Surname		Other Names	
Centre Number		Candidate Number	
Candidate Signature			

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General Certificate of Education
June 2003
Advanced Level Examination

CHEMISTRY CHM5
Unit 5 Thermodynamics and Further Inorganic Chemistry (including Synoptic Assessment)

Tuesday 24 June 2003 Morning Session

In addition to this paper you will require:
a calculator.

Time allowed: 2 hours

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 120.
- Mark allocations are shown in brackets.
- This paper carries 20 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 1 hour on **Section B**.

For Examiner's Use			
Number	Mark	Number	Mark
1			
2			
3			
4			
5			
6			
7			
8			
9			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

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.

Key

relative atomic mass — 6.9
Li
Lithium
atomic number — 3

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 †															

* 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

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

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SECTION A

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

1 Consider the following oxides.

Na_2O, MgO, Al_2O_3, SiO_2, P_4O_{10}, SO_3

(a) Identify one of the oxides from the above which

(i) can form a solution with a pH less than 3 ....

(ii) can form a solution with a pH greater than 12 ....

(2 marks)

(b) Write an equation for the reaction between

(i) MgO and HNO_3

....

(ii) SiO_2 and $NaOH$

....

(iii) Na_2O and H_3PO_4

....

(3 marks)

(c) Explain, in terms of their type of structure and bonding, why P_4O_{10} can be vaporised by gentle heat but SiO_2 cannot.

....

....

....

....

(4 marks)

9

Turn over ▶

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2 (a) Identify a reagent, or mixture of reagents, necessary to carry out each of the following conversions.

(i) $[Cr(H_2O)_6]^{3+}(aq) \rightarrow CrO_4^{2-}(aq)$

....

(ii) $VO_2^+(aq) \rightarrow [V(H_2O)_6]^{2+}(aq)$

....

(iii) $[Ag(NH_3)_2]^+(aq) \rightarrow Ag(s)$

....

(5 marks)

(b) In an acidic solution, hydrogen peroxide, H_2O_2, is oxidised to oxygen by manganate(VII) ions, which are reduced to Mn^{2+} ions.

(i) Write half-equations for the reactions occurring and use these to deduce the overall equation for this reaction.

Half-equation for the oxidation of H_2O_2

....

Half-equation for the reduction of manganate(VII) ions

....

Overall equation

....

....

....

(ii) 20.0 cm^3 of an acidified solution of H_2O_2 was found to react with exactly 15.7 cm^3 of a 0.0180 mol dm^{-3} solution of potassium manganate(VII).
Calculate the concentration, in g dm^{-3}, of the solution of hydrogen peroxide.
(If you have been unable to complete the overall equation in part (b)(i), assume that the mole ratio of manganate(VII) to H_2O_2 is 3:5. This is not the correct ratio.)

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(7 marks)

12

TURN OVER FOR THE NEXT QUESTION

Turn over ▶

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3 (a) The ion $C_2O_4^{2-}$ can act as a bidentate ligand.

(i) Explain the meaning of the term *bidentate ligand*.

....

....

(ii) Sketch the structure of the octahedral complex ion formed by Fe^{3+} ions which contains $C_2O_4^{2-}$ as the only ligand. Include the overall charge on the complex ion.

(5 marks)

(b) Explain the meaning of the term *chelate effect*.

....

....

(2 marks)

(c) The chloride ion can act as a monodentate ligand.

(i) Deduce the formula of the linear complex formed when an excess of concentrated hydrochloric acid is added to silver chloride.

....

(ii) Explain why metal(II) ions do not usually form octahedral complexes when chloride ions are the only ligands.

....

(2 marks)

(d) The concentration of $C_2O_4^{2-}$ ions can be determined by titration in acidic solution using a standard solution of potassium manganate(VII). At room temperature, the reaction proceeds very slowly at first but becomes faster after some of the manganate(VII) ions have reacted.

(i) Suggest why this reaction is very slow at first.

....

(ii) This is an example of an autocatalytic reaction. State the meaning of the term *autocatalytic* and identify the catalyst.

Meaning of the term autocatalytic ....

....

Catalyst ....

(iii) Suggest how this catalyst might be involved in the reaction.

....

....

....

(5 marks)

14

TURN OVER FOR THE NEXT QUESTION

Turn over ▶

4 (a) (i) Draw a fully-labelled Born–Haber cycle for the formation of solid barium chloride, $BaCl_2$, from its elements. Include state symbols for all species involved.

(ii) Use your Born–Haber cycle and the standard enthalpy data given below to calculate a value for the electron affinity of chlorine.

Enthalpy of atomisation of barium	+180 kJ mol^{-1}
Enthalpy of atomisation of chlorine	+122 kJ mol^{-1}
Enthalpy of formation of barium chloride	–859 kJ mol^{-1}
First ionisation enthalpy of barium	+503 kJ mol^{-1}
Second ionisation enthalpy of barium	+965 kJ mol^{-1}
Lattice formation enthalpy of barium chloride	–2056 kJ mol^{-1}

....

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....

....

(9 marks)

LEAVE MARGIN BLANK

(b) Use data from part (a)(ii) and the entropy data given below to calculate the lowest temperature at which the following reaction becomes feasible.

$$BaCl_2(s) \rightarrow Ba(s) + Cl_2(g)$$

	$BaCl_2(s)$	$Ba(s)$	$Cl_2(g)$
$S^{\ominus}$/ J K^{-1} mol^{-1}	124	63	223

....

