Surname		Other Names	
Centre Number		Candidate Number	
Candidate Signature			

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General Certificate of Education
June 2004
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

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

Tuesday 29 June 2004 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.
- Section B questions are provided on perforated sheets. Detach these sheets 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 $R = 8.31$ J K^{-1} 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			
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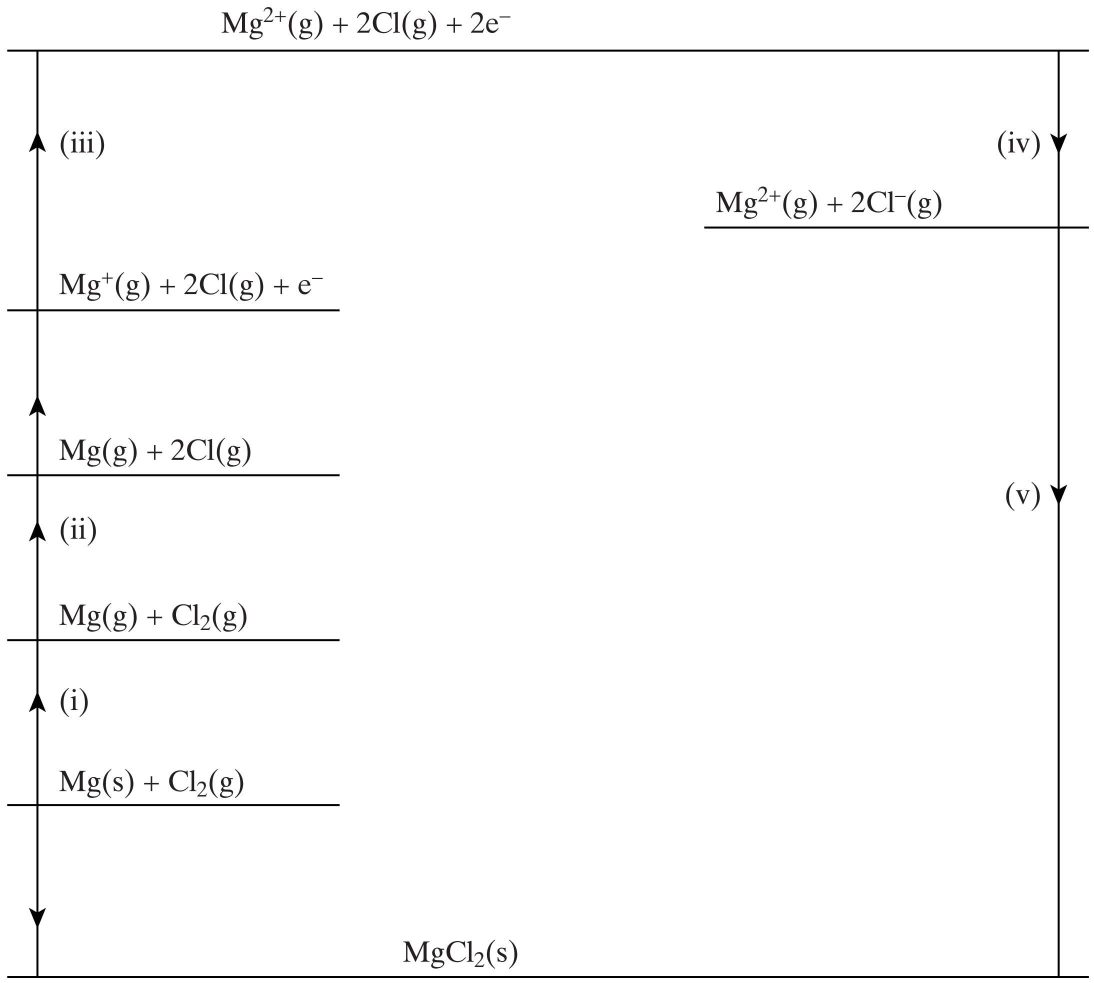
SECTION A

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

1 (a) A Born–Haber cycle for the formation of magnesium(II) chloride is shown below.



