Surname		Other Names	
Centre Number			Candidate Number	
Candidate Signature			

For Examiner's Use

General Certificate of Education
January 2008
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

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

Tuesday 22 January 2008 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 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 questions 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			
8			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

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SECTION A

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

1 In this question give all values of pH to 2 decimal places.

(a) The dissociation of water can be represented by the following equilibrium.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

(i) Write an expression for the ionic product of water, K_w

.....

(ii) The pH of a sample of pure water is 6.63 at 50 °C.

Calculate the concentration in mol dm^{-3} of H^+ ions in this sample of pure water.

.....

(iii) Deduce the concentration in mol dm^{-3} of OH^- ions in this sample of pure water.

.....

(iv) Calculate the value of K_w at this temperature.

.....

.....

.....

(4 marks)

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

Calculate the pH of a 0.136 mol dm^{-3} solution of KOH at 25 °C.

.....

.....

.....

.....

(2 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

* **58 – 71** Lanthanides	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
† **90 – 103** Actinides	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

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

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

2 In this question give all values of pH to 2 decimal places.

The acid dissociation constant, K_a, for propanoic acid has the value 1.35×10^{-5} mol dm^{-3} at 25 °C.

$$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

(a) Calculate the pH of a 0.169 mol dm^{-3} solution of propanoic acid.

.....

.....

.....

.....

.....

(3 marks)

(b) A buffer solution contains 0.250 mol of propanoic acid and 0.190 mol of sodium propanoate in 1000 cm^3 of solution.

A 0.015 mol sample of solid sodium hydroxide is then added to this buffer solution.

(i) Write an equation for the reaction of propanoic acid with sodium hydroxide.

.....

(ii) Calculate the number of moles of propanoic acid and of propanoate ions present in the buffer solution after the addition of the sodium hydroxide.

Moles of propanoic acid present .....

.....

Moles of propanoate ions present .....

.....

(iii) Hence, calculate the pH of the buffer solution after the addition of the sodium hydroxide.

.....

.....

.....

.....

.....

(6 marks)

3 Under suitable conditions the equilibrium represented below was established.

$$2CH_4(g) \rightleftharpoons 3H_2(g) + C_2H_2(g) \qquad \Delta H^{\ominus} = +377 \text{ kJ mol}^{-1}$$

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

.....

.....

(1 mark)

(b) At a given temperature and pressure, the equilibrium mixture contained 0.44 mol of methane, 0.28 mol of hydrogen and 0.12 mol of ethyne (C_2H_2) in a container of volume 0.25 dm^3.

Calculate the value of K_c under these conditions and deduce its units.

Calculation .....

.....

.....

.....

.....

Units .....

(4 marks)

(c) State the effect of an increase in temperature on the position of this equilibrium and on the value of K_c for this reaction.

Effect on position of equilibrium .....

Effect on the value of K_c .....

(2 marks)

(d) State the effect of an increase in pressure on the position of this equilibrium and on the value of K_c for this reaction.

Effect on position of equilibrium .....

Effect on the value of K_c .....

(2 marks)

(e) Calculate the mole fraction of ethyne (C_2H_2) in this equilibrium mixture.

.....

.....

.....

(2 marks)

(f) Calculate the partial pressure of ethyne in this mixture, given that the total pressure is 2.78×10^4 kPa.

.....

.....

(1 mark)

(g) A different equilibrium mixture was produced starting from methane alone.

$$2CH_4(g) \rightleftharpoons 3H_2(g) + C_2H_2(g)$$

When 3.0 mol of methane were used, the equilibrium mixture formed contained 1.6 mol of methane. Calculate the number of moles of hydrogen and the number of moles of ethyne present in this equilibrium mixture.

Moles of hydrogen .....

.....

Moles of ethyne .....

.....

(2 marks)

14

Turn over for the next question

4 (a) Each part below concerns a different pair of isomers.

Draw one possible structure for each of the compounds **A** to **J**.