....

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....

....

(4 marks)

13

TURN OVER FOR THE NEXT QUESTION

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5 Ethane, from North Sea gas, can be cracked to form ethene and hydrogen. In practice, the cracking reaction is incomplete and a mixture of ethane, ethene and hydrogen is obtained.

(a) Write an equation for this cracking reaction.

....

(1 mark)

(b) Calculate the total number of moles of gas in a $25.0\,cm^3$ sample of the gaseous mixture after cracking, measured at a temperature of 332 K and a pressure of 110 kPa.
($R = 8.31\,J\,K^{-1}\,mol^{-1}$)

....

....

....

....

(3 marks)

(c) The $25.0\,cm^3$ sample of the gaseous mixture from part (b) was treated with $75.0\,cm^3$ of gaseous bromine, also measured at 332 K and 110 kPa.

(i) Calculate the number of moles of bromine added to the gaseous mixture and write an equation for the reaction between ethene and bromine.

Calculation ....

....

....

Equation ....

After the reaction between ethene in the gaseous mixture and bromine was complete, the unreacted bromine was treated with an excess of aqueous potassium iodide. Iodine was formed.

(ii) Write an equation for the reaction between aqueous potassium iodide and bromine.

....

LEAVE MARGIN BLANK

Iodine reacts with aqueous sodium thiosulphate according to the following equation.

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

The iodine formed reacted with 22.1 cm^3 of a 0.250 mol dm^{-3} solution of sodium thiosulphate.

(iii) Calculate the number of moles of iodine formed. Hence, calculate the number of moles of bromine which reacted with the ethene present in the 25.0 cm^3 sample of the gaseous mixture.

Number of moles of iodine formed ....

....

....

....

Number of moles of bromine which reacted with ethene ....

....

....

(iv) Use these results to calculate the percentage by moles of ethene present in the gaseous mixture.

....

....

(8 marks)

12

TURN OVER FOR THE NEXT QUESTION

Turn over ▶

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SECTION B

Answer **all** of the questions below in the space provided on pages 16 to 20 of this booklet.

6 (a) State what is observed when aqueous ammonia is added dropwise, until present in excess, to a solution of cobalt(II) chloride, and the mixture obtained is then left to stand in air.
Give the formula of each cobalt-containing species formed. Explain the change which occurs when the mixture is left to stand in air. *(8 marks)*

(b) Explain why separate solutions of iron(II) sulphate and iron(III) sulphate of equal concentration have different pH values.
State what is observed when sodium carbonate is added separately to solutions of these two compounds. Give the formula of each iron-containing species formed. *(9 marks)*

7 Concentrated sulphuric acid is a useful laboratory reagent. Choosing appropriate examples, illustrate this statement by considering how you would use concentrated sulphuric acid

(a) to distinguish between solid samples of two sodium halides, *(6 marks)*

(b) to prepare isomeric alkenes from an alcohol, *(5 marks)*

(c) to prepare an aromatic nitro-compound. *(4 marks)*

Write equations for the reactions occurring and state the role(s) of sulphuric acid in each reaction.

LEAVE MARGIN BLANK

8 (a) A flask containing a mixture of 0.200 mol of ethanoic acid and 0.110 mol of ethanol was maintained at 25 °C until the following equilibrium had been established.

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

The ethanoic acid present at equilibrium required 72.5 cm^3 of a 1.50 mol dm^{-3} solution of sodium hydroxide for complete reaction.

(i) Calculate the value of the equilibrium constant, K_c, for this reaction at 25 °C.

(ii) The enthalpy change for this reaction is quite small. By reference to the number and type of bonds broken and made, explain how this might have been predicted. *(9 marks)*

(b) Aspirin can be prepared by acylation using either ethanoyl chloride or ethanoic anhydride, as represented by the equations shown below.

$$CH_3COCl + HOC_6H_4COOH \rightarrow CH_3COOC_6H_4COOH + HCl$$

$$(CH_3CO)_2O + HOC_6H_4COOH \rightarrow CH_3COOC_6H_4COOH + CH_3COOH$$

(i) By a consideration of the intermolecular forces involved, explain why the product HCl is a gas but the product CH_3COOH is a liquid at room temperature.

(ii) Give **two** industrial advantages of using ethanoic anhydride rather than ethanoyl chloride in the manufacture of aspirin. *(4 marks)*

9 You are required to plan an experiment to determine the percentage by mass of sulphate ions in some solid waste made up of the three compounds silicon dioxide, sodium carbonate and magnesium sulphate.

You are provided with dilute hydrochloric acid, a solution of barium chloride and simple laboratory equipment. (Hydrochloric acid reacts with carbonate ions and prevents the precipitation of barium and magnesium carbonates.)

(a) Outline how you would extract the sulphate ions from the solid waste and convert the extracted sulphate ions into a precipitate of barium sulphate.
Write equations for the reactions which occur. *(8 marks)*

(b) Describe how you would separate pure barium sulphate from other reaction products and how you would determine its mass.
Hence, explain how the percentage by mass of sulphate ions in the solid waste would be calculated. *(7 marks)*

END OF QUESTIONS

Turn over ▶