely together. The number of marks is given in brackets [] at the end of each question or part question.

Suggested Solutions

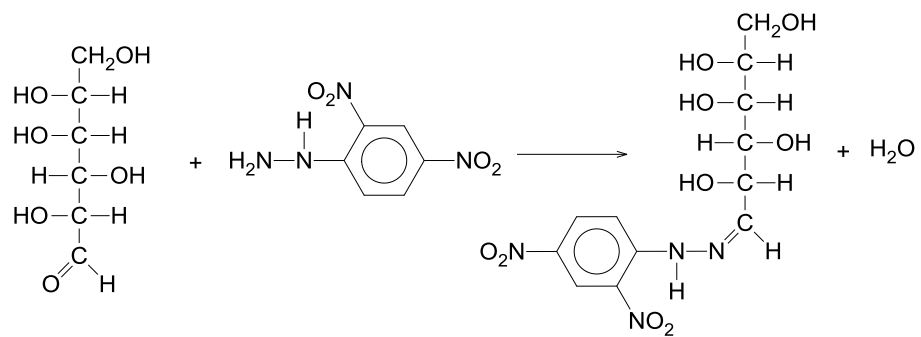
Section A

Answer **all** the questions in the spaces provided.

1	<p>Ascorbic acid is a naturally occurring organic compound with antioxidant properties. It dissolves well in water and is effective in the prevention of scurvy.</p> <div style="text-align: center;">  <p>Ascorbic acid</p> </div> <p>A student analysed the ascorbic acid content found in Vitamin-C tablets using the following experimental procedure.</p> <p>Step 1: He prepared a 250 cm³ mixture containing the following chemicals:</p> <ul style="list-style-type: none"> - Sulfuric acid, H₂SO₄ - Potassium iodide, KI - 0.664 g Potassium iodate, KIO₃ <p>This reaction mixture generates iodine which is essential for the analysis of ascorbic acid. The reaction is illustrated below.</p> $\text{KIO}_3 + 5\text{KI} + 6\text{H}^+ \rightarrow 3\text{I}_2 + 6\text{K}^+ + 3\text{H}_2\text{O}$
(a)	<p>Calculate the total number of moles of iodine liberated by the 250 cm³ reaction mixture.</p> <p style="text-align: right;">[2]</p>
	<p>Amount of KIO₃ = $\frac{0.664}{39.1+127+48} = \frac{0.664}{214.1} = 0.003101 \text{ mol}$</p> <p>Amount of iodine liberated in 250 cm³ = 0.003101 x 3 = 0.009304 mol</p>
	<p>Step 2: The student then separately weighted 6.863 g of Vitamin-C tablets and placed them into the 250 cm³ reaction mixture from step 1. The liberated iodine reacted with the ascorbic acid as follow.</p> $\text{C}_6\text{H}_8\text{O}_6 \text{ (ascorbic acid)} + \text{I}_2 \rightarrow \text{C}_6\text{H}_6\text{O}_6 \text{ (dehydroascorbic acid)} + 2\text{I}^- + 2\text{H}^+$ <p>Step 3: The student then pipetted 25.0 cm³ of the reaction mixture from step 2 before proceeding with iodometric titration to investigate the amount of iodine which did not react with the ascorbic acid.</p> $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$ <p>He found out that 9.60 cm³ of 0.0787 mol dm⁻³ sodium thiosulfate was required for the iodometric titration.</p>

	(b)	(i)	Using the information provided, calculate the number of moles of iodine that has reacted with the sodium thiosulfate in the 25.0 cm ³ sample in step 3 . [1]
			Amount of Na ₂ S ₂ O ₃ = $\frac{9.6}{1000} \times 0.0787 = 0.0007555$ mol Amount of unreacted iodine in 25 cm ³ = $0.0007555 \div 2 = 0.0003778$ mol
		(ii)	Hence, determine the amount of iodine that has reacted with ascorbic acid. [1]
			Amount of unreacted iodine in 250 cm ³ = $0.0003778 \times \frac{250}{25} = 0.003778$ mol Amount of iodine reacted with ascorbic acid = $0.009304 - 0.003778 = 0.005526$ mol
		(iii)	Using your answer in (b)(ii) , determine the percentage by mass of ascorbic acid in the Vitamin-C tablet. [1]
			Amount of ascorbic acid = 0.005526 mol Mass of ascorbic acid = $0.005526 \times 176 = 0.9726$ g Percentage by mass = $\frac{0.9726}{6.863} \times 100 = 14.2\%$
	(c)		When hot acidified potassium manganate(VII) is added to ascorbic acid, acidic hydrolysis and oxidation occur simultaneously. Draw all carbon-containing products. [2]
			 and CO ₂

	(d)	<p>The following reaction scheme shows the outdated but historically important synthesis of ascorbic acid from glucose</p> <div style="text-align: center;"> <p>glucose $\xrightarrow{\text{step 1}}$ Compound A $\xrightarrow{\text{step 2}}$ Compound B</p> <p style="text-align: right;">step 3 (O₂ & Pt)</p> <p style="text-align: right;">Compound C</p> <p style="text-align: center;">- H₂O + H₂O</p> </div>
	(i)	<p>Suggest the reagents and condition required to convert glucose to compound A.</p> <p style="text-align: right;">[1]</p>
		<p>LiAlH₄ in dry ether, room temperature or NaBH₄ in ethanol, room temperature or H₂ gas, Ni, heat or H₂ gas, Pt, r.t.p.</p>
	(ii)	<p>State the type of reaction that occur in step 2.</p> <p style="text-align: right;">[1]</p>
		<p>Oxidation</p>

