Surname		Other Names	
Centre Number			Candidate Number	
Candidate Signature			

For Examiner's Use

General Certificate of Education
June 2007
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

CHEMISTRY **CHM5**
Unit 5 Thermodynamics and Further Inorganic Chemistry

Monday 25 June 2007 9.00 am to 11.00 am

For this paper you must have
- 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 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 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.
- Your answers to the 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.

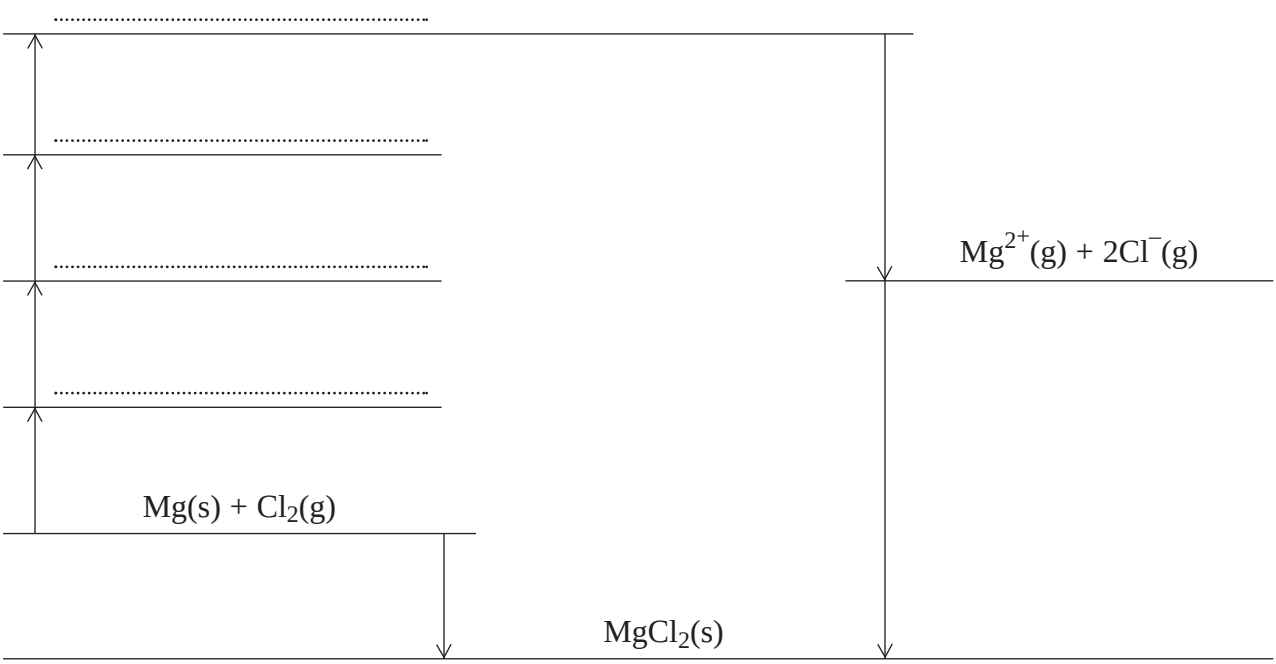
Advice
- You are advised to spend about 1 hour on **Section A** and about 1 hour on **Section B**.

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

SECTION A

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

1 Consider the incomplete Born–Haber cycle and the table of data below.



Name of standard enthalpy change	Substance to which enthalpy change refers	Value of enthalpy change / kJ mol^{-1}
Enthalpy of atomisation	chlorine	+121
Enthalpy of atomisation	magnesium	+150
Enthalpy of formation	magnesium chloride	–642
First ionisation enthalpy	magnesium	+736
Electron affinity	chlorine	–364
Enthalpy of lattice formation	magnesium chloride	–2493

(a) Complete the Born-Haber cycle above by writing the appropriate chemical formulae, with state symbols, on the dotted lines.

(4 marks)

(b) Use the cycle and the values given in the table to calculate the second ionisation enthalpy of magnesium.

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(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

* **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

(c) The standard enthalpies of hydration of the Mg^{2+} and the Cl^- ions are $-1920\,kJ\,mol^{-1}$ and $-364\,kJ\,mol^{-1}$, respectively. Use this information and data from the table in part (a) to calculate the enthalpy of solution of magnesium chloride.

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(3 marks)

(d) The standard enthalpy of solution of ammonium chloride, $NH_4^+Cl^-$, is $+15\,kJ\,mol^{-1}$.

