



Serangoon Junior College

2016 JC2 H2 CHEMISTRY (9647) Paper 2 Suggested Solutions

<b>1(P)</b>	<p>When a sparingly soluble salt, calcium hydroxide, <math>\text{Ca(OH)}_2</math>, is added to water, an equilibrium is established between the undissolved salt and a saturated solution of the salt.</p> $\text{Ca(OH)}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$ <p>The solubility product at laboratory temperature can be found by determining the equilibrium concentration of the hydroxide ions in a saturated solution of calcium hydroxide. This equilibrium concentration can be found by titration with a standard solution of hydrochloric acid.</p> <p>The numerical value of the solubility product of calcium hydroxide is approximately <math>5 \times 10^{-6}</math>.</p>
<b>(a)</b>	<p>Write an expression for the solubility product of calcium hydroxide, stating its units.</p> <p style="text-align: right;">[1]</p>
	<p><math>K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^{-}]^2</math>; units: <math>\text{mol}^3 \text{dm}^{-9}</math></p>
	<p>You are required to write a plan to determine the solubility product of calcium hydroxide at laboratory temperature.</p> <p>You may assume that you are provided with:</p> <ul style="list-style-type: none"><li>• Solid <math>\text{Ca(OH)}_2</math></li><li>• <math>0.200 \text{ mol dm}^{-3}</math> of stock solution of <math>\text{HCl}</math></li><li>• deionised water</li><li>• indicators normally found in a school laboratory</li><li>• equipment normally found in a school laboratory</li></ul>
<b>(b)</b>	<p><b>(i)</b> Calculate the minimum mass of <math>\text{Ca(OH)}_2</math> that needs to be weighed in order to obtain <math>250 \text{ cm}^3</math> of a saturated solution of <math>\text{Ca(OH)}_2</math> at laboratory temperature.</p> <p style="text-align: right;">[2]</p>
	<p><math>K_{\text{sp}} \approx 5.0 \times 10^{-6}</math> Let the solubility be <math>x \text{ mol dm}^{-3}</math>. <math>(x)(2x)^2 = 5.0 \times 10^{-6}</math> <math>4x^3 = 5.0 \times 10^{-6}</math> <math>x = 0.01077 \text{ mol dm}^{-3}</math></p> <p>solubility in <math>\text{g dm}^{-3} = 0.01077 \times (40.1 + 16.0 \times 2 + 1.0 \times 2) = 0.7982 \text{ g dm}^{-3}</math> Min mass of <math>\text{Ca(OH)}_2 = \frac{0.7982}{1000} \times 250 = 0.200\text{g}</math></p>
	<p><b>(ii)</b> Assuming that approximately <math>30.00 \text{ cm}^3</math> of <math>\text{HCl}</math> was required to react with <math>25.0 \text{ cm}^3</math> of saturated solution of <math>\text{Ca(OH)}_2</math>, calculate an appropriate concentration of <math>\text{HCl}</math> required. Hence, calculate the volume of the given solution of <math>\text{HCl}</math> required to prepare <math>250 \text{ cm}^3</math> of this solution.</p> <p style="text-align: right;">[2]</p>

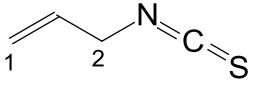
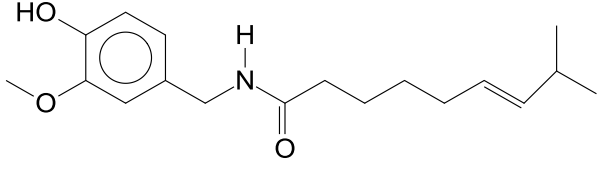
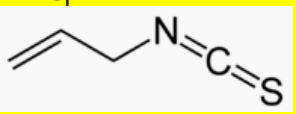

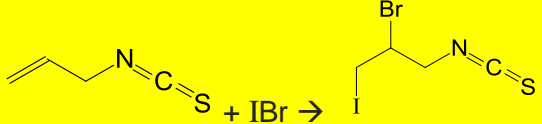
		$\text{Ca(OH)}_2 + 2\text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$ $\text{Amount of Ca(OH)}_2 = \frac{25}{1000} \times 0.01077 = 0.0002693\text{mol}$ $\text{Amount of HCl} = 0.0002693 \times 2 = 0.0005386\text{mol}$ $\text{Concentration of HCl required} = \frac{0.0005386}{30} \times 1000 = 0.0180\text{mol dm}^{-3}$ <p>Vol of the given solution needed =</p> $\frac{\frac{250}{1000} \times 0.0180}{0.2} = 0.0225\text{dm}^3 = 22.5\text{cm}^3$
	(iii)	<p>Using the information given above and the answers in <b>b(i)</b> and <b>b(ii)</b>, you are required to write a plan to determine the solubility product of calcium hydroxide.</p> <p>You are also required to explain how the data you obtain from this experiment may be used to determine the solubility product of calcium hydroxide.</p> <p>Your plan should include:</p> <ul style="list-style-type: none"> <li>the preparation of 250 cm<sup>3</sup> of the saturated solution of calcium hydroxide;</li> <li>the preparation of 250 cm<sup>3</sup> of standard solution of hydrochloric acid from the stock solution of hydrochloric acid;</li> <li>titration procedure;</li> <li>how the results obtained can be used to determine the solubility product of calcium hydroxide.</li> </ul> <p style="text-align: right;">[7]</p>
		<p><b><u>Preparation of saturated solution of calcium hydroxide</u></b></p> <ol style="list-style-type: none"> <li><b><u>Weigh</u></b> approximately <b><u>0.200 g</u></b> of solid.</li> <li>Using a <b><u>measuring cylinder</u></b>, place <b><u>250 cm<sup>3</sup> of deionised water</u></b> into a <b><u>dry conical flask/beaker</u></b>.</li> <li>Add <b><u>solid to water</u></b> and <b><u>stir with a glass rod</u></b> to dissolve the solid.</li> <li><b><u>Weigh</u></b> and <b><u>add more solid</u></b> to the water until <b><u>excess solid remains / no more solid dissolves</u></b>.</li> <li>Allow the mixture to <b><u>stand for a period of time</u></b> (e.g 30 mins) to establish equilibrium.</li> <li><b><u>Filter</u></b> the mixture to obtain the filtrate.</li> </ol>
		<p><b><u>Preparation of hydrochloric acid form the solution</u></b></p> <ol style="list-style-type: none"> <li>Fill a <b><u>burette</u></b> with the stock solution of <b><u>hydrochloric acid</u></b>. Drain <b><u>22.50 cm<sup>3</sup></u></b> of the hydrochloric acid from the burette into a <b><u>250 cm<sup>3</sup> volumetric flask</u></b>. Top-up the volumetric flask up <b><u>to the mark with de-ionised water</u></b>. Add the last few drops of de-ionised water using a dropper till the bottom of the meniscus coincides with the mark.</li> <li><b><u>Stopper</u></b> the volumetric flask firmly and <b><u>shake it</u></b> to ensure complete mixing. This is to ensure that a homogeneous solution is obtained.</li> </ol>


