Surname		Other Names	
Centre Number		Candidate Number	
Candidate Signature			

For Examiner's Use

General Certificate of Education
June 2009
Advanced Level Examination

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

Thursday 18 June 2009 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.
- Answer the questions in **Section A** and **Section B** in the spaces provided. **Answers written in margins or on blank pages will not be marked.**
- 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.
- The marks for questions 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.
- 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**.

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

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SECTION A

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

1 Use the following enthalpy data to answer the question.

	$\Delta H^{\ominus}$ / kJ mol^{-1}
$Mg(s) \longrightarrow Mg(g)$	+ 150
$Mg(g) \longrightarrow Mg^{+}(g) + e^{-}$	+ 736
$Mg^{+}(g) \longrightarrow Mg^{2+}(g) + e^{-}$	+ 1450
$\frac{1}{2}O_2(g) \longrightarrow O(g)$	+ 248
$O(g) + e^{-} \longrightarrow O^{-}(g)$	– 142
$O^{-}(g) + e^{-} \longrightarrow O^{2-}(g)$	+ 844
$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$	– 602

1 (a) Define the term *standard enthalpy of formation*.

....

....

....

....

(3 marks)

1 (b) Suggest why the enthalpy change for the process represented by the equation below is endothermic.

$$O^{-}(g) + e^{-} \longrightarrow O^{2-}(g)$$

....

(1 mark)

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

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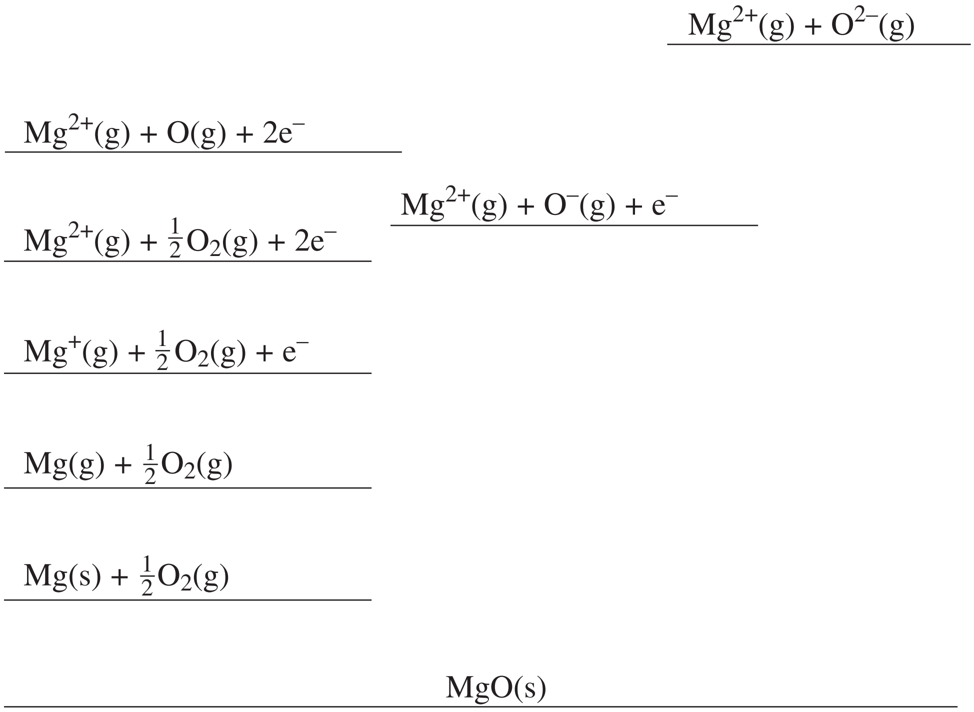
1 (c) Use the data from the table and the incomplete Born–Haber cycle below to calculate the standard enthalpy of lattice formation for magnesium oxide.



....

....

....

(3 marks)

1 (d) The enthalpies of lattice formation for calcium oxide and for barium oxide are $-3513\,kJ\,mol^{-1}$ and $-3152\,kJ\,mol^{-1}$ respectively. Suggest why the lattice enthalpy for CaO is more negative than that for BaO

....

....

....

(2 marks)

9

Turn over ▶

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DO NOT WRITE ON THIS PAGE
ANSWER IN THE SPACES PROVIDED

2 (a) Barium oxide reacts with water to form aqueous barium hydroxide.

2 (a) (i) Write an equation for this reaction.

....

(1 mark)

2 (a) (ii) Calculate the pH of the solution formed by reacting 2.00 g of BaO with water and making up to 100 cm^3 of solution at 298 K. Give your answer to two decimal places.
($K_w = 1.00 \times 10^{-14}\ mol^2\ dm^{-6}$ at 298 K)

....

....

....

....

....

....

....

