Surname		Other Names	
Centre Number		Candidate Number	
Candidate Signature			

For Examiner's Use

General Certificate of Education
January 2007
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

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

Tuesday 23 January 2007 9.00 am to 10.30 am

For this paper you must have
- 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.
- Answer the 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 to be 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.
- The marks for questions are shown in brackets.
- You are expected to use a calculator where appropriate.
- Write your answers to the question in **Section B** 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			
Question	Mark	Question	Mark
1			
2			
3			
4			
5			
6			
7			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

There are no questions printed on this page

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

Gas constant $R = 8.31$ J K^{-1} mol^{-1}

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

SECTION A

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

1 (a) The following data were obtained by studying the reaction between compounds **A**, **B** and **C** at a constant temperature.

Experiment	Initial concentration of **A** / mol dm^{-3}	Initial concentration of **B** / mol dm^{-3}	Initial concentration of **C** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.20	0.10	0.40	0.80×10^{-3}
2	0.20	0.40	0.40	3.20×10^{-3}
3	0.10	0.80	0.40	1.60×10^{-3}
4	0.10	0.30	0.20	0.60×10^{-3}

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

.....

.....

(ii) Deduce the order of reaction with respect to **B**.

.....

.....

(iii) Deduce the order of reaction with respect to **C**.

.....

.....

(3 marks)

(b) The rate equation for the reaction between compounds **D** and **E** at a given temperature is

$$\text{rate} = k[\mathbf{D}]^2[\mathbf{E}]$$

The initial rate of reaction is 8.36×10^{-4} mol dm^{-3} s^{-1} when the initial concentration of **D** is 0.84 mol dm^{-3} and the initial concentration of **E** is 1.16 mol dm^{-3}.
Calculate a value for the rate constant, k, at this temperature and deduce its units.

Value of k .....

.....

.....

Units of k .....

.....

(3 marks)

Turn over ▶

6

2 At high temperatures, PCl_5 dissociates according to the following equation.

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

A 2.60 mol sample of PCl_5 is placed in a sealed container and heated to a fixed temperature. At equilibrium, 1.40 mol of PCl_5 remain unreacted. The total pressure in the container is 125 kPa.

(a) Calculate the number of moles of Cl_2 and the total number of moles of gas present in the equilibrium mixture.

Moles of Cl_2 .....

Total number of moles .....

(2 marks)

(b) Calculate the mole fraction of PCl_5 and the mole fraction of Cl_2 in the equilibrium mixture.

Mole fraction of PCl_5 .....

.....

Mole fraction of Cl_2 .....

.....

(2 marks)

(c) (i) Write a general expression for the partial pressure of a gas, in a mixture of gases.

.....

.....

(ii) Calculate the partial pressure of PCl_5 and the partial pressure of Cl_2 in the equilibrium mixture.

Partial pressure of PCl_5 .....

.....

Partial pressure of Cl_2 .....

.....

(3 marks)

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

.....

.....

(1 mark)

(e) (i) State the effect, if any, on the value of K_p of adding more PCl_5 at a constant temperature.

.....

(ii) State the effect, if any, on the value of K_p of increasing the temperature of the container.

.....

(2 marks)

(f) In a further experiment, a second sample of PCl_5 is heated to a different temperature. In the equilibrium mixture produced at this temperature, the partial pressure of PCl_5 is 36.9 kPa and the partial pressure of Cl_2 is 42.6 kPa.
Calculate a value for the equilibrium constant, K_p, for this reaction at this temperature and give its units.

Calculation .....

.....

.....

Units .....

(3 marks)

13

Turn over for the next question

3 In this question, give all pH and pK_a values to 2 decimal places.

(a) Hydrochloric acid is described as a strong Brønsted-Lowry acid.

(i) State what is meant by the term *Brønsted-Lowry acid*.

.....

(ii) State why hydrochloric acid is described as *strong*.

.....

(2 marks)

(b) A sample of hydrochloric acid contains 7.05×10^{-3} mol of hydrogen chloride in $50\,cm^3$ of solution.

(i) Calculate the concentration, in mol dm^{-3}, of this hydrochloric acid.

.....

.....

(ii) Write an expression for the term *pH*.

.....

(iii) Calculate the pH of this hydrochloric acid.

.....

(iv) When water is added to this $50\,cm^3$ sample of acid the pH increases. Calculate the total volume of the solution when the pH becomes exactly 1.00

.....

.....

.....

.....