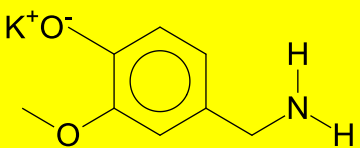
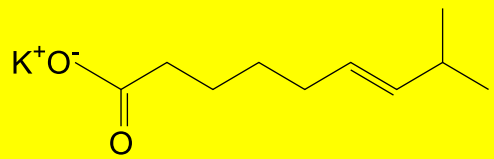
		<p><b><u>Titration procedure</u></b></p> <ol style="list-style-type: none"> <li>1. <b><u>Fill a clean burette</u></b> with the <b><u>hydrochloric acid</u></b> solution.</li> <li>2. <b><u>Pipette 25.0 cm<sup>3</sup> of calcium hydroxide</u></b> into a clean <b><u>conical flask</u></b>.</li> <li>3. Add <b><u>2 or 3 drops of methyl orange indicator</u></b> into the conical flask and <b><u>titrate</u></b> this solution with the <b><u>hydrochloric acid in the burette</u></b> with <b><u>constant swirling</u></b>, and <b><u>add drop-wise</u></b> as the titration is <b><u>near the end-point</u></b>.</li> <li>4. <b><u>Stop the titration</u></b> immediately when the first <b><u>drop of hydrochloric acid</u></b> added turns the solution from <b><u>yellow to orange</u></b>.</li> <li>5. <b><u>Repeat the titration</u></b> until <b><u>two accurate titre readings fall within 0.10 cm<sup>3</sup></u></b> of each other are obtained</li> </ol>
		<p><b><u>Results</u></b></p> <p>Assume that the volume obtained is <b><u>V cm<sup>3</sup></u></b></p> <p>Amount of Ca(OH)<sub>2</sub> in 25.0 cm<sup>3</sup> = <math>\frac{1}{2} \times \left( \frac{V}{1000} \times 0.0180 \right) \text{mol}</math></p> <p>Concentration of saturated Ca(OH)<sub>2</sub> =</p> $\left[ \frac{1}{2} \left( \frac{V}{1000} \times 0.0180 \right) \div \frac{25}{1000} \right] = z \text{ mol dm}^{-3}$ <p>[Ca<sup>2+</sup>] = z mol dm<sup>-3</sup></p> <p>[OH<sup>-</sup>] = 2z mol dm<sup>-3</sup></p> <p>K<sub>sp</sub> = z × (2z)<sup>2</sup> = 4z<sup>3</sup> mol<sup>3</sup> dm<sup>-9</sup></p>
		[Total: 12]

2	<p>The manufacture of ammonia from nitrogen and hydrogen takes place in two stages:</p> <p>First Stage: The manufacture of hydrogen from methane. Second Stage: The synthesis of ammonia (the Haber Process).</p> <p>The First Stage occurs via a two-step process.</p> <ul style="list-style-type: none"> <li>• <i>Steam Reforming</i></li> <li>• <i>Shift Reaction</i></li> </ul> <p>Both steps produce hydrogen gas that will be used in the Second Stage for the production of ammonia..</p>
	<p><b>(a)</b> <i>Steam Reforming</i> is a reaction that converts methane and steam to a mixture of carbon monoxide and hydrogen. There are two possible routes for it:</p> <p><i>Primary Steam Reforming:</i> Steam is supplied to start the reaction.  <math display="block">\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \quad \Delta H^\circ = +210 \text{ kJ mol}^{-1} \quad \text{eqm (1)}</math></p> <p><i>Secondary Steam Reforming:</i> Some hydrogen is burnt to form steam which then reacts with methane to generate more hydrogen.  <math display="block">2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) \quad \Delta H^\circ = -482 \text{ kJ mol}^{-1}</math> <math display="block">\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \quad \Delta H^\circ = +210 \text{ kJ mol}^{-1}</math></p>
	<p><b>(i)</b> State if the overall process of <i>Secondary Steam Reforming</i> is an exothermic or endothermic process. [1]</p>
	<p>Overall is exothermic.</p>
	<p><b>(ii)</b> Suggest which steam reforming process (<i>Primary</i> or <i>Secondary</i>) is favoured by high temperature. [2]</p>
	<p>Primary steam reforming is favoured by high temperature.</p> <p>For primary steam reforming, process is endothermic. By Le Chatelier's Principle (LCP), high temperature favoured the endothermic reaction which is the forward reaction as excess heat energy is being absorbed.</p>
	<p><b>(iii)</b> The methane gas used usually contains some organic sulfur compounds, R-SH, and hydrogen sulfide, H<sub>2</sub>S, both of which must be removed or it will poison the catalyst. Hence the methane mixture needs to be passed through a <i>desulfurisation unit</i> first.</p> <ul style="list-style-type: none"> <li>• These organic sulfur compounds are first converted into hydrogen sulfide and a hydrocarbon by reduction with hydrogen gas.</li> <li>• The hydrogen sulfide is reacted with zinc oxide (ZnO) to produce zinc sulfide (ZnS) as one of the products.</li> </ul> <p>Construct two balanced chemical equations showing the reactions that occurred in the <i>desulfurisation unit</i>, using R-SH to represent organic sulfur compounds and RH to represent hydrocarbon [2]</p>
	<p>R-SH + H<sub>2</sub> → RH + H<sub>2</sub>S ZnO + H<sub>2</sub>S → ZnS + H<sub>2</sub>O</p>

