Class Adm No

Candidate Name: _____

H

millennia institute

2011 Preliminary Examination II
Pre-university 3

H2 CHEMISTRY (Marking Scheme) 9647/03

Paper 3 Free Response **14 September 2011**

Candidates answer on separate paper. **2 hours**

Additional Materials: Writing Paper
Data Booklet

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

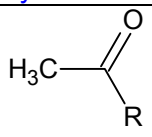
Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

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

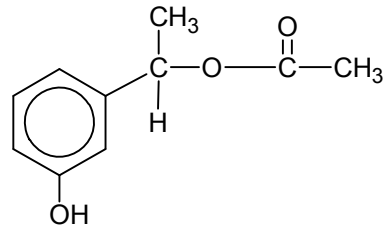
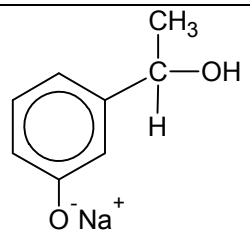
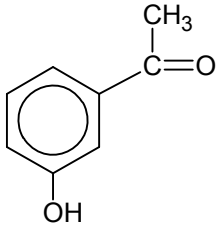
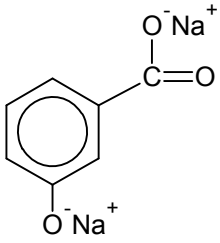
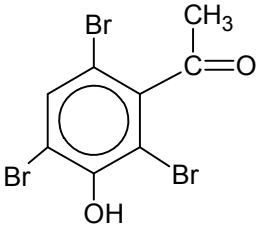
At the end of the examination, arrange your answers in numerical order and fasten all your work securely together.

1(a)	Ethanol is a renewable energy source because the energy is generated by using a resource, sunlight, which cannot be depleted. Creation of ethanol starts with photosynthesis causing a feedstock, such as sugar cane or corn, to grow. These feedstocks are processed into ethanol. Ethanol can be used in fuel cells, in the presence of aqueous potassium hydroxide electrolyte to produce electricity. During the reaction, ethanol is oxidised to ethanal.		
	(i)	Write ionic equations to illustrate the reactions that are happening at the cathode and anode respectively.	[2]
		Anode: $CH_3CH_2OH + 2OH^- \rightarrow CH_3CHO + 2\ H_2O + 2e$; Cathode: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$;	
	(ii)	Write an equation to represent the overall equation	[1]
		$2CH_3CH_2OH + O_2 \rightarrow 2\ CH_3CHO + 2\ H_2O$;	
	(iii)	An ethanol fuel cell is said to provide an e.m.f of 1.43V. Determine the reduction potential of the ethanol half cell.	[1]
		[O]: $CH_3CH_2OH + 2OH^- \rightarrow CH_3CHO + 2\ H_2O + 2e$ E =a [R]: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$ E = 0.40V a+ 0.40 = 1.43V a = 1.03 V Reduction potential = -1.03V ; (Reject if the answer is +1.03V)	
	(iv)	Assume that the current that is drawn by the ethanol fuel cell is 0.2 amperes per 10 hours, what is the mass of ethanol consumed by the ethanol fuel cell in **a day**?	[2]
		Q = It = 0.2 x 10 x 60 x 60 = 7200 C Amt of electrons consumed in 10 hours = $\frac{7200}{96500}$ = 0.07461 mol. Amt of ethanol consumed in 10 hours = 0.07461 x 0.5 = 0.03731 mol. ; Mass of ethanol consumed in 10 hours = 0.03731 x (2 x 12.0 + 6 x 1.0 + 16.0) = 1.72g Mass of ethanol consumed in a day = 1.72 x $\frac{24}{10}$ = 4.12g (3sf) ;	
	(v)	Suggest reagents and conditions to obtain ethanal from ethanol.	[1]
		Acidified $K_2Cr_2O_7$, distill. (reject $KMnO_4$/ H^+)	
1(b)	An organic compound **P** with molecular mass 180.0 contains the elements carbon, hydrogen and oxygen only. It was found to contain 66.7% carbon and 6.67% hydrogen by mass. **P** reacts with neutral $FeCl_3$ to give a violet colouration. When **P** was boiled under refluxed with aqueous NaOH, 2 compounds **Q**, $C_8H_9O_2^-Na^+$ and $CH_3CO_2^-Na^+$ were formed. **Q** can rotate plane polarized light. **Q** reacts with acidified potassium dichromate to give **R**, $C_8H_8O_2$. **R** gives **S** and a yellow precipitate with aqueous alkaline iodine. **R** decolourises aqueous bromine to give a white precipitate of **T**, $C_8H_5O_2Br_3$. Suggest the structures of **P**, **Q**, **R**, **S** and **T**. Explain the chemistry of the reactions		[10]

involved.