Taking care to note the direction of the indicated enthalpy change and the number of moles of species involved, give each of the enthalpy changes (i) to (v) above.

Enthalpy change (i) ....

Enthalpy change (ii) ....

Enthalpy change (iii) ....

Enthalpy change (iv) ....

Enthalpy change (v) ....

(5 marks)

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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.

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

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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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(b) Write an equation for the decomposition of $MgCl(s)$ into $MgCl_2(s)$ and $Mg(s)$ and use the following data to calculate a value for the enthalpy change of this reaction.

$\Delta H_f^{\ominus}$ $MgCl(s)$ $= -113\,kJ\,mol^{-1}$

$\Delta H_f^{\ominus}$ $MgCl_2(s)$ $= -653\,kJ\,mol^{-1}$

Equation ....

Calculation ....

....

....

....

(4 marks)

(c) Use the data below to calculate a value for the molar enthalpy of a solution of $MgCl_2(s)$.

Lattice formation enthalpy of $MgCl_2(s)$	$= -2502\,kJ\,mol^{-1}$
$\Delta H^{\ominus}_{hydration}$ of $Mg^{2+}(g)$	$= -1920\,kJ\,mol^{-1}$
$\Delta H^{\ominus}_{hydration}$ of $Cl^{-}(g)$	$= -364\,kJ\,mol^{-1}$

....

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....

(3 marks)

12

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2 In the questions below, each of the three elements **X**, **Y** and **Z** is one of the Period 3 elements Na, Mg, Al, Si or P.

(a) Both the chloride and the oxide of element **X** have high melting points. The oxide reacts readily with water. The chloride dissolves in water to form a neutral solution.

(i) Deduce the type of bonding present in the chloride of element **X**.

....

(ii) Identify element **X**.

....

(iii) Write an equation for the reaction between water and the oxide of element **X**.

....

(3 marks)

(b) Element **Y** has a chloride and an oxide which react vigorously with water to form solutions containing strong acids.

(i) Deduce the type of bonding present in the oxide of element **Y**.

....

(ii) Identify element **Y**.

....

(iii) Identify an acid which is formed when **both** the oxide and the chloride of element **Y** react separately with water.

....

(3 marks)

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(c) The oxide of element **Z** is a crystalline solid with a very high melting point. This oxide is classified as an acidic oxide but it is not soluble in water.

(i) Deduce the type of crystal shown by the oxide of element **Z**.

....

(ii) Identify element **Z**.

....

(iii) Write an equation for a reaction which illustrates the acidic nature of the oxide of element **Z**.

....

(4 marks)

10

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3 Use the data below, where appropriate, to answer the following questions.

Standard electrode potentials	$E^{\ominus}$/V
$S_2O_8^{2-}(aq) + 2e^- \longrightarrow 2SO_4^{2-}(aq)$	+2.01
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Cl_2(aq) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$NO_3^-(aq) + 3H^+(aq) + 2e^- \longrightarrow HNO_2(aq) + H_2O(l)$	+0.94
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77

(a) State the colours of the following species in aqueous solution.

(i) $Cr_2O_7^{2-}(aq)$ ....

(ii) $Cr^{3+}(aq)$ ....

(iii) $MnO_4^-(aq)$ ....

(3 marks)

(b) From the table above, select the species which is the most powerful reducing agent.

....

(1 mark)

(c) Deduce the oxidation state of

(i) chromium in $Cr_2O_7^{2-}$ ....

(ii) nitrogen in HNO_2 ....

(2 marks)

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(d) The concentration of iron(II) ions in aqueous solution can be determined by titrating the solution, after acidification, with a standard solution of potassium manganate(VII).

(i) Explain, by reference to the data given in the table opposite, why hydrochloric acid should not be used to acidify the solution containing iron(II) ions.

....

....

(ii) Explain, by reference to the data given in the table opposite, why nitric acid should not be used to acidify the solution containing iron(II) ions.

....

....

