Surname		Other Names	
Centre Number		Candidate Number	
Candidate Signature			

For Examiner's Use

General Certificate of Education
June 2008
Advanced Level Examination

CHEMISTRY CHM5
Unit 5 Thermodynamics and Further Inorganic Chemistry

Thursday 19 June 2008 9.00 am to 11.00 am

For this paper you must have
- a calculator.

Time allowed: 2 hours

Instructions
- Use black ink or black 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			
9			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

There are no questions printed on this page

DO NOT WRITE ON THIS PAGE
ANSWER IN THE SPACES PROVIDED

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

Turn over ▶

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

SECTION A

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

1 Ammonia can act as a base and as a nucleophile.

1 (a) Define the term *Brønsted–Lowry base*.

....

(1 mark)

1 (b) Define the term *Lewis base*.

....

(1 mark)

1 (c) Define the term *nucleophile*.

....

(1 mark)

1 (d) Write an ionic equation for the reaction between ammonia and hydrochloric acid in which the ammonia acts as a Brønsted–Lowry base.

....

(1 mark)

1 (e) Write an equation for the reaction between ammonia and aqueous copper(II) ions in which ammonia acts as a Lewis base with the copper ions. Give the colour of each of the copper-containing ions in your equation below its formula.

Equation .... → ....

Colours ....

(4 marks)

1 (f) Write an equation for the reaction between ammonia and ethanoyl chloride in which the ammonia acts as a nucleophile. Name and outline the mechanism for this reaction.

Equation ....

Name of mechanism ....

Mechanism

(6 marks)

14

Turn over ▶

2 Some enthalpy of vaporisation values, $\Delta H_v^\ominus$, and boiling points are given in the table below.

Substance	$\Delta H_v^\ominus$ **/ kJ mol^{-1}**	**Boiling point / K**
$NH_3(l)$	23.4	240
$HF(l)$	32.6	293

2 (a) State the equation that relates free-energy change, ΔG, to enthalpy change, ΔH, and entropy change, ΔS.

....

(1 mark)

2 (b) Suggest why the free-energy change is equal to zero ($\Delta G = 0$) when a liquid boils.

....

....

(1 mark)

2 (c) Use data from the table above to calculate the standard entropy change, in J K^{-1} mol^{-1}, when liquid ammonia boils.

....

....

....

(2 marks)

2 (d) Explain in terms of intermolecular forces why the enthalpy of vaporisation for liquid hydrogen fluoride is greater than that for liquid ammonia.

....

....

....

....

....

(3 marks)

7

3 Some data required for this question are given in the table below.

Substance	**$\Delta H_f^\ominus$/kJ mol^{-1}**	**$S^\ominus$/J K^{-1} mol^{-1}**
NH_3(g)	–46.2	193
N_2(g)	0	192
H_2(g)	0	131

3 (a) Write an equation to represent the formation of one mole of ammonia from its elements.

....

(1 mark)

3 (b) Using data from the table above calculate the entropy change for the formation of one mole of ammonia from its elements.

....

....

....

....

(3 marks)

3 (c) (i) Use your answer from part (b) and data from the table to calculate the value of the free-energy change, ΔG, for the formation of one mole of ammonia from its elements at 700 K. (If you have been unable to calculate an answer to part (b), you may assume that the entropy change for the formation of one mole of ammonia from its elements is –125 J K^{-1} mol^{-1}. This is not the correct value.)

....

....

....

....

3 (c) (ii) Predict in qualitative terms what would happen to the value of ΔG at temperatures lower than 700 K.

....

(3 marks)

3 (d) Suggest one advantage, in industry, of operating this reaction at temperatures higher than 700 K.

