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General Certificate of Education January 2004 Advanced Level Examination



CHEMISTRY CHM4 Unit 4 **Further Physical and Organic Chemistry**

Wednesday 21 January 2004 Morning Session

In addition to this paper you will require: a calculator.

Time allowed: 1 hour 30 minutes

Instructions

- Use blue or black ink or ball-point pen.
- Fill in the boxes at the top of this page.
- Answer all questions in **Section A** and **Section B** in the spaces provided. All working must be shown.
- Do all rough work in this book. Cross through any work you do not want marked.
- The Periodic Table/Data Sheet is provided on pages 3 and 4. Detach this perforated sheet at the start of the examination.
- Section B questions are provided on a perforated sheet. Detach this sheet at the start of the examination.

Information

- The maximum mark for this paper is 90.
- Mark allocations are shown in brackets.
- This paper carries 15 per cent of the total marks for Advanced Level.
- You are expected to use a calculator where appropriate.
- The following data may be required. Gas constant $R = 8.31 \,\mathrm{J \, K^{-1} \, mol^{-1}}$
- Your answers to questions in **Section B** should be written in continuous prose, where appropriate. You will be assessed on your ability to use an appropriate form and style of writing, to organise relevant information clearly and coherently, and to use specialist vocabulary, where appropriate.

Advice

• You are advised to spend about 1 hour on Section A and about 30 minutes on **Section B**.

	For Exam	iner's Use	•
Number	Mark	Number	Mark
1			
2			
3			
4			
5			
6			
7			
8			
Total (Column	1)	→	
Total (Column	2)	\rightarrow	
TOTAL			
Examine	r's Initials		

SECTION A

Answer all questions in the spaces provided.

The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Experiment	Initial concentration of A /mol dm ⁻³	Initial concentration of B /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
1	0.12	0.15	0.32×10^{-3}
2	0.36	0.15	2.88×10^{-3}
3	0.72	0.30	11.52×10^{-3}

(i)	Deduce the order of reaction with respect to A .
(ii)	Deduce the order of reaction with respect to B .
	(2 marks

The Periodic Table of the Elements

The atomic numbers and approximate relative atomic masses shown in the table are for use in the examination unless stated otherwise in an individual question.

