Surname		Other Names	
Centre Number			Candidate Number									
Candidate Signature												

For Examiner's Use

General Certificate of Education
January 2010
Advanced Level Examination

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

Monday 1 February 2010 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.
- 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 information clearly 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			
10			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

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

1 Chlorine is formed in a reversible reaction as shown by the equation

$$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$$

1 (a) Use the data below to calculate the standard enthalpy change, $\Delta H^{\ominus}$, and the standard entropy change, $\Delta S^{\ominus}$, for this reaction.

Substance	HCl(g)	O_2(g)	Cl_2(g)	H_2O(g)
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	–92	0	0	–242
$S^{\ominus}$ / J K^{-1} mol^{-1}	187	205	223	189

Standard enthalpy change, $\Delta H^{\ominus}$.....

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.....

Standard entropy change, $\Delta S^{\ominus}$.....

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(6 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

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
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

* **58 – 71** Lanthanides

† **90 – 103** Actinides

Turn over ▶

Gas constant $R = 8.31$ J K^{-1} 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

1 (b) The data below apply to a different gas phase reversible reaction.

Standard enthalpy change, $\Delta H^{\ominus} = +228\ \text{kJ mol}^{-1}$
Standard entropy change, $\Delta S^{\ominus} = +195\ \text{J K}^{-1}\ \text{mol}^{-1}$

Calculate the minimum temperature at which this reaction is feasible.

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(4 marks)

10

Turn over for the next question

2 Use the data below, where appropriate, to answer the following questions.

Standard electrode potentials	$E^{\ominus}$/V
$S_2O_8^{2-}(aq) + 2e^- \longrightarrow 2SO_4^{2-}(aq)$	+2.01
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Cl_2(aq) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$NO_3^-(aq) + 3H^+(aq) + 2e^- \longrightarrow HNO_2(aq) + H_2O(l)$	+0.94
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77

2 (a) From the table above, select the species that is the most powerful reducing agent.

.....

(1 mark)

2 (b) Deduce the oxidation state of

2 (b) (i) chromium in $Cr_2O_7^{2-}$ .....

2 (b) (ii) nitrogen in HNO_2 .....

(2 marks)

2 (c) The concentration of iron(II) ions in aqueous solution can be determined by titrating the solution, after acidification, with a standard solution of potassium manganate(VII).

2 (c) (i) Explain, by reference to the data given in the table opposite, why hydrochloric acid should **not** be used to acidify the solution containing iron(II) ions.

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2 (c) (ii) Explain, by reference to the data given in the table opposite, why nitric acid should **not** be used to acidify the solution containing iron(II) ions.

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(4 marks)

2 (d) (i) Calculate the e.m.f. of the cell represented by

$Pt|Mn^{2+}(aq),MnO_4^-(aq)\|S_2O_8^{2-}(aq),SO_4^{2-}(aq)|Pt$

.....

2 (d) (ii) Deduce an equation for the reaction that occurs when an excess of $S_2O_8^{2-}(aq)$ ions is added to an aqueous solution containing $Mn^{2+}(aq)$ ions.

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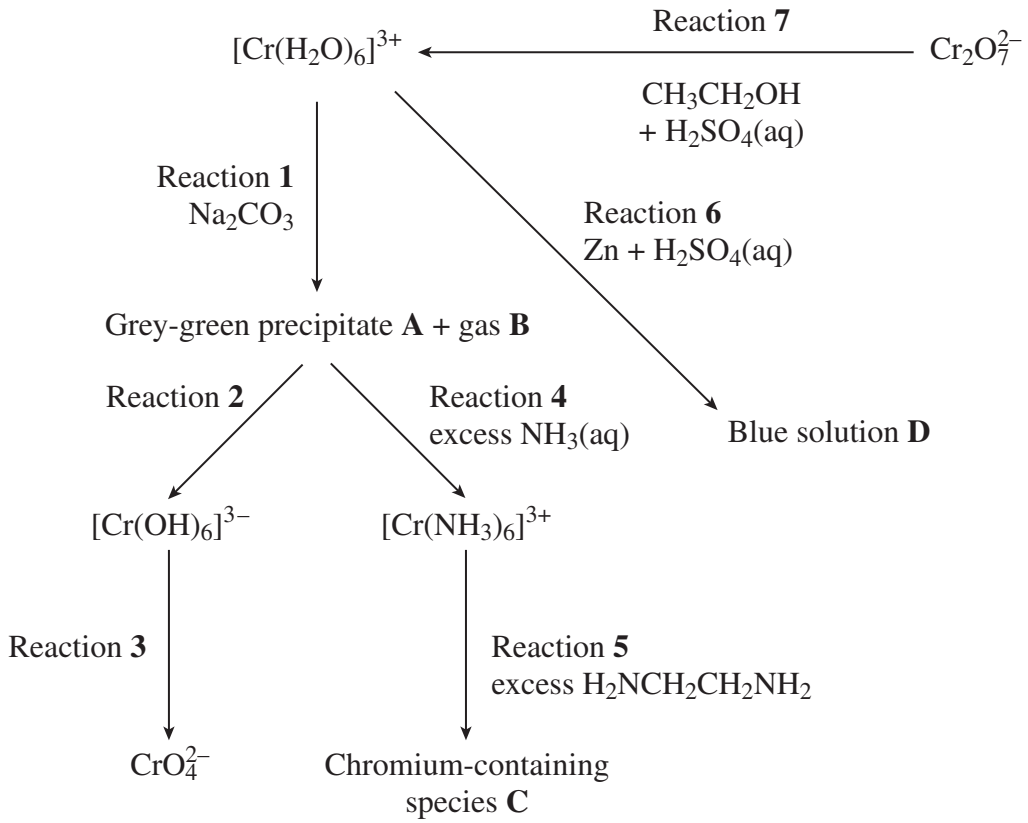
(3 marks)

10

Turn over for the next question

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



3 (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)

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

.....

