Candidate Name: _____

Class	Adm No 822

H

millennia institute

2013 Preliminary Examination II
Pre-university 3

H2 CHEMISTRY **9647/02**

Paper 2 Structured Questions **Wednesday, 18 Sep 2013**

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces provided at the top of this page.
Write in dark blue or black pen in the spaces provided.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** 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.

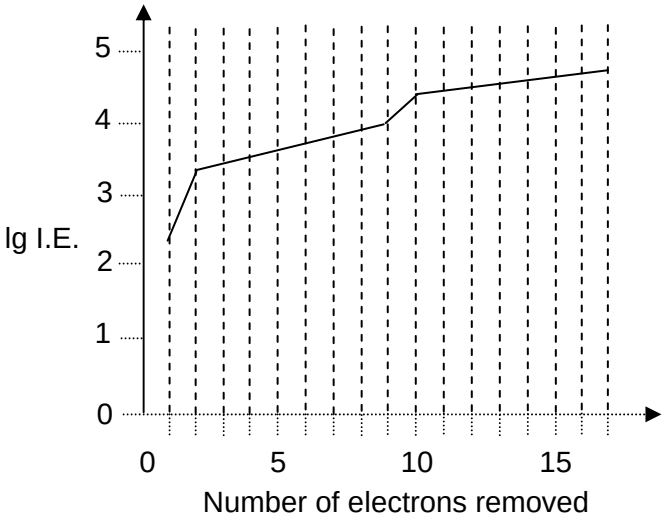
For Examiner's Use	
1	/12
2	/10
3	/13
4	/12
5	/13
6	/12
Total	/72

1	**Planning (P)**			*For Examiner's Use*
	You are to design an experiment to determine the enthalpy change of reaction between solid $Mg(OH)_2$ and hydrochloric acid. You are provided with the following list of apparatus and reagents. [You may assume that all other common laboratory apparatus not listed below are also available.] Reagents: • **FA1**: 2.50 mol dm^{-3} of HC*l* • **FA2**: $Mg(OH)_2$ solid Apparatus: • A thermometer with 0.2 °C interval • A 100 cm^3 styrofoam cup **with a lid** • 50 m*l* measuring cylinder			
	(a)	Write a balanced equation (including state symbols) for the reaction between solid $Mg(OH)_2$ and hydrochloric acid. [1]		
		$Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$ 1m for balanced equation with state symbols		
	(b)	Given that the **enthalpy change of reaction** between solid $Mg(OH)_2$ and hydrochloric acid is approximately – 30.0 kJ mol^{-1}, prove with calculations whether 50.0 cm^3 of 2.5 mol dm^{-3} HC*l* and 1.50 g of $Mg(OH)_2$ are suitable quantities to use at the start of the experiment. Justify your answer. [Assuming the specific heat capacity of the solution is 4.2 J g^{-1} K^{-1}] [4]		
		Amount of HC*l* = 50/1000 x 2.5 = 0.125 mol Amount of $Mg(OH)_2$ = 1.50 ÷ (24.3 + 17.0 x 2) = 0.02573 mol (L.R.) Heat released by reaction = heat absorbed by solution 30000 x 0.02573 = 50 x 4.2 x ΔT ΔT = 3.68 °C Amount of solid $Mg(OH)_2$ is not suitable as ΔT is not within 5-10 °C. A very small ΔT will give rise to a large experimental error. *1m for calculating amount of both reagents* *1m for determining L.R.* *1m for determining ΔT* *1m for justification*		