0	4.0 He Helium	Ne Ne	Neon	هُ	Argon	∞ ,	rypton	131.3 Xe	(enon	222.0 Rn	Radon 86		175.0 Lu Lutetium	(0) Lr rencium
	0.4 H		10 J	39.	ы	83.	ы 36 _К	131		222	ы 86 8		175 m	(260) (260) Lr Lawrenc 103
=		19.0 H	Fluorii 9	32.5	Chlorine 17	79.9 Br	Bromii 35	126.9 –	lodin 53	210.0 At	Astatine 85		73.0 Yb Ytterbium	(259) Nobeliu 102
5		16.0 O	Oxygen 8	32.1 S	Sulphur 16	79.0 Se	Selenium 34	127.6 Te	Tellurium 52	210.0 Po	Polonium 84		168.9 Tm Thulium	(258) Md Mendelevium 101
>		14.0 Z	Nitrogen 7	31.0 P	Phosphorus Sulphur 15	74.9 As	Arsenic 33	121.8 Sb	Antimony 51	209.0 Bi	Bismuth 83		167.3 Er Erbium	(257) Fm Fermium 100
≥		ر د د	Carbon 6	1.82 S .1	Silicon 14	72.6 Ge	Germaniur 32	118.7 Sn	Tin 50	207.2 Pb	Lead 82		164.9 Ho Holmium	67 (252) Es Einsteinium 99
=		10.8 B	Boron 5	27.0 Al	Aluminium 13	69.7 Ga	Gallium 31	114.8 In	Indium 49	204.4 T	Thallium 81		162.5 164.9 Ho Dysprosium Holmium	bb bb bf bb bb bb bb bb bb car bb bb
						65.4 Zn	Zinc 30	112.4 Cd	Cadmium 48	200.6 Hg	Mercury 80		140.9 144.2 144.9 150.4 152.0 157.3 158.9 Praseodymium Neodymium Promethium Samarium Europium Gadolinium Terbium Promethium Samarium Europium Gadolinium Terbium Cardolinium Cardolin	247.1 BK Berkelium 97
						63.5 Cu	Copper 29	107.9 Ag	Silver 47	197.0 Au	Gold 79		157.3 Gd Gadolinium	Cm Curium 96
						58.7 Z	Nickel 28	106.4 Pd	Palladium 46	195.1	Platinum 78		152.0 Eu Europium	237.0 239.1 243.1 Am Neptunium Plutonium Americium 93
						28.9 0	Cobalt 27	102.9 Rh	Rhodium 45	192.2 Ir	Iridium 77		150.4 Sm Samarium	239.1 Pu Plutonium 94
						55.8 5a	Iron 26	101.1 Ru	Ruthenium 44	190.2 Os	Osmium 76		144.9 Pm Promethium	51 237.0 Np Neptunium 93
		-6.9 Li	Lithium -3			54.9 Mn	Manganese 25	98.9 Tc	Technetium 43	186.2 Re	Rhenium 75		144.2 Nd Neodymium	238.0 U Uranium 92
		ass ——				ن د	Chromium 24	95.9 98.9 101.1 102.9 11 Mo Tc Ru Rh	Molybdenum 42	183.9 W	Tungsten 74		140.9 Pr Praseodymium	231.0 2 Pa Protactinium 91
		relative atomic mass	umber –			2 0.9	Vanadiui 23	92.9 Nb	Niobiun 41	180.9 Ta	Tantalur 73		140.1 Ce Cerium	232.0 Th Thorium 90
	Key	relative	atomic number			47.9 T i	Titanium 22	91.2 Zr	E	178.5 H	Hafnium 72			
						45.0 SC	_	8 8.9	Yttrium 39	138.9 La	Lanthanum 57 *	227 Ac Actinium 89 +	anides	ides
=		9.0 Be	Beryllium 4	24.3 Mg	⊑	40.1 Ca	Calcium 20	87.6 Sr	Strontium 38	137.3 Ba	Barium 56	226.0 Ra Radium 88	* 58 – 71 Lanthanides	† 90 – 103 Actinides
_	1.0 H Hydrogen 1	6.9 Li	Lithium 3	23.0 Na	Sodium 11	39.1 X	Potassium 19	85.5 Rb	Rubidium 37	132.9 Cs	Caesium 55	223.0 Fr Francium 87	* 58 – 7	+ 90 – 1
	WW	/\ <u>\</u>	<u>, X</u>	tr	er	ne	<u>P2</u>	g	<u>er</u>	S.	ne	t wv	vw.theallp	apers.com

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	140.1 Ce	40.1 140.9 144.2 Ce Pr N	₅	144.9 Pm	150.4 Sm	152.0 Eu	157.3 Gd	158.9 Tb	162.5 Dy	164.9 Ho	167.3 Er	168.9 Tm	173.0 Yb	175.0 Lu
anides	Cerium F	Praseodymium 59	Neodymiun 60	Promethium Samarium Europium Gadolinium Terbium Dysprosium Holmium Erbium 61 65 66 67 68	Samarium 62	Europium 63	Gadolinium 64	Terbium 65	Dysprosium 66	Holmium 67	Erbium 68	n Thulium Ytterbium 70 70	Ytterbium 70	ר Lutetiu 71
1	232.0 Th	231.0 238.0 Da		237.0 Np	239.1 Pu	243.1 Am	247.1 Cm	247.1 BK	247.1 252.1 (252) (257) (258) (259) Bk Cf Es Fm Md No	(252) Es	(257) Fm	(258) Md	(259) No	(260) L
lides	Thorium 90	Protactinium 91	Ę	Neptunium 93	Plutonium 94	Americium 95	Curium 96	Berkelium 97	Californium 98	Einsteinium 99	Fermium 100	Mendelevium 101	Nobelium 102	n Lawrenci

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Table 1 Proton n.m.r chemical shift data

Type of proton	δ/ppm
RCH_3	0.7–1.2
R_2CH_2	1.2–1.4
R_3 CH	1.4–1.6
$RCOCH_3$	2.1–2.6
$ROCH_3$	3.1–3.9
$RCOOCH_3$	3.7–4.1
ROH	0.5–5.0

Table 2 Infra-red absorption data

Bond	Wavenumber/cm ⁻¹
С—Н	2850-3300
С—С	750–1100
C=C	1620–1680
C=O	1680–1750
С—О	1000-1300
O—H (alcohols)	3230–3550
O—H (acids)	2500-3000

The following data were obtained in a series of experiments on the rate of the reaction between NO and O₂ at a constant temperature.