(4 marks)

(e) (i) Calculate the e.m.f. of the cell represented by

$Pt | Mn^{2+}(aq), MnO_4^-(aq) || S_2O_8^{2-}(aq), SO_4^{2-}(aq) | Pt$

....

(ii) Deduce an equation for the reaction which occurs when an excess of $S_2O_8^{2-}(aq)$ is added to an aqueous solution of $Mn^{2+}(aq)$ ions.

....

....

....

(3 marks)

13

TURN OVER FOR THE NEXT QUESTION

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4 (a) State what is meant by each of the following terms.

(i) *Ligand* ....

....

(ii) *Complex ion* ....

....

(iii) *Co-ordination number* ....

....

(3 marks)

(b) Using complex ions formed by Co^{2+} with ligands selected from H_2O, NH_3, Cl^-, $C_2O_4^{2-}$ and $EDTA^{4-}$, give an equation for each of the following.

(i) A ligand substitution reaction which occurs with no change in either the co-ordination number or in the charge on the complex ion.

....

(ii) A ligand substitution reaction which occurs with both a change in the co-ordination number and in the charge on the complex ion.

....

(iii) A ligand substitution reaction which occurs with no change in the co-ordination number but a change in the charge on the complex ion.

....

(iv) A ligand substitution reaction in which there is a large change in entropy.

....

(8 marks)

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(c) An aqueous solution of iron(II) sulphate is a pale-green colour. When aqueous sodium hydroxide is added to this solution a green precipitate is formed. On standing in air, the green precipitate slowly turns brown.

(i) Give the formula of the complex ion responsible for the pale-green colour.

....

(ii) Give the formula of the green precipitate.

....

(iii) Suggest an explanation for the change in the colour of the precipitate.

....

....

(4 marks)

15

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5 (a) State what is meant by the term *homogeneous* as applied to a catalyst.

....

(1 mark)

(b) (i) State what is meant by the term *autocatalysis*.

....

....

(ii) Identify the species which acts as an autocatalyst in the reaction between ethanedioate ions and manganate(VII) ions in acidic solution.

....

(2 marks)

(c) When petrol is burned in a car engine, carbon monoxide, carbon dioxide, oxides of nitrogen and water are produced. Catalytic converters are used as part of car exhaust systems so that the emission of toxic gases is greatly reduced.

(i) Write an equation for a reaction which occurs in a catalytic converter between two of the toxic gases. Identify the reducing agent in this reaction.

Equation ....

Reducing agent ....

(ii) Identify a transition metal used in catalytic converters and state how the converter is constructed to maximise the effect of the catalyst.

Transition metal ....

How effect is maximised ....

....

(5 marks)

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(d) The strength of the adsorption of reactants and products onto the surface of a transition metal helps to determine its activity as a heterogeneous catalyst.

(i) Explain why transition metals which adsorb strongly are not usually good catalysts.

....

(ii) Explain why transition metals which adsorb weakly are not usually good catalysts.

....

(2 marks)

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SECTION B

Detach these two perforated sheets.
Answer **all** questions in the space provided on pages 19 to 24 of this booklet.

6 When anhydrous iron(III) chloride is added to water the following reactions occur.

$$FeCl_3 + 6H_2O \longrightarrow [Fe(H_2O)_6]^{3+} + 3Cl^-$$

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$

(a) State the type of acidity shown by $FeCl_3$ and by $[Fe(H_2O)_6]^{3+}$ in these reactions. Explain your answers.

(4 marks)

(b) (i) A 0.150 mol dm^{-3} solution of iron(III) chloride was found to have a pH of 1.52
For the acid $[Fe(H_2O)_6]^{3+}$, calculate a value for the acid dissociation constant, K_a, and a pK_a value.
(You should assume that all the hydrogen ion concentration is due to the reaction shown below.)

$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$$

(ii) A 50.0 cm^3 sample of a 0.250 mol dm^{-3} solution of iron(III) chloride was diluted by the addition of 150 cm^3 of water.

Use the value of K_a determined in part (b)(i) to calculate the pH of the diluted solution.
(If you have failed to complete part (b)(i) you should assume that the value of K_a is 4.50×10^{-3} mol dm^{-3}. This is not the correct value.)