		(iii)	State the functional group that is present in glucose and compound B which is not present in compound A . Hence, with an aid of a chemical equation, suggest how this functional group can be positively identified. (You may use either glucose or compound B for the equation.) [4]
			<p>Carbonyl compound To positively test for carbonyl compound, use 2,4-DNPH Orange ppt will be observed.</p> 
		(iv)	Propose a simple test-tube reaction to differentiate compound B and C . [2]
			<p>Test: Add sodium carbonate to the test tube containing the compound separately. [***(<i>optional</i>) Bubble the gas produced into a test tube of Ca(OH)_2.] Observation: Effervescence will be observed for compound C not B. [***(<i>optional</i>) white ppt formed in Ca(OH)_2.]</p>
		(v)	Propose a chemical test to differentiate compound B and glucose. [2]
			<p>Use Tollen's reagent Silver mirror will be observed in glucose but not in compound B</p> <p>OR</p> <p>Use Fehling's reagent Reddish brown ppt observed in glucose but not in compound B.</p>
			[Total: 17]

2	(a)	Carboxylic acid and alcohol react together in the presence of sulfuric acid to produce ester. The following equilibrium will be established. $\text{RCOOH (l)} + \text{R'OH (l)} \rightleftharpoons \text{RCOOR' (l)} + \text{H}_2\text{O (l)}$																						
	(i)	Write an expression for the equilibrium constant, K_c , for the reaction between alcohol and carboxylic acid.																						
		$K_c = \frac{[\text{RCOOR'}][\text{H}_2\text{O}]}{[\text{RCOOH}][\text{R'OH}]}$																						
	(ii)	State Le Chatelier's Principle and suggest how it can be used to predict the effect of increasing concentration of RCOOH on the equilibrium concentration of RCOOR'.																						
		Le Chatelier's Principle states that when a system in equilibrium is disturbed , the system will react to counteract the effect of the change until a new equilibrium is reached. When [RCOOH] is increased, by Le Chatelier's Principle, the position of equilibrium shifts to the right to counteract the increase in the RCOOH. Hence, [RCOOR'] will increase																						
	(iii)	An alcohol of molecular formula $\text{C}_3\text{H}_8\text{O}$ can react with ethanoic acid to generate the sweet-smelling compound. Draw two possible structures for the alcohol and state the type of isomerism involved.																						
		<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;"> $\begin{array}{c} \text{OH} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{H} \end{array}$ </div> <div style="margin: 0 10px;">and</div> <div style="text-align: center;"> $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{OH} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ </div> </div> <p>Positional isomerism (Do not accept structural isomerism)</p>																						
	(iv)	3.00 moles of ethanoic acid are mixed with 3.00 moles of ethanol. When equilibrium was established, 2.33 moles of ethyl ethanoate are present. The total volume of the reaction mixtures is 1.5 dm^3 . Using the information provided, calculate a value for K_c .																						
		<table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <tr> <td></td><td>CH_3COOH</td><td>$\text{C}_2\text{H}_5\text{OH}$</td><td>$\text{CH}_3\text{COOC}_2\text{H}_5$</td><td>$\text{H}_2\text{O}$</td></tr> <tr> <td>Initial</td><td>3</td><td>3</td><td>0</td><td>0</td></tr> <tr> <td>Change</td><td>-2.33</td><td>-2.33</td><td>2.33</td><td>2.33</td></tr> <tr> <td>Eqm</td><td>0.67</td><td>0.67</td><td>2.33</td><td>2.33</td></tr> </table>				CH_3COOH	$\text{C}_2\text{H}_5\text{OH}$	$\text{CH}_3\text{COOC}_2\text{H}_5$	H_2O	Initial	3	3	0	0	Change	-2.33	-2.33	2.33	2.33	Eqm	0.67	0.67	2.33	2.33
	CH_3COOH	$\text{C}_2\text{H}_5\text{OH}$	$\text{CH}_3\text{COOC}_2\text{H}_5$	H_2O																				
Initial	3	3	0	0																				
Change	-2.33	-2.33	2.33	2.33																				
Eqm	0.67	0.67	2.33	2.33																				

