



UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS General Certificate of Education Advanced Level

CANDIDATE NAME					
CENTRE NUMBER			CANDIDATE NUMBER		



CHEMISTRY 9701/43

Paper 4 Structured Questions

October/November 2011

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Write in dark blue or black pen.

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

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

DO NOT WRITE ON 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.

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 Examiner's Use		
1		
2		
3		
4		
5		
6		
7		
8		
Total		

This document consists of 17 printed pages and 3 blank pages.



Section A

For Examiner's Use

Answer all questions in the spaces provided.

1

(a)	Complete the electronic configurations of the following ions.				ving ions.
	Cr ³	+:	1s ² 2s ² 2p ⁶		
	Mn²	2+:	1s ² 2s ² 2p ⁶		[2]
(b)	Bot	h Ki	MnO ₄ and K ₂ Cr	r ₂ O ₇ are used as oxidising a	gents, usually in acidic solution.
	(i)			om the <i>Data Booklet</i> to expla the solution increases.	in why their oxidising power increases
	(ii)		nat colour char	-	en each of these oxidising agents is
		•	KMnO ₄	from	to
		•	K ₂ Cr ₂ O ₇	from	to[4]
(c)	Pas	sing	g a stream of S		d, insoluble in water and dilute acids. on of MnO ₂ in water does, however,
	(i)				n for this reaction, and explain what e and of sulfur during the reaction.
	(ii)			spension of MnO ₂ is reduced ct, if any, this would have on	
					[4]

(d) The main ore of manganese, pyrolusite, is mainly MnO_2 . A solution of $SnCl_2$ can be used to estimate the percentage of MnO_2 in a sample of pyrolusite, using the following method.

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- A known mass of pyrolusite is warmed with an acidified solution containing a known amount of SnCl₂.
- The excess Sn²⁺(aq) ions are titrated with a standard solution of KMnO₄.

In one such experiment, 0.100 g of pyrolusite was warmed with an acidified solution containing $2.00 \times 10^{-3} \, \text{mol} \, \text{Sn}^{2+}$. After the reaction was complete, the mixture was titrated with $0.0200 \, \text{mol} \, \text{dm}^{-3} \, \text{KMnO}_4$, and required $18.1 \, \text{cm}^3$ of this solution to reach the end point.

The equation for the reaction between $\mathrm{Sn^{2+}}(\mathrm{aq})$ and $\mathrm{MnO_4^-}(\mathrm{aq})$ is as follows.

$$2\mathsf{MnO_4}^- + 5\mathsf{Sn^{2+}} + 16\mathsf{H^+} \longrightarrow 2\mathsf{Mn^{2+}} + 5\mathsf{Sn^{4+}} + 8\mathsf{H_2O}$$

(i) Use the Data Booklet to construct an equation for the reaction between ${\rm MnO_2}$ and ${\rm Sn^{2+}}$ ions in acidic solution.

- (ii) Calculate the percentage of MnO₂ in this sample of pyrolusite by the following steps.
 - number of moles of MnO₄⁻ used in the titration
 - number of moles of Sn²⁺ this MnO₄⁻ reacted with
 - number of moles of Sn²⁺ that reacted with the 0.100 g sample of pyrolusite
 - number of moles of MnO₂ in 0.100 g pyrolusite. Use your equation in (i).
 - mass of MnO₂ in 0.100 g pyrolusite
 - percentage of MnO₂ in pyrolusite

percentage =%

ĮΟJ

[Total: 16]

2 (a) (i) What is meant by the term *ligand* as applied to the chemistry of the transition elements?

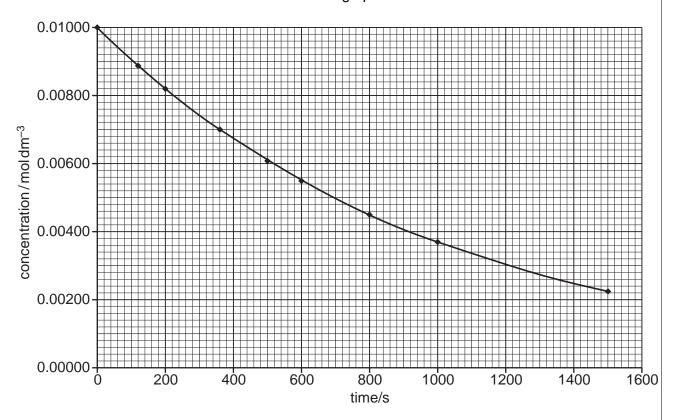
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(ii) Describe the type of bonding that occurs between a ligand and a transition element.

