

Surname						Other Names					
Centre Number						Candidate Number					
Candidate Signature											

For Examiner's Use

General Certificate of Education
June 2007
Advanced Level Examination



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

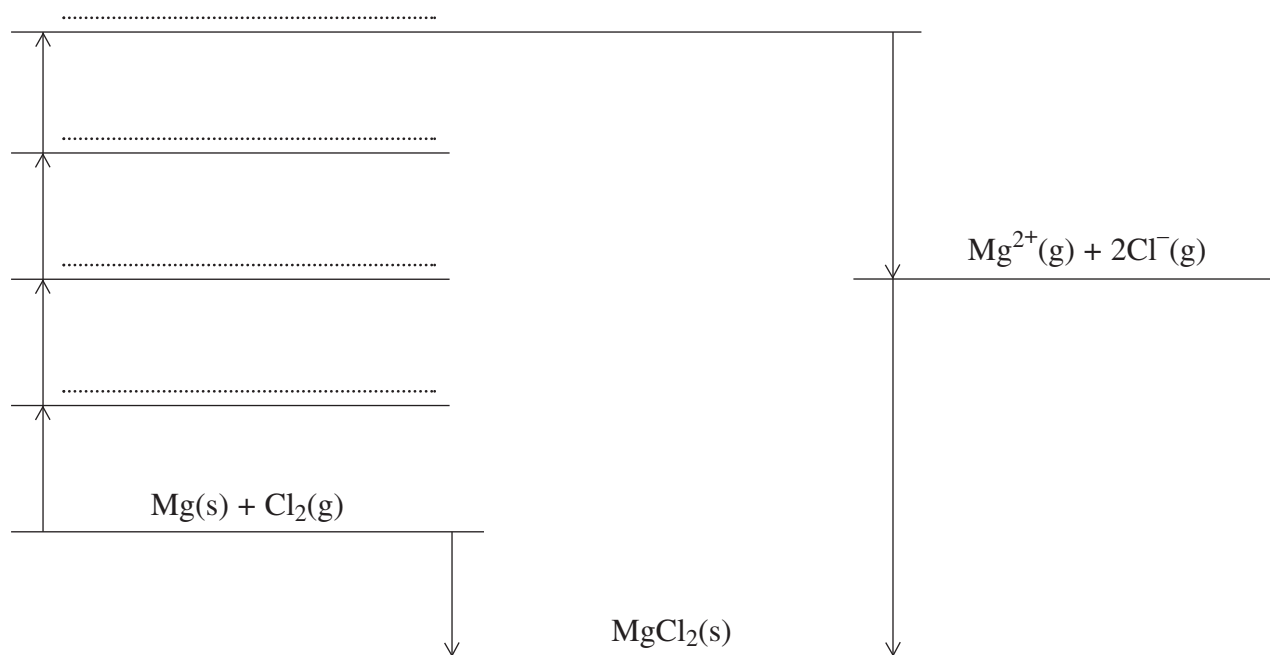
- You are advised to spend about 1 hour on **Section A** and about 1 hour on **Section B**.

For Examiner's Use			
Question	Mark	Question	Mark
1			
2			
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Total (Column 1) →			
Total (Column 2) →			
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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)

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 $-1920 \text{ kJ mol}^{-1}$ 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 $+15 \text{ kJ mol}^{-1}$.

- (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 $4.2 \text{ J K}^{-1} \text{ g}^{-1}$.

Temperature change

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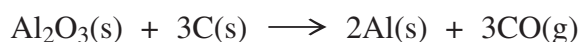
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Final temperature of solution

(5 marks)

Turn over ►

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



Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$
$\text{Al}_2\text{O}_3(\text{s})$	-1669	51
$\text{C}(\text{s})$	0	6
$\text{Al}(\text{s})$	0	28
$\text{CO}(\text{g})$	-111	198

- (a) Calculate the values of ΔH^\ominus , ΔS^\ominus and ΔG^\ominus for the above reaction at 298 K and suggest why this reaction is not feasible at 298 K.

ΔH^\ominus

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ΔS^\ominus

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ΔG^\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 ΔH^\ominus and ΔS^\ominus in part (a) you may assume that they are $+906 \text{ kJ mol}^{-1}$ and $+394 \text{ J K}^{-1} \text{ mol}^{-1}$ 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)

3 The table below shows some standard electrode potentials.

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

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

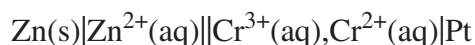
Products, if any

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.

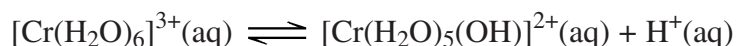


e.m.f.

Equation

(2 marks)

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



The value of K_a for this reaction is $1.15 \times 10^{-4} \text{ mol dm}^{-3}$.

Calculate the pH of a $0.500 \text{ mol dm}^{-3}$ solution of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$.

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(5 marks)

- (d) State what you would observe after addition of the following reagents to separate aqueous solutions containing $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ions.
In each case give the formula of the chromium-containing product.

- (i) an excess of $\text{NaOH}(\text{aq})$

Observation(s)

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Formula of product

- (ii) $\text{Na}_2\text{CO}_3(\text{aq})$

Observation(s)

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Formula of product

(5 marks)

- 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 P₄O₁₀

Bonding in MgO

Bonding in P₄O₁₀

- (ii) Explain how the type of bonding in P₄O₁₀ can be predicted by a consideration of electronegativity.

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(3 marks)

- (d) Write equations for the reaction of Na₂O and of SO₂ with water.

Equation for Na₂O

Equation for SO₂

(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 P₄O₁₀ 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.

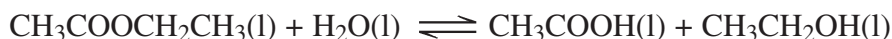
- 5 (a) Explain why the ester methyl ethanoate has a lower boiling point than its isomer, propanoic acid. (2 marks)

- (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.



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 $\text{Mn}^{2+}(\text{aq})$ 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 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 $0.140 \text{ mol dm}^{-3}$ solution of $\text{Q}^{2+}(\text{aq})$ required 29.2 cm^3 of a $0.040 \text{ mol dm}^{-3}$ solution of potassium dichromate(VI) for complete reaction.

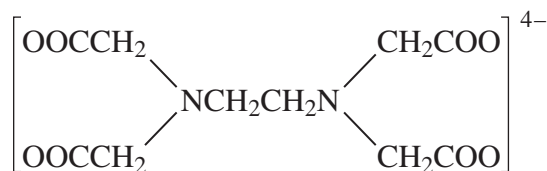
Determine the oxidation state of the metal Q after reaction with the potassium dichromate(VI). (6 marks)

Turn over ►

- 7 The reaction scheme below shows a two-stage synthesis of ethane-1,2-diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.



- (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 $\text{CH}_3\text{CH}_2\text{Cl}$ 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