P: 66.7% carbon and 6.67% hydrogen by mass.	M.F of **P** = $C_{10}H_{12}O_3$
P reacts with neutral $FeCl_3$ to give a violet colouration.	Phenol is present in **P**.
P was boiled under refluxed with aqueous NaOH, 2 compounds **Q**, $C_8H_9O_2^-Na^+$ and $CH_3CO_2^-Na^+$ were formed.	**P** is an ester. Or Hydrolysis in an alkaline medium
Q can rotate plane polarized light.	Chiral carbon is present in **Q**.
Q reacts with acidified potassium dichromate to give **R**, $C_8H_8O_2$.	Oxidation reaction. No change in number of oxygen. **Q** is a secondary alcohol. R is a ketone.
R gives **S** and yellow precipitate with aqueous alkaline iodine.	 **R** has the structure.
R decolourises aqueous bromine to give a white precipitate of **T**, $C_8H_5O_2Br_3$.	The side-chain is not at the 2,4,6 position as phenol is tri-substituted.

Deductions: Max 5.

P: 	**Q:** 
R: 	**S:** 
T: 	

Structures: 1 mark per correct structure.

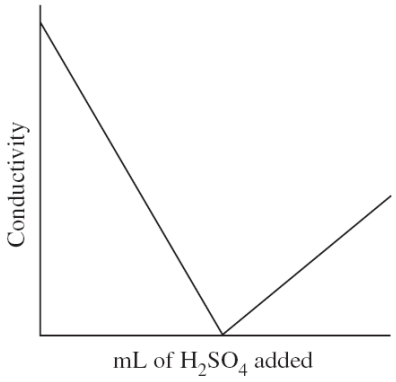
1(c)	Explain the relative ease of hydrolysis of ethanoyl chloride, chlorobenzene and chloroethane.	[3]

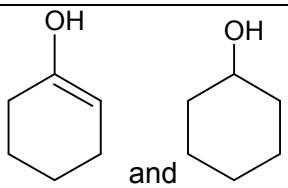
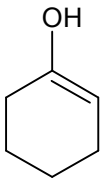
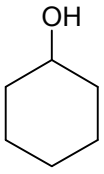
Most readily hydrolysed: Ethanoyl chloride, chloroethane, chlorobenzene. ;

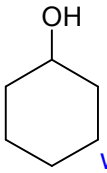
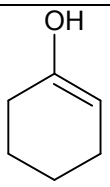
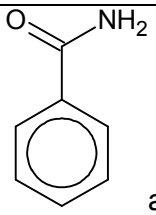
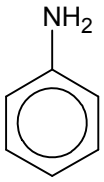
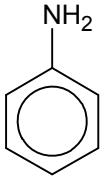
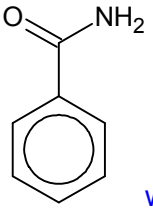
Ethanoyl chloride hydrolyses the most readily in water because one of the carbon atoms is bonded to 2 highly electronegative elements, O and Cl. Hence, the carbon atom is highly electron deficient, making it highly susceptible to nucleophilic attack.;