(i) Explain why ammonium chloride dissolves spontaneously in water even though this process is endothermic.

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(2 marks)

(ii) A 2.0 g sample of ammonium chloride is dissolved in 50 g of water. Both substances are initially at 20 °C.
Calculate the temperature change and the final temperature of the solution.
Assume that the specific heat capacity of the solution is $4.2\,J\,K^{-1}\,g^{-1}$.

Temperature change .....

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Final temperature of solution .....

(5 marks)

2 Data for the following reaction, which represents the reduction of aluminium oxide by carbon, are shown in the table below.

$$Al_2O_3(s) + 3C(s) \longrightarrow 2Al(s) + 3CO(g)$$

Substance	$\Delta H_f^{\ominus}$ **/ kJ mol^{-1}**	$S^{\ominus}$ **/ J K^{-1} mol^{-1}**
$Al_2O_3(s)$	–1669	51
C(s)	0	6
Al(s)	0	28
CO(g)	–111	198

(a) Calculate the values of $\Delta H^{\ominus}$, $\Delta S^{\ominus}$ and $\Delta G^{\ominus}$ for the above reaction at 298 K and suggest why this reaction is not feasible at 298 K.

$\Delta H^{\ominus}$.....

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$\Delta S^{\ominus}$.....

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$\Delta G^{\ominus}$.....

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Reason why this reaction is not feasible at 298 K .....

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(8 marks)

(b) Calculate the temperature above which this reaction is feasible.

(If you have been unable to calculate values for $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ in part (a) you may assume that they are $+906\,kJ\,mol^{-1}$ and $+394\,J\,K^{-1}\,mol^{-1}$ respectively. These are not the correct values.)

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(2 marks)

(c) The reaction between aluminium oxide and carbon to form aluminium and carbon monoxide does not occur to a significant extent until the temperature reaches a value about 1000 K above that of the answer to part (b). Give one reason for this.

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(1 mark)

(d) State the method used to reduce aluminium oxide on an industrial scale. Give the essential conditions for this industrial process.

Method .....

Conditions .....

.....

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(3 marks)

14

3 The table below shows some standard electrode potentials.

	$E^{\ominus}$/V
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$Cr^{3+}(aq) + e^- \longrightarrow Cr^{2+}(aq)$	−0.41
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$Cr^{2+}(aq) + 2e^- \longrightarrow Cr(s)$	−0.91

(a) Predict the products, if any, when the following substances are mixed. In each case use $E^{\ominus}$ values from the table to explain your answer.

(i) iron metal with aqueous zinc(II) ions

Products, if any .....

Explanation .....

.....

(ii) aqueous iron(III) ions with aqueous chromium(II) ions

Products, if any .....

Explanation .....

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(5 marks)

(b) Calculate the e.m.f. of the following standard cell and deduce an equation for the overall cell reaction.

$$Zn(s)|Zn^{2+}(aq)||Cr^{3+}(aq),Cr^{2+}(aq)|Pt$$

e.m.f. .....

Equation .....

(2 marks)

(c) Chromium(III) ions are weakly acidic in aqueous solution as shown by the following equation.

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

The value of K_a for this reaction is 1.15×10^{-4} mol dm^{-3}.

Calculate the pH of a 0.500 mol dm^{-3} solution of $[Cr(H_2O)_6]^{3+}(aq)$.

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(5 marks)

(d) State what you would observe after addition of the following reagents to separate aqueous solutions containing $[Cr(H_2O)_6]^{3+}$ ions.
In each case give the formula of the chromium-containing product.

(i) an excess of NaOH(aq)

Observation(s) .....

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Formula of product .....

(ii) $Na_2CO_3(aq)$

Observation(s) .....

.....

Formula of product .....

(5 marks)

17

4 (a) Give the meaning of the term *electronegativity*.

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(2 marks)

(b) State and explain the trend in electronegativity across Period 3 from Na to Cl.

Trend .....

Explanation .....

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(3 marks)

(c) (i) Name the main type of bonding in each of the oxides MgO and P_4O_{10}

Bonding in MgO .....

Bonding in P_4O_{10} .....

(ii) Explain how the type of bonding in P_4O_{10} can be predicted by a consideration of electronegativity.

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(3 marks)

(d) Write equations for the reaction of Na_2O and of SO_2 with water.

Equation for Na_2O .....

Equation for SO_2 .....

(2 marks)

(e) Write an equation for the reaction of MgO with dilute hydrochloric acid.

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(1 mark)

(f) Write an equation for the reaction of P_4O_{10} with an excess of aqueous sodium hydroxide.