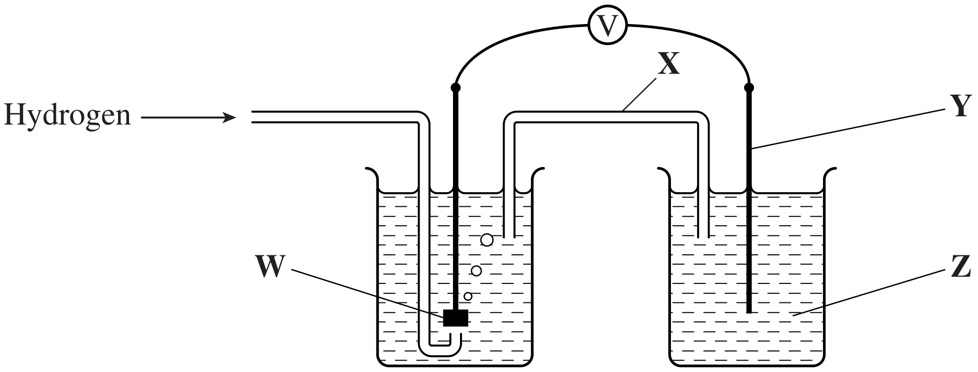
....

(1 mark)

8

Turn over ▶

4 (a) The cell shown below can be used to measure the electrode potential of magnesium.



4 (a) (i) Identify possible chemical substances for **W**, **X**, **Y** and **Z** labelled in the diagram above.

W ....

X ....

Y ....

Z ....

4 (a) (ii) Give the conventional representation for this cell (conventional cell diagram).

....

(6 marks)

4 (b) An alkaline cell that is used to provide electricity has electrodes which can be represented by the following half-equations. The zinc electrode is the negative electrode.

$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad E = -0.76\ V$$
$$MnO_2 + H_2O + e^- \longrightarrow MnO(OH) + OH^- \qquad \textit{E is to be determined}$$

4 (b) (i) The e.m.f. of this cell is 1.60 V. Calculate a value for the electrode potential of the manganese oxide electrode.

....

4 (b) (ii) Deduce the oxidation state of manganese in MnO(OH)

....

4 (b) (iii) Write an equation for the overall cell reaction.

....

4 (b) (iv) Identify the oxidising agent and the reducing agent in this alkaline cell.

Oxidising agent ....

Reducing agent ....

4 (b) (v) Give one reason why the e.m.f. of the cell decreases to a very low value after the cell has been used for a long time.

....

(6 marks)

4 (c) A redox reaction occurs when concentrated sulphuric acid reacts with solid potassium bromide.

4 (c) (i) Write half-equations and an overall equation for this reaction.

Half-equation 1 ....

Half-equation 2 ....

Overall equation ....

4 (c) (ii) Give one reason why a redox reaction does not occur when concentrated sulphuric acid is mixed with solid potassium chloride.
Write an equation for the reaction that **does** occur.

Reason ....

....

Equation ....

(5 marks)