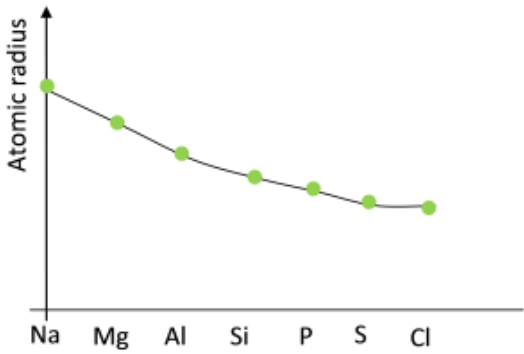
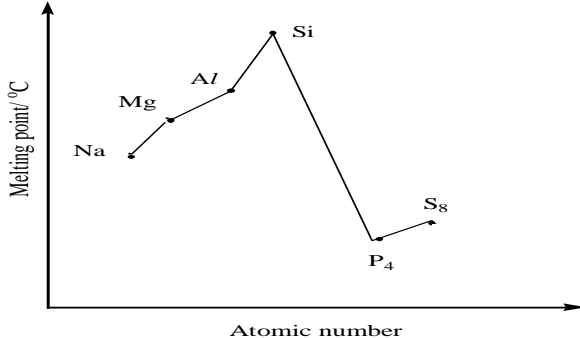
			$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{\left[\frac{2.33}{1.5}\right]\left[\frac{2.33}{1.5}\right]}{\left[\frac{0.67}{1.5}\right]\left[\frac{0.67}{1.5}\right]} = 12.1$										
		(v)	<p>Given the enthalpy change of formation of the following molecules, calculate the enthalpy change of reaction when ethanoic acid and ethanol undergo esterification process.</p> <table><tr><th>Molecules</th><th>$\Delta H_f^\circ / \text{kJ mol}^{-1}$</th></tr><tr><td>Ethanoic acid</td><td>-487</td></tr><tr><td>Ethanol</td><td>-287</td></tr><tr><td>Ethyl ethanoate</td><td>-481</td></tr><tr><td>Water</td><td>-286</td></tr></table> <p style="text-align: right;">[2]</p>	Molecules	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	Ethanoic acid	-487	Ethanol	-287	Ethyl ethanoate	-481	Water	-286
Molecules	$\Delta H_f^\circ / \text{kJ mol}^{-1}$												
Ethanoic acid	-487												
Ethanol	-287												
Ethyl ethanoate	-481												
Water	-286												
			<p style="text-align: center;">$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$</p> <p>Using formula method $\Delta H^\circ = \Delta H_f^\circ(\text{products}) - \Delta H_f^\circ(\text{reactants})$ $= \{\Delta H_f^\circ(\text{ethyl ethanoate}) + \Delta H_f^\circ(\text{water})\} - \{\Delta H_f^\circ(\text{ethanoic acid}) + \Delta H_f^\circ(\text{ethanol})\}$ $\Delta H = (-481 - 286) - (-487 - 287)$ $= +7 \text{ kJ mol}^{-1}$</p>										
		(vi)	<p>Hence, state the enthalpy change of reaction when ethyl ethanoate undergo acidic hydrolysis</p> <p style="text-align: right;">[1]</p>										
			- 7 kJ mol ⁻¹										
		(vii)	<p>Construct a reaction pathway diagram illustrating the acidic hydrolysis of ethyl ethanoate.</p> <p style="text-align: right;">[2].</p>										
			<p style="text-align: center;">Energy ↑</p> <p style="text-align: center;">Ethyl ethanoate</p> <p style="text-align: center;">E_a</p> <p style="text-align: center;">ΔH = - 7 kJ mol⁻¹</p> <p style="text-align: center;">Ethanoic acid + ethanol</p> <p style="text-align: center;">Reaction pathway →</p>										

	(b)	(i)	Comment on the acidity between ethanoic acid and chloroethanoic acid. [3]
			<p><u>Chloroethanoic acid</u> is <u>more acidic</u> than <u>ethanoic acid</u>.</p> <p>Presence of a <u>electron-withdrawing chlorine</u> in chloroethanoic acid.</p> <p>The <u>negative charge</u> on the <u>conjugate base</u> of chloroethanoic acid is <u>dispered to a greater</u> extent as compared to that of ethanoic acid.</p> <p>Hence the conjugate base of chloroethanoic is <u>stablised to a greater extent</u> resulting in more H^+ being dissociated.</p>
		(ii)	State the reagent and condtion required for the formation of chloroethanoic acid from ethanoic acid.
			Limited amount of chlorine gas, u.v. light
			[Total: 17]

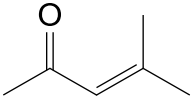
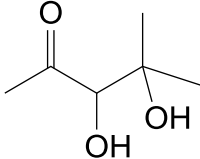
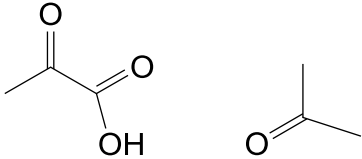
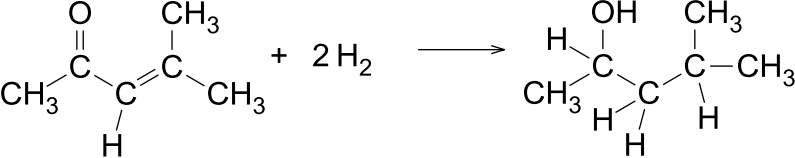
3	(a)	(i)	Write equations to show the reaction of the elements magnesium and phosphorous with excess oxygen.
			$2 \text{Mg (s)} + \text{O}_2 \text{(g)} \rightarrow 2 \text{MgO (s)}$ $\text{P}_4 \text{(s)} + 5 \text{O}_2 \text{(g)} \rightarrow \text{P}_4\text{O}_{10} \text{(s)}$
		(ii)	State the types of structure present in the oxides of magnesium, silicon and phosphorus.
			oxide of magnesium: giant ionic lattice structure oxide of silicon: giant covalent structure oxides of phosphorus: simple molecular structure
		(iii)	Suggest if each of the oxides of magnesium, silicon and phosphorus dissolves in water or undergoes a reaction with water. Write equation, if any, to support your answer.
			MgO react less vigorously with water to form basic solution $\text{MgO(s)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{Mg(OH)}_2\text{(aq)}$ SiO ₂ does not react with water P ₄ O ₁₀ reacts readily with water $\text{P}_4\text{O}_{10}\text{(s)} + 6\text{H}_2\text{O(l)} \rightarrow 4 \text{H}_3\text{PO}_4\text{(aq)}$
			[Total: 6]