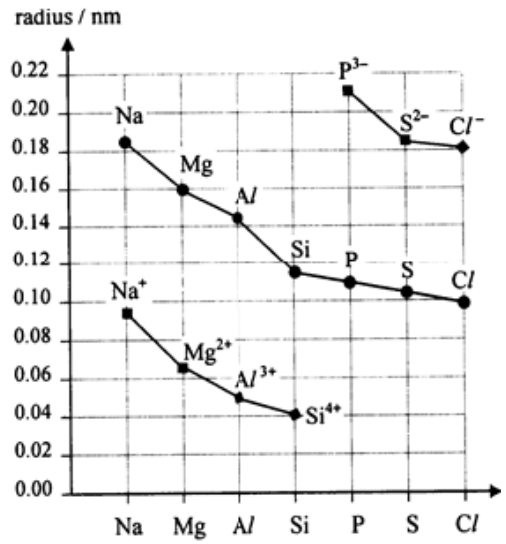
	(c)	Hence give a detailed procedure to determine the enthalpy change of reaction between solid $Mg(OH)_2$ and HC*l*. [4]		*For Examiner's Use*
		Note: *Use double the mass of $Mg(OH)_2$ solid (i.e. 3.00 g) so that ΔT is doubled to 7.36 $^{\circ}C$ and dilute HCl is still present in excess.* 1. Weigh accurately about 3.00 g of $Mg(OH)_2$ using a weighing bottle. 2. Using a 50 m*l* measuring cylinder, measure 50 cm^3 of HC*l* into a styrofoam cup supported in a beaker. 3. Measure the initial temperature of HC*l* solution. 4. Add solid $Mg(OH)_2$ into the styrofoam cup and replace the lid immediately. 5. Stir with the thermometer and measure the highest temperature reached. 6. Weigh the mass of weighing bottle and residual solid and calculate the actual mass of $Mg(OH)_2$ used. 7. Wash the styrofoam cup and dry it thoroughly before the next experiment. 8. Repeat experiment for consistent results. *1m for M1* *(accept any mass of $Mg(OH)_2$: 2.05 g < **m** < 3.60 g in order for it to still be the L.R.)* *1m for M2 – M4* *1m for M5 – M6* *1m for M7 – M8*		
	(d)	Both Group I and Group II hydroxides are white solids. A student accidentally mixes up two **unlabelled** bottles of white solids, known to contain either KOH or $Ba(OH)_2$. Briefly describe an experiment in which the student can perform in order to determine the identity of the white solids. You are provided with two unknown colourless solutions both at the same concentration of 1.00 mol dm^{-3}, either containing KOH (aq) or $Ba(OH)_2$ (aq) and **FA1**: 2.50 mol dm^{-3} of HC*l*. [3]		
		1. Using a measuring cylinder, measure 25 cm^3 of each unknown solution into separate Styrofoam cups and measure its initial temperature. **2. Add *50 cm^3* of FA1 into each cup. Stir the mixture with a thermometer and record the highest temperature reached.** **3. Determine the temperature change for both solutions. The two temperature changes should be mathematically related by: $\Delta T_1 = 2\Delta T_2$.** **4. The mixture which give rises to the higher temperature change (twice) contains Ba(OH)2, due to two moles of water produced during the neutralisation reaction.**		

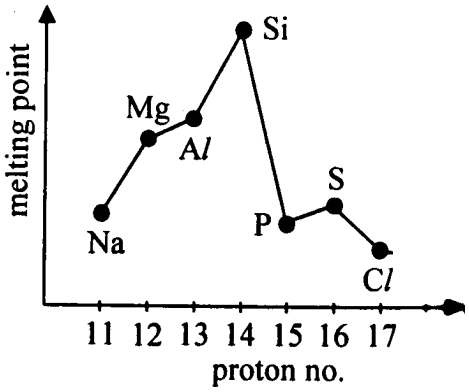
4

		Note: Volume of FA1 chosen must allow FA1 used to be in excess. *1m for M1&M2* *1m for M3* *1m for M4*		
		[Total: 12]		

2	The graph shows the logarithm, lg, of the ionization energies for the outermost electrons of element **X** in Period 4.  			*For Examiner's Use*
(a)	From the graph above, deduce the group in the Periodic Table to which **X** is likely to belong to and explain your reasoning. Hence, suggest an identity for element **X**. [2]			
	Group I. **Largest increase in energy to remove the second outermost electron.** **The second electron was removed from a lower principal quantum shell ;** **X is potassium. ;**			
(b)	**(i)**	Sketch a graph for elements of the third period (**sodium to chlorine**) to show how each property changes across the period. I. Atomic and Ionic Radius (**on the same graph**) II. Melting Point Explain your sketches.		

