Surname		Other Names	
Centre Number		Candidate Number	
Candidate Signature			

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General Certificate of Education
January 2004
Advanced Level Examination

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

Friday 23 January 2004 Afternoon Session

In addition to this paper you will require:
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 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.
- The following data may be required.
  Gas constant $R = 8.31\,J\,K^{-1}\,mol^{-1}$
- Your answers to 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			
Number	Mark	Number	Mark
1			
2			
3			
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8			
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10			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

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SECTION A

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

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

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

(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, $\Delta H^\ominus$ ....

....

....

....

....

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

....

....

....

....

(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.

Key

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

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

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

Standard enthalpy change, $\Delta H^{\ominus} = +208\ \text{kJ mol}^{-1}$
Standard entropy change, $\Delta S^{\ominus} = +253\ \text{J K}^{-1}\ \text{mol}^{-1}$

(i) Deduce the effect of an increase in temperature on the position of the equilibrium in this reaction. Use Le Chatelier's principle to explain your answer.

Effect ....

Explanation ....

....

(ii) Calculate the minimum temperature at which this reaction is feasible.

....

....

....

....

(7 marks)

13

TURN OVER FOR THE NEXT QUESTION

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2 (a) Silicon dioxide is a solid with a high melting point. When a mixture of silicon dioxide and carbon is heated in a stream of chlorine, silicon tetrachloride and carbon monoxide are formed. At room temperature, silicon tetrachloride is a colourless liquid.

(i) State the type of bonding and structure present in solid silicon dioxide and explain why it has a high melting point.

Type of bonding ....

Type of structure ....

Reason for high melting point ....

....

(ii) Write an equation for the reaction described above in which silicon tetrachloride is formed.

....

(iii) State the type of bonding present in silicon tetrachloride molecules. Explain why silicon tetrachloride has a low melting point.

Type of bonding ....

Reason for low melting point ....

....

(6 marks)

(b) Describe what you would observe and write an equation for the reaction occurring when silicon tetrachloride is added to an excess of water.

Observations ....

....

Equation ....

(3 marks)

9

3 The Group II element **A** burns when heated in chlorine forming the solid chloride **B** which has a high melting point.

When aqueous sodium hydroxide is added to an aqueous solution of **B** a white precipitate **C** is formed.

Precipitate **C** does not dissolve when an excess of aqueous sodium hydroxide is added but does dissolve when aqueous sulphuric acid is added.

(a) State the type of bonding present in **B**.

....

(1 mark)

(b) Identify **B**.

....

(1 mark)

(c) Write an equation for the formation of chloride **B** from element **A**.

....

(1 mark)

(d) Identify the precipitate **C**.

....

(1 mark)

(e) Write an equation for the reaction in which **C** is formed.

....

(1 mark)

(f) Write an equation for the reaction of **C** with aqueous sulphuric acid.

....

(1 mark)

6

TURN OVER FOR THE NEXT QUESTION

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4 Use the data below, where appropriate, to answer the questions which follow.

Standard electrode potentials	$E^{\ominus}$/V
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+1.09
$2BrO_3^-(aq) + 12H^+(aq) + 10e^- \longrightarrow Br_2(aq) + 6H_2O(l)$	+1.52

Each of the above can be reversed under suitable conditions.

(a) State the hydrogen ion concentration and the hydrogen gas pressure when, at 298 K, the potential of the hydrogen electrode is 0.00 V.

Hydrogen ion concentration ....

Hydrogen gas pressure ....

(2 marks)

(b) The electrode potential of a hydrogen electrode changes when the hydrogen ion concentration is reduced. Explain, using Le Chatelier's principle, why this change occurs and state how the electrode potential of the hydrogen electrode changes.

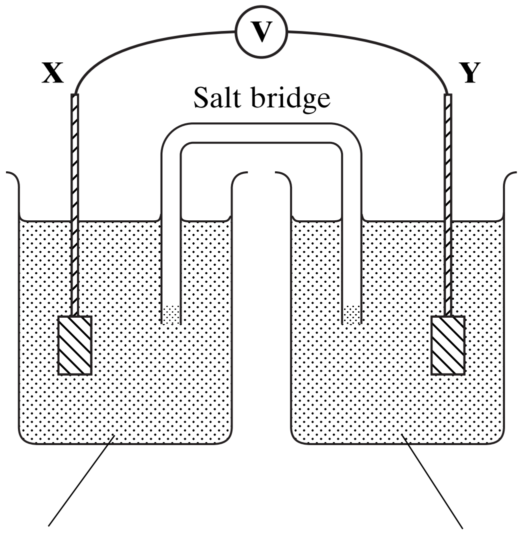
Explanation of change ....

....

Change in electrode potential ....

(3 marks)

(c) A diagram of a cell using platinum electrodes **X** and **Y** is shown below.



Solution containing Br_2(aq) and Br^-(aq)

Solution containing BrO_3^-(aq), H^+(aq) and Br_2(aq)

(i) Use the data above to calculate the e.m.f. of the above cell under standard conditions.