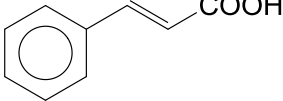
Section B

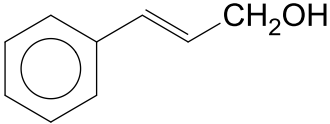
Answer **two** questions from this section on separate answer paper.

4	(a)	Sodium, magnesium, aluminium, silicon, phosphorus and sulfur are elements in Period 3 of the Periodic Table. Sketch and explain the trend for the following:	
	(i)	Atomic radius	[2]
		 <p>Na Mg Al Si P S Cl</p> <ul style="list-style-type: none"> • Across the period, valence electrons are added to the same valence shell thus the shielding effect is similar. • The number of protons increases hence causing an increase in nuclear charge. • Electrostatic forces of attraction between the nucleus and electrons increases thus pulling the electrons closer to the nucleus. 	
	(ii)	Melting point	[8]
		 <p>Melting point/°C</p> <p>Na Mg Al Si P₄ S₈</p> <p>Atomic number</p> <ul style="list-style-type: none"> - Melting point increases from Na to Al. - Number of valence electrons contributed per atom for metallic bonding increases from Na to Al. - In addition, cationic radii decrease across the metals in a period, leading to stronger electrostatic forces of attraction between cations and sea of delocalised electrons. - Therefore, metallic bonds strength progressively increase across the period among the metals. - Si has a very high melting point as it has a giant molecular structure. - Very large amount of energy required to overcome the extensive 	

		<p><u>covalent bonds</u> between atoms in the <u>three dimensional network structure</u></p> <ul style="list-style-type: none"> - <u>S₈ and P₄ have simple molecular structure</u> and thus <u>small amount of energy is required</u> to overcome the <u>weaker instantaneous dipole-induced dipole interaction</u> resulting in lower melting point than Na to Si. - However, <u>melting point of S₈ > P₄</u> - <u>Number of electrons</u> of S₈ > P₄ - The greater the number of electrons in a molecule, the greater unsymmetrical distribution of the shared electron cloud (i.e. greater dipole moment). - Hence, the <u>extensiveness of intermolecular van der Waals' forces of attraction</u> of S₈ > P₄ - The amount of <u>energy</u> required to overcome the stronger intermolecular van der Waals forces of S₈ > P₄
	(b)	<p>Using equations, suggest what will happen when aluminium oxide and phosphorus pentoxide is placed in separated test-tubes containing aqueous sodium hydroxide and hydrochloric acid.</p> <p style="text-align: right;">[3]</p>
		<p> $Al_2O_3(s) + 6 HCl(aq) \rightarrow 2 AlCl_3(aq) + 3 H_2O(l)$ $Al_2O_3(s) + 2 NaOH(aq) + 3 H_2O(l) \rightarrow 2 Na[Al(OH)_4](aq)$ </p> <p>P₄O₁₀ do not react with HCl</p> <p> $P_4O_{10}(s) + 12 NaOH(aq) \rightarrow 4 Na_3PO_4(aq) + 6 H_2O(l)$ </p>
	(c)	<p>Aluminium chloride is an inorganic substance that can be used in organic chemistry. Suggest, with an equation, the pH of the solution when aluminium chloride undergo hydrolysis with water.</p> <p style="text-align: right;">[2]</p>
		<p>pH = 3</p> <p> $AlCl_3 + 6 H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3 Cl^-$ $[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H^+$ </p>

(d)	<p>Compound E is an intermediate use in the synthesis of MIBK which is commonly found in paint solvent.</p> <div style="text-align: center;">  <p>Compound E</p> </div> <p>Draw the structural formula of the products form when compound E undergo reaction with</p>
(i)	<p>Cold alkaline potassium manganate(VII) [1]</p>
	<div style="text-align: center;">  </div>
(ii)	<p>Hot acidified potassium manganate(VII) [2]</p>
	<div style="text-align: center;">  </div>
(e) (i)	<p>Write a balanced chemical equation illustrating the reduction process when hydrogen gas is bubbled into compound E.</p>
	<div style="text-align: center;">  </div>
(ii)	<p>Using relevant data from the <i>Data Booklet</i>, determine the enthalpy change of reaction for the reduction process in (e)(i).</p>
	$\Delta H^\circ = \sum BE \text{ (rxts)} - \sum BE \text{ (pds)}$ $\Delta H^\circ = [BE(C=O) + BE(C=C) + 2BE(H-H)] - [BE(C-O) + BE(C-C) + 3BE(C-H) + BE(O-H)]$ $= [740 + 610 + 2(436)] - [360 + 350 + 3(410) + 460]$ $= -178 \text{ kJ mol}^{-1}$ <p style="text-align: right;">[Total: 20]</p>