Use **Table 2** on the Data Sheet where appropriate.

(i) Compounds **A** and **B** have the molecular formula C_6H_{12}
Both have only one peak in their proton n.m.r. spectra.
A has an absorption at 1650 cm^{-1} in its infra-red spectrum but **B** does not.

A **B**

(ii) Compounds **C** and **D** have the molecular formula $C_5H_{10}O$ and both have only two peaks in their proton n.m.r. spectra.
C forms a silver mirror with Tollens' reagent but **D** does not.

C **D**

(iii) Compounds **E** and **F** have the molecular formula $C_3H_6O_2$ and both have only a quartet, a triplet and a singlet peak in their proton n.m.r. spectra.
E gives an effervescence with aqueous sodium hydrogencarbonate but **F** does not.

E **F**

(iv) Compounds **G** and **H** have the molecular formula C_6H_{12}
G shows geometrical isomerism but not optical isomerism.
H shows optical isomerism but not geometrical isomerism.

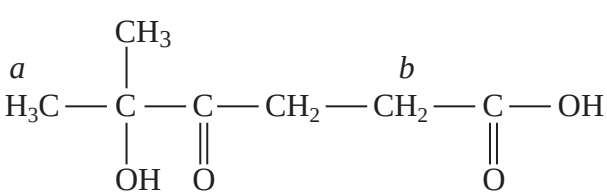
G **H**

(v) Compounds **I** and **J** have the molecular formula $C_5H_{12}O$
I cannot be oxidised by acidified potassium dichromate(VI) but can be dehydrated to form an alkene.
J can be oxidised by acidified potassium dichromate(VI) but cannot be dehydrated to form an alkene.

I **J**

(10 marks)

(b) Consider the compound below.



(i) Predict the number of peaks in its proton n.m.r. spectrum.

.....

(ii) The protons labelled *a* and *b* each produce a peak in the proton n.m.r. spectrum. Name the splitting pattern for each of these peaks.

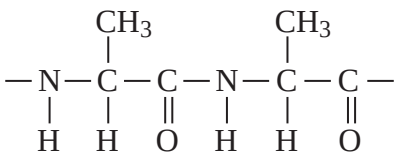
Splitting pattern for the protons labelled a .....

Splitting pattern for the protons labelled b .....

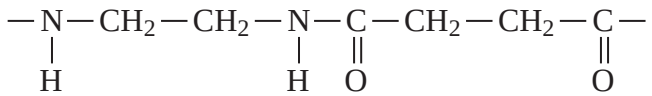
(3 marks)

5 Sections of different polymers **P** to **U** are shown below.

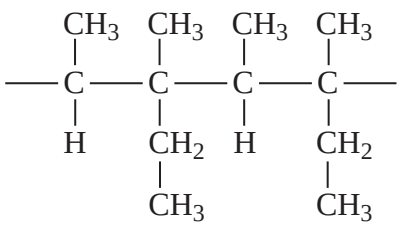
P



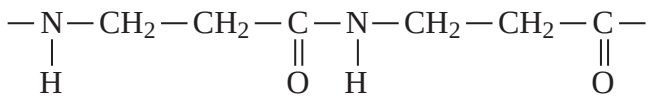
Q



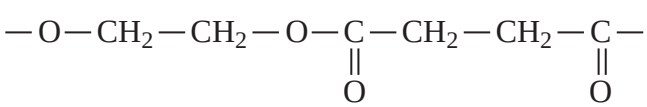
R



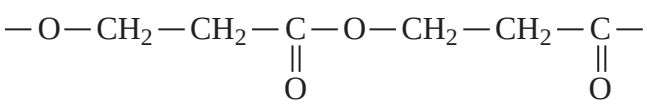
S



T



U



(a) (i) Polymer **P** is formed from the single amino acid, 2-aminopropanoic acid. Draw the structure of the zwitterion of this amino acid.

