Surname		Other Names	
Centre Number		Candidate Number	
Candidate Signature			

General Certificate of Education
June 2006
Advanced Level Examination

AQA

ASSESSMENT and
QUALIFICATIONS
ALLIANCE

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

Monday 26 June 2006   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.
- Answer 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 a perforated sheet. Detach this sheet at the start of the examination.

Information
- The maximum mark for this paper is 120.
- The marks for part 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 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			

CHM5

SECTION A

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

1   A 0.263 g sample of impure iron, containing an unreactive impurity, was reacted with an excess of hydrochloric acid. All of the iron in the sample reacted, evolving hydrogen gas and forming a solution of iron(II) chloride. The volume of hydrogen evolved was $102 \, cm^3$, measured at 298 K and 110 kPa.

The percentage, by mass, of iron in the sample can be determined using either the volume of hydrogen produced or by titrating the solution of iron(II) chloride formed against a standard solution of potassium dichromate(VI).

(a)   (i)   Write an equation for the reaction between iron and hydrochloric acid.

....

(ii)   Calculate the number of moles of hydrogen produced in the reaction.

....

....

....

....

(iii)   Use your answers to parts (a)(i) and (ii) to determine the number of moles of iron and the mass of iron in the original sample.
(If you have been unable to complete part (a)(ii) you should assume the answer to be 4.25×10^{-3} mol. This is not the correct answer.)

Moles of iron ....

Mass of iron ....

(iv)   Calculate the percentage of iron in the original sample.

....

....

(7 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.

Key

relative atomic mass ——— 6.9 **Li** Lithium
atomic number ——— 3

I	II														III	IV	V	VI	VII	0
																				4.0 **He** Helium 2
1.0 **H** Hydrogen 1																				
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	252.0 **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

(b) (i) Write half-equations for the oxidation of Fe^{2+} and for the reduction of $Cr_2O_7^{2-}$ in acidic solution, and use these to construct an overall equation for the reaction between these two ions.

Half-equation for the oxidation of Fe^{2+}

....

Half-equation for the reduction of $Cr_2O_7^{2-}$

....

Overall equation

....

(ii) The number of moles of iron in the sample was determined in part (a)(iii). Use this answer to calculate the volume of a $0.0200 \, mol \, dm^{-3}$ solution of potassium dichromate(VI) which would react exactly with the solution of iron(II) chloride formed in the reaction.
(If you have been unable to complete part (a)(iii) you should assume the answer to be 3.63×10^{-3} mol. This is not the correct answer.)

....

....

....

....

....

(iii) Explain why an incorrect value for the number of moles of iron(II) chloride formed would have been obtained if the original solution had been titrated with potassium manganate(VII).

....

....

(7 marks)

14

Turn over ▶

2 The sketch graph below shows how the entropy of a sample of water varies with temperature.
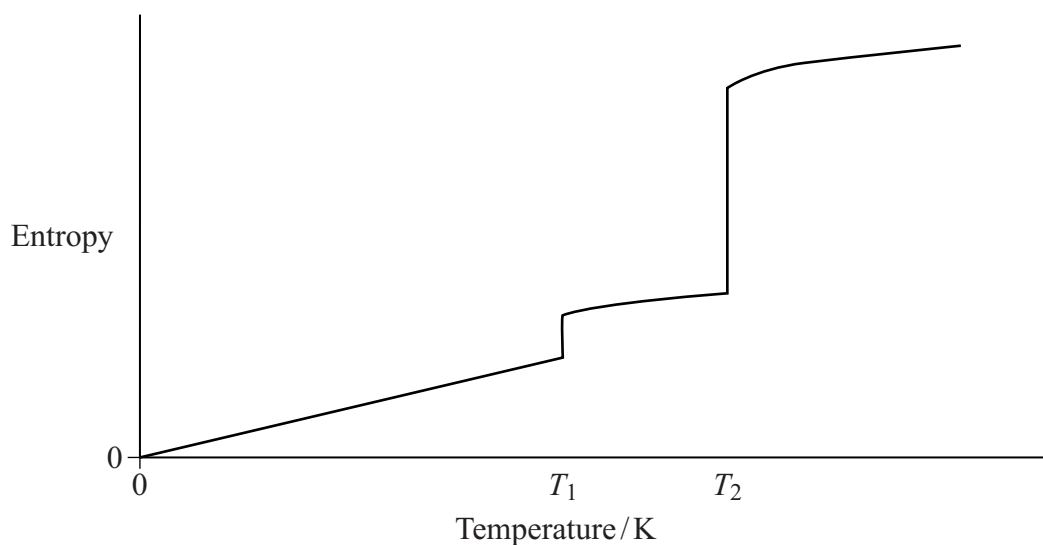
(a) Suggest why the entropy of water is zero at 0 K.

