Surname		Other Names	
Centre Number			Candidate Number									
Candidate Signature												

For Examiner's Use

General Certificate of Education
June 2008
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

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

Thursday 12 June 2008 1.30 pm to 3.00 pm

For this paper you must have
- a calculator.

Time allowed: 1 hour 30 minutes

Instructions

- Use black ink or black 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. Answers written in margins or blank pages will not be marked.
- 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			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

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

1 In this question you are required to calculate the pH values of some acidic solutions. Give all values of pH to 2 decimal places.

1 (a) Calculate the pH of 0.0380 mol dm^{-3} hydrochloric acid.

.....

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(1 mark)

1 (b) Calculate the pH of the solution formed when 100 cm^3 of pure water are added to 100 cm^3 of this 0.0380 mol dm^{-3} hydrochloric acid.

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(2 marks)

1 (c) HX is a weak Brønsted–Lowry acid.

1 (c) (i) Explain the terms *weak* and *Brønsted–Lowry acid* as applied to HX.

Weak .....

.....

Brønsted–Lowry acid .....

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1 (c) (ii) Write an expression for the dissociation constant, K_a, for the acid HX.

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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

1 (c) (iii) The pH of 0.0630 mol dm^{-3} solution of HX is 3.48
Calculate the value of K_a for HX.

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(6 marks)

1 (d) An aqueous buffer solution which contains 0.0550 mol of a different weak acid, HA, and 0.0250 mol of NaA in 100 cm^3 of solution has a pH of 4.20

The value of K_a for the acid HA is 2.87×10^{-5} mol dm^{-3} at 25 °C.

1 (d) (i) Deduce the pH of the solution formed when 100 cm^3 of pure water are added to 100 cm^3 of this buffer solution.

.....

1 (d) (ii) Calculate the pH of the solution formed when 10.0 cm^3 of 0.130 mol dm^{-3} aqueous sodium hydroxide are added to 100 cm^3 of the original buffer solution.

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(6 marks)

15

2 (a) The table below shows the results of three experiments to investigate the rate of reaction between compounds **A** and **B**. All three experiments were carried out at the same temperature.

	Experiment 1	Experiment 2	Experiment 3
Initial concentration of **A**/mol dm^{-3}	3.90×10^{-2}	7.80×10^{-2}	7.80×10^{-2}
Initial concentration of **B**/mol dm^{-3}	9.60×10^{-2}	2.40×10^{-2}	1.20×10^{-2}
Initial rate/mol dm^{-3} s^{-1}	5.00×10^{-5}	5.00×10^{-5}	2.50×10^{-5}

Use the data in the table to deduce the order of reaction with respect to **A** and the order of reaction with respect to **B**.

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

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

(2 marks)

2 (b) The reaction between compounds **C** and **D** at a given temperature is first order with respect to **C** and second order with respect to **D**.

2 (b) (i) Write a rate equation for this reaction.

.....

2 (b) (ii) When the initial concentration of **C** is 2.50×10^{-2} mol dm^{-3} and the initial concentration of **D** is 6.65×10^{-2} mol dm^{-3}, the initial rate of reaction is 1.45×10^{-4} mol dm^{-3} s^{-1}. Calculate the value of the rate constant at this temperature and deduce its units.

Calculation .....

.....

.....

Units of rate constant .....

(4 marks)

6

3 The equation for the catalytic decomposition of hydrazine into its elements is shown below.

$$N_2H_4(g) \rightleftharpoons N_2(g) + 2H_2(g)$$

3 (a) A sample of hydrazine and a catalyst were placed in a container and heated to a given temperature. In the equilibrium mixture of gases produced at a total pressure of 150 kPa, the mole fraction of hydrazine was 0.22

3 (a) (i) Calculate the partial pressure of hydrazine under these conditions.

.....

.....

3 (a) (ii) Hence, calculate the partial pressure of nitrogen and the partial pressure of hydrogen in the mixture.

Partial pressure of nitrogen .....

.....

Partial pressure of hydrogen .....

.....

(5 marks)

3 (b) A different mixture of hydrazine, nitrogen and hydrogen was prepared and allowed to reach equilibrium in the presence of a catalyst at a temperature *T*. In this new equilibrium mixture, the partial pressure of hydrazine was 75.0 kPa, the partial pressure of nitrogen was 27.0 kPa and the partial pressure of hydrogen was 48.0 kPa.

3 (b) (i) Write an expression for the equilibrium constant, K_p, for the decomposition of hydrazine.

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3 (b) (ii) Calculate the value of K_p at this temperature and deduce its units.

Calculation .....

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Units .....

(4 marks)

3 (c) The gas mixture from part (b) was transferred to a different container of half the original volume. When equilibrium was re-established at temperature *T*, the partial pressure of hydrazine had more than doubled. Explain why halving the volume has not simply doubled the partial pressure of hydrazine.

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(2 marks)

11

Turn over ▶

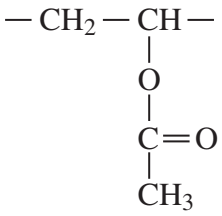
4 (a) A polymer is formed when propane-l,3-diamine reacts with pentanedioic acid. Name the type of polymerisation reaction which occurs and draw the structure of the repeating unit of the polymer formed.

Type of polymerisation .....

Repeating unit

(3 marks)

4 (b) The repeating unit shown below represents the polymer commonly known as poly(vinyl acetate) or PVA.

