Surname		Other Names	
Centre Number			Candidate Number									
Candidate Signature												

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General Certificate of Education
January 2004
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

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 $R = 8.31\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$
- 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 Examiner's Use			
Number	Mark	Number	Mark
1			
2			
3			
4			
5			
6			
7			
8			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

Answer **all** questions in the spaces provided.

1 (a) 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.

I	II										III	IV	V	VI	VII	0
1.0 **H** Hydrogen 1																4.0 **He** Helium 2
6.9 **Li** Lithium 3	9.0 **Be** Beryllium 4										10.8 **B** Boron 5	12.0 **C** Carbon 6	14.0 **N** Nitrogen 7	16.0 **O** Oxygen 8	19.0 **F** Fluorine 9	20.2 **Ne** Neon 10
23.0 **Na** Sodium 11	24.3 **Mg** Magnesium 12										27.0 **Al** Aluminium 13	28.1 **Si** Silicon 14	31.0 **P** Phosphorus 15	32.1 **S** Sulphur 16	35.5 **Cl** Chlorine 17	39.9 **Ar** Argon 18
39.1 **K** Potassium 19	40.1 **Ca** Calcium 20	45.0 **Sc** Scandium 21	47.9 **Ti** Titanium 22	50.9 **V** Vanadium 23	52.0 **Cr** Chromium 24	54.9 **Mn** Manganese 25	55.8 **Fe** Iron 26	58.9 **Co** Cobalt 27	58.7 **Ni** Nickel 28	63.5 **Cu** Copper 29	65.4 **Zn** Zinc 30	69.7 **Ga** Gallium 31	72.6 **Ge** Germanium 32	74.9 **As** Arsenic 33	79.0 **Se** Selenium 34	79.9 **Br** Bromine 35	83.8 **Kr** Krypton 36
85.5 **Rb** Rubidium 37	87.6 **Sr** Strontium 38	88.9 **Y** Yttrium 39	91.2 **Zr** Zirconium 40	92.9 **Nb** Niobium 41	95.9 **Mo** Molybdenum 42	98.9 **Tc** Technetium 43	101.1 **Ru** Ruthenium 44	102.9 **Rh** Rhodium 45	106.4 **Pd** Palladium 46	107.9 **Ag** Silver 47	112.4 **Cd** Cadmium 48	114.8 **In** Indium 49	118.7 **Sn** Tin 50	121.8 **Sb** Antimony 51	127.6 **Te** Tellurium 52	126.9 **I** Iodine 53	131.3 **Xe** Xenon 54
132.9 **Cs** Caesium 55	137.3 **Ba** Barium 56	138.9 **La** Lanthanum 57 *	178.5 **Hf** Hafnium 72	180.9 **Ta** Tantalum 73	183.9 **W** Tungsten 74	186.2 **Re** Rhenium 75	190.2 **Os** Osmium 76	192.2 **Ir** Iridium 77	195.1 **Pt** Platinum 78	197.0 **Au** Gold 79	200.6 **Hg** Mercury 80	204.4 **Tl** Thallium 81	207.2 **Pb** Lead 82	209.0 **Bi** Bismuth 83	210.0 **Po** Polonium 84	210.0 **At** Astatine 85	222.0 **Rn** Radon 86
223.0 **Fr** Francium 87	226.0 **Ra** Radium 88	227 **Ac** Actinium 89 †															

Key

relative atomic mass — 6.9 **Li** Lithium

atomic number — 3

140.1 **Ce** Cerium 58	140.9 **Pr** Praseodymium 59	144.2 **Nd** Neodymium 60	144.9 **Pm** Promethium 61	150.4 **Sm** Samarium 62	152.0 **Eu** Europium 63	157.3 **Gd** Gadolinium 64	158.9 **Tb** Terbium 65	162.5 **Dy** Dysprosium 66	164.9 **Ho** Holmium 67	167.3 **Er** Erbium 68	168.9 **Tm** Thulium 69	173.0 **Yb** Ytterbium 70	175.0 **Lu** Lutetium 71
232.0 **Th** Thorium 90	231.0 **Pa** Protactinium 91	238.0 **U** Uranium 92	237.0 **Np** Neptunium 93	239.1 **Pu** Plutonium 94	243.1 **Am** Americium 95	247.1 **Cm** Curium 96	247.1 **Bk** Berkelium 97	252.1 **Cf** Californium 98	(252) **Es** Einsteinium 99	(257) **Fm** Fermium 100	(258) **Md** Mendelevium 101	(259) **No** Nobelium 102	(260) **Lr** Lawrencium 103

*** 58 – 71** Lanthanides

† 90 – 103 Actinides

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_3CH	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}**
C—H	2850–3300
C—C	750–1100
C═C	1620–1680
C═O	1680–1750
C—O	1000–1300
O—H (alcohols)	3230–3550
O—H (acids)	2500–3000

(b) The following data were obtained in a series of experiments on the rate of the reaction between NO and O_2 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)

6

TURN OVER FOR THE NEXT QUESTION

2 At high temperatures, SO_2Cl_2 dissociates according to the following equation.

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

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

(a) Write an expression for the equilibrium constant, K_p, for this reaction.

.....

.....

(1 mark)

(b) Calculate 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_2Cl_2 .....

.....