6





1m for each correctly labelled sketch (total 2m)

Across the period, nuclear charge ↑ as proton number ↑change in the screening effect is negligible (Same no. of inner shells of e⁻s across the period), the outer e⁻s are more strongly attracted by the nucleus
∴ atomic radii ↓

cations have one shell less than neutral atoms, the outer e⁻s are more strongly attracted by the nucleus, thus smaller in radius than the parent atom.

anions have more e⁻s than protons and so, the effective attractive force on the outer e⁻s is less than that in neutral atoms, the outer e⁻s are less strongly attracted by the nucleus, thus bigger in radius as compared to the parent atom.

1m for explanation of atomic radius
1m for explanation of <u>both</u> cationic and anionic radius

<u>Na to Al</u>
giant metallic structure
strong electrostatic forces of attraction between metal cations and delocalised electrons, large amount of energy required to overcome those forces ∴ high m.p.

delocalised electrons ↑, size of cations ↓, (charge on cation ↑)
strength of metallic bond ↑∴m.p. ↑

<u>Si</u>
giant covalent structure
⇒ large amount of energy required to break strong covalent bonds between Si atoms.∴ high m.p.

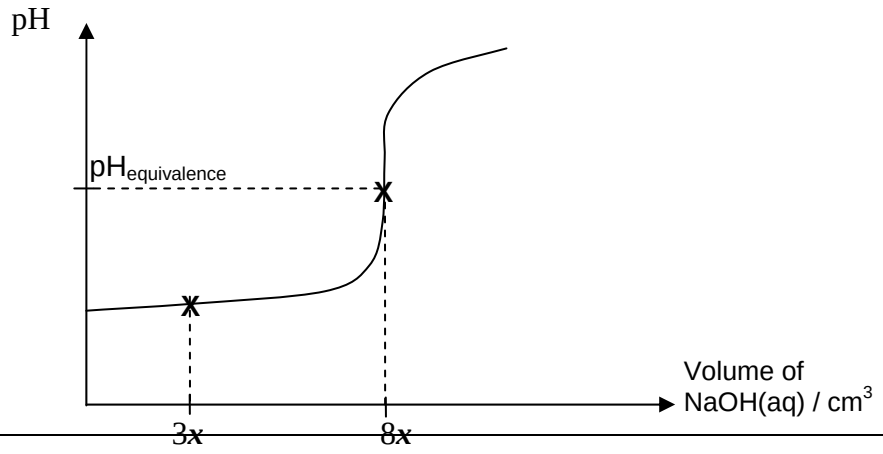
<u>P to Cl</u>

		Simple molecular structure **weak temporary dipole – induced dipole forces of attraction between molecules** **⇒ relatively smaller amount of energy required to overcome those forces** **∴ low m.p.** **size of electron cloud of molecules varies, S_8>P_4>CI_2** **size of electron cloud of molecules ↑, strength of temporary dipole – induced dipole forces of attraction ↑. ∴ m.p.: S_8>P_4>CI_2** *1m for explanation of Na-Al* *1m for explanation of Si* *1m for explanation of P - Cl*		
	(ii)	State and explain the trend of atomic radius of transition metals across the period from titanium to copper. [8]		*For Examiner's Use*
		⇒ Electrons are being added to <u>inner 3d subshell</u>. **⇒ Screening effect of 3d electrons effectively cancels almost all increase in nuclear charge across period** **⇒ Thus, <u>metallic radius remains almost constant.</u>**		
		[Total: 10]		
3	Explain the following observations as fully as you can. Write equations where appropriate.			
(a)	**(i)**	When NH_3(aq) is added to a solution containing Cu^{2+}(aq), a light blue precipitate which is soluble in an excess of NH_3(aq) to form a dark blue solution is formed.		
		$[Cu(H_2O)_6]^{2+}$(aq) + $2OH^-$(aq) → $Cu(OH)_2$(s) + $6H_2O$(*l*) **Light blue ppt** **OR $[Cu(H_2O)_6]^{2+}$(aq) + $2OH^-$(aq) → $[Cu(OH)_2(H_2O)_4]$(s) + $2H_2O$(*l*) ;** **$Cu(OH)_2$(s) + $4NH_3$ → $[Cu(NH_3)_4]^{2+}$(aq) + $2OH^-$(aq)** **Dark blue solution** **OR $[Cu(OH)_2(H_2O)_4]$ + $4NH_3$ → $[Cu(NH_3)_4(H_2O)_2]^{2+}$(aq) + $2OH^-$ + $2H_2O$;**		
	(ii)	When concentrated hydrochloric acid is added to another solution containing Cu^{2+}(aq), there is a colour change from blue to pale yellowish-green. No such colour change occurs when concentrated sulfuric acid is added to Cu^{2+}(aq). [4]		