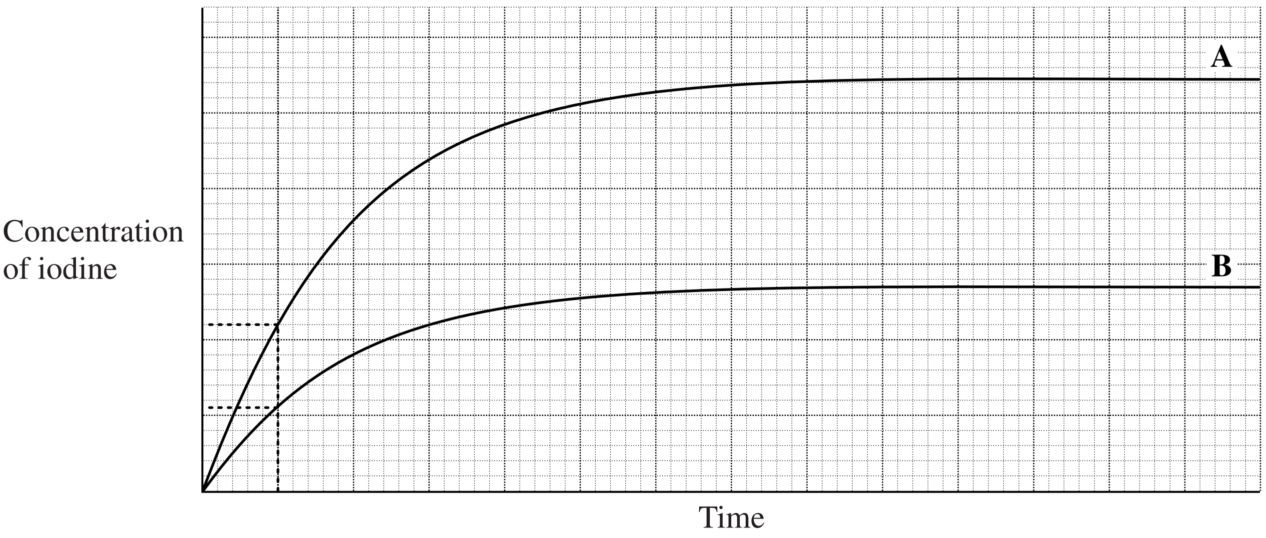
17

Turn over for the next question

5 Iodide ions are oxidised to iodine by peroxodisulphate ions, $S_2O_8^{2-}$. The reaction can be catalysed by Fe^{2+}(aq) ions and by Fe^{3+}(aq) ions.

In an experiment to investigate the uncatalysed reaction, the concentration of iodine was determined at different times. Curve **A** shown below was obtained.

The experiment was repeated using half the original concentration of iodide ions but keeping other conditions the same. Curve **B** was obtained.



5 (a) Use these curves and the dotted lines to deduce the order of the reaction with respect to iodide ions. Explain how you deduced the order.

Order ....

Explanation ....

....

(2 marks)

5 (b) On the axes above, sketch a curve to show how the results will change if the experiment leading to curve **B** is repeated under the same conditions of concentration but at a lower temperature. Label this curve **X**.

(2 marks)

5 (c) On the axes above, sketch a curve to show how the results will change if the experiment leading to curve **A** is repeated in the presence of a catalyst containing Fe^{2+}(aq) ions. Label this curve **Y**.

(2 marks)

5 (d) In the oxidation of iodide ions by peroxodisulphate ions, the Fe^{2+} ions act as a catalyst in a two-step process.

5 (d) (i) Write an equation for each of the two steps.

Equation for step 1 ....

Equation for step 2 ....

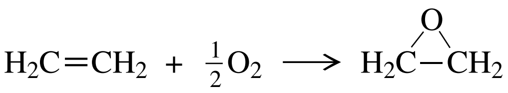
5 (d) (ii) Give two reasons why the Fe^{2+} ions are regarded as a catalyst in this reaction.

Reason 1 ....

Reason 2 ....

(4 marks)

5 (e) Silver is used as a heterogeneous catalyst for the exothermic process illustrated by the following equation.



$$H_2C{=}CH_2 + \tfrac{1}{2}O_2 \longrightarrow H_2C{-}CH_2 \text{ (with O bridging both C atoms)}$$

5 (e) (i) Explain the meaning of the term *heterogeneous* as applied to the silver catalyst.

....

5 (e) (ii) Give one reason why silver is a poor heterogeneous catalyst.

....

....

5 (e) (iii) Explain why it is **not** desirable to use a very effective catalyst for this reaction.

....

....

....

(4 marks)

14

Turn over ▶

SECTION B

Detach this perforated sheet.
Answer questions 6, 7, 8 and 9 on page 12 and pages 15-20 of this booklet.

6 (a) Each of the following pairs of compounds, in aqueous solution, can be distinguished by using a suitable reagent in test-tube reactions.

For each pair, identify a reagent, describe what you would observe and write equations for any reactions that occur.

6 (a) (i) separate solutions of $CuSO_4(aq)$ and of $Cu(NO_3)_2(aq)$
6 (a) (ii) separate solutions of $CrCl_3(aq)$ and of $FeCl_2(aq)$ *(9 marks)*

6 (b) Separate aqueous solutions of potassium manganate(VII) ($KMnO_4$) and sodium manganate(VII) ($NaMnO_4$), each contained 1.000 g of the compound in 250 cm^3 of solution.
A 25.0 cm^3 sample of **one** of these solutions reacted with exactly 17.60 cm^3 of a 0.100 $mol\,dm^{-3}$ acidified solution of sodium ethanedioate, $Na_2C_2O_4$

6 (b) (i) Write an equation for the reaction between MnO_4^- ions and $C_2O_4^{2-}$ ions in an acidified solution. In this reaction, 2 mol of MnO_4^- ions reacted with 5 mol of $C_2O_4^{2-}$ ions.