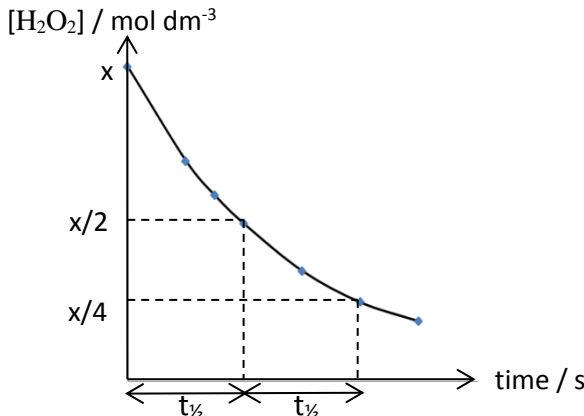
5	(a)	<p>Cinnamic acid has a honey-like odour and is obtained from the oil of cinnamon. It has a pK_a of 4.44.</p> <div style="text-align: center;">  <p><i>cinnamic acid</i></p> </div>
	(i)	<p>Calculate the pH of a 0.1 mol dm^{-3} solution of cinnamic acid. [2]</p> <p> $pK_a = 4.44$ $K_a = 10^{-4.44} = 3.631 \times 10^{-5}$ $K_a = \frac{[H^+][RCOO^-]}{[RCOOH]}$ $[H^+] = \sqrt{3.631 \times 10^{-5} \times 0.1} = 1.905 \times 10^{-3}$ $pH = -\lg(1.905 \times 10^{-3})$ $= \underline{2.72}$ </p>
	(ii)	<p>Explain with the aid of two balanced equations, how cinnamic acid and sodium cinnamate, acts as a buffer solution. [You may represent the formula of cinnamic acid by $RCOOH$.]</p> <p>Upon addition of <u>small amount</u> of H^+, $H^+ + RCOO^- \rightarrow RCOOH$</p> <p>The added <u>$H^+$ is removed as $RCOOH$</u> and <u>pH remains fairly constant</u></p> <p>Upon addition of <u>small amount</u> of OH^-, $OH^- + RCOOH \rightarrow H_2O + RCOO^-$ The added <u>OH^- is removed as $H_2O + RCOO^-$</u> and <u>pH remains fairly constant</u></p>
		[2]

	(b)	<p>A student carried out an experiment to measure the standard enthalpy change of neutralisation between cinnamic acid and sodium hydroxide.</p> <p>The student added 25.0 cm³ of 2.5 mol dm⁻³ cinnamic acid to 40.0 cm³ of 1.5 mol dm⁻³ sodium hydroxide in a polystyrene cup. The maximum temperature rise recorded is 10.4 °C.</p> <p>Given that the neutralisation process was 85 % efficient, calculate the standard enthalpy change of neutralisation for the reaction between cinnamic acid and sodium hydroxide.</p>
		<p>Amount of cinnamic acid = $\frac{25}{1000} \times 2.5 = 0.0625 \text{ mol}$</p> <p>Amount of NaOH = $\frac{40}{1000} \times 1.5 = 0.06 \text{ mol}$</p> <p>Amount of H₂O = 0.06 mol</p> <p>Heat absorbed by the water = $mc\Delta T = 65 \times 4.18 \times 10.4 = 2825.68 \text{ J}$</p> <p>Actual heat given out = $\frac{100}{85} \times 2825.68 = 3324.3 \text{ J}$</p> <p>$\Delta H_n = -\frac{Q}{n_{H_2O}} = \frac{3324.3}{0.06} = \underline{\underline{-55.4 \text{ kJ mol}^{-1}}}$</p>
		[2]
	(c)	Lithium aluminium hydride is a useful reducing agent in organic chemistry. It can be used to reduce cinnamic acid.
	(i)	Draw the structure of the product formed from the reduction of cinnamic acid by LiAlH ₄ .
		

