2 hours



# UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS General Certificate of Education Advanced Level

Paper 4 Struct	ured Questions		May/June 2013
CHEMISTRY			9701/42
CENTRE NUMBER		CANDIDATE NUMBER	
CANDIDATE NAME			

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

#### **READ THESE INSTRUCTIONS FIRST**

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

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

DO NOT WRITE IN ANY BARCODES.

#### **Section A**

Answer all questions.

#### Section B

Answer all questions.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

Electronic calculators may be used.

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.

For Exam	iner's Use
1	
2	
3	
4	
5	
6	
7	
8	
Total	

This document consists of 16 printed pages and 4 blank pages.



#### Section A

For Examiner's Use

Answer all the questions in the spaces provided.

A bromoalkane, R-Br, is hydrolysed by aqueous sodium hydroxide. 1 (a) (i) Write a balanced equation for this reaction.

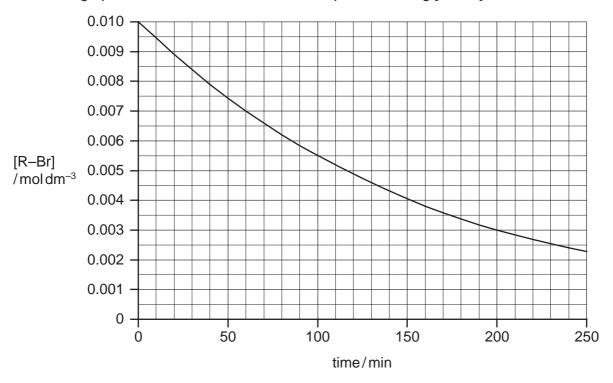
.....

(ii) What type of reaction is this?

[2]

(b) The concentration of bromoalkane was determined at regular time intervals as the reaction progressed.

Two separate experiments were carried out, with different NaOH concentrations. The graph below shows the results of an experiment using [NaOH] = 0.10 mol dm<sup>-3</sup>.



When the experiment was repeated using [NaOH] = 0.15 mol dm<sup>-3</sup>, the following results were obtained.

time/min	[R-Br]/moldm <sup>-3</sup>
0	0.0100
40	0.0070
80	0.0049
120	0.0034
160	0.0024
200	0.0017
240	0.0012

(i) Plot these data on the axes above, and draw a line of best fit.

(ii) Use one of the graphs to confirm that the reaction is first order with respect to R–Br. Show all your working, and show clearly any construction lines you draw.

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(iii) Use the graphs to calculate the order of reaction with respect to NaOH. Show all your working, and show clearly any construction lines you draw on the graphs.

(iv) Write the rate equation for this reaction, and calculate the value of the rate constant.

rate =

[7]

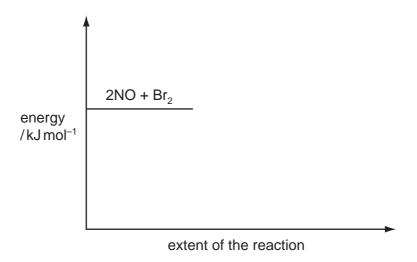
(c) Nitric oxide, NO, and bromine vapour react together according to the following equation.

$$2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$$
  $\Delta H = -23 \text{ kJ mol}^{-1}$ 

The reaction has an activation energy of +5.4 kJ mol<sup>-1</sup>.

Use the following axes to sketch a fully-labelled reaction pathway diagram for this reaction.

Include all numerical data on your diagram.



[2]

[Total: 11]

2	(a)	(i)	With the aid of a fully-labelled diagram, describe the standard hydrogen electrode.
		(ii)	Use the <i>Data Booklet</i> to calculate the standard cell potential for the reaction between $Cr^{2+}$ ions and $Cr_2O_7^{2-}$ ions in acid solution, and construct a balanced equation for the reaction.
			<i>E</i> <sup>o</sup> <sub>cell</sub> = ∨
			equation
		(iii)	Describe what you would see if a blue solution of $Cr^{2+}$ ions was added to an acidified solution of $Cr_2O_7^{2-}$ ions until reaction was complete.
			[8]

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Use

**(b)** A buffer solution is to be made using  $1.00\,\mathrm{mol\,dm^{-3}}$  ethanoic acid,  $\mathrm{CH_3CO_2H}$ , and  $1.00\,\mathrm{mol\,dm^{-3}}$  sodium ethanoate,  $\mathrm{CH_3CO_2Na}$ .