....
(1 mark)

(b) What change of state occurs at temperature T_1?

....
(1 mark)

(c) Explain why the entropy change, ΔS, at temperature T_2 is much larger than that at temperature T_1.

....

....

....
(2 marks)

(d) It requires 3.49 kJ of heat energy to convert 1.53 g of liquid water into steam at 373 K and 100 kPa.

(i) Use these data to calculate the enthalpy change, ΔH, when 1.00 mol of liquid water forms 1.00 mol of steam at 373 K and 100 kPa.

....

....

....

....

(ii) Write an expression showing the relationship between free-energy change, ΔG, enthalpy change, ΔH, and entropy change, ΔS.

....

(iii) For the conversion of liquid water into steam at 373 K and 100 kPa, $\Delta G = 0\,\text{kJ mol}^{-1}$

Calculate the value of ΔS for the conversion of one mole of water into steam under these conditions. State the units.
(If you have been unable to complete part (d)(i) you should assume that $\Delta H = 45.0\,\text{kJ mol}^{-1}$. This is not the correct answer.)

Calculation ....

....

....

Units ....
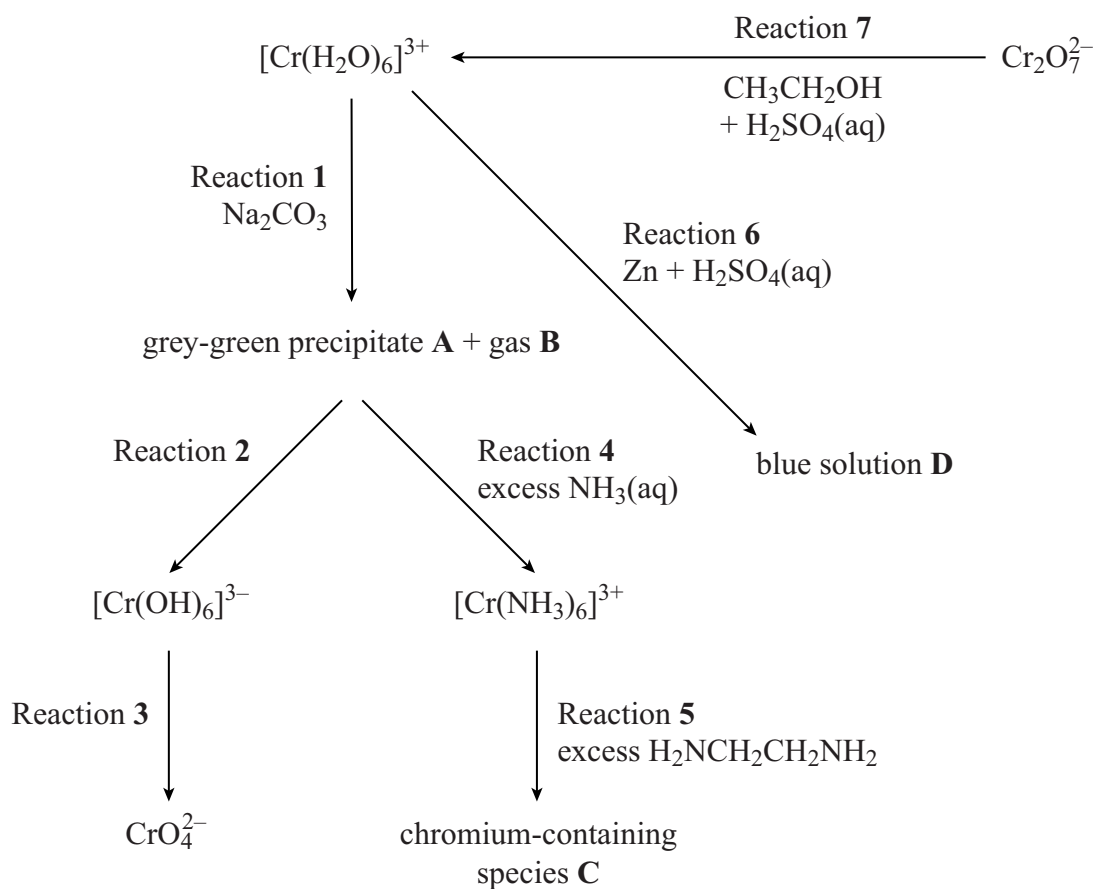
(6 marks)