Experiment	Initial concentration of NO/mol dm ⁻³	Initial concentration of O ₂ /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
4	5.0×10^{-2}	2.0×10^{-2}	6.5×10^{-4}
5	6.5×10^{-2}	3.4×10^{-2}	To be calculated

The rate equation for this reaction is

$$rate = k[NO]^2[O_2]$$

(i)	Use the data from experiment 4 to calculate a value for the rate constant, k , at this temperature, and state its units.
	Value of k
	Units of k
(ii)	Calculate a value for the initial rate in experiment 5.
	(4 marks)



TURN OVER FOR THE NEXT QUESTION

2 At high temperatures, SO₂Cl₂ dissociates according to the following equation.

$$SO_2Cl_2(g) \implies SO_2(g) + Cl_2(g) \qquad \Delta H^{\Theta} = +93 \text{ kJ mol}^{-1}$$

When $1.00\,\text{mol}$ of SO_2Cl_2 dissociates, the equilibrium mixture contains $0.75\,\text{mol}$ of Cl_2 at 673 K and a total pressure of 125 kPa.

(a)		e an expression for the equilibrium constant, K_p , for this reaction.
		(1 mark)
(b)		ulate the total number of moles of gas present in the equilibrium mixture.
		(2 marks)
(c)	(i)	Write a general expression for the partial pressure of a gas in a mixture of gases in terms of the total pressure.
	(ii)	Calculate the partial pressure of SO_2Cl_2 and the partial pressure of Cl_2 in the equilibrium mixture.
		Partial pressure of SO ₂ Cl ₂
		Partial pressure of Cl ₂
		(5 marks)
(d)	Calc	ulate a value for the equilibrium constant, K_p , for this reaction and give its units.

(3 marks)

(e)	State the effect, if any, of an increase in temperature on the value of K_p for this reaction. Explain your answer.
	Effect on K _p
	Explanation
	(2 marks)
(f)	State the effect, if any, of an increase in the total pressure on the value of K_p for this reaction.
	(1 mark)

TURN OVER FOR THE NEXT QUESTION

3

(a)	The	pH of a 0.120 mol dm ⁻³ solution of the weak monoprotic acid, HX, is 2.56 at 298 K.
	(i)	Write an expression for the term pH .
	(ii)	Write an expression for the dissociation constant, K_a , for the weak acid HX and calculate its value at 298 K.
		Expression for K _a
		Calculation
		(5 marks)
(b)	(i)	Write an expression for the ionic product of water, $K_{\rm w}$, and give its value at 298 K.
		Expression for K _w
		Value of K _w
	(ii)	Hence, calculate the pH of a $0.0450\mathrm{moldm^{-3}}$ solution of sodium hydroxide at $298\mathrm{K}$.
		(4 marks)
		(

(c)	A titration curve is plotted showing the change in pH as a $0.0450 \text{ mol dm}^{-3}$ solution of sodium hydroxide is added to 25.0 cm^3 of a solution of ethanedioic acid, $H_2C_2O_4$ The titration curve obtained has two equivalence points (end points).						
	(i)	Write an equation for the reaction which is completed at the first equivalence point.					
	(ii)	When the second equivalence point is reached, a total of 41.6 cm ³ of 0.0450 mol dm ⁻³ sodium hydroxide has been added. Calculate the concentration of the ethanedioic acid solution.					
		(4 marks)					
(d)	Draw the structure of the organic product formed in each case when, in the presence of a small amount of concentrated sulphuric acid, ethanedioic acid reacts with						
	a sm						
	a sm (i)						
		all amount of concentrated sulphuric acid, ethanedioic acid reacts with					
		all amount of concentrated sulphuric acid, ethanedioic acid reacts with					
		all amount of concentrated sulphuric acid, ethanedioic acid reacts with					
		all amount of concentrated sulphuric acid, ethanedioic acid reacts with					
	(i)	all amount of concentrated sulphuric acid, ethanedioic acid reacts with an excess of methanol,					
	(i)	all amount of concentrated sulphuric acid, ethanedioic acid reacts with an excess of methanol,					
	(i)	all amount of concentrated sulphuric acid, ethanedioic acid reacts with an excess of methanol,					

Turn over ▶

(a) Consider the following amino acid.