(b) Chromium hexacarbonyl undergoes the following ligand replacement reaction.

$$Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_5PR_3 + CO$$

Two separate experiments were carried out to study the rate of this reaction. In the first experiment, the ligand PR_3 was in a large excess and $[Cr(CO)_6]$ was measured with time. The results are shown on the graph below.



In the second experiment, $Cr(CO)_6$ was in a large excess, and $[PR_3]$ was measured with time. The following results were obtained.

time/s	[PR ₃]/moldm ⁻³
0	0.0100
120	0.0076
200	0.0060
360	0.0028

(i) Plot the data in the table on the graph above, using the same axis scales, and draw the best-fit line through your points.

Use the graphs to determine the order of reaction with respect to ${\rm Cr(CO)}_6$ and ${\rm PR}_3$. In each case explain how you arrived at your answer.							
Cr(CO) ₆							
PR	3						
Sta	te the units of the rate constant.						
the	letter next to the one mechanism which is						
Α	$Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ $Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5 PR_3$	fast slow					
В	$Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ $Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5 PR_3$	slow fast					
С							
D	$Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_6 PR_3$ $Cr(CO)_6 PR_3 \rightarrow Cr(CO)_5 PR_3 + CO$	slow fast					
Explain your answer.							
	Cr(In each case explain how you arrived at your $Cr(CO)_6$ Write the rate equation for the reaction, and of using the method of initial rates, or any other state the units of the rate constant. Four possible mechanisms for this reaction at the letter next to the one mechanism which is have written in (iii) . A $Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ $Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5 PR_3$ B $Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ $Cr(CO)_6 \rightarrow Cr(CO)_5 PR_3 \rightarrow Cr(CO)_6 PR_3$ $Cr(CO)_6 \rightarrow Cr(CO)_6 PR_3 \rightarrow$					

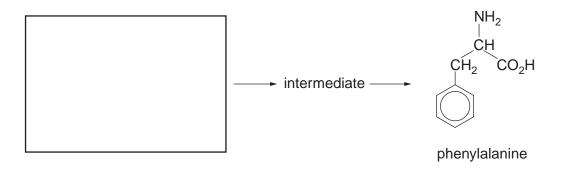
[Total: 11]

For Examiner's Use **3 (a)** Amino acids such as alanine are essential building blocks for making proteins. They can be synthesised by a general reaction of which the following is an example.

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$$\begin{array}{c|c} \text{CH}_3\text{CHO} & & \\ \hline & & \\ \hline & & \\ \text{CH}_3\text{CHO} & \\ \hline & & \\$$

- (i) Suggest the structure of the intermediate compound **E** by drawing its structural formula in the box above.
- (ii) Suggest, in the box below, the structural formula of the starting material needed to synthesise phenylalanine by the above general reaction.



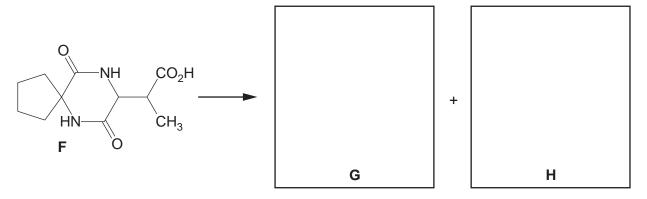
[2]

- (b) (i) What is a protein?
 - (ii) Using alanine as an example, draw a diagram to show how proteins are formed from amino acids. Show two repeat units in your answer.

[3]

(c) The hydrolysis of compound F produces two compounds G and H.





(i) State the reagents and conditions needed for this hydrolysis.

(ii) Draw the structures of the two products **G** and **H** in the boxes above.

[3]

(d) (i) Draw the zwitterionic structure of alanine.