		(ii)	The following data will be useful in this question.										
			<table border="1"> <tr> <td></td> <td>kJ mol^{-1}</td> </tr> <tr> <td>$\text{Li (s)} \rightarrow \text{Li (g)}$</td> <td>+159.5</td> </tr> <tr> <td>$\text{Al (s)} \rightarrow \text{Al (g)}$</td> <td>+314</td> </tr> <tr> <td>$\text{Al (g)} + 4\text{H (g)} + \text{e}^- \rightarrow \text{AlH}_4^- \text{ (g)}$</td> <td>-1341</td> </tr> <tr> <td>$\text{Li}^+ \text{ (g)} + \text{AlH}_4^- \text{ (g)} \rightarrow \text{LiAlH}_4 \text{ (s)}$</td> <td>-640</td> </tr> </table>		kJ mol^{-1}	$\text{Li (s)} \rightarrow \text{Li (g)}$	+159.5	$\text{Al (s)} \rightarrow \text{Al (g)}$	+314	$\text{Al (g)} + 4\text{H (g)} + \text{e}^- \rightarrow \text{AlH}_4^- \text{ (g)}$	-1341	$\text{Li}^+ \text{ (g)} + \text{AlH}_4^- \text{ (g)} \rightarrow \text{LiAlH}_4 \text{ (s)}$	-640
				kJ mol^{-1}									
			$\text{Li (s)} \rightarrow \text{Li (g)}$	+159.5									
			$\text{Al (s)} \rightarrow \text{Al (g)}$	+314									
$\text{Al (g)} + 4\text{H (g)} + \text{e}^- \rightarrow \text{AlH}_4^- \text{ (g)}$	-1341												
$\text{Li}^+ \text{ (g)} + \text{AlH}_4^- \text{ (g)} \rightarrow \text{LiAlH}_4 \text{ (s)}$	-640												
The enthalpy change of formation of LiAlH_4 can be found using the energy cycle below.													
			In the energy cycle above, what enthalpy change is represented by ΔH_7 ?										
			<u>Lattice energy of $\text{LiAlH}_4 \text{ (s)}$.</u>										
		(iii)	Use the <i>Data Booklet</i> to obtain the value of the enthalpy change for ΔH_4 and ΔH_5 .										
			$\Delta H_4 = \textbf{+436 kJ mol}^{-1}$										
			$\Delta H_5 = \textbf{+519 kJ mol}^{-1}$										
		(iv)	Use the energy cycle to calculate the enthalpy change of formation of LiAlH_4 .										
			$\Delta H_1 = +159.5 + 314 + 2(436) + 519 - 1341 - 640 = \textbf{-116.5 kJ mol}^{-1}$										
			[4]										

	<p>(d) An organic compound F has the molecular formula C_4H_7Cl.</p> <p>F is known to react with the following inorganic chemicals to generate other organic substances.</p> <p>(1) Hot alcoholic potassium hydroxide to form compound G, C_4H_6. (2) Steam in the presence of acid catalyst to generate compound H, C_4H_9C/O.</p> <p>When compound G is reacted with hot acidified potassium manganate(VII), only carbon dioxide and water are produced.</p> <p>Compound H is known to undergo oxidation with acidified potassium dichromate(VI) to produce compound L, C_4H_7C/O.</p> <p>Compound H and L both produce compound K, $C_3H_6O_3$ when heated with sodium hydroxide followed by aqueous iodine with subsequent acidification with dilute hydrochloric acid.</p> <p>Deduce the identities of F, G, H, L and K.</p>										
	<div style="text-align: right;">[9]</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> F reacts with hot alcoholic potassium hydroxide to form compound G, C_4H_6 </td><td style="width: 50%; padding: 5px;"> F undergoes <u>elimination</u> G contains <u>alkene</u> </td></tr> <tr> <td style="padding: 5px;"> F reacts with steam in the presence of acid catalyst to generate compound H, C_4H_9C/O </td><td style="padding: 5px;"> F undergoes <u>electrophilic addition</u>. F contains <u>alkene</u> </td></tr> <tr> <td style="padding: 5px;"> G reacted with hot acidified $KMnO_4$ forming only CO_2 and water </td><td style="padding: 5px;"> G undergoes <u>oxidation</u> G contains <u>terminal $C=C$</u> </td></tr> <tr> <td style="padding: 5px;"> Compound H known to undergo oxidation with acidified potassium dichromate(VI) to produce compound L </td><td style="padding: 5px;"> Compound H contains <u>secondary alcohol</u> as it oxidises to form a compound with one 'O' atom. Compound L contains <u>ketone</u> </td></tr> <tr> <td style="padding: 5px;"> Compound H and L both produces compound K, $C_3H_6O_3$ when reacted with warm sodium hydroxide followed by aqueous iodine with subsequent acidification with dilute hydrochloric acid </td><td style="padding: 5px;"> H and L undergo <u>nucleophilic substitution</u> with NaOH When reacted with aq iodine, mild <u>oxidation</u> occur. <div style="text-align: center;"> $\begin{array}{c} H \\ \\ -C-OH \\ \\ CH_3 \end{array}$ </div> H contains <div style="text-align: center;"> $\begin{array}{c} O \\ \\ -C-CH_3 \end{array}$ </div> L contains </td></tr> </table>	F reacts with hot alcoholic potassium hydroxide to form compound G , C_4H_6	F undergoes <u>elimination</u> G contains <u>alkene</u>	F reacts with steam in the presence of acid catalyst to generate compound H , C_4H_9C/O	F undergoes <u>electrophilic addition</u> . F contains <u>alkene</u>	G reacted with hot acidified $KMnO_4$ forming only CO_2 and water	G undergoes <u>oxidation</u> G contains <u>terminal $C=C$</u>	Compound H known to undergo oxidation with acidified potassium dichromate(VI) to produce compound L	Compound H contains <u>secondary alcohol</u> as it oxidises to form a compound with one 'O' atom. Compound L contains <u>ketone</u>	Compound H and L both produces compound K , $C_3H_6O_3$ when reacted with warm sodium hydroxide followed by aqueous iodine with subsequent acidification with dilute hydrochloric acid	H and L undergo <u>nucleophilic substitution</u> with NaOH When reacted with aq iodine, mild <u>oxidation</u> occur. <div style="text-align: center;"> $\begin{array}{c} H \\ \\ -C-OH \\ \\ CH_3 \end{array}$ </div> H contains <div style="text-align: center;"> $\begin{array}{c} O \\ \\ -C-CH_3 \end{array}$ </div> L contains
F reacts with hot alcoholic potassium hydroxide to form compound G , C_4H_6	F undergoes <u>elimination</u> G contains <u>alkene</u>										
F reacts with steam in the presence of acid catalyst to generate compound H , C_4H_9C/O	F undergoes <u>electrophilic addition</u> . F contains <u>alkene</u>										
G reacted with hot acidified $KMnO_4$ forming only CO_2 and water	G undergoes <u>oxidation</u> G contains <u>terminal $C=C$</u>										
Compound H known to undergo oxidation with acidified potassium dichromate(VI) to produce compound L	Compound H contains <u>secondary alcohol</u> as it oxidises to form a compound with one 'O' atom. Compound L contains <u>ketone</u>										
Compound H and L both produces compound K , $C_3H_6O_3$ when reacted with warm sodium hydroxide followed by aqueous iodine with subsequent acidification with dilute hydrochloric acid	H and L undergo <u>nucleophilic substitution</u> with NaOH When reacted with aq iodine, mild <u>oxidation</u> occur. <div style="text-align: center;"> $\begin{array}{c} H \\ \\ -C-OH \\ \\ CH_3 \end{array}$ </div> H contains <div style="text-align: center;"> $\begin{array}{c} O \\ \\ -C-CH_3 \end{array}$ </div> L contains										