		$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(aq)$ **Ligand exchange occurs. Yellow-green solution is due to the formation of $[CuCl_4]^{2-}(aq)$. ;** **When H_2SO_4 is added to $Cu^{2+}(aq)$, no complexes are formed thus no colour change is observed. ;**		
(b)	3-bromo-3-methylhexane, $CH_3CH_2C(Br)(CH_3)CH_2CH_2CH_3$, reacts with ethanolic sodium cyanide to form a mixture that does not rotate light. [2]		
	The reaction proceeds via S_N1 mechanism. **The carbocation intermediate formed (sp^2 hybridised) has a trigonal planar shape, hence CN^- nucleophile has equal probability of attacking from either side of the carbocation intermediate, forming a racemic mixture. ;** **The racemic mixture contains equal proportions of each enantiomer, thus is optically inactive. ;**			
(c)	The entropy of the following systems increases. [Both systems are kept under constant volumes.] I. 1 mol of Br_2 (g) is added to 1 mol of N_2 (g) at 298 K. II. 1 mol of I_2 (g) is heated from 298 K to 373 K. [2]			
	I. **Entropy increases as the system becomes more disorderly due to the process of mixing which results in more ways of arranging the particles.** II. **Entropy increases as the system becomes more disorderly as the particles gain more kinetic energy due to the increase in temperature which results the particles moving further apart from each other, losing its structure.** ***1m each***			
(d)	**(i)**	The kinetics of the chlorination of PCl_3 was investigated in three experiments at constant temperature. The initial rate of the experiment was measured at different concentrations of PCl_3 and Cl_2. The results are shown in the following table.		

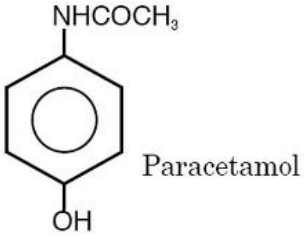
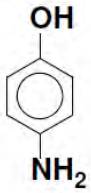
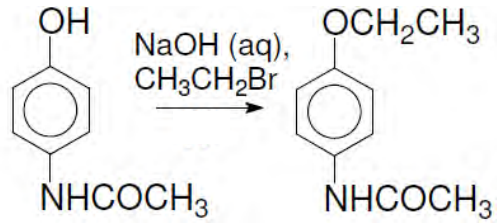
Experiment	**$[PCl_3]$ / mol dm^{-3}**	**$[Cl_2]$ mol dm^{-3}**	**Relative Rate/ mol dm^{-3} s^{-1}**
1	0.005	0.005	1.00
2	0.006	0.006	1.44
3	0.008	0.006	1.92

		Show that the units for the rate constant, ***k***, of the above experiment is $mol^{-1}\,dm^3\,s^{-1}$.		
		Order wrt CI_2 = 1 ; **Order wrt PCI_3 = 1 ;** **Rate = k[PCI_3] [CI_2]** **Thus, units for *k* for an overall second order reaction is $mol^{-1}\,dm^3\,s^{-1}$. ;** ***Appropriate working must be shown to be awarded the marks***		