(ii) One other polymer represented above is formed from a single amino acid. Give the formula of this amino acid.

.....

(iii) Name the monomers used in the formation of polymer **Q**.

Name of first monomer .....

Name of second monomer .....

(4 marks)

(b) Polymer **R** is formed from an alkene monomer.

(i) Name the type of polymerisation involved in the formation of polymer **R**.

.....

(ii) Name the alkene monomer.

.....

(2 marks)

(c) Polymers **T** and **U** are polyesters.

(i) Draw the structures of the monomers used to produce polymer **T**.

First monomer

Second monomer

(ii) Draw the structure of the species formed when polymer **U** is hydrolysed by heating with aqueous sodium hydroxide.

(3 marks)

(d) (i) Name the strongest type of intermolecular force in polymer **R**.

.....

(ii) Name the strongest type of intermolecular force in polymer **T**.

.....

(2 marks)

6 (a) The initial rate of the reaction between compounds **X** and **Y** was measured in a series of experiments at a fixed temperature. The following rate equation was deduced.

$$\text{rate} = k[\mathbf{X}]^2[\mathbf{Y}]^0$$

(i) Complete the table of data below for the reaction between **X** and **Y**.

Expt	Initial [**X**] / mol dm^{-3}	Initial [**Y**] / mol dm^{-3}	Initial rate / mol dm^{-3}
1	1.20×10^{-3}	3.30×10^{-3}	2.68×10^{-4}
2	1.20×10^{-3}	6.60×10^{-3}	
3	2.40×10^{-3}	6.60×10^{-3}	
4		9.90×10^{-3}	8.04×10^{-4}

(ii) Using the data for experiment 1, calculate a value for the rate constant, *k*, and deduce its units.

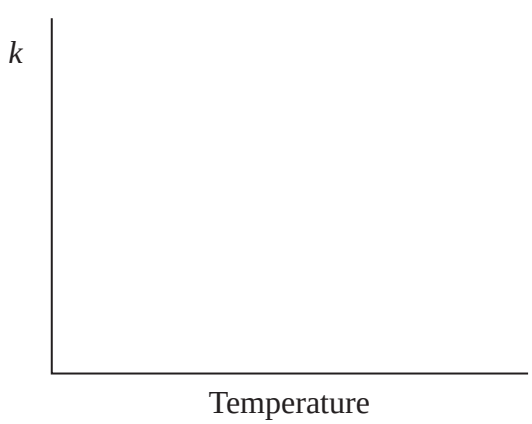
Calculation .....

.....

Units .....

(6 marks)

(b) Sketch a graph to show how the value of the rate constant, *k*, varies with temperature.



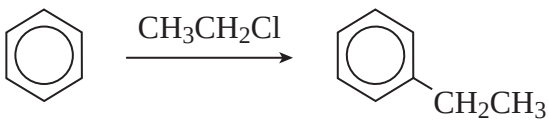
(1 mark)

7

SECTION B

Answer **both** questions 7 and 8 in the space provided on pages 15–20.

7 Chloroethane (CH_3CH_2Cl) can be used as a reagent in each of the following reactions.

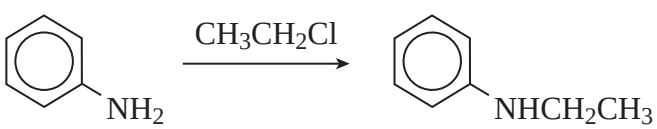
(a) 

Identify a catalyst for this reaction and show how the catalyst reacts and is regenerated.

Name and outline a mechanism for this reaction.

Name the product shown and identify an important industrial chemical manufactured from it.

(9 marks)

(b) 

Name and outline a mechanism for this reaction and name the product shown.