6 (b) (ii) Calculate the number of moles of $C_2O_4^{2-}$ ions that have reacted and hence the number of moles of MnO_4^- ions used.

6 (b) (iii) Hence, calculate the mass of one mole of the manganate(VII) compound. Use your answer to identify this compound as either $KMnO_4$ or $NaMnO_4$ *(6 marks)*

7 (a) Draw the shape of each of the following and, in each case, name the shape.

7 (a) (i) HCHO
7 (a) (ii) $[CoCl_4]^{2-}$
7 (a) (iii) $[IF_4]^-$
7 (a) (iv) $[Ag(CN)_2]^-$ *(8 marks)*

7 (b) Draw a structure, including all the bonds, to show how **one** ethanedioate ion, $C_2O_4^{2-}$, bonds as a bidentate ligand to a Co^{2+} ion. On your structure represent each co-ordinate bond with an arrow. *(2 marks)*

7 (c) Outline a mechanism for the reaction of HCN with CH_3CHO
Use the mechanism to explain why two stereoisomers are formed in this reaction.
Draw structures to show the shapes of the two stereoisomers. *(5 marks)*

Turn over ▶

8 The tables below contain some data about aqueous solutions.

	Na^+	Mg^{2+}	Al^{3+}	Cl^-
Enthalpy of hydration, $\Delta H^\ominus_{hyd}$ / kJ mol^{-1}	–406	–1920	–4690	–364

	NaCl	$MgCl_2$
Enthalpy of solution, $\Delta H^\ominus_{sol}$ / kJ mol^{-1}	+3.9	–155

8 (a) Use these data to calculate the lattice enthalpy of dissociation of sodium chloride and of magnesium chloride. *(3 marks)*

8 (b) Explain why the lattice enthalpy of dissociation of sodium chloride is less than that of magnesium chloride. *(2 marks)*

8 (c) Suggest why the enthalpy of hydration of aluminium ions is much more exothermic than that for magnesium ions. *(2 marks)*

8 (d) Aqueous solutions of $AlCl_3$ are acidic.

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

The acid dissociation constant for this reaction, $K_a = 1.26 \times 10^{-5}$ mol dm^{-3}.
Calculate the pH of a 2.0 mol dm^{-3} solution of $AlCl_3$ *(4 marks)*

8 (e) Write an equation for the reaction that occurs when silicon tetrachloride is added to water. Predict the pH of the resulting solution. *(2 marks)*

9 Methanol is a possible alternative to hydrocarbons as a liquid fuel.

9 (a) Calculate the mass of methanol that should be burned in order to raise the temperature of 1.00 kg of water from 20.0 °C to 100 °C. The enthalpy of combustion of methanol has the value of –715 kJ mol^{-1}.
Assume that 50% of the heat obtained from burning the methanol is lost to the surroundings and that the specific heat capacity of water is 4.18 J K^{-1} g^{-1}. *(5 marks)*

9 (b) Methanol can be produced by using a reversible reaction between carbon monoxide and hydrogen.

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

When 2.00 mol of hydrogen and 1.00 mol of carbon monoxide are mixed and heated to a high temperature in a container of volume 1.50 dm^3, the equilibrium yield of methanol is 0.80 mol.

Calculate a value for the equilibrium constant, K_c, for this reaction at this temperature and give its units. *(7 marks)*

9 (c) The ester, methyl ethanoate (CH_3COOCH_3), can be distinguished from its isomer, ethyl methanoate ($HCOOCH_2CH_3$), by proton n.m.r. spectroscopy. For each of these isomers indicate the number of peaks and the splitting, if any, of each peak in the proton n.m.r. spectrum. *(5 marks)*

END OF QUESTIONS

Areas outside the box will not be scanned for marking

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Areas outside the box will not be scanned for marking

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