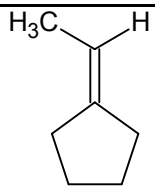
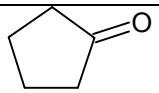
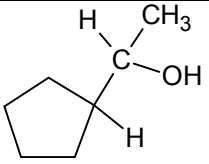
		The p-orbital of C*l* in chlorobenzene is able to overlap with the p-orbitals of benzene ring, hence, forming a partial pi bond which makes the C-C*l* bond resistant to hydrolysis.;	
		[Total: 20 marks]	
2(a)	(i)	An environmental chemist investigated the bromide content of river water. He decided to convert the bromide ions into bromine using acidified $KMnO_4$. Suggest, with the aid of equations, whether using HC*l* or H_2SO_4 would be more suitable for his investigation.	[3]
		The use of H_2SO_4 will be more suitable. ; (no marks for merely quoting the correct answer) $2Cl^- \rightarrow Cl_2 + 2e$ E = -1.36V $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H2O$ E=+1.52V Overall E = +1.52 – 1.36 = 0.16V > 0V ; If HC*l* was used to acidify the solution, $KMnO_4$ will be used to oxidise both Cl^- and Br^- ; hence rendering the volume of $KMnO_4$ required to be more than actual. ; (bonus) Max 3	
2(b)	Electrowinning, also called electroextraction, is the electrodeposition of metals from their ores that have been put in solution or liquefied. In electrowinning, a current is passed from an inert anode through a liquid leach solution containing the metal so that the metal is extracted as it is deposited in an electroplating process onto the cathode. The most common electrowon metals are lead, copper, gold, silver, zinc, aluminium, chromium, cobalt, manganese, and the rare-earth and alkali metals. For aluminium, this is the only production process employed. Several industrially important active metals like sodium and potassium are produced commercially by electrolysis of their pyrochemical molten salts.		
	(i)	Suggest 1 similarity and 1 difference between electrowinning and electropurification of copper.	[2]
		Similarity: Metals are deposited at the cathode.; Difference: For electroplating, the metal to be plated is placed at the anode (metal participates in the reaction.) In electrowinning, the anode is inert.;	
	(ii)	Draw a setup to illustrate how sodium metal can be extracted from its molten salts, stating: • the name of the salt used, • the electrode used, • the equations at the respective electrodes.	[3]
		Electrode: Graphite, Molten salt: Molten sodium choride. ; Setup; Equations at the respective electrodes.;	
	(iii)	Suggest why the reduction potential of reactive metals like sodium and potassium cannot be measured directly when they are connected to the standard hydrogen electrode.	[1]
		Sodium and potassium electrodes will react vigorously with the electrolyte to form a hydroxide solution.;	

2(c)	(i)	State two assumptions of the kinetic theory of ideal gas.	[2]
		• There is insignificant intermolecular force of attraction between the particles. ; • The volume of the gas particles is insignificant when compared to the volume of the container.; • There is elastic collision between the particles.; (Any 2)	
	(ii)	Would you expect carbon monoxide to behave as an ideal gas at high temperature?	[1]
		CO will behave like an ideal gas at high temperature. At high T, carbon monoxide particles gain kinetic energy and moves rapidly. Hence, the intermolecular forces of attraction between the particles will be insignificant. ;	
	(iii)	Explain the environmental consequences of excessive production of carbon monoxide arising from the combustion of car engines.	[1]
		CO will bond with haemoglobin, hence, reducing the ability of blood to carry oxygen round the body.	
2(d)	0.500 mole of ethanoic acid and 1.00 mole of ethanol were shaken together. The total volume of the mixture is 0.5 dm^3. The equilibrium mixture required 80 cm^3 of 1.00 mol dm^{-3} of sodium hydroxide for complete reaction.		
	(i)	Write an equation for the reaction between ethanoic acid and ethanol.	[1]
		$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$; [No marks will be awarded if an irreversible arrow is used.]	
	(ii)	Explain why the reaction mixture has to be titrated with sodium hydroxide rapidly.	[1]
		This is to reduce the effects of equilibrium changes as when more ethanoic acid is removed when NaOH is added, the equilibrium mixture may shift to the left to produce more ethanoic acid.;	
	(iii)	Write the K_c expression for the reaction formed between ethanoic acid and ethanol.	[1]
		$K_c = \frac{[ethylethanoate][water]}{[ethanoic][ethanol]}$;	
	(iv)	Calculate the equilibrium constant for the equilibrium.	[4]
		Amount of NaOH used = Amt of excess CH_3COOH at equilibrium = 80/1000 x 1 = 0.0800 mol ; $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$ I/mol: 0.5	1	0	0 C/mol: -x	-x	+x	+x E/ mol: 0.5 -x	1-x	+x	+x E/ mol; 0.08	0.58	0.42	0.42 E/ moldm^{-3}: 0.16	1.16	0.84	0.84 x = 0.5 – 0.0800 = 0.42 ; $K_c = \frac{[0.84][0.84]}{[0.16][1.16]} = 3.80$; [-1 mark if the student did not include V or 0.5dm^3 in their calculation.]	