	(ii)	Phosphorus trichloride, PCI_3, and NCI_3 react in different ways with water although they each give two products. In the reaction, PCI_3 gives HC*l* as the only chlorine containing product, while NCI_3 gives HOC*l* as the only chlorine-containing product. Suggest why PCI_3 and NCI_3 behave differently. [5]		
		P is in period 3 and has empty d-orbitals to accept a lone pair of electrons from water to form dative bonding. Thus PCI_3 is readily hydrolysed to give HC*l*. ; **N does not form dative bonding with water. However, due to the greater electronegativity of N as compared to P, the δ- on the N will be attracted to the δ+ end of the water molecule. Thus forming NH_3 + 3HOC*l* as products. ;**		*For Examiner's Use*
		[Total: 13]		
4	A biochemist needs to prepare a CH_3COOH / $CH_3COO^-Na^+$ buffer solution to stimulate the growth of a particular fungus. In order to investigate the composition of a $CH_3COOH/CH_3COO^-Na^+$ buffer solution of pH 4.16, the biochemist titrated 25.0 cm^3 of this buffer solution with 1.0 mol dm^{-3} aqueous sodium hydroxide. The graph below shows the titration curve obtained.  		

	Upon the addition of $3x$ cm^3 of aqueous sodium hydroxide, the buffer solution becomes most effective. The equivalence point of titration is attained when $8x$ cm^3 of aqueous sodium hydroxide is added.		
(a)	Show that the ratio of $[CH_3COOH]$: $[CH_3COO^-Na^+]$ is 4 : 1 in the original buffer solution. [3]		
	At maximum buffer capacity, **Mol ratio of CH_3COOH : $CH_3COO^-Na^+$ = 1 : 1** **From 3x to 8x of NaOH used, 5x of CH_3COOH is converted to $CH_3COO^-Na^+$** **Hence at maximum buffer capacity,** **CH_3COOH : $CH_3COO^-Na^+$ = 5x : 5x ;** **Working backwards, at the beginning of titration,** **mol ratio of CH_3COOH : $CH_3COO^-Na^+$** **= 5x + 3x : 5x – 3x ;** **= 8x : 2x = 4:1 ;** **$[CH_3COOH]$: $[CH_3COO^-Na^+]$ = 4:1**		
			For Examiner's Use
(b)	Determine the K_a of CH_3COOH. [2]		
	$pH = pK_a + lg \frac{[NaA]}{[HA]}$ **$4.16 = pK_a + lg (\frac{1}{4})$** **$pK_a$ = 4.76 ;** **Hence, $K_a = 1.73 \times 10^{-5}$ mol dm^{-3} ;**		
(c)	State and explain if the K_a value of $CH_2ClCOOH$ is higher or lower than the K_a value of CH_3COOH. [2]		
	The K_a value of $CH_2ClCOOH$ is higher. ; **The presence of the electron withdrawing Cl atom disperses the negative charge on the oxygen atom of the carboxylate anion, increasing the stability of the carboxylate anion. Thus, the acid has a higher tendency of donating H^+, resulting in $CH_2ClCOOH$ being a stronger acid.** ;		
(d)	**(i)** Using your answer in **(b)**, determine the pH of the solution formed when 50.0 cm^3 of 0.100 mol dm^{-3} $CH_3COOH(aq)$ is mixed with 30.0 cm^3 of 0.100 mol dm^{-3} $CH_3COO^-Na^+(aq)$.		
	$[CH_3COOH]$ in buffer = 0.0625 $moldm^{-3}$; **$[CH_3COO^-Na^+]$ in buffer = 0.0375 $moldm^{-3}$;** **$pH = -lg(1.73 \times 10^{-5}) + lg\{0.0375/0.0625\} = 4.54$;** ***allow e.c.f from (b)***		