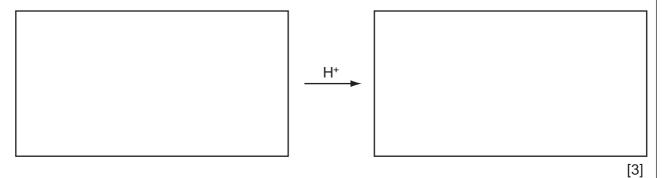
Calculate to the nearest 1 cm³ the volumes of each solution that would be required to make 100 cm³ of a buffer solution with pH 5.50.

Clearly show all steps in your working.

 $K_a (CH_3CO_2H) = 1.79 \times 10^{-5} \,\text{mol dm}^{-3}$ 

volume of 1.00 mol dm <sup>-3</sup> $CH_3CO_2H = \dots$	cm <sup>3</sup>
volume of 1.00 mol dm <sup>-3</sup> CH <sub>3</sub> CO <sub>2</sub> Na =	cm <sup>3</sup>

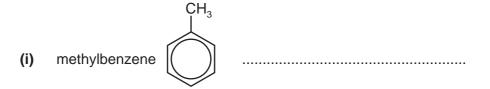
- (c) Write an equation to show the reaction of this buffer solution with each of the following.
  - (i) added HC1 .....
  - (ii) added NaOH ......[2]
- (d) Choose **one** reaction in organic chemistry that is catalysed by an acid, and write the structural formulae of the reactants and products in the boxes below.



[Total: 17]

**3 (a)** Describe the reagents and conditions required to form a nitro compound from the following.

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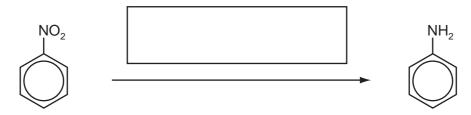
(ii) phenol

[3]

**(b)** Draw the structure of the intermediate organic ion formed during the nitration of benzene.

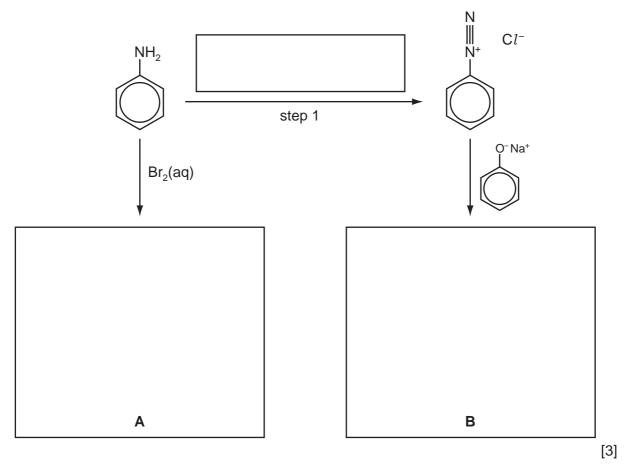
[1]

(c) In the box over the arrow below, write the reagents needed to convert nitrobenzene into phenylamine.



[1]

- (d) Phenylamine can be converted into the organic compounds A and B.
  - (i) Suggest the structural formulae of A and B in the boxes below.
  - (ii) Suggest suitable reagents and conditions for step 1, and write them in the box over the arrow.



- **(e)** When phenylamine is treated with propanoyl chloride a white crystalline compound, **C**, C<sub>9</sub>H<sub>11</sub>NO, is formed.
  - (i) Name the functional group formed in this reaction.
  - (ii) Calculate the percentage by mass of nitrogen in  ${\bf C}$ .

percentage = ..... %

(iii) Draw the structural formula of C.

[3]

[Total: 11]

4 (a)		(i)	Suggest why transition elements show variable oxidation states in their compounds whereas s-block elements like calcium do not.		
		(ii)	Calculate the oxidation number of the metal in each of the following ions.		
			VO <sub>2</sub> <sup>+</sup>		
			CrF <sub>6</sub> <sup>2-</sup>		
			MnO <sub>4</sub> <sup>2-</sup> [4]		
	(b)		blain why transition element complexes are often coloured whereas compounds of lock elements such as calcium and sodium are not.		
			[4]		
	(c)	SO	<sub>2</sub> and MnO₄⁻ react together in acidic solution.		
	, ,		Use the Data Booklet to construct a balanced equation for this reaction.		
		(ii)	Describe the colour change you would see when $SO_2(aq)$ is added to a sample of acidified $KMnO_4$ until the $SO_2$ is in excess.		
			from to		
			[3]		
	(d)		scribe the observations you would make when $NH_3$ (aq) is added gradually to a solution staining $Cu^{2+}$ ions, until the $NH_3$ is in an excess.		
			[3]		
			[0]		

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[Total: 14]

5 Coffee beans contain chlorogenic acid.

chlorogenic acid

(a) (i)	Draw circles around any chiral centres in the above structure.
(ii)	Write down the molecular formula of chlorogenic acid.
(iii)	How many moles of $H_2(g)$ will be evolved when 1 mol of chlorogenic acid reacts with an excess of sodium metal?
(iv)	How many moles of NaOH(aq) will react with 1 mol of chlorogenic acid under each of the following conditions?
	in the cold
	on heating[6]

**(b)** On heating with dilute aqueous acid, chlorogenic acid produces two compounds, **D** and **E**.

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(iii) Name the functional groups in compound F that would react with the following.