(5 marks)

2 (b) State why the pH of a solution formed by adding an excess of magnesium hydroxide to water is lower than the pH of the solution formed in part (a) (ii).

....

....

(1 mark)

7

3 (a) Give the equation that relates the free-energy change for a reaction to the enthalpy change and the entropy change.

....

(1 mark)

3 (b) Consider the following equation that represents the first step in the extraction of titanium.

$$TiO_2(s) + 2C(s) + 2Cl_2(g) \longrightarrow 2CO(g) + TiCl_4(g) \qquad \Delta H = -30\,kJ\,mol^{-1}$$

3 (b) (i) Deduce the sign of the entropy change for this reaction and explain your answer.

Sign of entropy change ....

Explanation ....

....

....

(3 marks)

3 (b) (ii) Use your answers to part (a) and part (b) (i) to explain why this reaction will be feasible at all temperatures.

....

....

....

(2 marks)

3 (b) (iii) Give one reason why, despite being feasible at all temperatures, the reaction is carried out at 900 °C.

....

(1 mark)

3 (c) The following data refer to the second step in the extraction of titanium.

	$TiCl_4(g)$	Na(l)	NaCl(s)	Ti(s)
Standard enthalpy of formation, $\Delta H_f^{\ominus}$ / kJ mol^{-1}	–720	3	–411	0
Standard entropy, $S^{\ominus}$ / J K^{-1} mol^{-1}	329	58	72	30

3 (c) (i) Use the data from the table to calculate values for the enthalpy change and the entropy change for the following reaction.

$$TiCl_4(g) + 4Na(l) \longrightarrow 4NaCl(s) + Ti(s)$$

Value of ΔH ....

....

....

Value of ΔS ....

....

....

(5 marks)

3 (c) (ii) Use your answers to part (c) (i) to calculate the temperature above which this reaction is not feasible.
(If you have been unable to calculate answers to part (c) (i) you may assume that the enthalpy change has the value –812 kJ mol^{-1} and the entropy change has the value –312 J K^{-1} mol^{-1}. These are not the correct values.)

....

....

....

(3 marks)

15

Turn over ▶

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4 (a) In terms of electrons, state what happens to the oxidising agent in a redox reaction.

....

(1 mark)

4 (b) State the value of the standard electrode potential for the following half-equation. Give a reason why it has this value.

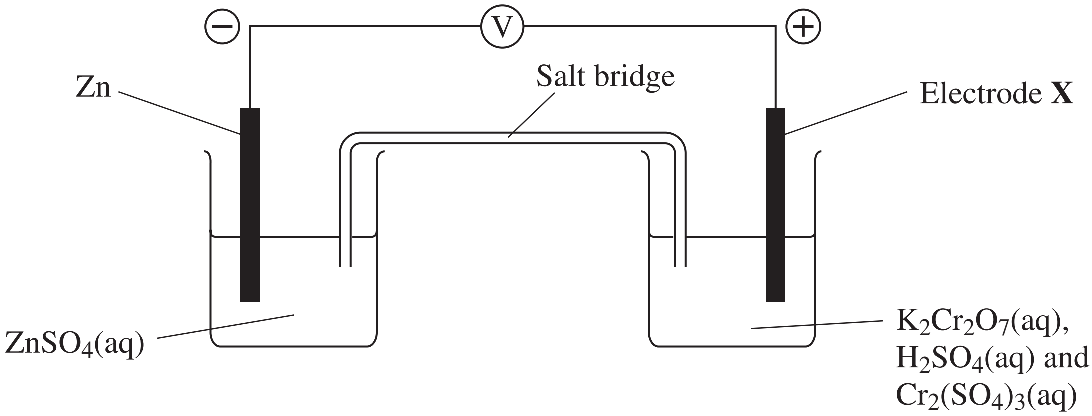
$$H^+(aq) + e^- \longrightarrow \tfrac{1}{2}H_2(g)$$

Value of $E^\ominus$ ....

Reason ....

(2 marks)

4 (c) Consider the electrochemical cell shown below. The aqueous mixture in the right-hand part of the cell contains the oxidising agent and the reducing agent for that part of the cell.



State the purpose of the salt bridge and of the electrode **X**. Identify the substance or substances from which each of these is made.

Purpose of salt bridge...

....

Salt bridge is made from...

Purpose of electrode **X** ....

....

Electrode **X** *is made from* ....

(4 marks)

4 (d) Give the oxidation state of chromium in $K_2Cr_2O_7$

....

(1 mark)

4 (e) Write half-equations for the reactions at each electrode and an overall equation for the cell reaction.

Positive electrode half-equation

....

Negative electrode half-equation

....

Overall equation for cell reaction

....

(3 marks)

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

....