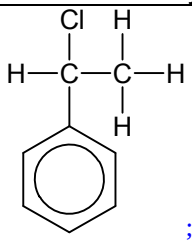
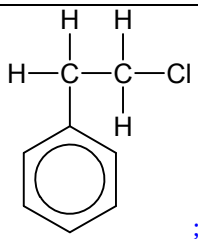
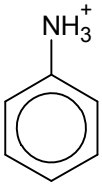
		[Allow ecf if student did not include [water] in the K_c expression.	
		[Total: 20 marks]	
3(a)	Barium sulfate is a sparingly soluble salt. A 20 mL sample of 0.100 mol dm^{-3} barium hydroxide was titrated with 0.200 mol dm^{-3} sulfuric acid. The conductivity of the solution was measured throughout the titration and the results graphed, as shown.  		
	(i)	Write an equation with state symbols to illustrate the reaction between barium hydroxide and sulphuric acid.	[1]
		$Ba(OH)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2H_2O(l)$; [No marks if state symbols are not included.]	
	(ii)	Calculate the volume of H_2SO_4 added when the conductivity of the solution is zero.	[1]
		1 $Ba(OH)_2(aq)$: 1 $H_2SO_4(aq)$ Volume of H_2SO_4 required = $10.0cm^3$	
	(iii)	Explain the changes in conductivity shown by the graph.	[3]
		Electrical conductivity of the solution is dependent on the amount of free ions in the solution to carry the electrical charges. ; The electrical conductivity decreases from 0 ml of H_2SO_4 to $10cm^3$ of H_2SO_4 because of the decrease in the amount of free Ba^{2+} and SO_4^{2-} to conduct electricity where acid is the limiting reagent. ; However, when $10cm^3$ of H_2SO_4 is added to $20cm^3$ of $Ba(OH)_2$, only solid $BaSO_4$ is present. Absence of free moving ion to conduct electricity. ; When more H_2SO_4 is added, the free H^+ and SO_4^{2-} ions from the acid will be able to carry the electrical current since acid is now in excess.; Max 3 pts.	
	(iv)	Write the K_{sp} expression for the solubility product of barium sulfate. State the units.	[2]
		$K_{sp} = [Ba^{2+}][SO_4^{2-}]$; Units: $mol^2\ dm^{-6}$;	
	(v)	The solubility of barium sulfate is 2.42×10^{-3} g dm^{-3} at 25°C. Calculate the K_{sp} value for barium sulfate in terms of $(mol\ dm^{-3})^n$.	[2]
		Solubility of barium sulfate = $2.42 \times 10^{-3} / (137 + 32 + 4 \times 16.0)$ = 1.039×10^{-5} mol dm^{-3}	

		$K_{sp} = s^2$ $= (1.039 \times 10^{-5})^2$ $= 1.08 \times 10^{-10}$ mol^2 dm^{-6}	
3(b)	Beryllium is another element in Group II. However, the temperature required for thermal decomposition of $BeCO_3$ is much lower than $BaCO_3$. Explain the observation, quoting relevant data from the data booklet.		[2]
		Cationic radius: Be^{2+} : 0.031nm Ba^{2+} : 0.135nm ; Since Be^{2+} has a much lower cationic radius than Ba^{2+}, the charge density of Be^{2+} will be much higher. Hence, Be^{2+}will be able to polarize the electron cloud of CO_3^{2-} much easily, leading to lower temperature required for thermal decomposition. ;	
3(c)	When BF_3 is dissolved in HF, the solution became acidic. Suggest reasons for the observations. Illustrate your answer with a diagram.		[3]
		Boron in BF_3 has an empty orbital to form dative bonding with the lone pair of electrons in F^-.; $HF \rightleftharpoons H^+ + F^-$ $BF_3 + F^- \rightarrow BF_4^-$ Since F^- is constantly used to form $BF_4^-$with BF_3, HF will dissociate to produce more H^+ and F^-, hence increasing the acidity of the solution.; Diagram;	
3(d)	Suggest and explain one simple chemical method for distinguishing between the members of each of the following pair, making clear observations you would expect to make for each substance.		[6]
	(i)		
		Reagents: Aqueous bromine solution. ;  Observations: will decolourise brown aqueous bromine solution while  will not. ; Or Reagents: PCl_5 ;	