(iv) Suggest structures for compounds **F** and **G** and draw them in the relevant boxes above.

(v)	Compound <b>E</b> is one of a pair of stereoisomers.
	What type of stereoisomerism is shown by compound E?
(vi)	Draw the structure of the other stereoisomer in the box below.
	[8]
(c) Cal	ulate the volume of 0.1 mol dm <sup>-3</sup> NaOH that is needed to react completely with 0.1 g
	mpound E.
	volume = cm <sup>3</sup> [3]
	[Total: 17]

Answer all the questions in the spaces provided.

				oo. an		opasto providodi	
6	There are two important polymerisations that occur within living organisms – protein synthesis and the formation of DNA.						
	(a)		-	e table by plac nce could be u		orrect column to indi	cate in which process
				substance	protein synthesis	formation of DNA	
				cysteine			
				cytosine			
				glutamine			
				guanine			
							[3]
	(b)	DN.	A consist	s of a double h	nelical structure.		
		(i)	strand is	s joined by it.			te which part of each
		(ii)	How do DNA?	es the strength		ate to the mechanisn	
	(c)			ses are caused se changes.	d by changes in the	structure of proteins	[4]
							[3]

[Total: 10]

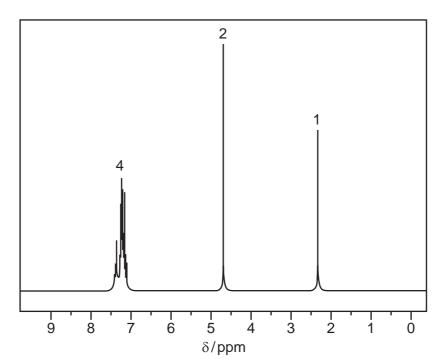
7 The techniques of mass spectrometry and NMR spectroscopy are useful in determining the structures of organic compounds.

- (a) The three peaks of highest mass in the mass spectrum of organic compound L correspond to masses of 142, 143 and 144.

  The ratio of the heights of the M:M+1 peaks is 43.3:3.35, and the ratio of heights of the M:M+2 peaks is 43.3:14.1.
  - (i) Use the data to calculate the number of carbon atoms present in L.

(ii)	Explain what element is indicated by the M+2 peak.

Compound  ${\bf L}$  reacts with sodium metal. The NMR spectrum of compound  ${\bf L}$  is given below.




(iv)	Use the information given and your answers to (i), (ii) and (iii) to deduce a structure for L.					
	Explain how you arrive at your answer.					
	structure of L					
					[7]	
					[,]	
<b>(b)</b> The	e molecular formula	C₃H <sub>6</sub> represents	the compounds pro	opene and c	yclopropane.	
			H			
			H C	H		
	CH₃CH	≕CH.	Ç H	—ç		
	0.130.1	32	 H	 H		
	prop	ene	cyclopropa	ane		
(i)	Suggest <b>one</b> difference in the fragmentation patterns of the mass spectra of these compounds.					
(ii)	Suggest two differen	ences in the NM	R spectra of these	compounds.		

I

[Total: 10]

[3]

For Examiner's Use 8 In recent years there has been considerable interest in a range of polymers known as 'hydrogels'. These polymers are hydrophilic and can absorb large quantities of water.

For Examiner's Use

(a) The diagram shows part of the structure of a hydrogel.

The hydrogel is formed from chains of one polymer which are cross-linked using another molecule.

(i) Draw the structure of the monomer used in the polymer chains.

(ii)	State the type of polymerisation used to form these chains.				

(iii) Draw the structure of the molecule used to cross-link the polymer chains.

	(iv)	During the cross-linking, a small molecule is formed as a by-product. Identify this molecule.
(b)		[5] ce a hydrogel has absorbed water, it can be dried and re-used many times. Plain why this is possible, referring to the structure on the opposite page.
		TO3
(c)		every available side chain in the polymer is cross-linked, and the amount of ss-linking affects the properties of the hydrogel.
	(i)	The amount of cross-linking has little effect on the ability of the gel to absorb water. Suggest why this is the case.
	(ii)	Suggest <b>one</b> property of the hydrogel that will change if more cross-linking takes place. Explain how the increased cross-linking brings about this change.
		[3]
		[Total: 10]

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