			<p>F:</p> $ \begin{array}{ccccccc} & & \text{H} & \text{H} & \text{H} & & \\ & & & & & & \\ \text{H} & & \text{C} = \text{C} & - \text{C} & - \text{C} & - \text{Cl} \\ & & & & & & \\ \text{H} & & & \text{H} & \text{H} & & \end{array} $ <p>G:</p> $ \begin{array}{ccccccc} & & \text{H} & & \text{H} & & \\ & & & & & & \\ \text{H} & & \text{C} = \text{C} & - \text{C} = \text{C} & & \text{H} \\ & & & & & & \\ \text{H} & & & & & & \end{array} $ <p>L:</p> $ \begin{array}{ccccccc} & & \text{H} & \text{O} & \text{H} & \text{H} & \\ & & & & & & \\ \text{H} & - & \text{C} & - \text{C} & - \text{C} & - \text{C} & - \text{Cl} \\ & & & & & & \\ & & \text{H} & & \text{H} & \text{H} & \end{array} $ <p>H:</p> $ \begin{array}{ccccccc} & & \text{H} & \text{H} & \text{H} & \text{H} & \\ & & & & & & \\ \text{H} & - & \text{C} & - \text{C} & - \text{C} & - \text{C} & - \text{Cl} \\ & & & & & & \\ & & \text{H} & \text{OH} & \text{H} & \text{H} & \end{array} $ <p>K:</p> $ \begin{array}{ccccccc} & & \text{O} & \text{H} & \text{H} & & \\ & & & & & & \\ \text{HO} & - & \text{C} & - \text{C} & - \text{C} & - \text{OH} \\ & & & & & & \\ & & & \text{H} & \text{H} & & \end{array} $
			[Total: 20]

6	(a)	<p>Pure hydrogen peroxide, H_2O_2, was long believed to be unstable. Its decomposition follows a first order reaction.</p> $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$
	(i)	<p>Sketch a graph of $[\text{H}_2\text{O}_2]$ against time and use your graph to show clearly how you could determine the order of reaction with respect to H_2O_2. [2]</p>
		
		<p><i>Marker's comment</i> Many candidates understood that they need to draw a curve indicating at two constant half-lives with clearly labelled axes and annotations.</p>
	(ii)	<p>As H_2O_2 decomposes slowly at room temperature, catalysts such as manganese(IV) oxide are often added. Explain the effect of a catalyst on the rate constant for this reaction. [2]</p>
		<p>The rate constant will increase.</p> <p><u>Addition of catalyst will result in increase in rate despite concentrations of reactants remaining the same</u>, thus the value of k must have increased.</p> <p>OR</p> <p>Using Arrhenius equation, <u>$k = A e^{-E_a/RT}$</u>, if <u>activation energy, E_a, decreases, k will increase</u>. (not in syllabus)</p>
		<p><i>Marker's comment</i> Many candidates has the misconception that rate constant is only affected by temperature and hence, this question is not well attempted.</p>
	(iii)	<p>Raising temperatures is another method to increase the rate of decomposition. Use the Maxwell-Boltzmann curve to describe how a higher temperature does so. [3]</p>