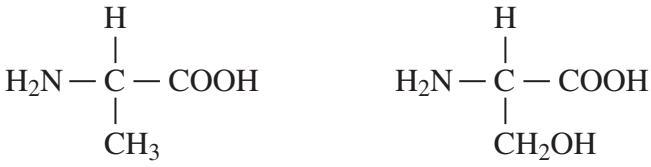


4 (b) (i) Draw the structure of the monomer which is used to make PVA.

4 (b) (ii) Draw the repeating unit of the polymer formed when PVA reacts with an excess of aqueous sodium hydroxide.

(2 marks)

4 (c) The amino acids *alanine* and *serine* are shown below.



alanine *serine*

4 (c) (i) Draw the structures of the two dipeptides formed by the reaction of *alanine* with *serine*.

4 (c) (ii) Draw the structure of the zwitterion of *serine*.

4 (c) (iii) Draw the structure of the organic compound formed when *alanine* reacts with methanol in the presence of a small amount of concentrated sulphuric acid.

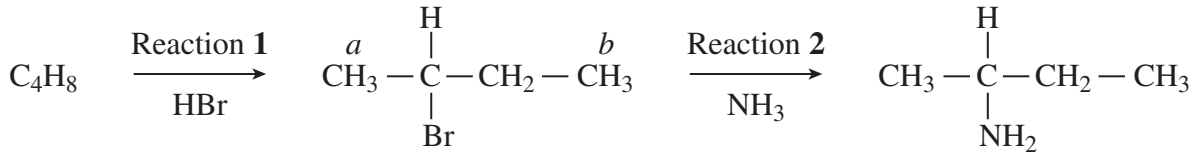
4 (c) (iv) Draw the structure of the organic compound formed when one molecule of *serine* reacts with two molecules of ethanoyl chloride.

(6 marks)

11

Turn over ▶

5 Consider the reaction sequence shown below.



E **F** **G**

5 (a) (i) Name the mechanism for Reaction **1**.

.....

5 (a) (ii) Compound **F** is the **only** product formed in Reaction **1**. Deduce the structure of compound **E**.

(2 marks)

5 (b) Name and outline a mechanism for Reaction **2**.

Name of mechanism .....

Mechanism

(5 marks)

5 (c) Compound **G** is a primary amine with molecular formula $C_4H_{11}N$
In Reaction **2**, the percentage conversion of **F** into **G** is 53.4%.

5 (c) (i) Calculate the mass of **G** formed in Reaction **2** from 10.0 g of **F**.

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5 (c) (ii) Suggest a reason, other than experimental technique, for the relatively low percentage conversion of **F** into **G** in Reaction **2**.

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.....

(4 marks)

5 (d) Predict the total number of peaks in the proton n.m.r. spectrum of **F**. State the splitting pattern of the peak for the protons labelled *a* and the splitting pattern of the peak for the protons labelled *b*.

Total number of peaks .....

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

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

(3 marks)

5 (e) Draw the structure of the following isomers of **G**.

5 (e) (i) The isomer which is a primary amine and has two peaks in its proton n.m.r. spectrum.

5 (e) (ii) The isomer which is a secondary amine and has four peaks in its proton n.m.r. spectrum.

5 (e) (iii) The isomer which is a tertiary amine.

(3 marks)

17

SECTION B

Detach this perforated sheet.
Answer **both** questions in the space provided on page 12 and pages 15-20 of this booklet.

6 Propanoyl chloride, CH_3CH_2COCl, reacts with water and with benzene.

6 (a) Write a balanced equation for the reaction of propanoyl chloride with water.
Name and outline a mechanism for this reaction.

(6 marks)

6 (b) Write a balanced equation for the overall reaction of propanoyl chloride with benzene.

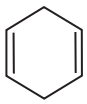
Identify a suitable catalyst for this reaction. Write equations to show how this catalyst reacts and how it is regenerated.

Name and outline a mechanism for the reaction involving benzene.

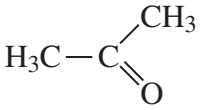
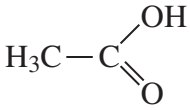
(8 marks)

Turn over for the next question

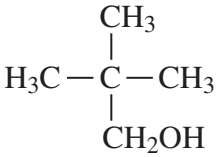
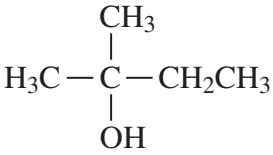
7 (a) Describe, by giving reagents and stating observations, how you could distinguish between the compounds in the following pairs. Use **one** simple test-tube reaction for each pair.

7 (a) (i)  and 

P **Q**

7 (a) (ii)  and 

R **S**

7 (a) (iii)  and 

T **U**

(9 marks)

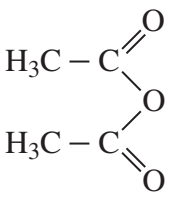
7 (b) Compound **T** in part (a)(iii) has a mass spectrum with a peak at $m/z = 57$

Draw the structure of the ion responsible for this peak and write an equation for the fragmentation of the molecular ion of **T** to produce this species.

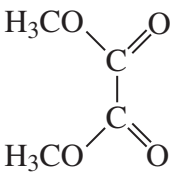
(3 marks)

7 (c) Identify a solvent used for samples in proton n.m.r. spectroscopy.

Give the names of compounds **V** and **W**, shown below, and describe how they can be distinguished using their proton n.m.r. spectra.



V



W

(4 marks)

END OF QUESTIONS