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(1 mark)

SECTION B

Detach this perforated sheet.
Answer **all** questions in the spaces provided on pages 13 to 20 of this booklet.

5 (a) Explain why the ester methyl ethanoate has a lower boiling point than its isomer, propanoic acid. *(2 marks)*

(b) A polyester is formed when ethane-1,2-diol reacts with butanedioic acid. Draw the structure of the repeating unit of this polymer.

Suggest why this polyester begins to melt at a higher temperature than poly(ethene) which has molecules of a similar size to those in the polyester. *(4 marks)*

(c) Outline a mechanism for the formation of an ester by the reaction between ethanoyl chloride and an alcohol. *(4 marks)*

(d) The ester ethyl ethanoate is hydrolysed when it is heated with water in the presence of an acid catalyst. An equilibrium is established.

$$CH_3COOCH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3COOH(l) + CH_3CH_2OH(l)$$

A 0.50 mol sample of ethyl ethanoate was heated with 4.0 mol of water. At equilibrium, 70 % of the ester was hydrolysed. Calculate a value of K_c for this reaction. *(5 marks)*

6 One characteristic property of transition metals is variable oxidation state.

(a) For each of the following processes, write two equations to show how the transition metal catalyst reacts and is reformed. Identify the different oxidation states shown by the transition metal catalyst in each process.

(i) the Contact Process catalysed by vanadium(V) oxide

(ii) the oxidation of ethanedioate ions by acidified potassium manganate(VII), autocatalysed by $Mn^{2+}(aq)$ ions.

(6 marks)

(b) Cobalt(II) ions cannot easily be oxidised to cobalt(III) ions in water. Suggest why this oxidation can be carried out in aqueous ammonia and identify a suitable oxidising agent. *(3 marks)*

(c) Metal ions $\mathbf{Q}^{2+}$ in acidified aqueous solution can be oxidised by aqueous potassium dichromate(VI).

In a titration, an acidified 25.0 cm^3 sample of a 0.140 mol dm^{-3} solution of $\mathbf{Q}^{2+}(aq)$ required 29.2 cm^3 of a 0.040 mol dm^{-3} solution of potassium dichromate(VI) for complete reaction.

Determine the oxidation state of the metal **Q** after reaction with the potassium dichromate(VI). *(6 marks)*

7 The reaction scheme below shows a two-stage synthesis of ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$.

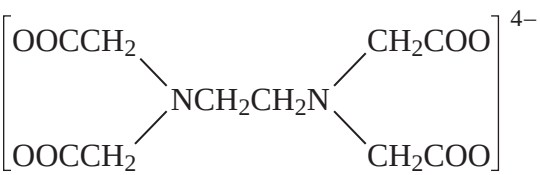
$$H_2C=CH_2 \xrightarrow{\text{Reaction } \mathbf{1}} BrCH_2CH_2Br \xrightarrow{\text{Reaction } \mathbf{2}} H_2NCH_2CH_2NH_2$$

(a) Suggest a reagent for Reaction **1**. Name and outline a mechanism for this reaction. *(5 marks)*

(b) Suggest a reagent for Reaction **2**. Name the type of mechanism involved and write an equation for the overall reaction. *(3 marks)*

(c) Draw the structure of the complex ion formed when aqueous cobalt(II) ions react with an excess of ethane-1,2-diamine. *(2 marks)*

(d) Ethane-1,2-diamine can be converted into the $EDTA^{4-}$ ion shown below.



State why this ion can act as a multidentate ligand.

Write an equation for the reaction of $EDTA^{4-}$ with aqueous cobalt(II) ions. In your equation represent the ligand by $EDTA^{4-}$

Explain why the $EDTA^{4-}$ ion readily displaces unidentate ligands such as water. *(5 marks)*

8 (a) The compounds CH_3CH_2Cl and CH_3CHCl_2 can be distinguished by comparing their proton n.m.r. spectra.

For each compound, describe its proton n.m.r. spectrum by giving the number of peaks, the integration ratio and the splitting patterns. *(6 marks)*

(b) The following pairs of compounds can be distinguished using the reagents indicated. Each compound is in a separate aqueous solution. For each one of the compounds, describe what you would observe and write equations for any reactions that occur.

(i) KBr and KI using chlorine water

(ii) $BaCl_2$ and $MgCl_2$ using dilute sulphuric acid

(iii) $CoCl_2$ and $CuCl_2$ using concentrated hydrochloric acid

(9 marks)

END OF QUESTIONS

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