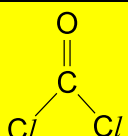
	<p><b>(b)</b> In the <i>Shift Reaction</i>, the carbon monoxide produced during the <i>Steam Reforming</i> process was converted to carbon dioxide and hydrogen gas. <i>Shift Reaction</i> is done via a two-step process:</p> <ul style="list-style-type: none"> <li>• <i>High Temperature Shift Reaction</i> with iron(III) oxide catalyst.</li> <li>• <i>Low Temperature Shift Reaction</i> with thermally unstable copper catalyst at 500 K. The carbon monoxide concentration is further reduced to 0.2%.</li> </ul> <p>The reaction involved in the <i>Shift Reaction</i> is illustrated in the following equation.</p> $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)} \quad \Delta H^\circ = -42 \text{ kJ mol}^{-1} \quad \textbf{eqm (2)}$
	<p><b>(i)</b> State the full electronic configuration of iron(III) ion and copper metal. [2]</p>
	<p>Fe<sup>3+</sup>: 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>5</sup>      Cu: 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>10</sup>4s<sup>1</sup></p>
	<p><b>(ii)</b> With reference to the <i>Shift Reaction</i>, state and explain if iron(III) oxide and copper is functioning as homogeneous or heterogeneous catalyst. [2]</p>
	<p>They are <b>heterogeneous catalysts</b></p> <p><b><u>The availability of partially-filled 3d orbitals allow reactant molecules to be adsorbed onto</u></b> the catalyst surface via van der Waals' interactions.</p>
	<p><b>(c)</b> Traces of carbon dioxide produced in the <i>Shift Reaction</i> is subsequently removed by passing it with hydrogen gas over a nickel catalyst at 600 K, a process known as <i>Methanation</i>.</p> $\text{CO}_2\text{(g)} + 4\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + 2\text{H}_2\text{O(g)}$ <p>Using the enthalpy change values of <b>eqm(1)</b> and <b>eqm(2)</b> of this question, determine the enthalpy change for this <i>Methanation</i> process. [2]</p>
	<p>Using algebraic method:</p> <p>(1) <math>\text{CH}_4\text{(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO(g)} + 3\text{H}_2\text{(g)} \quad \Delta H^\circ = +210 \text{ kJ mol}^{-1}</math></p> <p>(2) <math>\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)} \quad \Delta H^\circ = -42 \text{ kJ mol}^{-1}</math></p> <p>Reverse (1) + Reverse (2)</p> <p><math>\text{CO(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + \text{H}_2\text{O(g)} \quad \Delta H^\circ = +210 \text{ kJ mol}^{-1}</math></p> <p><math>\text{CO}_2\text{(g)} + \text{H}_2\text{(g)} \rightleftharpoons \text{CO(g)} + \text{H}_2\text{O(g)} \quad \Delta H^\circ = +42 \text{ kJ mol}^{-1}</math></p> <p>Overall: <math>\text{CO}_2\text{(g)} + 4\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + 2\text{H}_2\text{O(g)} \quad \Delta H^\circ = -168 \text{ kJ mol}^{-1}</math></p> <p>OR</p> <p>Using energy cycle:</p> <div style="text-align: center;"> <pre> graph TD     A["CO2 (g) + 4 H2(g)"] -- "ΔH" --&gt; C["CH4(g) + 2H2O"]     A -- "+ 42" --&gt; B["CO(g) + H2O(g) + 3H2(g)"]     B -- "-210" --&gt; C </pre> </div> <p>By Hess Law  <math>\Delta H = +42 - 210 = -168 \text{ kJ mol}^{-1}</math></p>

