Surname		Other Names	
Centre Number			Candidate Number									
Candidate Signature												

For Examiner's Use

General Certificate of Education
June 2009
Advanced Level Examination

AQA

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

Thursday 11 June 2009 1.30 pm to 3.00 pm

For this paper you must have
- a calculator.

Time allowed: 1 hour 30 minutes

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			

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 on 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**.

SECTION A

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

1 (a) The initial rate of the reaction between the gases **P** and **Q** was measured in a series of experiments at a constant temperature and the following rate equation was determined.

$$\text{rate} = k[\mathbf{P}][\mathbf{Q}]^2$$

1 (a) (i) Complete the table of data below for the reaction between **P** and **Q**.

Expt	Initial [**P**] / mol dm^{-3}	Initial [**Q**] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	1.2×10^{-3}	2.0×10^{-3}	1.8×10^{-5}
2		2.0×10^{-3}	2.7×10^{-5}
3	0.60×10^{-3}	6.0×10^{-3}	
4	1.8×10^{-3}		0.30×10^{-5}

(3 marks)

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

Calculation .....

.....

.....

.....

Units .....

(3 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

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

Table 1
Proton n.m.r. chemical shift data

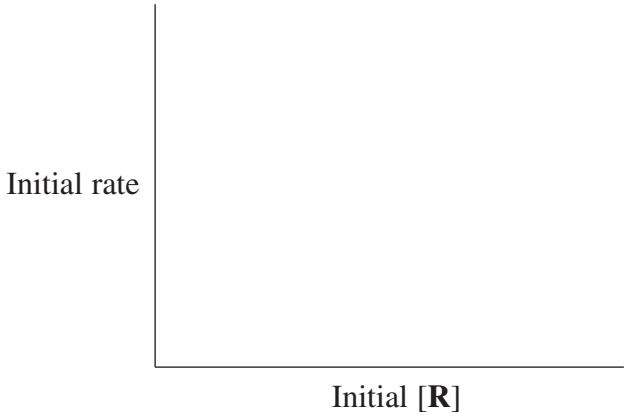
Type of proton	δ/ppm
RCH_3	0.7–1.2
R_2CH_2	1.2–1.4
R_3CH	1.4–1.6
$RCOCH_3$	2.1–2.6
$ROCH_3$	3.1–3.9
$RCOOCH_3$	3.7–4.1
ROH	0.5–5.0

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 (b) The decomposition of compound **R** is a zero order reaction.

On the axes below sketch a line to show the relationship between the initial rate of reaction of **R** and the initial concentration of **R** at constant temperature.



(1 mark)

7

Turn over for the next question

2 Dinitrogen tetraoxide dissociates into nitrogen dioxide as shown in the equation below.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

2 (a) In an experiment, 1.20 mol of dinitrogen tetraoxide were sealed in a flask and heated to a given temperature. The equilibrium mixture formed at this temperature contained 0.36 mol of nitrogen dioxide.

Calculate the mole fraction of nitrogen dioxide present in this equilibrium mixture.

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.....

.....

(3 marks)

2 (b) In a second experiment, a different equilibrium mixture was established at a different temperature. In this mixture, the mole fraction of nitrogen dioxide was found to be 0.28 at a total pressure of 180 kPa.

2 (b) (i) Write a general expression to show how the partial pressure of a gas is related to its mole fraction.

.....

(1 mark)

2 (b) (ii) Calculate the partial pressure of nitrogen dioxide in this mixture and hence deduce the partial pressure of dinitrogen tetraoxide.

Partial pressure of nitrogen dioxide .....

.....

Partial pressure of dinitrogen tetraoxide .....

.....

(2 marks)

2 (c) In a third experiment at a given temperature, an equilibrium mixture is formed in which the partial pressure of NO_2 is 49.6 kPa and the partial pressure of N_2O_4 is 132.0 kPa.

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

.....

.....

(1 mark)

2 (c) (ii) Calculate a value for K_p for this equilibrium at this temperature and give its units.

Calculation .....

.....

.....

Units .....

(3 marks)

10

Turn over for the next question

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

3 (a) (i) Write an expression for the term *pH*.

.....

(1 mark)

3 (a) (ii) A 5.0 cm^3 sample of 0.135 mol dm^{-3} hydrochloric acid is added to 995 cm^3 of water. Calculate the pH of the solution formed.

.....

.....

.....

(2 marks)

3 (b) At 298 K, the value of the dissociation constant for the weak acid 2-chloropropanoic acid ($CH_3CHClCOOH$), $K_a = 1.48 \times 10^{-3}$ mol dm^{-3}.