Partial pressure of Cl_2 .....

.....

(5 marks)

(d) Calculate 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)

14

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_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 mol dm^{-3} solution of sodium hydroxide at 298 K.

.....

.....

.....

(4 marks)

(c) A titration curve is plotted showing the change in pH as a 0.0450 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

(i) an excess of methanol,

.....

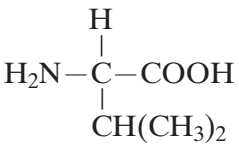
(ii) an equimolar amount of ethane-1,2-diol.

.....

(2 marks)

15

4 (a) Consider the following amino acid.



(i) 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)

7

5 Compound **Q** has the molecular formula C_4H_7ClO and does not produce misty fumes when added to water.

(a) The infra-red spectrum of **Q** contains a major absorption at 1724 cm^{-1}. Identify the bond responsible for this absorption.

.....

(1 mark)

(b) The mass spectrum of **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 **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 **Q**.

Fragment ion .....

Equation .....

(3 marks)

(c) The proton n.m.r. spectrum of **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)

(d) The proton n.m.r. spectrum of **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**.

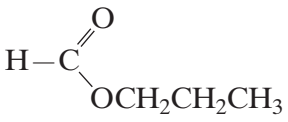
(1 mark)

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

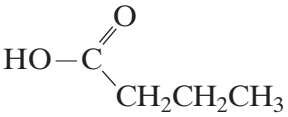
(1 mark)

9

6 (a) Consider the following pair of isomers.



C



D

(i) Name compound **C**.

.....

(ii) 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.

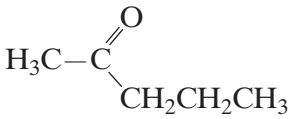
Reagent .....

*Observation with **C*** .....

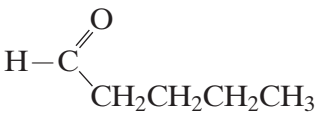
*Observation with **D*** .....

(4 marks)

(b) Consider the following pair of isomers.



E



F

(i) Name compound **E**.

.....

(ii) 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)

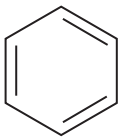
(c) Draw the structure of the chain isomer of **F** which shows optical isomerism.

(1 marks)

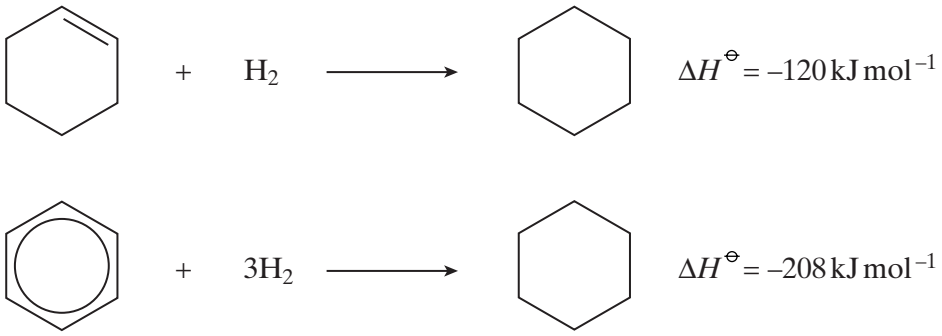
SECTION B

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

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

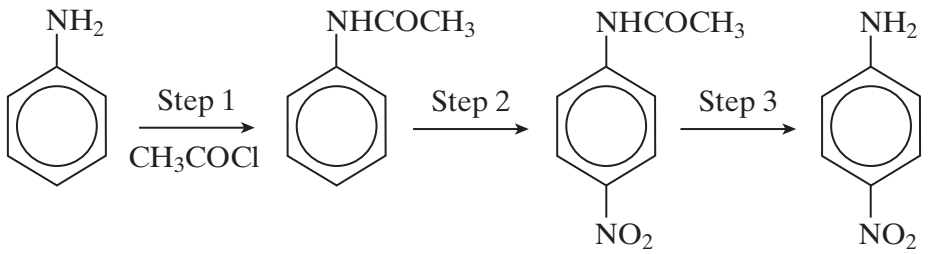


Give a reason for this difference in stability.



(4 marks)

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



(i) 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.

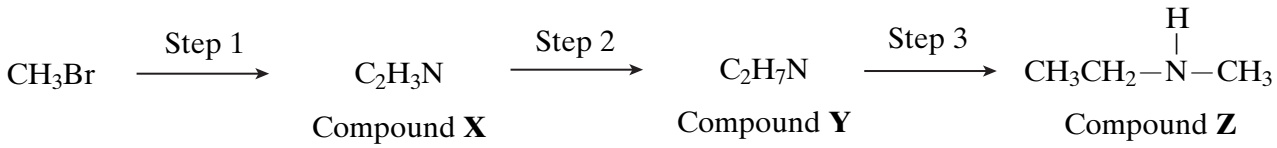
(iii) The mechanism of Step 2 involves attack by an electrophile. Give the reagents used in this step and write an equation showing the formation of the electrophile. Outline a mechanism for the reaction of this electrophile with benzene.

(iv) Name the type of linkage which is broken in Step 3 and suggest a suitable reagent for this reaction.

(17 marks)

Turn over ▶

8 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