		  Observations: will give white fumes with aq NH_3 while will not. ;	
	(ii)	 and 	
		Reagents and conditions: Aqueous bromine solution.;  Observations: will decolourise brown aqueous bromine but  will not. ;	
	(iii)	HCO_2H and CH_3COOH	
		Reagents and conditions: Acidified $KMnO_4$, heat under reflux. Pass the gas produced through $Ca(OH)_2$ / limewater.; Observations: Effervescence produced for HCOOH. Gas produced formed a white ppt with limewater/ $Ca(OH)_2$.;	
		[Total: 20 marks]	
4(a)	Compound **E**, C_7H_{12} reacts with acidified $KMnO_4$, heated under refluxed to produce 2 compounds **F**, $C_2H_4O_2$ and **G**, C_5H_8O. Compound **F** produces effervescence when reacted with sodium carbonate. Compound **G** does not give silver mirror with Tollen's reagent. Compound **E** reacts with steam to give compound **H**, $C_7H_{14}O$. Compound **H** can be further oxidised by $KMnO_4$ to give a compound that gives a orange precipitate with Brady's reagent. Suggest the structures of **E**, **F**, **G** and **H**. Explain the chemistry of the reactions involved.	[7]
		Compound **E**, C_7H_{12} reacts with acidified $KMnO_4$, heated under refluxed to produce 2 compounds **F**, $C_2H_4O_2$ and **G**, C_5H_8O. OR Compound **E** reacts with steam in the presence of steam to give compound **H**, $C_7H_{14}O$.	Compound **E** is an alkene.

		Compound **F** produces effervescence when reacted with sodium carbonate.	Compound **F** is a 2 C carboxylic acid. **F** is CH_3COOH.
		Compound **G** does not give silver mirror with Tollen's reagent.	Compound **G** is a ketone.
		Compound **H** can be further oxidised by $KMnO_4$ to give a compound that gives a orange precipitate with Brady's reagent.	Compound **H** is a secondary alcohol.
		Deductions: max 3 marks	
		E 	**F** CH_3COOH.
		G 	**H** 
		1 mark per correct structure.	
4(b)	Manganese is an element in the transition metal series.		
	(i)	Write down the electronic configuration of the transition ion present in Mn_2O_3.	[1]
		Mn^{3+} : [Ar] $3d^4$;	
	(ii)	Explain, with the aid of equations, the use of Mn^{2+} and Mn^{3+} as catalyst in an I^-/ $S_2O_8^{2-}$ reaction.	[4]
		Mn^{2+} and Mn^{3+} acts as homogeneous catalyst in the reaction by providing an alternative pathway with a lowered activation energy for the reaction to happen. ; $S_2O_8^{2-}$ + 2e ⇌ $2SO_4^{2-}$ $E^{\ominus}$ = +2.01V $2I^-$ ⇌ I_2 + 2e $E^{\ominus}$ = -0.54V [R]Mn^{3+} + e ⇌ Mn^{2+} $E^{\ominus}$ = +1.49V [O] $2I^-$ ⇌ I_2 + 2e $E^{\ominus}$ = -0.54V Overall: $2Mn^{3+}$ + $2I^-$ ⇌ $2Mn^{2+}$ + I_2 ; $E^{\ominus}$ = +0.95V [R] $S_2O_8^{2-}$ + 2e ⇌ $2SO_4^{2-}$ $E^{\ominus}$ = +2.01V [O] Mn^{2+} ⇌ Mn^{3+} + e $E^{\ominus}$ = -1.49V Overall: $S_2O_8^{2-}$ + 2 Mn^{2+} ⇌ $2SO_4^{2-}$ + $2Mn^{3+}$; $E^{\ominus}$ = +0.52V Overall $E^{\ominus}$ calculated for BOTH equation;	
	(iii)	How does the addition of catalyst affect the rate constant of the I^-/ $S_2O_8^{2-}$ reaction? Explain.	[2]
		It increases the rate constant of the reaction.; When a catalyst is used, the lowered activation energy will allow more particles to possess the minimum energy to collide together. Hence, frequency of effective collision increases.;	