Draw the structure of the amino acid species present in a solution at pH 12.

(ii) Draw the structure of the dipeptide formed from two molecules of this amino acid.

(iii) Protein chains are often arranged in the shape of a helix. Name the type of interaction that is responsible for holding the protein chain in this shape.

(3 marks)

- (b) Consider the hydrocarbon G, $(CH_3)_2C=CHCH_3$, which can be polymerised.
 - (i) Name the type of polymerisation involved and draw the repeating unit of the polymer.

Type of polymerisation

Repeating unit

(ii) Draw the structure of an isomer of **G** which shows geometrical isomerism.

(iii) Draw the structure of an isomer of **G** which does not react with bromine water.

(4 marks)



5

Compound Q has the molecular formula C_4H_7CIO and does not produce misty fumes when added to water.
(a) The infra-red spectrum of \mathbf{Q} contains a major absorption at 1724 cm ⁻¹ . Identify the bond responsible for this absorption.
(1 mark)
(b) The mass spectrum of \mathbf{Q} contains two molecular ion peaks at $m/z = 106$ and $m/z = 108$. It also has a major peak at $m/z = 43$.
(i) Suggest why there are two molecular ion peaks.
(ii) A fragment ion produced from \mathbf{Q} has $m/z = 43$ and contains atoms of three different elements. Identify this fragment ion and write an equation showing its formation from the molecular ion of \mathbf{Q} .
Fragment ion
Equation(3 marks)
(c) The proton n.m.r. spectrum of \mathbf{Q} was recorded.
(i) Suggest a suitable solvent for use in recording this spectrum of Q .
(ii) Give the formula of the standard reference compound used in recording proton n.m.r. spectra.
(2 marks)

The proton n.m.r. spectrum of \mathbf{Q} shows three peaks. Complete the table below to show the number of adjacent, non-equivalent protons responsible for the splitting pattern.

	Peak 1	Peak 2	Peak 3
Integration value	3	3	1
Splitting pattern	doublet	singlet	quartet
Number of adjacent, non-equivalent protons	1		

(1 mark)

(e) Using the information in parts (a), (b) and (d), deduce the structure of compound **Q**.

(1 *mark*)

(f) A structural isomer of **Q** reacts with cold water to produce misty fumes. Suggest a structure for this isomer.

(1 mark)



(a) Consider the following pair of isomers.

D

 \mathbf{C}

Identify a reagent which could be used in a test-tube reaction to distinguish between C and D. In each case, state what you would observe.

Reagent

Observation with C

Observation with **D**

(4 marks)

Consider the following pair of isomers.

 \mathbf{E}



F

(i) Name compound **E**.

Identify a reagent which could be used in a test-tube reaction to distinguish between E and F. In each case, state what you would observe.

Reagent

Observation with E

Observation with **F**.....

(4 marks)

(c) Draw the structure of the chain isomer of **F** which shows optical isomerism.

(1 marks)

SECTION B

Detach this perforated sheet.

Answer **both** questions in the space provided on pages 17 to 20 of this booklet.

Use the following data to show the stability of benzene relative to the hypothetical cyclohexa-1,3,5-triene.



Give a reason for this difference in stability.

+
$$H_2$$
 \rightarrow $\Delta H^{\Theta} = -120 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$

+
$$3H_2$$
 \rightarrow $\Delta H^{\Theta} = -208 \text{ kJ mol}^{-1}$

(4 marks)

(b) Consider the following reaction sequence which starts from phenylamine.

- State and explain the difference in base strength between phenylamine and ammonia.
- (ii) Name and outline a mechanism for the reaction in Step 1 and name the organic product of Step 1.
- (iii) The mechanism of Step 2 involves attack by an electrophile. Give the reagents used in this step and write an equation showing the formation of the electrophile. Outline a mechanism for the reaction of this electrophile with benzene.
- Name the type of linkage which is broken in Step 3 and suggest a suitable reagent for this reaction.

(17 marks)

Compound **Z** can be formed via compounds **X** and **Y** in the three step synthesis shown below.

Identify compounds **X** and **Y** and give reagents and conditions for Steps 1 and 2.

State the **type** of compound of which **Z** is an example.

Compound **Z** reacts with a large excess of bromomethane to form a solid product. Draw the structure of this product and name the type of mechanism for this reaction.

(9 marks)

END OF QUESTIONS