(d)	<p>The main process of the Haber Process occurs in a fixed bed reactor.</p> $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H^\circ = -92 \text{ kJ mol}^{-1}$ <p>The proportion of ammonia in the equilibrium mixture increases with increasing pressure and with falling temperature. Quantitative data are given the table below.</p> <table><tr><th>Pressure/atm</th><th colspan="3">Percentage ammonia present at equilibrium at a range of temperature</th></tr><tr><td></td><th>373 K</th><th>473 K</th><th>573 K</th></tr><tr><td>10</td><td>-</td><td>50.7</td><td>14.7</td></tr><tr><td>25</td><td>91.7</td><td>63.6</td><td>27.4</td></tr><tr><td>50</td><td>94.5</td><td>74.0</td><td>39.5</td></tr><tr><td>100</td><td>96.7</td><td>81.7</td><td>52.5</td></tr><tr><td>200</td><td>98.4</td><td>89.0</td><td>66.7</td></tr><tr><td>400</td><td>99.4</td><td>94.6</td><td>79.7</td></tr><tr><td>1000</td><td>-</td><td>98.3</td><td>92.6</td></tr></table>	Pressure/atm	Percentage ammonia present at equilibrium at a range of temperature				373 K	473 K	573 K	10	-	50.7	14.7	25	91.7	63.6	27.4	50	94.5	74.0	39.5	100	96.7	81.7	52.5	200	98.4	89.0	66.7	400	99.4	94.6	79.7	1000	-	98.3	92.6
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(i)	<p>To obtain a reasonable yield with favourable rate, high pressures, moderate temperatures and a catalyst are used. Using the data, select the temperature and pressure which will result in the highest yield of ammonia.</p> <p>[1]</p>																																				
	<p>Temperature: 373 K Pressure: 400 atm</p>																																				
(ii)	<p>Hence, using the data you have selected in (a)(i), determine the volume of ammonia gas, nitrogen gas and hydrogen gas at equilibrium when 10 cm<sup>3</sup> of nitrogen gas is reacted with 30 cm<sup>3</sup> of hydrogen gas in the Haber Process. Leave your answer to two decimal places.</p> <p>[3]</p>																																				
	<p>Let x be the volume of NH<sub>3</sub> at equilibrium</p> <table><tr><td></td><td>N<sub>2</sub>(g)</td><td>+</td><td>3H<sub>2</sub>(g)</td><td></td><td>2NH<sub>3</sub>(g)</td></tr><tr><td>Initial</td><td>10</td><td></td><td>30</td><td></td><td>0</td></tr><tr><td>Change</td><td>-0.5x</td><td></td><td>-1.5x</td><td></td><td>+x</td></tr><tr><td>Eqm</td><td>10 – 0.5x</td><td></td><td>30 – 1.5x</td><td></td><td>x</td></tr></table> <p>Total volume of gas at eqm = 10 – 0.5x + 30 – 1.5x + x = 40 – x</p> <p>From (a)(i) Since at 373 K and 400 atm, percentage ammonia present is 99.4% <math>99.4 = \frac{x}{40-x} \times 100</math></p> <p>(0.994)(40-x) = x 39.76 – 0.994x = x x = 19.94</p> <p>Hence at eqm: Volume of NH<sub>3</sub> = <b>19.94 cm<sup>3</sup></b> Volume of N<sub>2</sub> = 10 – 9.97 = <b>0.03 cm<sup>3</sup></b> Volume of H<sub>2</sub> = 30 – 1.5(19.94) = <b>0.09 cm<sup>3</sup></b></p>		N <sub>2</sub> (g)	+	3H <sub>2</sub> (g)		2NH <sub>3</sub> (g)	Initial	10		30		0	Change	-0.5x		-1.5x		+x	Eqm	10 – 0.5x		30 – 1.5x		x												
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	<p>[Total: 15]</p>																																				

3	(a)	<p>Allyl isothiocyanate (AITC) is responsible for the pungent taste of wasabi while capsaicin is an active component of chilli pepper and is found in spiced products like curry.</p> <div style="text-align: center;">  <p>AITC</p> </div> <div style="text-align: center;">  <p>Capsaicin</p> </div>
	(i)	Using your concept of VSEPR, state the shape about the carbon labelled 1 and 2 on AITC. [2]
		Carbon 1: Trigonal planar Carbon 2: Tetrahedral
	(ii)	Suggest the type of hybridisation for all carbons present in AITC. [2]
		<div style="text-align: center;"> <math>sp^2</math>    <math>sp^2 \quad sp^3 \quad sp</math> </div>
	(iii)	<p>Besides the ether group , state the other functional groups that are present in Capsaicin. [3]</p> <p>Alkene, secondary amide, phenol</p>
	(iv)	<p>Ignoring the effect of the <math>-N=C=S</math> group, write an equation showing how AITC reacts with liquid IBr. Hence, with reference to the <i>Data Booklet</i> and given that the bond energy of I-Br to be <math>180 \text{ kJ mol}^{-1}</math>, determine the enthalpy change of reaction when AITC reacts with liquid IBr. [2]</p> <div style="text-align: center;">  </div> $\Delta H = BE(C=C) + BE(I-Br) - BE(C-I) - BE(C-Br) - BE(C-C)$ $= 610 + 180 - 240 - 280 - 350$ $= -80 \text{ kJ mol}^{-1}$
	(v)	Using your knowledge in chemical bonding, suggest why the burning sensation of capsaicin cannot be washed away with water. [2]
		Capsaicin is a simple molecular structure. There is <u>no favourable solute-solvent interaction</u> between capsaicin and water. Hence, the burning effect could not be washed away with water.