10

Turn over for the next question

3   The following scheme shows some reactions of chromium compounds in aqueous solution.

Reaction **7**

$[Cr(H_2O)_6]^{3+}$ ⟵ $Cr_2O_7^{2-}$

CH_3CH_2OH
$+ H_2SO_4(aq)$

Reaction **1**
Na_2CO_3

Reaction **6**
$Zn + H_2SO_4(aq)$

grey-green precipitate **A** + gas **B**

Reaction **2**

Reaction **4**
excess $NH_3(aq)$

blue solution **D**

$[Cr(OH)_6]^{3-}$ $[Cr(NH_3)_6]^{3+}$

Reaction **3**

Reaction **5**
excess $H_2NCH_2CH_2NH_2$

CrO_4^{2-}

chromium-containing
species **C**

(a)   Identify the grey-green precipitate **A** and the gas **B** formed in Reaction **1**. Write an equation for this reaction.

Precipitate A ....

Gas B ....

Equation ....

....
(3 marks)

(b)   (i)   Identify a reagent for Reaction **2**.

....

(ii)   Deduce the oxidation state of chromium in CrO_4^{2-}

....

(iii)   Identify a reagent needed for Reaction **3**. Write a half-equation for the conversion of $[Cr(OH)_6]^{3-}$ into CrO_4^{2-}

Reagent ....

Half-equation ....
(4 marks)

(c) (i) Draw the structure of the chromium-containing species **C** formed in Reaction **5**. Indicate the charge on species **C**.

(ii) Explain, by reference to the changes in bonding, why the enthalpy change, ΔH, in Reaction **5** is close to zero.

....

....

(iii) Explain why the free-energy change, ΔG, for Reaction **5** is negative.

....

....

....

....

(7 marks)

(d) Identify the chromium-containing species present in the blue solution **D** formed in Reaction **6** and state the role of zinc in its formation.

Chromium-containing species ....

Role of zinc ....

(2 marks)

(e) Two organic compounds are formed in Reaction **7**. One of these compounds has a low boiling point and can be distilled readily from the reaction mixture. The other compound has a higher boiling point and is the main organic product formed when the reaction mixture is refluxed.

(i) Identify the organic product which has a low boiling point.

....

(ii) Identify the main organic product formed when the mixture is refluxed.

....

(2 marks)

18

Turn over ▶

4 A sealed flask containing gases **X** and **Y** in the mole ratio 1:3 was maintained at 600 K until the following equilibrium was established.

$$X(g) + 3Y(g) \rightleftharpoons 2Z(g)$$
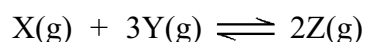
The partial pressure of **Z** in the equilibrium mixture was 6.0 MPa when the total pressure was 22.0 MPa.

(a) (i) Write an expression for the equilibrium constant, K_p, for this reaction.

....

....

(ii) Calculate the partial pressure of **X** and the partial pressure of **Y** in the equilibrium mixture.

Partial pressure of X ....

....

Partial pressure of Y ....

(iii) Calculate the value of K_p for this reaction under these conditions and state its units.

Value of K_p ....

....

....

Units of K_p ....
(6 marks)

(b) When this reaction is carried out at 300 K and a high pressure of 100 MPa, rather than at 600 K and 22.0 MPa, a higher equilibrium yield of gas **Z** is obtained.

Give two reasons why an industrialist is unlikely to choose these reaction conditions.

Reason 1 ....