3 (b) (ii) 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 .....

(3 marks)

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

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

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

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(7 marks)

3 (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)

3 (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.

3 (e) (i) Identify the organic product that has a low boiling point.

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

.....

(2 marks)

17

Turn over ▶

4 (a) State what is meant by the term *homogeneous* as applied to a catalyst.

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(1 mark)

4 (b) (i) State what is meant by the term *autocatalysis*.

.....

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4 (b) (ii) Identify the species that acts as an autocatalyst in the reaction between ethanedioate ions and manganate(VII) ions in acidic solution.

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(2 marks)

4 (c) When petrol is burned in a car engine, carbon monoxide, carbon dioxide, oxides of nitrogen and water are produced. Catalytic converters are used as part of car exhaust systems so that the emission of toxic gases is greatly decreased.

4 (c) (i) Write an equation for a reaction that occurs in a catalytic converter between **two** of the toxic gases. Identify the reducing agent in this reaction.

Equation .....

Reducing agent .....

4 (c) (ii) Identify a transition metal used in catalytic converters and state how the converter is constructed to maximise the effect of the catalyst.

Transition metal .....

How effect is maximised .....

.....

.....

(5 marks)

8

5 (a) State what is meant by the term *buffer solution*. Identify a reagent that could be added to a solution of ammonia in order to form a buffer solution.

Buffer solution .....

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Reagent .....

(3 marks)

5 (b) An acidic buffer solution is obtained when sodium ethanoate is dissolved in aqueous ethanoic acid.

5 (b) (i) Calculate the pH of the buffer solution formed at 298 K when 0.160 mol of sodium ethanoate is dissolved in 250 cm^3 of a 1.00 mol dm^{-3} solution of ethanoic acid.
The acid dissociation constant, K_a, for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 298 K.

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5 (b) (ii) Write an ionic equation for the reaction that occurs when a small volume of dilute hydrochloric acid is added to this buffer solution.

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(5 marks)

8

6 (a) Aqueous silver nitrate, followed by an excess of aqueous ammonia, can be used to identify halide ions in solution.

6 (a) (i) State what is observed when aqueous silver nitrate is added to a solution of aluminium chloride. Write an equation for the reaction that occurs.

Observation .....

Equation .....

6 (a) (ii) Explain why the addition of aqueous ammonia cannot be used to confirm the presence of chloride ions when the solution also contains aluminium ions.

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(4 marks)

6 (b) Concentrated sulphuric acid reacts with solid sodium chloride.

6 (b) (i) State what is observed in this reaction.

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6 (b) (ii) Write an equation for this reaction.

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6 (b) (iii) State the role of concentrated sulphuric acid in this reaction.

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(3 marks)

7

SECTION B

Detach this perforated sheet.
Answer Questions 7, 8, 9 and 10 in the spaces provided on pages 15 to 20 of this booklet.

7 Addition reactions to both alkenes and carbonyl compounds can result in the formation of isomeric compounds.

7 (a) Choose an alkene with molecular formula C_4H_8 that reacts with HBr to form two structural isomers. Give the structures of these two isomers and name the type of structural isomerism shown.

Outline a mechanism for the formation of the major product. *(7 marks)*

7 (b) Using HCN and a suitable carbonyl compound with molecular formula C_3H_6O, outline a mechanism for an addition reaction in which two isomers are produced.

Give the structures of the two isomers formed and state the type of isomerism shown. *(7 marks)*

8 When anhydrous iron(III) chloride is added to water the following reactions occur.

$$FeCl_3 + 6H_2O \longrightarrow [Fe(H_2O)_6]^{3+} + 3Cl^-$$

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$

8 (a) State the type of acidity shown by $FeCl_3$ and by $[Fe(H_2O)_6]^{3+}$ in these reactions. Explain your answers. *(4 marks)*

8 (b) A 0.125 mol dm^{-3} solution of iron(III) chloride was found to have a pH of 1.87
For the acid $[Fe(H_2O)_6]^{3+}$, calculate a value for the acid dissociation constant, K_a, and a pK_a value.
You should assume that all the hydrogen ion concentration is due to the reaction shown below.

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

(6 marks)

8 (c) Explain why the pH of a solution of iron(II) chloride is higher than that of a solution of iron(III) chloride of the same concentration. *(2 marks)*

Turn over ▶

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

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

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

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

10 (a) Iron is extracted by the reduction of iron(III) oxide using carbon. Titanium is extracted by the reduction of titanium(IV) chloride using sodium in an inert atmosphere.

Explain why these methods are used and state how the method chosen influences the cost of extraction of titanium compared to that of iron. *(6 marks)*

10 (b) A 1.35 g sample of impure iron obtained from the Blast Furnace was reacted with an excess of dilute sulphuric acid. All of the iron in the sample was converted into aqueous iron(II) sulphate, and hydrogen was evolved. The solution formed was made up to 250 cm^3. A 25.0 cm^3 sample of this solution reacted completely with exactly 20.8 cm^3 of a 0.0210 mol dm^{-3} solution of potassium manganate(VII).

10 (b) (i) Calculate the percentage by mass of iron in the sample.

10 (b) (ii) Write an equation for the reaction between iron and dilute sulphuric acid.

10 (b) (iii) Calculate the volume of hydrogen evolved, measured in cm^3, at 298 K and 101 kPa. (If you have been unable to complete the calculation in part (b) (i) above, assume that the sample contained 1.82×10^{-2} mol of iron. This is **not** the correct value.) *(11 marks)*

END OF QUESTIONS