(6 marks)

(c) The value of the acid dissociation constant, K_a, for the weak acid HX is 6.10×10^{-5} mol dm^{-3} at 25 °C.

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

.....

.....

(ii) Calculate the pH of a 0.255 mol dm^{-3} solution of HX at 25 °C.

.....

.....

.....

.....

(4 marks)

(d) A given volume of a buffer solution contains 6.85×10^{-3} mol of the weak acid HY and 2.98×10^{-3} mol of the salt NaY. The pH of the buffer solution is 3.78

(i) Calculate the value of pK_a for the acid HY at this temperature.

.....

.....

.....

.....

.....

.....

(ii) State and explain the effect on the pH of the buffer solution when a small amount of hydrochloric acid is added.

Effect on pH .....

Explanation .....

.....

.....

.....

(7 marks)

19

4 Compounds **J**, **K**, **L** and **M** are structural isomers of $C_4H_{10}O_2$
Some of these isomers are ethers. Ethers contain the C–O–C linkage.
Isomers **J**, **K**, **L** and **M** can be distinguished using proton n.m.r. spectroscopy and infra-red spectroscopy.

(a) The substance TMS is used as a standard in recording proton n.m.r. spectra.

Draw the structure of TMS and give two reasons why it is used as a standard.

Structure of TMS

Reason 1 .....

Reason 2 .....

(3 marks)

(b) State the number of peaks in the proton n.m.r. spectrum of isomer **J**, $CH_3OCH_2CH_2OCH_3$

.....

(1 mark)

(c) (i) Isomer **K**, shown below, has five peaks in its proton n.m.r. spectrum. Predict the splitting pattern of the peaks due to the protons labelled *a* and *b*.

$$CH_3\overset{a}{C}H_2O\overset{b}{C}H_2CH_2OH$$

a .....

b .....

(ii) Identify the wavenumber of an absorption which would be present in the infra-red spectrum of **K** but which would not be present in the infra-red spectrum of **J**.

.....

(3 marks)

(d) Isomer **L**, $HOCH_2CH_2CH_2CH_2OH$, can be used to form polyesters.

(i) Give the name of **L**.

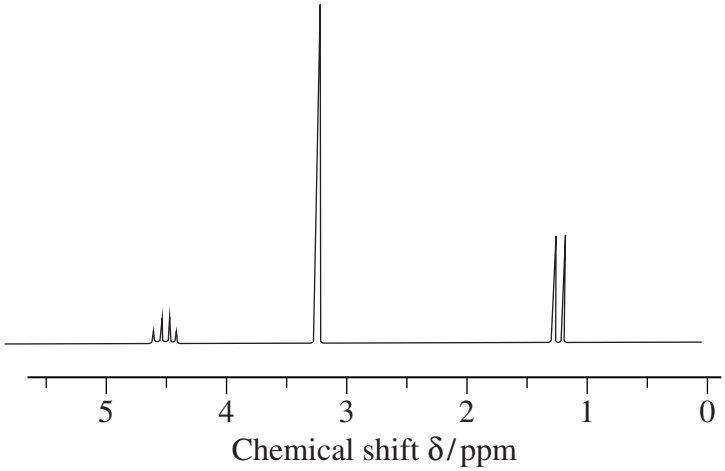
.....

(ii) Isomer **L** reacts with pentanedioic acid to form a polyester. Name the type of polymerisation involved and draw the repeating unit of the polyester formed.

Type of polymerisation .....
Repeating unit

(4 marks)

(e) The proton n.m.r. spectrum of isomer **M** is shown below. The measured integration trace gives the ratio 0.4 to 2.4 to 1.2 for the peaks at δ 4.6, 3.3 and 1.3, respectively.



(i) State what you can deduce from the integration value for the peak at δ 3.3

.....

(ii) Use **Table 1** on the reverse of the Periodic Table to help you identify the type of proton leading to the peak at δ 3.3

.....

(iii) Draw the part of the structure which can be deduced from the splitting of the peaks at δ 1.3 and δ 4.6 and from their integration values.

.....

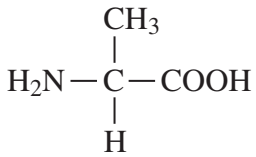
(iv) Hence, deduce the structure of **M**.

(4 marks)

Turn over ►

15

5 The amino acid *alanine* is shown below.



(a) Give the systematic name for alanine.

.....

(1 mark)

(b) (i) Draw the structure of the dipeptide formed from two alanine molecules, showing clearly the full structure of the peptide link.