(1 mark)

12

Turn over for the next question

5 The following compounds can be distinguished by observing what happens in test-tube reactions.

For each pair, suggest a suitable reagent that could be added separately to each compound. Describe what you would observe in each case. Write an equation or equations where required.

5 (a) $MgCl_2(aq)$ and $BaCl_2(aq)$

Reagent ....

Observation with $MgCl_2(aq)$ ....

Observation with $BaCl_2(aq)$ ....

(3 marks)

5 (b) $CH_3COOH(aq)$ and $CH_3COCH_3(aq)$

Reagent ....

Observation with $CH_3COOH(aq)$...

Observation with $CH_3COCH_3(aq)$ ....

Equation either with $CH_3COOH(aq)$ or with $CH_3COCH_3(aq)$

....

(4 marks)

5 (c) KF(aq) and KCl(aq)

Reagent ....

Observation with KF(aq)...

Observation with KCl(aq)..

(3 marks)

5 (d) $CrCl_3(aq)$ and $FeCl_2(aq)$

Reagent ....

Observation with $CrCl_3(aq)$..

Observation with $FeCl_2(aq)$..

(3 marks)

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5 (e) $AlCl_3(aq)$ and $MgCl_2(aq)$

Reagent ....

Observation with $AlCl_3(aq)$ ....

Observation with $MgCl_2(aq)$ ....

Equation(s) with $AlCl_3(aq)$ ....

....

(4 marks)

17

Turn over for the next question

Turn over ▶

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SECTION B

Detach this perforated sheet.
Answer **all** questions in the spaces provided on page 14 and pages 17–20 of this booklet.

6 (a) Define the term *electronegativity*. *(2 marks)*

6 (b) Explain why the bonding in sodium chloride is ionic but there is covalent bonding in anhydrous aluminium chloride. *(3 marks)*

6 (c) The table below shows the melting points of some Period 3 chlorides.

	$MgCl_2$	$SiCl_4$	PCl_5
Melting point / K	987	203	435

By considering the structures and the bonding involved explain the following.

6 (c) (i) $MgCl_2$ has a high melting point. *(2 marks)*

6 (c) (ii) $SiCl_4$ is a liquid at room temperature but PCl_5 is a solid with a higher melting point. *(5 marks)*

6 (d) Write equations for the reactions that occur when each of $MgCl_2$, $SiCl_4$ and PCl_5 is added to separate samples of water. *(3 marks)*

7 (a) State the meaning of each of the terms *ligand* and *co-ordination number* as they apply to transition metal complex ions. *(2 marks)*

7 (b) Explain why transition metal ions are usually coloured. *(3 marks)*

7 (c) The colour of an aqueous solution containing pink $[Co(H_2O)_6]^{2+}(aq)$ ions can be changed by

7 (c) (i) changing the ligand but keeping the co-ordination number the same *(3 marks)*

7 (c) (ii) changing both the co-ordination number and the ligand *(3 marks)*

7 (c) (iii) changing the oxidation state. *(4 marks)*

In each case, identify the reagent or reagents required to bring about the change, give the formula of the cobalt-containing ion formed and state its colour.

Turn over for the next question

8 (a) State the meaning of each of the terms *rate of reaction* and *catalyst*. *(2 marks)*

8 (b) Identify the main feature of transition metal ions that enables them to act as good catalysts for redox reactions.

Explain how and why Fe^{2+}(aq) ions are able to catalyse the reaction between I^-(aq) ions and $S_2O_8^{2-}$(aq) ions. Illustrate your answer with equations. *(6 marks)*

8 (c) For each of the following processes, suggest a catalyst and write an equation for the overall reaction.

8 (c) (i) the cracking of octane to form 2,2-dimethylbutane and one other product *(2 marks)*

8 (c) (ii) the removal of nitrogen monoxide from the exhaust gases of a petrol engine *(2 marks)*

8 (c) (iii) the acylation of benzene. *(3 marks)*

9 (a) Bromine molecules react with propene at room temperature. Outline a mechanism for this reaction. *(4 marks)*

9 (b) Bromine atoms are involved in the reaction between bromine and methane to form bromomethane. Write equations for the two propagation steps in this reaction. *(2 marks)*

9 (c) When heated, bromine molecules can be atomised as shown in the equation below.

$$Br_2(g) \rightleftharpoons 2Br\bullet(g)$$

In an experiment, 6.30 g of bromine in a sealed container of volume 2.00 dm^3 were heated to a high temperature. Under these conditions, at equilibrium, 20% of the bromine is converted into atoms.

9 (c) (i) Write an expression for the equilibrium constant, K_c, for this reaction. *(1 mark)*

9 (c) (ii) Calculate a value for K_c under these conditions. *(5 marks)*

9 (c) (iii) Suggest what happens to the value of K_c when the reaction is carried out at a higher temperature. Explain your answer. *(3 marks)*

END OF QUESTIONS

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