		(vi)	<p>Draw the structural formula of the products formed when capsaicin is reacted with hot aqueous potassium hydroxide.</p> <p>[You are to ignore the effect of the  group]</p> <p style="text-align: right;">[2]</p>
			<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div> </div> <p style="text-align: right;">[Total: 13]</p>

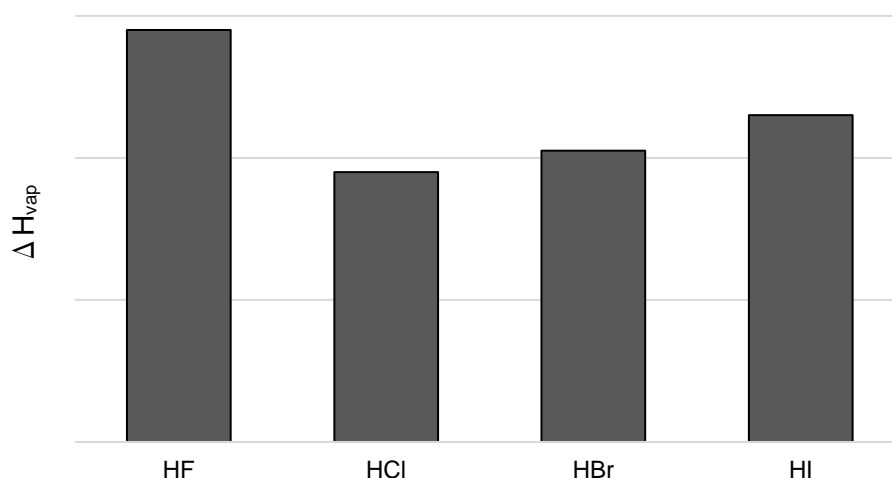


4	(a)	<p>Phosgene is the chemical compound with the formula <math>\text{COCl}_2</math>. It is not to be confused with cobalt(II) chloride with the formula <math>\text{CoCl}_2</math>.</p> <p>Phosgene is produced industrially with carbon dioxide and chlorine gas.</p> $\text{CO (g)} + \text{Cl}_2 \text{ (g)} \rightleftharpoons \text{COCl}_2 \text{ (g)} \quad \Delta H^\circ = -107.6 \text{ kJ mol}^{-1}$ <p>The <math>K_p</math> of this process is <math>0.05 \text{ atm}^{-1}</math> at 300 K. A mixture contains 2 mol of carbon monoxide and 2 mol of chlorine initially was reacted and allow to reach equilibrium. The equilibrium mixture is found to contain 1.5 mol of phosgene.</p>																		
	(i)	<p>Draw the Lewis structure of phosgene.</p> <p style="text-align: right;">[1]</p>																		
		<div></div>																		
	(ii)	<p>Write an expression for <math>K_p</math> for the equilibrium between <math>\text{CO}</math>, <math>\text{Cl}_2</math> and phosgene and hence using the information provided calculate the total pressure of the system at equilibrium.</p> <p style="text-align: right;">[3]</p>																		
		<div><math display="block">K_p = \frac{P_{\text{COCl}_2}}{P_{\text{CO}} P_{\text{Cl}_2}}</math><table><tr><td></td><td colspan="2"><math>\text{CO (g)} + \text{Cl}_2 \text{ (g)} \rightleftharpoons \text{COCl}_2 \text{ (g)}</math></td><td></td></tr><tr><td>Initial no. of moles</td><td>2</td><td>2</td><td>0</td></tr><tr><td>Change in no. of moles</td><td>-1.5</td><td>-1.5</td><td>+1.50</td></tr><tr><td>Eqm. no. of moles</td><td>0.5</td><td>0.5</td><td>1.50</td></tr></table><p>Total no. of moles of gases at eqm = <math>0.5 + 0.5 + 1.50 = 2.5</math></p><math display="block">K_p = \frac{(P_{\text{COCl}_2})}{(P_{\text{CO}}) \times (P_{\text{Cl}_2})}</math><math display="block">0.05 = \left( \frac{1.50}{2.50} \times P_T \right) \div \left( \left( \frac{0.5}{2.50} \times P_T \right) \left( \frac{0.5}{2.50} \times P_T \right) \right)</math><p><math>0.05 = 0.6 P_T \div (0.2 P_T \times 0.2 P_T)</math> <math>0.05 = 0.6 P_T \div (0.04 P_T^2)</math> <math>0.05 = 15/P_T</math> <math>P_T = 300 \text{ atm}</math></p></div>				$\text{CO (g)} + \text{Cl}_2 \text{ (g)} \rightleftharpoons \text{COCl}_2 \text{ (g)}$			Initial no. of moles	2	2	0	Change in no. of moles	-1.5	-1.5	+1.50	Eqm. no. of moles	0.5	0.5	1.50
	$\text{CO (g)} + \text{Cl}_2 \text{ (g)} \rightleftharpoons \text{COCl}_2 \text{ (g)}$																			
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Change in no. of moles	-1.5	-1.5	+1.50																	
Eqm. no. of moles	0.5	0.5	1.50																	
	(iii)	<p>Suggest if chlorine or phosgene will deviate more from ideal gas behaviour.</p> <p style="text-align: right;">[2]</p>																		
		<p><u>Phosgene gas deviates more from ideality</u> <u>The permanent dipole – permanent dipole interaction between phosgene molecules is stronger as compared to the instantaneous dipole – induced dipole between chlorine molecules.</u></p>																		