(ii) Draw the structure of the organic compound formed by the reaction of alanine with propan-2-ol in the presence of a small amount of the catalyst concentrated sulphuric acid.

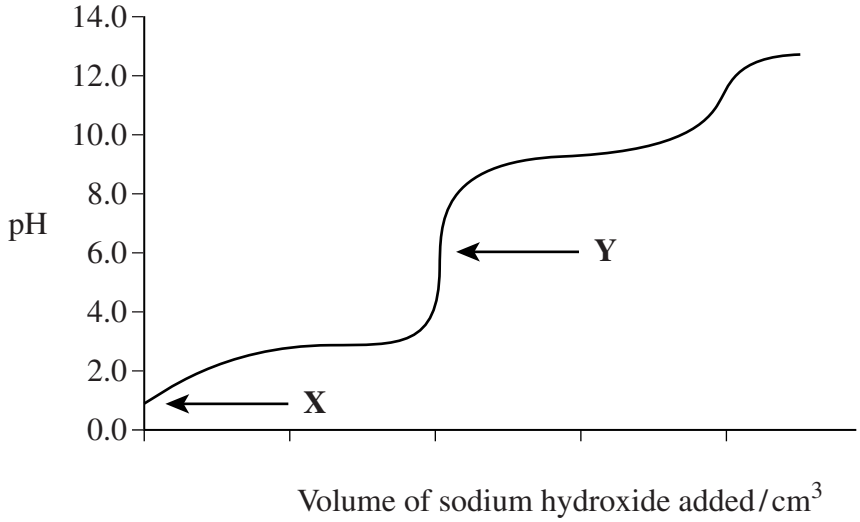
(iii) Draw the structure of the *N*–substituted amide formed by the reaction of alanine with ethanoyl chloride. Name the type of mechanism involved.

Structure

Name of mechanism .....

(4 marks)

(c) A solution was prepared by reacting alanine with an equal number of moles of hydrochloric acid. This solution was titrated with aqueous sodium hydroxide. The titration curve obtained is shown below.



(i) Draw the structure of the alanine species present at point **X** on the curve.

(ii) Draw the structure of the alanine species present at point **Y** on the curve.

(2 marks)

7

LEAVE MARGIN BLANK

SECTION B

Detach this perforated sheet.
Answer **both** questions 6 and 7 in the space provided on page 14 and pages 17-20.

6 (a) An acylium ion has the structure $R{-}\overset{+}{C}{=}O$ where R is any alkyl group.

In the conversion of benzene into phenylethanone, $C_6H_5COCH_3$, an acylium ion $CH_3\overset{+}{C}O$ reacts with a benzene molecule.
Write an equation to show the formation of this acylium ion from ethanoyl chloride and one other substance.
Name and outline the mechanism of the reaction of this acylium ion with benzene.

(6 marks)

(b) Phenylethanone, $C_6H_5COCH_3$, reacts with HCN according to the equation below.

$$C_6H_5COCH_3 + HCN \longrightarrow C_6H_5-\underset{\displaystyle CN}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-CH_3$$

Name and outline the mechanism of this reaction.

The product formed exists as a racemic mixture. State the meaning of the term *racemic mixture* and explain why such a mixture is formed in this reaction.

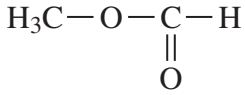
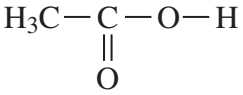
(8 marks)

(c) Acylium ions are also formed by the fragmentation of molecular ions in a mass spectrometer.
Give the name of compound **Z**, $CH_3CH_2COCH(CH_3)_2$
Draw the structures of the **two** possible acylium ions formed in the fragmentation of the molecular ion of **Z** in a mass spectrometer.
Write an equation for the formation of **one** of these acylium ions from the molecular ion of **Z**.

(5 marks)

19

7 (a) Describe, by giving reagents and stating observations, how you could distinguish between the compounds in the following pairs using simple test-tube reactions.

(i)  and 

P **Q**

(ii) CH_3CH_2COCl and CH_3CH_2Cl

R **S**

(6 marks)

(b) (i) Give the reagents needed for the reduction of nitrobenzene to form phenylamine. Write an equation for the reaction. Use [H] to represent the reductant.

(ii) Name the type of mechanism for the reaction between phenylamine and bromomethane. Draw the structure of the product of the reaction of phenylamine with a large excess of bromomethane.

(5 marks)

11

END OF QUESTIONS

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