		<p>No. of molecules with energy, E</p> <p>Key:</p> <p> No. of particles with $E \geq E_a$ at higher temperature No. of particles with $E \geq E_a$ at lower temperature </p> <p>for diagram (start from origin, peaks of 2 curves with lower peak for higher temp, label of E_a and correct shading)</p> <p>When temperature of the reaction increases,</p> <ul style="list-style-type: none"> • <u>average kinetic energy</u> of the reactant particles <u>increases</u> • <u>more reactant particles with energy $\geq E_a$</u> • <u>more effective collisions</u> • Since rate of reaction is proportional to the frequency of effective collisions, <u>rate</u> of reaction <u>increases</u>
	(b)	In the presence of UV light, H_2O_2 decomposes to form hydroxyl free radicals, $\cdot\text{OH}$.
	(i)	Draw the 'dot-and-cross' diagram for H_2O_2 . [1]
	(ii)	Using relevant data from the <i>Data Booklet</i> , suggest the relative rate of the formation of $\cdot\text{Cl}$ from chlorine gas as compared to $\cdot\text{OH}$ from hydrogen peroxide. [2]
		<p>Bond energy: <u>$\text{O}-\text{O}$ (150 kJ mol^{-1}) $<$ $\text{Cl}-\text{Cl}$ (244 kJ mol^{-1})</u></p> <p><u>Ease of cleavage of bond: $\text{O}-\text{O} > \text{Cl}-\text{Cl}$</u></p> <p><u>Rate of formation of $\cdot\text{OH}$ radicals is faster than $\cdot\text{Cl}$.</u></p>
	(iii)	<p>Propylamine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, may be formed via the following reaction pathway involving free radical substitution in the first step.</p> $\text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow[\text{Cl}_2, \text{uv}]{\text{Step I}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{Step II}} \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ <p>State the reagents and condition required in step II. [1]</p> <p><u>Alcoholic NH_3, heat in sealed tube</u></p>

		(iv)	As the yield from the reaction in (iii) is low, propose a 3-step synthetic route to produce propylamine from ethene instead. Show clearly the reagents and conditions as well as intermediates involved. <div style="text-align: right;">[3]</div>																									
			<div style="text-align: center;">$\text{CH}_2=\text{CH}_2 \xrightarrow{\text{HCl}} \text{CH}_3\text{CH}_2\text{Cl} \xrightarrow[\text{heat}]{\text{ethanolic KCN}} \text{CH}_3\text{CH}_2\text{CN}$<div style="display: inline-block; vertical-align: middle; text-align: center;">\downarrow $\text{LiAlH}_4 \text{ in dry ether}$ \downarrow $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$</div></div> <p style="text-align: right;"><i>Step III: students may use <u>H₂, Ni, heat</u></i></p>																									
	(c)		<p>The kinetics of the reaction between hydrogen peroxide and iodide ions in acidic solution was studied.</p> $\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{I}_2$ <p>Four separate experiments were carried out to determine the relative rates by varying the concentrations of the reactants. The results obtained are given in the table below.</p> <table border="1"><thead><tr><th>Expt</th><th>[H₂O₂] / mol dm⁻³</th><th>[I⁻] / mol dm⁻³</th><th>[H⁺] / mol dm⁻³</th><th>relative rate</th></tr></thead><tbody><tr><td>1</td><td>0.03</td><td>0.03</td><td>0.03</td><td>1.0</td></tr><tr><td>2</td><td>0.05</td><td>0.03</td><td>0.03</td><td>1.6</td></tr><tr><td>3</td><td>0.05</td><td>0.01</td><td>0.06</td><td>0.53</td></tr><tr><td>4</td><td>0.03</td><td>0.01</td><td>0.03</td><td>0.33</td></tr></tbody></table>	Expt	[H ₂ O ₂] / mol dm ⁻³	[I ⁻] / mol dm ⁻³	[H ⁺] / mol dm ⁻³	relative rate	1	0.03	0.03	0.03	1.0	2	0.05	0.03	0.03	1.6	3	0.05	0.01	0.06	0.53	4	0.03	0.01	0.03	0.33
Expt	[H ₂ O ₂] / mol dm ⁻³	[I ⁻] / mol dm ⁻³	[H ⁺] / mol dm ⁻³	relative rate																								
1	0.03	0.03	0.03	1.0																								
2	0.05	0.03	0.03	1.6																								
3	0.05	0.01	0.06	0.53																								
4	0.03	0.01	0.03	0.33																								
		(i)	Use the data to deduce the orders of reaction with respect to H ₂ O ₂ , I ⁻ and H ⁺ . Show your working clearly. <div style="text-align: right;">[3]</div>																									
			<p>Using expt 1 and 2, as [I⁻] and [H⁺] are constant while <u>[H₂O₂] increases 1.6 times, rate increases 1.6 times.</u> → Order of rxn wrt H₂O₂ is <u>1</u></p> <p>Using expt 2 and 4, $\frac{\text{Rate}_2}{\text{Rate}_4} = \frac{1.6}{0.33} = \frac{k[0.05]^1[0.03]^x[0.03]^y}{k[0.03]^1[0.01]^x[0.03]^y}$$4.84 = \left(\frac{5}{3}\right)(3)^x$$x = 1$ → Order of rxn wrt I⁻ is <u>1</u></p> <p>Using expt 2 and 3, <u>as [H₂O₂] is constant while [I⁻] decreases 3 times and [H⁺] increases 2 times, rate decreases 3 times.</u> Hence, change in [H⁺] does not affect relative rate. → Order of rxn wrt H⁺ is <u>0</u> (or use mathematical approach)</p>																									

		(ii)	Hence write the rate equation and state the units of the rate constant. [2]
			rate = $k[\text{H}_2\text{O}_2][\text{I}^-]$ Units for k = <u>$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$</u>
		(iii)	Unreacted iodide ions may be easily separated by adding silver nitrate solution, followed by filtration. State the identity of the precipitate and its colour. [1]
			<u>AgI</u> , pale <u>yellow</u> ppt
			Total: 20 marks

END