	(b)	Crystals of hydrated cobalt(II) chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , lose water when they are heated, forming anhydrous cobalt(II) chloride, $\text{CoCl}_2$ .  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{s}) \rightarrow \text{CoCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{l})$										
	(i)	<p>The standard enthalpy change for the reaction, <math>\Delta H^\ominus</math>, is <math>+88.1 \text{ kJ mol}^{-1}</math>. Given that the calculation for entropy change to be similar to that of enthalpy change, use the following entropy data to determine the standard entropy change of the reaction at 298 K. Give your answer to <b>four</b> significant figures.</p> <table><tr><th>Compound</th><th><math>S^\ominus</math> / <math>\text{J mol}^{-1}\text{K}^{-1}</math></th></tr><tr><td><math>\text{CoCl}_2 \cdot 6\text{H}_2\text{O} (\text{s})</math></td><td>343.0</td></tr><tr><td><math>\text{CoCl}_2 (\text{s})</math></td><td>109.2</td></tr><tr><td><math>\text{H}_2\text{O} (\text{l})</math></td><td>69.9</td></tr><tr><td><math>\text{H}_2\text{O} (\text{g})</math></td><td>188.7</td></tr></table> <p style="text-align: right;">[1]</p>	Compound	$S^\ominus$ / $\text{J mol}^{-1}\text{K}^{-1}$	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O} (\text{s})$	343.0	$\text{CoCl}_2 (\text{s})$	109.2	$\text{H}_2\text{O} (\text{l})$	69.9	$\text{H}_2\text{O} (\text{g})$	188.7
Compound	$S^\ominus$ / $\text{J mol}^{-1}\text{K}^{-1}$											
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$\text{H}_2\text{O} (\text{l})$	69.9											
$\text{H}_2\text{O} (\text{g})$	188.7											
		$\Delta S^\ominus = 109.2 + 6(69.9) - 343$ $= +185.6 \text{ J mol}^{-1}\text{K}^{-1} \text{ (to 4 s.f.)}$										
	(ii)	<p>Hence, explain by using calculation, whether hydrated cobalt(II) chloride can be stored at 298K without decomposition.</p> <p style="text-align: right;">[2]</p>										
		$\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus$ $= +88.1 \times 10^3 - 298(185.6)$ $= 88100 - 55308.8$ $= 32791.2$ $\approx +32800 \text{ J mol}^{-1}$ <p>Yes it can be stored without decomposition as <math>\Delta G^\ominus</math> is positive.</p>										
	(c)	<p>With the aid of a chemical equation, explain why a solution of cobalt(II) chloride has a pH of 4.6.</p> <p style="text-align: right;">[2]</p>										
		<p>(FYI for <math>\text{Co}^{2+}</math>: charge +2, ionic radius 0.065 nm) (FYI for <math>\text{Al}^{3+}</math>: charge +3, ionic radius 0.053 nm) (FYI for <math>\text{Mg}^{2+}</math>: charge +2, ionic radius 0.072 nm)</p> <p><b><math>\text{Co}^{2+}</math> ion</b> has <b>high charge density</b> or has <b>high polarising power</b> which can distort the electron cloud of the water ligand.</p> $[\text{Co}(\text{H}_2\text{O})_6]^{2+} \rightleftharpoons [\text{Co}(\text{H}_2\text{O})_5(\text{OH})]^+ + \text{H}^+$ <p>Thus, solution is acidic.</p> <p style="text-align: right;">[Total: 11]</p>										

- 5 Group VII hydrides are colourless gases at room temperature. The figures below shows the relative enthalpy change of vaporisation of the hydrides

Figure 1:  $\Delta H_{\text{vap}}$  of HX



- (a) With reference to **Figure 1**, explain the abnormally high enthalpy change of vaporisation of hydrogen fluoride. [2]

HF molecules are held together by stronger **intermolecular hydrogen bonds** as compared to the other HX molecules held by weaker **permanent dipole-permanent dipole interactions**.

**More energy** is needed to overcome **stronger** intermolecular hydrogen bonds in HF, explaining its abnormally high enthalpy change of vaporisation.

- (b) The table below shows the  $pK_a$  of the respective compounds when they are dissolved in water

Compounds	$pK_a$	Compounds	$pK_a$
		Hydrogen bromide	-9.00
Hydrogen chloride	-7.00	Hydrogen iodide	-10.00
Methanoic acid	3.77	Water	7.00

- (i) Using relevant information from the *Data Booklet*, rank the acid strength of aqueous solution containing HCl, HBr and HI, in increasing order. Explain your answer. [2]

**From *Data Booklet*, Bond energy:**  $\text{H}-\text{Cl}$  (431) >  $\text{H}-\text{Br}$  (366) >  $\text{H}-\text{I}$  (299)