3 (b) (i) Write an expression for the dissociation constant, K_a, for 2-chloropropanoic acid.

.....

.....

(1 mark)

3 (b) (ii) Calculate a value for the pH of a 0.350 mol dm^{-3} solution of 2-chloropropanoic acid at this temperature.

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.....

(3 marks)

3 (c) The dissociation of 2-chloropropanoic acid in aqueous solution is an endothermic reaction. Predict how the pH of an aqueous solution of 2-chloropropanoic acid would change, if at all, when the temperature of the solution is increased. Explain your prediction.

Effect on pH .....

Explanation .....

.....

.....

.....

(3 marks)

3 (d) Name the type of stereoisomerism shown by 2-chloropropanoic acid. State how you could distinguish between separate samples of its stereoisomers.

Type of stereoisomerism .....

How to distinguish between stereoisomers .....

.....

.....

(3 marks)

3 (e) A buffer solution has a pH of 4.69 and contains 0.15 mol of propanoic acid and 0.10 mol of sodium propanoate. Use these data to calculate a value of K_a for propanoic acid.

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(3 marks)

16

4 (a) (i) Give the meaning of the term *Brønsted–Lowry base*.

.....

(1 mark)

4 (a) (ii) State which of ammonia and butylamine ($CH_3CH_2CH_2CH_2NH_2$) is the stronger base. Explain your answer.

Stronger base .....

Explanation .....

.....

.....

(3 marks)

4 (b) Draw the structure of the tertiary amine which is an isomer of butylamine.

(1 mark)

4 (c) (i) Draw the structure of the species formed when the amine $CH_3(CH_2)_{17}NH_2$ reacts with an excess of CH_3Br

(1 mark)

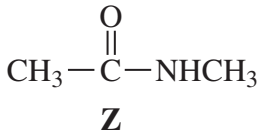
4 (c) (ii) Name the type of compound formed in part (c) (i) and give a use for such compounds.

Type of compound .....

Use .....

(2 marks)

4 (d) (i) Name compound **Z** shown below.



Z

.....

(1 mark)

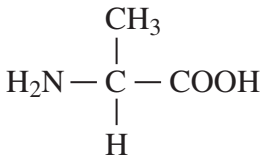
4 (d) (ii) Name and outline a mechanism for the reaction in which **Z** is formed from CH_3NH_2 and CH_3COCl

Name of mechanism .....

Mechanism

(5 marks)

4 (e) Consider the amino acid *alanine*



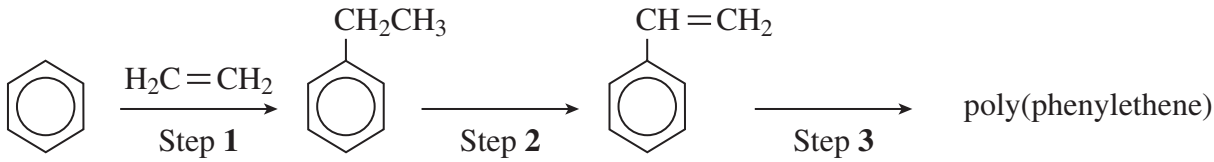
Complete the table below to show the structure of the species formed when alanine

dissolves in water	
reacts with hydrochloric acid	
reacts with methanol in the presence of a small amount of concentrated sulphuric acid.	

(3 marks)

17

5 Poly(phenylethene) can be manufactured from benzene and ethene as shown below.



ethylbenzene phenylethene

5 (a) (i) Identify **two** other substances needed to carry out the reaction in Step **1**.

Write an equation for the reaction of these two substances with ethene to form the reactive intermediate $CH_3CH_2^+$

Substance 1 .....

Substance 2 .....

Equation .....

(3 marks)

5 (a) (ii) Name and outline a mechanism for the reaction of this intermediate with benzene in Step **1**.

Name of mechanism .....

Mechanism

(4 marks)

5 (b) An alternative way of making ethylbenzene from benzene uses chloroethane instead of ethene. Give **one** reason why ethene is the preferred reagent.

.....

(1 mark)

5 (c) Draw the repeating unit of poly(phenylethene) and name the type of polymerisation involved in its formation.

Repeating unit

Type of polymerisation .....

(2 marks)

10

Turn over for the next question

SECTION B

Detach this perforated sheet.
Answer **Questions 6** to **8** in the space provided on page 14 and pages 17 to 20 of this booklet.