(ii) Suggest the structural formulae of the zwitterions that could be formed from the following compounds.

compound	zwitterion
H_2N — CO_2H	
OH NHCH ₃	
HO S NH ₂	

[4]

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(e)	Sol	plutions of amino acids are good buffers.				
	(i)	What is meant by the term buffer?				
	(ii)	Write an equation to show how a solution of alanine, $\mathrm{CH_3CH(NH_2)CO_2H}$, behaves as a buffer in the presence of an acid such as $\mathrm{HC}\mathit{l}(\mathrm{aq})$.				
	(iii)	Briefly describe how the pH of blood is controlled.				
	(iv)	Calculate the pH of the buffer formed when $10.0\mathrm{cm^3}$ of $0.100\mathrm{moldm^{-3}}$ NaOH is added to $10.0\mathrm{cm^3}$ of $0.250\mathrm{moldm^{-3}}$ CH ₃ CO ₂ H, whose p K_a = 4.76.				
		pH =[7]				
		[Total: 19]				

4

(a)	Write an equation representing the action of heat on calcium nitrate, ${\rm Ca(NO_3)_2}$.			
		[1]		
(b)		cribe and explain the trend in the thermal stabilities of the nitrates of the Group II nents.		
		[3]		
(c)	Sod CO ₂	ium carbonate is stable to heat, but heating lithium carbonate readily produces (g).		
	(i)	Suggest an equation for the action of heat on lithium carbonate.		
	(ii)	Suggest a reason for the difference in reactivity of these two carbonates.		
	(iii)	Predict what you would see if a sample of lithium nitrate was heated. Explain your answer.		
		[4]		
		[Total: 8]		

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5	Alkanes are generally considered to be unreactive compounds, showing an inertness common reagents such as NaOH, H ₂ SO ₄ , and K ₂ Cr ₂ O ₇ .					
	(a)	Sug	gest a reason why these reagents	do not attack an alkane such as CH ₄ .		
				[1]		
	(b)	can	occur due to the fast exothermic re	e gas is exposed to strong sunlight, an explosion eaction. rever, the following reaction occurs.		
			$C_2H_6 + Cl_2 \rightarrow$	$C_2H_5Cl + HCl$		
		(i)	What is the name of this type of re	eaction?		
		(ii)	Use equations to describe the involved.	mechanism of this reaction, naming the steps		
		(iii)				
	;	struc	tural formula of by-product	formed by		

(iv) It is found by experiment that, during this type of reaction, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

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reaction	relative rate
$RCH_3 \rightarrow RCH_2Cl$	1
$R_2CH_2 \rightarrow R_2CHCl$	7
$R_3CH \rightarrow R_3CCl$	21

Using this information, and considering the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule, predict the relative ratio of the two possible products $\bf J$ and $\bf K$ from the chlorination of 2-methylpropane. Explain your answer.

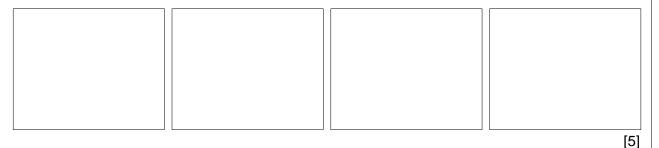
ratio **J**/**K** =

ners of

[10]

(c) In the boxes below draw the **skeletal** formulae of **four** different structural isomers of $C_5H_{11}Cl$ that could be obtained from the chlorination of 2-methylbutane. Indicate any chiral centres in your structures by an asterisk (*).

2-methylbutane



. . .

[3]

CH₂OH

Answer all questions in the spaces provided.

- 6 The formation of proteins is a key process in the growth and repair of tissues in living organisms.
 - Study the structures of the three molecules below. One of the molecules could be (a) (i) a building block for a protein while the other two could be building blocks for other biological polymers.