**Ease of cleavage** of HX bond:  $\text{H}-\text{Cl}$  <  $\text{H}-\text{Br}$  <  $\text{H}-\text{I}$

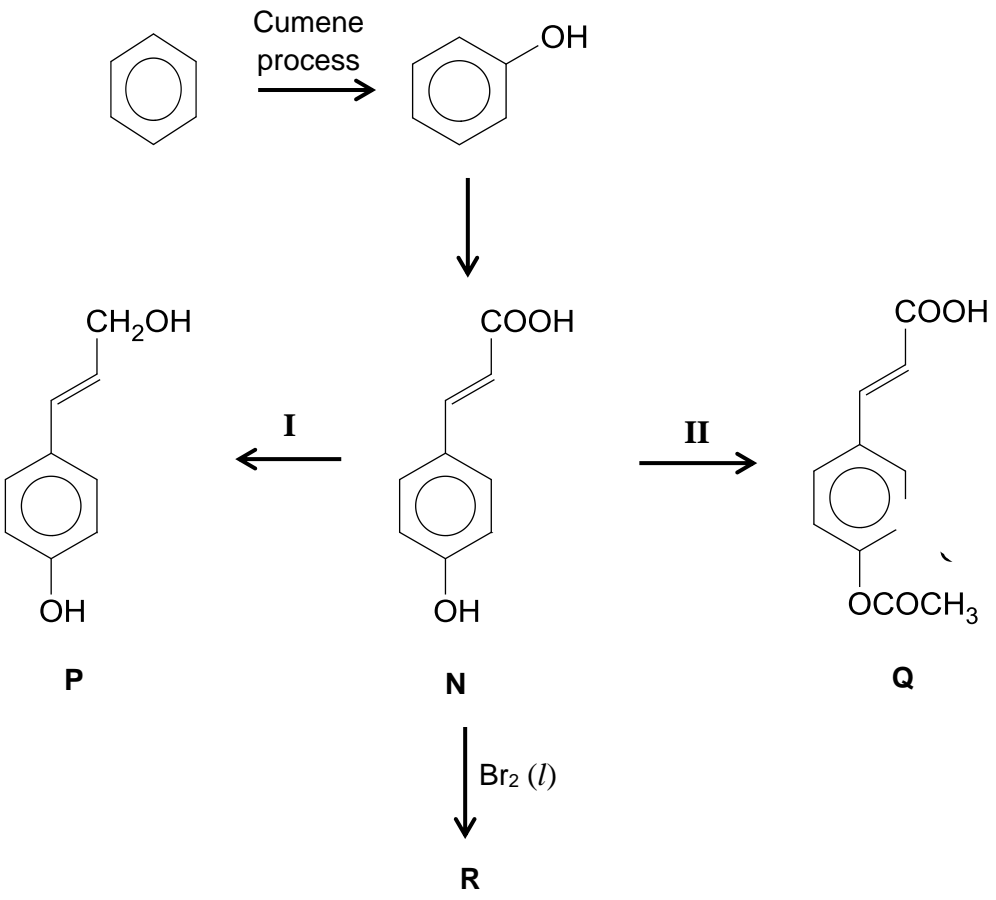
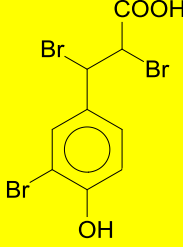
Or **energy needed to break HX bond:**  $\text{H}-\text{Cl}$  >  $\text{H}-\text{Br}$  >  $\text{H}-\text{I}$

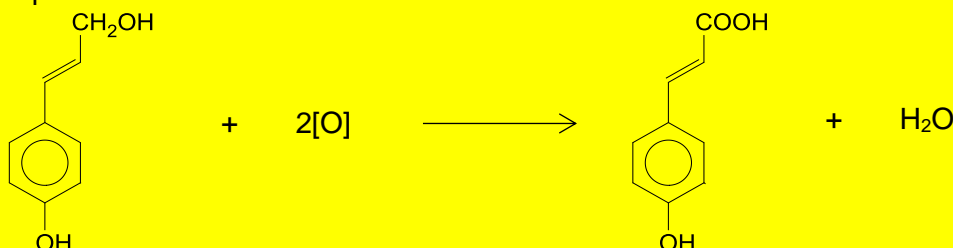
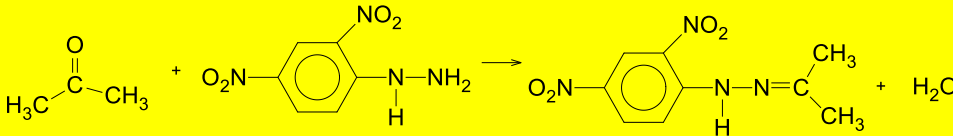
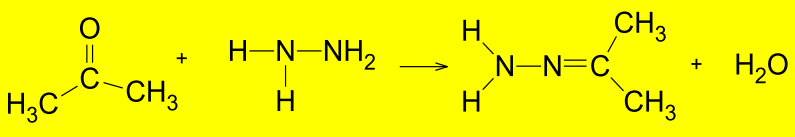
Ease of release of  $\text{H}^+$  ion:  $\text{HCl}$  <  $\text{HBr}$  <  $\text{HI}$

**Acidity :**  $\text{HCl}$  <  $\text{HBr}$  <  $\text{HI}$

		(ii)	Account for the relative acidities of methanoic acid and water. <div>[2]</div>																								
			Methanoic acid is a <b>stronger acid</b> than water as its <b>conjugate base / carboxylate anion</b> ( $\text{RCOO}^-$ ) is resonance <b>stabilised by the delocalisation of the negative charge over the C atom and both oxygen atoms</b> .  As such, methanoic acid is less likely to accept a proton from HX than water.																								
	(c)	Unlike other Group VII hydrides, hydrogen fluoride, HF, behaves as a weak acid in water.  A solution of HF was titrated against aqueous potassium hydroxide until 25% of the HF present was neutralised.																									
		(i)	Write the acid dissociation constant expression, $K_a$ , for HF. <div>[1]</div>																								
			$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$																								
		(ii)	Given that the pH of the resulting solution described above is 2.88, calculate $K_a$ of HF. <div>[3]</div>																								
			<p><math>\text{pH} = -\log_{10}[\text{H}^+]</math> <math>[\text{H}^+] = 10^{-2.88} = \underline{1.32 \times 10^{-3} \text{ mol dm}^{-3}}</math></p> <p>Let x be the initial [HF]</p> <table><tr><td></td><td>HF</td><td><math>\rightleftharpoons</math></td><td>H<sup>+</sup></td><td>+</td><td>F<sup>-</sup></td></tr><tr><td>Initial/mol dm<sup>-3</sup></td><td>x</td><td></td><td>0</td><td></td><td>0</td></tr><tr><td>Change/mol dm<sup>-3</sup></td><td>-0.25x</td><td></td><td>+0.25x</td><td></td><td>+0.25x</td></tr><tr><td>Eqm/mol dm<sup>-3</sup></td><td>0.75x</td><td></td><td>0.25x</td><td></td><td>0.25x</td></tr></table> <p><math display="block">K_a = \frac{[\text{H}^+][0.25x]}{[0.75x]} = \frac{(1.32 \times 10^{-3}) \times 1}{3} = \underline{4.40 \times 10^{-4} \text{ mol dm}^{-3}}</math></p> <p>Alternative solution</p> <p><math>\text{pH} = \text{p}K_a + \lg \{[\text{salt}]/[\text{acid}]\}</math> <math>2.88 = \text{p}K_a + \lg \{[\text{F}^-]/[\text{HF}]\}</math> <math>2.88 = \text{p}K_a + \lg (0.25/0.75)</math> <math>K_a = 4.39 \times 10^{-4} \text{ mol dm}^{-3}</math></p>		HF	$\rightleftharpoons$	H <sup>+</sup>	+	F <sup>-</sup>	Initial/mol dm <sup>-3</sup>	x		0		0	Change/mol dm <sup>-3</sup>	-0.25x		+0.25x		+0.25x	Eqm/mol dm <sup>-3</sup>	0.75x		0.25x		0.25x
	HF	$\rightleftharpoons$	H <sup>+</sup>	+	F <sup>-</sup>																						
Initial/mol dm <sup>-3</sup>	x		0		0																						
Change/mol dm <sup>-3</sup>	-0.25x		+0.25x		+0.25x																						
Eqm/mol dm <sup>-3</sup>	0.75x		0.25x		0.25x																						