(6 marks)

15

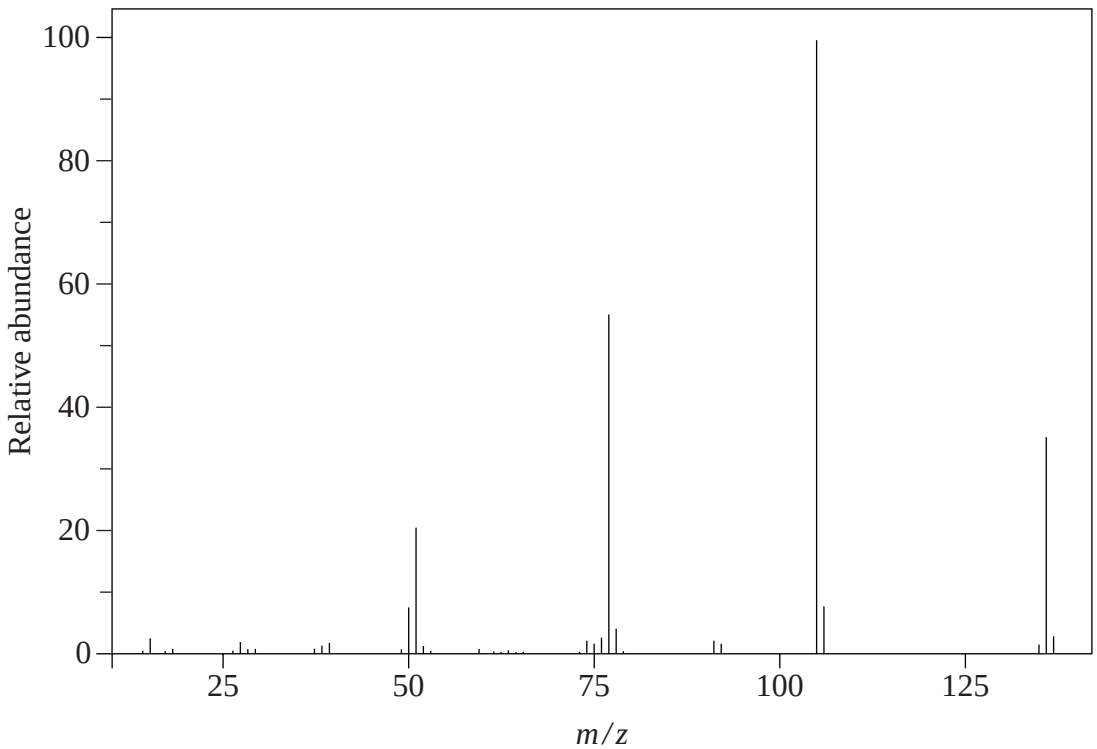
Turn over for the next question

8 The ester methyl benzenecarboxylate ($C_6H_5COOCH_3$) can be prepared by the reaction of methanol with benzenecarbonyl chloride, C_6H_5COCl

(a) Name and outline a mechanism for this reaction.

(5 marks)

(b) The mass spectrum of methyl benzenecarboxylate is shown below.



Suggest structures for the fragment ions which produce peaks at *m/z* = 105 and *m/z* = 77 in the mass spectrum above.

Write an equation for the fragmentation of the molecular ion to give the ion which produces the peak at *m/z* = 105.

(4 marks)

(c) Esters **V** and **W** are isomers of methyl benzenecarboxylate and both contain a benzene ring.

V has a major peak at *m/z* = 43 in its mass spectrum. Suggest a structure for the fragment ion which produces this peak and hence suggest a structure for **V**.

W has a major peak at *m/z* = 91 in its mass spectrum. Suggest a structure for the fragment ion which produces this peak and hence suggest a structure for **W**.

(4 marks)

(d) (i) Infra-red spectroscopy can be used to distinguish between esters and carboxylic acids. Identify an absorption that would enable you to distinguish between methyl benzenecarboxylate and its isomer 4-methylbenzenecarboxylic acid.

(ii) State how infra-red spectroscopy can be used to show that an unknown ester is definitely methyl benzenecarboxylate.

(2 marks)

END OF QUESTIONS

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