4(c)	A buffer solution is prepared as follows: 53.5 g of ammonium chloride dissolved in 400 cm^3 of 15.0 mol dm^{-3} ammonia, and the mixture is diluted to 1.00 dm^3. K_a of NH_4^+ = 6.00 x 10^{-10} mol dm^{-3}		
	(i)	Explain what is meant by a buffer solution with reference to ammonium chloride and ammonia. Illustrate your answers with equations.	[2]
		A buffer solution is a mixture made up by a weak base, ammonia and its salt, ammonium chloride. It is able to resist changes in pH values when a little acid or base is added to it. $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ $NH_3 + H^+ \rightarrow NH_4^+$;	
	(ii)	Calculate the pH of the prepared buffer solution.	[3]
		$K_b = \frac{1.00 \times 10^{-14}}{6.00 \times 10^{-10}}$ = 1.667 x 10^{-5} mol dm^{-3} pK_b = 4.78 ; [salt] = 53.5/ 53.5 = 1.00 mol dm^{-3} [base] = $\frac{\frac{400}{1000} \times 15}{1}$ = 6.00 mol dm^{-3} pOH = pKb + lg $\frac{[salt]}{[base]}$ = 4.78 + lg $\frac{1}{6}$; = 4.00 pH = 10.0;	
	(iii)	Suggest the indicator that can be used in a titration between aqueous ammonia and hydrochloric acid to produce ammonium chloride salt.	[1]
		Methyl orange/ methyl red.;	
		[Total: 20 marks]	
5(a)	(i)	Name and describe the mechanism for the reaction of HCN with $CH_3COCH_2CH_3$.	[3]
		Name of mechanism: Nucleophilic addition. ; Correct intermediate; Correct arrows + lone pair of electrons shown on CN^-;	
	(ii)	Explain with the aid of equation, the importance of adding trace quantity of NaOH to the reaction in (i)	[2]
		$HCN \rightleftharpoons H^+ + CN^-$ HCN is a weak acid that dissociates partially in water only.; When NaOH is added, NaOH will react with H^+. By LCP, the system will shift to	

		the right to produce more H^+ and CN^-, hence generating more CN^- nucleophiles.;	
5(b)	Benzene is a common starting reagent for many reactions.		
	(i)	Describe structural isomerism.	[1]
		Structural isomerism arises when molecules have the same molecular formula but the atoms are arranged differently to form molecules.	
	(ii)	Describe and explain the shape of benzene in relation to *sigma* and *pi* bonds.	[1]
		Planar. Each carbon atoms forms 3 sigma bonds with other atoms. Hence, each carbon atom undergoes sp^2 hybridisation leading to its planar shape.;	
	(iii)	Ethylbenzene reacts with chlorine in the presence of UV light. Draw the displayed formula of the products that can be formed during the reaction. Describe the type of isomerism involved.	[3]
		 ;  ; Positional isomerism. ;	
	(ii)	Benzene reacts with concentrated nitric acid and concentrated sulfuric acid to form nitrobenzene. However, the reaction does not work if dilute nitric acid was added. Explain the observation.	[2]
		Reaction of benzene with concentrated nitric acid and concentrated sulfuric acid to form nitrobenzene involves an electrophilic substitution mechanism.; Concentrated sulphuric acid is a catalyst to generate a strong electrophile.; In benzene, the ring is not bonded to any electron donating groups. Hence, the ring is not activated. Thus, more extreme condition is required for the reaction to occur.; (Max 2 marks)	
	(iii)	Nitrobenzene can be converted to phenylamine in a 2 step reaction. State the conditions, reagents used for the conversion. Draw the full structural formula of the intermediate that is formed.	[3]
		Step 1: Conc HC*l*, Sn, Heat under reflux. ; Step 2: NaOH (aq) ; Intermediate: 	
5(c)	(i)	Describe the reactions of oxides of Period 3 elements (sodium to silicon) with water, stating their pH values, with reference to their structure and bonding.	[3]
		$Na_2O + H_2O \rightarrow 2NaOH$ pH= 13 $MgO + H_2O \rightleftharpoons Mg(OH)_2$ pH = 9 MgO dissolves sparingly in water because of its high lattice energy.	

		Al_2O_3 and SiO_2 do not react with water because their relative high lattice energy. pH = 7.	
	(ii)	Describe the difference in melting of sodium oxide and oxides of sulphur with reference to their structure and bonding.	[2]
		Sodium oxide is an ionic oxide with strong electrostatic forces of attraction between the oppositely charged Na^+ and O^{2-} ions. Hence, a lot of energy is required to overcome the strong forces of attraction. High melting point. ; Oxides of sulphur are simple covalent compounds with weak intermolecular forces of attractions between molecules. Hence, little energy is required to overcome the weaker forces of attraction between the molecules. Low melting point. ;	
		[Total: 20 marks]	