(9 marks)

(c) Explain why the pH of a solution of iron(II) chloride is higher than that of a solution of iron(III) chloride of the same concentration.

(2 marks)

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7 Butenedioic acid, HOOCCH=CHCOOH, occurs as two stereoisomers. One of the isomers readily forms the acid anhydride $C_4H_2O_3$ when warmed.

(a) Draw the structures of the two isomers of butenedioic acid and name the type of isomerism shown.
Use the structures of the two isomeric acids to suggest why only one of them readily forms an acid anhydride when warmed. Draw the structure of the acid anhydride formed.

(6 marks)

(b) Identify one electrophile which will react with butenedioic acid and outline a mechanism for this reaction.

(4 marks)

(c) Write an equation for a reaction which occurs when butenedioic acid is treated with an excess of aqueous sodium hydroxide.

(2 marks)

(d) Describe and explain the appearance of the proton n.m.r. spectrum of butenedioic acid.

(3 marks)

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8 (a) The gaseous reactants **W** and **X** were sealed in a flask and the mixture left until the following equilibrium had been established.

$$2W(g) + X(g) \rightleftharpoons 3Y(g) + 2Z(g) \quad \Delta H = -200\,kJ\,mol^{-1}$$

Write an expression for the equilibrium constant, K_p, for this reaction.
State one change in the conditions which would both increase the rate of reaction and decrease the value of K_p. Explain your answers.

(7 marks)

(b) Ethyl ethanoate can be prepared by the reactions shown below.

Reaction 1

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l) \quad \Delta H^{\ominus} = -2.0\,kJ\,mol^{-1}$$

Reaction 2

$$CH_3COCl(l) + C_2H_5OH(l) \rightarrow CH_3COOC_2H_5(l) + HCl(g) \quad \Delta H^{\ominus} = -21.6\,kJ\,mol^{-1}$$

(i) Give one advantage and one disadvantage of preparing ethyl ethanoate by **Reaction 2** rather than by **Reaction 1**.

(ii) Use the information given above and the data below to calculate values for the standard entropy change, $\Delta S^{\ominus}$, and the standard free-energy change, $\Delta G^{\ominus}$, for **Reaction 2** at 298 K.

	$CH_3COCl(l)$	$C_2H_5OH(l)$	$CH_3COOC_2H_5(l)$	$HCl(g)$
$S^{\ominus}/J\,K^{-1}\,mol^{-1}$	201	161	259	187

(8 marks)

TURN OVER FOR THE NEXT QUESTION

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9 The following two-stage method was used to analyse a mixture containing the solids magnesium, magnesium oxide and sodium chloride.

Stage 1

A weighed sample of the mixture was treated with an excess of dilute hydrochloric acid. The sodium chloride dissolved in the acid. The magnesium oxide reacted to form a solution of magnesium chloride. The magnesium also reacted to form hydrogen gas and a solution of magnesium chloride. The hydrogen produced was collected.

(a) Write equations for the two reactions involving hydrochloric acid.

(b) State how you would collect the hydrogen. State the measurements that you would make in order to calculate the number of moles of hydrogen produced. Explain how your results could be used to determine the number of moles of magnesium metal in the sample.

(8 marks)

Stage 2

Sodium hydroxide solution was added to the solution formed in **Stage 1** until no further precipitation of magnesium hydroxide occurred. This precipitate was filtered off, collected, dried and heated strongly until it had decomposed completely into magnesium oxide. The oxide was weighed.

(c) Write equations for the formation of magnesium hydroxide and for its decomposition into magnesium oxide.

(d) When a 2.65 g sample of the mixture of the three solids was analysed as described above, the following results were obtained.

Hydrogen obtained in **Stage 1**	0.0528 mol
Mass of magnesium oxide obtained in **Stage 2**	6.41 g

Use these results to calculate the number of moles of original magnesium oxide in 100 g of the mixture.

(7 marks)

END OF QUESTIONS

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