6 Compounds **A** to **F** are all isomers of $C_6H_{10}O_4$

6 (a) Isomer **A** ($HOOC(CH_2)_4COOH$) is used to make nylon 6,6

Name **A** and draw the repeating unit of nylon 6,6

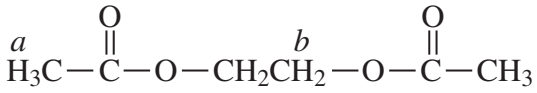
Draw the structure of the anhydride formed when one molecule of water is lost by one molecule of **A** *(4 marks)*

6 (b) Draw the structure of Isomer **B** ($C_6H_{10}O_4$), a dicarboxylic acid which contains two chiral centres. *(1 mark)*

6 (c) Isomer **C** is a propyl ester which also contains a carboxylic acid group.

Draw the structure of **C** *(1 mark)*

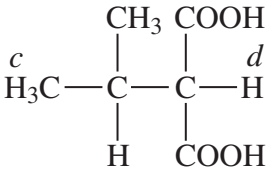
6 (d) Isomer **D** is the diester shown below. Some of the protons have been labelled.



Deduce the number of peaks in the proton n.m.r. spectrum of **D**

Use **Table 1** of the Data Sheet to predict the δ range of the peaks produced by the protons labelled *a* and *b*. *(3 marks)*

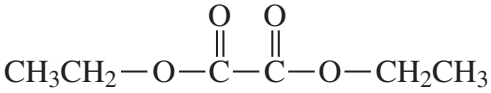
6 (e) Isomer **E** is the dicarboxylic acid shown below. Some of the protons have been labelled.



The protons labelled *c* and *d* each produce a peak in the proton n.m.r. spectrum.

Name the splitting pattern of the peak due to the protons labelled *c* and name the splitting pattern of the peak due to the proton labelled *d*. *(2 marks)*

6 (f) Isomer **F** is shown below.



The mass spectrum of Isomer **F** contains major peaks at $m/z = 45$ and $m/z = 29$

Draw the structure of the fragment which causes the peak at $m/z = 45$

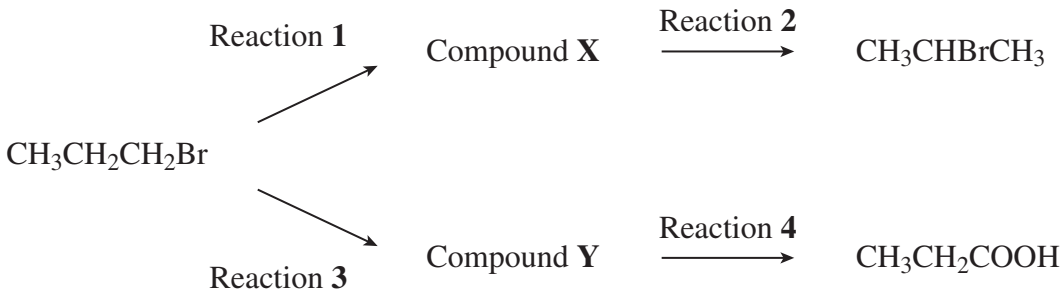
Write an equation for the fragmentation of the molecular ion to produce the fragment which causes the peak at $m/z = 29$ *(3 marks)*

Turn over for the next question

7 Consider the reaction sequences shown below.

Reaction **1** is an elimination.

Reaction **3** is a substitution.



Identify compounds **X** and **Y**.

Give reagents and conditions for each of Reactions **1**, **2**, **3** and **4**. *(9 marks)*

8 An aqueous solution contained both sodium carbonate and sodium hydrogencarbonate.

A 25.0 cm^3 sample of the solution was transferred into a conical flask. After the addition of a few drops of phenolphthalein, 0.150 mol dm^{-3} hydrochloric acid was then added from a burette.

The indicator changed colour when exactly 20.80 cm^3 of the 0.150 mol dm^{-3} hydrochloric acid had been added to the conical flask. This end-point showed that the reaction in Stage **1** had been completed.

Stage **1** $\quad CO_3^{2-} + H^+ \longrightarrow HCO_3^-$

A few drops of methyl orange were then added to the conical flask. A further 33.25 cm^3 of 0.150 mol dm^{-3} hydrochloric acid were required before this second indicator changed colour. This end-point showed that the reaction in Stage **2** had been completed.

Stage **2** $\quad HCO_3^- + H^+ \longrightarrow CO_2 + H_2O$

8 (a) Use the data about Stage **1** to calculate the concentration of sodium carbonate in the original solution. *(3 marks)*

8 (b) State why the volume of hydrochloric acid used in Stage **2** is greater than that used in Stage **1**. Hence calculate the concentration of sodium hydrogencarbonate in the original solution. *(4 marks)*

END OF QUESTIONS