HO、	OH OH OH	OH N H	CH ₂ OH H OOH HOOH H HOOH	
	J	К	L	
	Which of the three could be a building block for a protein? Explain your answer.			
(ii)	For which biologica block?	I polymer could one of the	other molecules form a building	
	molecule	polymer	[2]	
	otein molecules have ape.	four levels of structure as the	ne long molecules fold and take	
(i)	The primary structure is the sequence of amino acids in the protein chain. What type of bonding exists between the amino acids in this chain?			
(ii)	What type of bondin	g can exist in all of the other	types of structure?	
(iii)		onding that does not occur in tl		

(c)		y proteins play an important role in catalysing chemical reactions in living nisms.	For Examiner's Use
	(i)	What name is given to these catalysts?	
	(ii)	Give two changes in conditions under which these catalysts may be inactivated, explaining the chemical reason for this in each case.	
		[4]	
		[Total: 9]	

7 Different analytical techniques are used to build up a picture of complex molecules. Each technique on its own provides different information about complex molecules but together the techniques can give valuable structural information.

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(a) Complete the table, identifying the technique which can provide the appropriate structural information.

structural information	analytical technique	
three-dimensional arrangement of atoms and bonds in a molecule		
chemical environment of protons in a molecule		
identity of amino acids present in a polypeptide		

[3]

(b)	One general method of separating organic molecules is chromatography. Briefly explain the chemical principles involved in each of the following techniques.		
	(i)	paper chromatography	
	(ii)	thin-layer chromatography	
	` ,		
		[2]	

(c) A combination of mass spectrometry and NMR spectroscopy is often enough to determine the structure of a simple organic compound. The organic compound N produced a mass spectrum in which the ratio of the M:M+1 peaks was 5.9:0.20, and which had an M+2 peak of similar height to the M peak.

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(i) Calculate how many carbon atoms are present in one molecule of N.

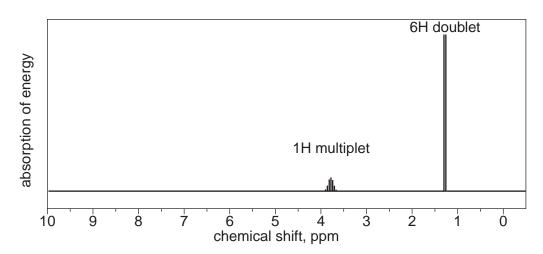
(ii) Deduce which element, other than carbon and hydrogen, is present in N.

.....

(iii) Explain how many atoms of this element are present in one molecule of N.

.....

The NMR spectrum of **N** is shown.



(iv) State the empirical formula of **N** and, using the NMR data, suggest the structural formula of **N**, explaining your reasons.

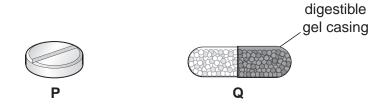
[6]

[Total: 11]

8 Drugs can be delivered in a number of ways. The method chosen depends both on the nature of the drug, and the problem it is being used to treat.

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(a) Many common drugs are taken by mouth in forms similar to those shown.



(i)	Some drugs are available in solution. How would the speed of action of this form compare with P and Q ? Explain your answer.
(ii)	Explain which of the two forms, ${\bf P}$ or ${\bf Q}$, would act the most rapidly when taken by mouth.
(iii)	Some drugs are broken down before they can be absorbed by the intestine. Suggest how the design of ${\bf Q}$ prevents this.
	[3]
into	er an abdominal operation drugs are often delivered by means of a 'drip' inserted a blood vessel in the patient's arm. Explain why this is more effective than taking akillers by mouth.
	[2]

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(b)

(c)		e of the molecules that has found a variety of uses in drug delivery is poly(ethylene ol) or PEG. It is formed from dihydroxyethane, HOCH ₂ CH ₂ OH.	For Examiner's Use
	2n	$HOCH_2CH_2OH \rightarrow H-(OCH_2CH_2OCH_2CH_2)_n-OH + (2n-1) \; H_2O$	
	(i)	What type of reaction is this?	
	brok this:	ching a PEG molecule to a drug increases the time that it takes for the drug to be sen down and flushed from the body. There are thought to be two major reasons for firstly the PEG can form bonds to slow the passage of the drug around the body; andly it may reduce the efficiency of breakdown of the drug by enzymes.	
	(ii)	What type of bonds would the PEG part of the molecule form with molecules in the body?	
	(iii)	Suggest why attaching a PEG molecule to a drug molecule would reduce the rate of the drug's decomposition by enzymes.	
	(iv)	Drugs are often protein or polypeptide molecules. What type of reaction might occur in the breakdown of such a drug?	
		[5]	
		[Total: 10]	

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