	(d)	One of the most common ways to make hydrogen chloride is to react sodium chloride with concentrated sulfuric acid, $\text{H}_2\text{SO}_4$ or concentrated phosphoric(V) acid, $\text{H}_3\text{PO}_4$ . Both reactions occur similarly, releasing white fumes of gas.
	(i)	Construct a balanced equation involving sodium chloride and concentrated phosphoric(V) acid. [1]
		$\text{NaCl} + \text{H}_3\text{PO}_4 \rightarrow \text{HCl} + \text{NaH}_2\text{PO}_4$
	(ii)	In reaction with sodium bromide, concentrated sulfuric acid produces reddish-brown solution while concentrated phosphoric(V) acid produces white fumes.  Suggest a reason for the observations above. [1]
		Concentrated sulphuric acid is able to oxidise $\text{Br}^-$ to reddish-brown $\text{Br}_2$ while concentrated phosphoric(V) acid cannot. Thus, concentrated phosphoric(V) acid is a <b><u>weaker oxidising agent</u></b> .
		[Total: 12]

6	(a)	<p>The chemical structure and some reactions involving compound <b>N</b> are shown below.</p> <div style="text-align: center;">  <p>The diagram illustrates the following chemical transformations:</p> <ul style="list-style-type: none"> <li>Benzene ring <math>\xrightarrow{\text{Cumene process}}</math> Phenol (benzene ring with -OH)</li> <li>Phenol <math>\downarrow</math> 4-(hydroxymethyl)benzoic acid (<b>N</b>)</li> <li><b>N</b> <math>\xrightarrow{\text{I}}</math> 4-(hydroxymethyl)phenol (<b>P</b>)</li> <li><b>N</b> <math>\xrightarrow{\text{II}}</math> 4-(acetoxy)benzoic acid (<b>Q</b>)</li> <li><b>N</b> <math>\xrightarrow{\text{Br}_2(l)}</math> <b>R</b></li> </ul> </div>
	(i)	<p>State the reagents and conditions involved in Steps <b>I</b> and <b>II</b>.</p> <p>Step <b>I</b>: Step <b>II</b>:</p> <p style="text-align: right;">[2]</p>
		<p>Step <b>I</b>: <u>LiAlH<sub>4</sub> in dry ether, rtp</u> Step <b>II</b>: <u>CH<sub>3</sub>COCl, rtp</u></p>
	(ii)	<p>Draw the structure of organic product <b>R</b>.</p> <p style="text-align: right;">[1]</p>
		<div style="text-align: center;">  </div>

		(iii)	Propose a chemical test to distinguish between <b>P</b> and <b>N</b> , in which a positive test is observed for <b>P only</b> . Write a balanced chemical equation for the reaction that has occurred. <div style="text-align: right;">[3]</div>
			<p>Test: Add <b><u>K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in dilute H<sub>2</sub>SO<sub>4</sub>, heat</u></b>  Observation: <b><u>Orange K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> turns green</u></b></p> <p><i>*KMnO<sub>4</sub> is not suitable as ferulic acid may be [O] as well due to presence of C=C and benzylic H</i>  <i>*distillation with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to form aldehyde is not preferred when carrying out simple chemical tests</i></p> <p>Equation:</p> <div style="text-align: center;">  </div>
	(b)		In the cumene process one mole of benzene reacts with one mole of propene in the presence of oxygen from air to form phenol and organic substance <b>T</b> . Substance <b>T</b> does not give any positive observation with diammine silver complex.
	(i)		From the information provided, identify substance <b>T</b> . <div style="text-align: right;">[1]</div>
			$\text{O}_2 + \text{C}_6\text{H}_6 + \text{H}_2\text{C}=\text{CH}_2 \longrightarrow \text{H}_3\text{C}-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_3 + \text{C}_6\text{H}_5\text{OH}$ <p style="text-align: center;"><b>T</b></p>
	(ii)		Hence, with an aid of a chemical equation, suggest how the functional group in substance <b>T</b> can be positively identified. <div style="text-align: right;">[2]</div>
			<p><b><u>orange ppt</u></b> will be observed</p> <div style="text-align: center;">  </div> <p>Or</p> <div style="text-align: center;">  </div>
			[Total: 9]

END