Surname		Other Names	
Centre Number			Candidate Number									
Candidate Signature												

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General Certificate of Education
June 2003
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

CHEMISTRY CHM4
Unit 4 Further Physical and Organic Chemistry

Wednesday 18 June 2003 Afternoon 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.

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 $R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$
- 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			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

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

1 The rate of the reaction between substance **A** and substance **B** was studied in a series of experiments carried out at the same temperature. In each experiment the initial rate was measured using different concentrations of **A** and **B**. These results were used to deduce the order of reaction with respect to **A** and the order of reaction with respect to **B**.

(a) What is meant by the term *order of reaction* with respect to **A**?

.....

.....

(1 mark)

(b) When the concentrations of **A** and **B** were both doubled, the initial rate increased by a factor of 4. Deduce the **overall** order of the reaction.

.....

(1 mark)

(c) In another experiment, the concentration of **A** was increased by a factor of three and the concentration of **B** was halved. This caused the initial rate to increase by a factor of nine.

(i) Deduce the order of reaction with respect to **A** and the order with respect to **B**.

*Order with respect to **A*** .....

*Order with respect to **B*** .....

(ii) Using your answers from part (c)(i), write a rate equation for the reaction and suggest suitable units for the rate constant.

Rate equation .....

Units for the rate constant .....

.....

(4 marks)

6

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

2 When a mixture of 0.345 mol of PCl_3 and 0.268 mol of Cl_2 was heated in a vessel of fixed volume to a constant temperature, the following reaction reached equilibrium.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \qquad \Delta H^{\ominus} = -93\,kJ\,mol^{-1}$$

At equilibrium, 0.166 mol of PCl_5 had been formed and the total pressure was 225 kPa.

(a) (i) Calculate the number of moles of PCl_3 and of Cl_2 in the equilibrium mixture.

Moles of PCl_3 .....

Moles of Cl_2 .....

(ii) Calculate the total number of moles of gas in the equilibrium mixture.

.....

(3 marks)

(b) Calculate the mole fraction and the partial pressure of PCl_3 in the equilibrium mixture.

Mole fraction of PCl_3 .....

.....

Partial pressure of PCl_3 .....

.....

(3 marks)

(c) (i) Write an expression for the equilibrium constant, K_p, for this equilibrium.

.....

.....

(ii) The partial pressures of Cl_2 and PCl_5 in the equilibrium mixture were 51.3 kPa and 83.6 kPa, respectively, and the total pressure remained at 225 kPa. Calculate the value of K_p at this temperature and state its units.

.....

.....

.....

(4 marks)

(d) State the effect on the mole fraction of PCl_3 in the equilibrium mixture if

(i) the volume of the vessel were to be increased at a constant temperature,

.....

(ii) the temperature were to be increased at constant volume.

.....

(2 marks)

Turn over ▶

3 (a) At 50 °C, the ionic product of water, K_w, has the value 5.48×10^{-14} mol^2 dm^{-6}.

(i) Define the term K_w

.....

(ii) Define the term *pH*

.....

(iii) Calculate the pH of pure water at 50 °C. Explain why pure water at 50 °C is still neutral even though its pH is not 7.

Calculation .....

.....

.....

Explanation .....

.....

(5 marks)

(b) At 25 °C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}. Calculate the pH at 25 °C of

(i) a 0.150 mol dm^{-3} solution of sodium hydroxide,

.....

.....

.....

(ii) the solution formed when 35.0 cm^3 of this solution of sodium hydroxide is mixed with 40.0 cm^3 of a 0.120 mol dm^{-3} solution of hydrochloric acid.

.....

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(8 marks)

(c) In a 0.150 mol dm^{-3} solution of a weak acid HX at 25 °C, 1.80 % of the acid molecules are dissociated into ions.

(i) Write an expression for K_a for the acid HX.

.....

.....

(ii) Calculate the value of K_a for the acid HX at this temperature and state its units.

.....

.....

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.....

.....

(5 marks)

18

TURN OVER FOR THE NEXT QUESTION

4 (a) Outline a mechanism for the reaction of $CH_3CH_2CH_2CHO$ with HCN and name the product.

Mechanism

Name of product .....