Reason 2 ....
(2 marks)

8

5 Use the data in the table below, where appropriate, to answer the questions which follow.

Standard electrode potentials	$E^{\ominus}$/V
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$2BrO_3^-(aq) + 12H^+(aq) + 10e^- \longrightarrow Br_2(aq) + 6H_2O(l)$	+1.52
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O(l)$	+2.08
$F_2O(g) + 2H^+(aq) + 4e^- \longrightarrow 2F^-(aq) + H_2O(l)$	+2.15

Each of the above can be reversed under suitable conditions.

(a) (i) Identify the most powerful reducing agent in the table.

....

(ii) Identify the most powerful oxidising agent in the table.

....

(iii) Identify **all** the species in the table which can be oxidised in acidic solution by $BrO_3^-(aq)$.

....

(4 marks)

(b) The cell represented below was set up.

$$Pt\,|\,Fe^{2+}(aq), Fe^{3+}(aq)\,\|\,BrO_3^-(aq), Br_2(aq)\,|\,Pt$$

(i) Deduce the e.m.f. of this cell.

....

(ii) Write a half-equation for the reaction occurring at the negative electrode when current is taken from this cell.

....

(iii) Deduce what change in the concentration of $Fe^{3+}(aq)$ would cause an increase in the e.m.f. of the cell. Explain your answer.

Change in concentration ....

Explanation ....

....

....

(6 marks)

10

Turn over ▶

There are no questions printed on this page

SECTION B

Detach this perforated sheet.
Answer **all** questions in the space provided on pages 15 to 24 of this booklet.

6 (a) (i) Write an equation for the reaction of ammonia with water. Explain how, in this reaction, ammonia behaves as a Brønsted-Lowry base. Draw the shape of the species formed from ammonia.

(ii) Write an equation for the reaction of ammonia with boron trifluoride. Explain how, in this reaction, ammonia behaves as a Lewis base. Draw the shape of the species formed.

(6 marks)

(b) Outline the mechanism for the addition-elimination reaction between ammonia and an acyl chloride. Name the organic product formed in the reaction you have given.

(5 marks)

(c) Amines can be made by the reaction between a haloalkane and ammonia. Explain why, in an excess of ammonia, a primary amine is the major organic product.

(2 marks)

(d) When ammonia reacts with potassium metal, a redox reaction occurs. Hydrogen and NH_2^- ions are produced.

Write a half-equation for the formation of hydrogen and NH_2^- ions from ammonia. Use this to deduce an overall equation for the reaction between potassium and ammonia.

(2 marks)

(e) Boiling point data for three hydrides are given in the table below.

Hydride	M_r	Boiling point / K
Methane	16	91.1
Ammonia	17	240
Water	18	373

Explain why these three hydrides have very different boiling points.   *(4 marks)*

Turn over ▶

7 (a) Explain why the melting point of magnesium chloride is much higher than the melting point of silicon tetrachloride. *(5 marks)*

(b) Suggest why the melting point of magnesium oxide is much higher than the melting point of magnesium chloride. *(2 marks)*

(c) Magnesium oxide and sulphur dioxide are added separately to water. In each case describe what happens. Write equations for any reactions which occur and state the approximate pH of any solution formed. *(6 marks)*

(d) Write equations for two reactions which together show the amphoteric character of aluminium hydroxide. *(4 marks)*

8 (a) State the trend in the reducing power of the halide ions Cl^- to I^-.
Identify all the reduction products formed when solid sodium iodide reacts with concentrated sulphuric acid. Write an overall equation for **one** of these redox reactions. *(6 marks)*

(b) Outline a mechanism for the formation of a chloroalkane by the reaction between an alkane and chlorine. *(3 marks)*

(c) Name and outline a mechanism for the reaction of a chloroalkane with benzene in the presence of anhydrous aluminium chloride. *(5 marks)*

9 (a) Explain why the reaction between sodium ethanedioate, $Na_2C_2O_4$, and potassium manganate(VII) in acidified aqueous solution is initially slow but gradually increases in rate. Write equations to illustrate your answer. *(6 marks)*

(b) State what is meant by the term *active site* as applied to a heterogeneous catalyst.
Explain how the number of active sites can be increased for a given mass of catalyst.
The efficiency of a heterogeneous catalyst often decreases during use. Explain, using a specific example, why this happens. *(4 marks)*

END OF QUESTIONS

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

Turn over ▶

Turn over ▶

Turn over ▶