	(ii)	2 cm^3 of 0.100 mol dm^{-3} of hydrochloric acid was accidentally added to the solution in **(d)(i).** It was found that the pH of the resulting solution did not differ much from the pH obtained in **(d)(i)**. Explain why this is so. Write equations to support your answer. [5]		
		A buffer solution is obtained in (d)(i). A buffer solution is a solution that resists pH changes when a small amount of acids or bases is added to it, as shown in the following equation: ; **CH_3COO^- (aq) + H^+(aq) → CH_3COOH (aq) ;**		
		[Total: 12]		

5	Paracetamol is classified as a mild painkiller. It is commonly used for the relief of headaches and other minor aches and pains and is a major ingredient in numerous cold and flu remedies.  Paracetamol		
(a)	Paracetamol can be made from phenol as a starting material. Describe a synthesis route for the production of paracetamol from phenol in no more than 3 steps. You are to include all intermediates and reagents and conditions used in each step of your synthesis. [5]		
	Step I: Dilute nitric acid, room temperature **Step II: Sn and conc. HC*l*, heat under reflux, followed by NaOH (aq)** **Step III: limited CH_3COCl, in the cold.** **A**  **B**  ***1m for each intermediate (total 2m)*** ***1m for each set of reagents and conditions (3m)***		
(b)	Paracetamol can be converted into another painkiller, Phenacetin, as shown below.  *Paracetamol* *Phenacetin* With reference to the mechanism of the reaction, suggest why NaOH(aq) is added in the conversion. [2]		
	• NaOH will neutralize the phenol group in Paracetamol to form the phenoxide ion, which is a stronger nucleophile. ; • The phenoxide ion attacks the electron-deficient C in CH_3CH_2Br, substituting the		

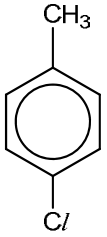
halogen atom to form Phenacetin. ;

(c) Suggest a method by which the following compounds could be distinguished from each other by a chemical test. State the observations you would expect for each compound.

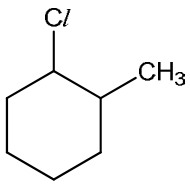
(i) Paracetamol and Phenacetin

Test: add neutral $FeCl_3$ to each compound
Observations: Violet colouration observed for paracetamol only.

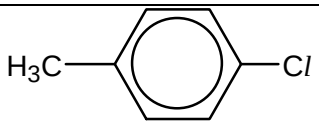
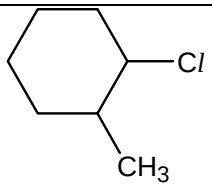
(ii)



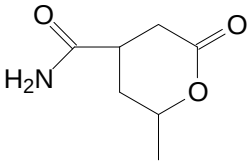
and



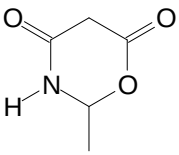
Test: Add aq NaOH and boil followed by excess dilute HNO_3 and $AgNO_3$.

	
No white ppt observed	**White ppt observed**

(iii)



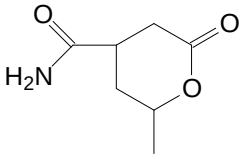
and



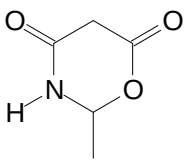
[6]

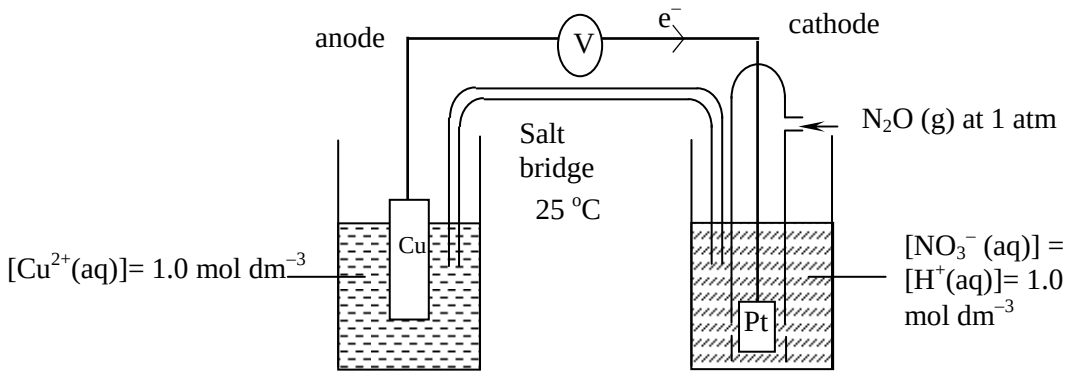
Add NaOH (aq) to each compound and heat under reflux. Test any gas evolved with damp red litmus paper.