(5 marks)

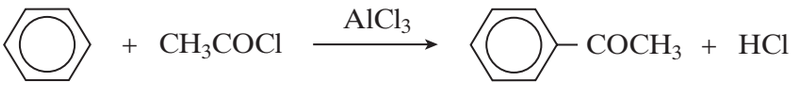
(b) Outline a mechanism for the reaction of CH_3OH with CH_3CH_2COCl and name the organic product.

Mechanism

Name of organic product .....

(5 marks)

(c) An equation for the formation of phenylethanone is shown below. In this reaction a reactive intermediate is formed from ethanoyl chloride. This intermediate then reacts with benzene.



(i) Give the formula of the reactive intermediate.

.....

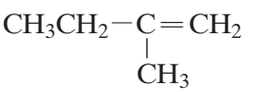
(ii) Outline a mechanism for the reaction of this intermediate with benzene to form phenylethanone.

(4 marks)

14

TURN OVER FOR THE NEXT QUESTION

5 (a) The hydrocarbon **M** has the structure shown below.



(i) Name hydrocarbon **M**.

.....

(ii) Draw the repeating unit of the polymer which can be formed from **M**. State the type of polymerisation occurring in this reaction.

Repeating unit

Type of polymerisation .....

(iii) The reaction between **M** and benzene in the presence of HCl and $AlCl_3$ is similar to the reaction between ethene and benzene under the same conditions. Name the type of mechanism involved and draw the structure of the major product formed in the reaction between **M** and benzene.

Name of mechanism .....

Major product

(iv) Draw a structural isomer of **M** which shows geometrical isomerism.

(6 marks)

(b) Draw the repeating unit of the polymer formed by the reaction between butanedioic acid and hexane-1,6-diamine. State the type of polymerisation occurring in this reaction and give a name for the linkage between the monomer units in this polymer.

Repeating unit

Type of polymerisation .....

Name of linkage .....

(4 marks)

SECTION B

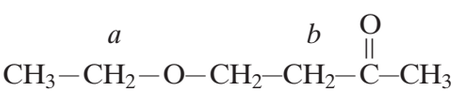
Answer **both** the questions in the space provided on pages 12 to 16 of this booklet.

6 Use the data given on the back of the Periodic Table on page 3 of this booklet to help you answer this question.
Compounds **A** to **G** are all isomers with the molecular formula $C_6H_{12}O_2$

(a) Isomer **A**, $C_6H_{12}O_2$, is a neutral compound and is formed by the reaction between compounds **X** and **Y** in the presence of a small amount of concentrated sulphuric acid.
X and **Y** can both be formed from propanal by different redox reactions.
X has an absorption in its infra-red spectrum at 1750 cm^{-1}.
Deduce the structural formulae of **A**, **X** and **Y**. Give suitable reagents, in each case, for the formation of **X** and **Y** from propanal and state the role of concentrated sulphuric acid in the formation of **A**. *(7 marks)*

(b) Isomers **B**, **C**, **D** and **E** all react with aqueous sodium carbonate to produce carbon dioxide.
Deduce the structural formulae of the three isomers that contain an asymmetric carbon atom.
The fourth isomer has only three singlet peaks in its proton n.m.r. spectrum. Deduce the structural formula of this isomer and label it **E**. *(4 marks)*

(c) Isomer **F**, $C_6H_{12}O_2$, has the structural formula shown below, on which some of the protons have been labelled.



A proton n.m.r. spectrum is obtained for **F**. Using Table 1 on page 4 of this booklet, predict a value of δ for the protons labelled *a* and also for those labelled *b*. State and account for the splitting patterns of the peaks assigned to the protons *a* and *b*.
(6 marks)

(d) Isomer **G**, $C_6H_{12}O_2$, contains six carbon atoms in a ring. It has an absorption in its infra-red spectrum at 3270 cm^{-1} and shows only three different proton environments in its proton n.m.r. spectrum. Deduce a structural formula for **G**. *(2 marks)*

Turn over ▶

7 (a) Outline a mechanism for the formation of ethylamine from bromoethane. State why the ethylamine formed is contaminated with other amines. Suggest how the reaction conditions could be modified to minimise this contamination. *(6 marks)*

(b) Suggest one reason why phenylamine cannot be prepared from bromobenzene in a similar way. Outline a synthesis of phenylamine from benzene. In your answer you should give reagents and conditions for each step, but equations and mechanisms are not required. *(5 marks)*

END OF QUESTIONS