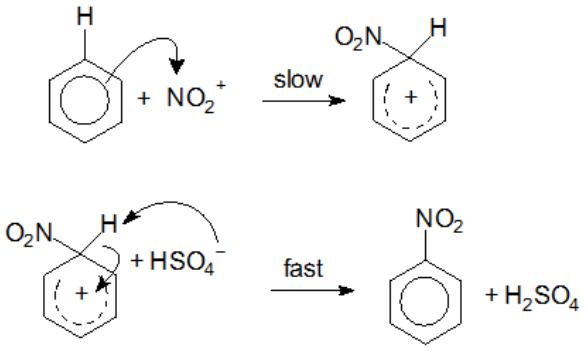
Observation:



Effervescence seen ; colourless gas evolved turns damp red litmus paper turns blue



		damp red litmus paper remains unchanged.		
		For each part, *1m for correct chemical test, including all reagents and observations* *1m for observations for both compounds*		
		[Total: 13]		
6	Nitrous oxide is naturally present in the atmosphere as part of the Earth's nitrogen cycle. Human activities such as agriculture, fossil fuel combustion, wastewater management, and industrial processes contribute to the amount of N_2O in the atmosphere.			
(a)	Draw a fully labelled experimental set–up for a voltaic cell made up of an NO_3^-/N_2O half–cell and a Cu^{2+}/Cu half–cell under standard conditions. Indicate clearly the anode and cathode and show the flow of electrons. [4]			
	 *1m for correctly indicating anode cathode* *1m for salt bridge, voltmeter, labeling all standard conditions and flow of electrons* *1m each for each complete, labelled half-cell (total 2m)*			
(b)	*The use of the Data Booklet is relevant to this question.* The standard electrode potential of the NO_3^-/N_2O half–cell is given below: $2NO_3^- + 10H^+ + 8e^- \rightleftharpoons N_2O + 5H_2O$ $\quad E^\ominus = +1.11$ V Calculate the $E^\ominus_{cell}$ and write an equation for the reaction that occurs. [2]			
	$E^\ominus_{cell}$ = +1.11 – 0.34 V = +0.77 V ; **$2NO_3^-(aq) + 10H^+(aq) + 4Cu(s) \rightarrow N_2O(g) + 5H_2O(l) + 4Cu^{2+}(aq)$;** ***Accept answers without state symbols***			
(c)	Benzene is nitrated by warming it in a mixture of concentrated nitric acid and			

	concentrated sulfuric acid. With the help of equations, describe the mechanism of the nitration of benzene. [4]		
	Nitration of benzene proceeds via the electrophilic substitution mechanism. The electrophile, NO_2^+ is generated in the reaction between conc. H_2SO_4 and conc. HNO_3 as follows: $2H_2SO_4 + HNO_3 \rightleftharpoons 2HSO_4^- + H_3O^+ + NO_2^+$  *1m for generation of electrophile step* *1m for all correctly-drawn curly arrows* *1m for intermediate and indicating slow step* *1m for regeneration of H_2SO_4*		
(d)	The bromination of benzene occurs via a similar mechanism to that in **(c)**. Iron(III) bromide is required to catalyse the reaction. Suggest why this is so. [2]		
	Due to delocalisation, π–electrons in benzene are not polarising enough to generate Br^+ from Br_2. ; $FeBr_3$ is therefore needed to generate Br^+ as follows: $FeBr_3 + Br_2 \rightarrow Br^+ + FeBr_4^-$;		
	[Total: 12]		

END OF PAPER