....

(ii) Write a half-equation for the reaction occurring at electrode **X** and an overall equation for the cell reaction which occurs when electrodes **X** and **Y** are connected.

Half-equation ....

Overall equation ....

....

(4 marks)

9

TURN OVER FOR THE NEXT QUESTION

Turn over ▶

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5 (a) By reference to the forces between molecules, explain why ammonia is very soluble in water.

....

....

(2 marks)

(b) Aqueous solutions of ammonia have a pH greater than 7.

(i) Write an equation for the reaction of ammonia with water.

....

(ii) Explain why the pH of a solution containing 1.0 mol dm^{-3} of ammonia is less than 14 at 298 K.

....

....

(3 marks)

(c) An ammonium ion in aqueous solution can behave as a Brønsted–Lowry acid. State what is meant by the term *Brønsted–Lowry acid*.

....

(1 mark)

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

Buffer solution ....

....

Reagent ....

(3 marks)

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

(i) Calculate the pH of the buffer solution formed at 298 K when 0.125 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 1.70×10^{-5} mol dm^{-3} at 298 K.

....

....

....

....

....

....

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

....

(5 marks)

14

TURN OVER FOR THE NEXT QUESTION

Turn over ▶

6 (a) Explain why complex ions with partially filled d sub-levels are usually coloured.

....

....

(2 marks)

(b) (i) When aqueous ammonia was added to an aqueous solution of cobalt(II) sulphate, a blue precipitate **M** was formed. Identify the cobalt-containing species present in aqueous cobalt(II) sulphate and the precipitate **M**.

Cobalt-containing species ....

*Precipitate **M*** ....

(ii) Precipitate **M** dissolved when an excess of concentrated aqueous ammonia was added. The solution formed was pale brown due to the presence of the cobalt-containing species **P**. Identify **P**.

....

(iii) On standing in air, the colour of the solution containing **P** slowly darkened as the cobalt-containing species **Q** was formed. State the type of reaction occurring when **P** changes into **Q** and identify the reactant responsible for this change.

Type of reaction ....

Reactant responsible ....

(iv) When potassium iodide was added to the solution containing **Q** and the mixture was acidified, a dark red-brown colour due to the presence of **R** was produced. On addition of starch solution the mixture turned blue-black.
Identify **R** and explain its formation.

*Identity of **R*** ....

Explanation ....

....

(7 marks)

9

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SECTION B

Detach this perforated sheet.
Answer **all** of the questions below in the space provided on pages 15 to 20 of this booklet.

7 (a) When methane reacts with chlorine in sunlight, a mixture of chlorinated substitution products is obtained. Outline mechanisms for the formation of two of the chlorinated substitution products. *(5 marks)*

(b) Two different organic products can be formed when 2-chloropropane, $CH_3CHClCH_3$, reacts with potassium hydroxide. The major product formed depends on the solvent in which the potassium hydroxide is dissolved.

Write equations showing the formation of these different products. In each case state the solvent which could be used to obtain the best yield of that product. *(4 marks)*

(c) State why the hydrogen ion concentration in aqueous iron(II) chloride is lower than that in aqueous iron(III) chloride of the same concentration. *(3 marks)*

(d) State what is observed when aqueous sodium hydroxide is added slowly, until present in excess, to aqueous chromium(III) chloride.
Write equations for the reactions occurring. *(4 marks)*

8 (a) Vanadium(V) oxide is used as a heterogeneous catalyst in the Contact Process.

Explain what is meant by the terms *heterogeneous* and *catalyst* and state, in general terms, how a catalyst works.

State the essential feature of vanadium chemistry which enables vanadium(V) oxide to function as a catalyst and, by means of equations, suggest how it might be involved in the Contact Process. *(7 marks)*

(b) The following method was used to determine the percentage by mass of vanadium in a sample of ammonium vanadate(V).

A solution was made up by dissolving 0.160 g of ammonium vanadate(V) in dilute sulphuric acid. The ammonium vanadate(V) formed VO_2^+ ions in this solution. When an excess of zinc was added to this solution, the VO_2^+ ions were reduced to V^{2+} ions and the zinc was oxidised to Zn^{2+} ions.

After the unreacted zinc had been removed, the solution was titrated against a 0.0200 mol dm^{-3} solution of potassium manganate(VII). In the titration, 38.5 cm^3 of potassium manganate(VII) solution were required to oxidise all vanadium(II) ions to vanadium(V) ions.

Using half-equations, construct an overall equation for the reduction of VO_2^+ to V^{2+} by zinc in acidic solution.

Calculate the percentage by mass of vanadium in the sample of ammonium vanadate(V). *(8 marks)*

Turn over ▶

9 The three compounds $CH_3CH_2CH_2CH_2OH$, $(CH_3)_3COH$ and $CH_3CH_2CH_2CHO$ can be distinguished by use of the following three reagents

1. potassium dichromate(VI) acidified with dilute sulphuric acid
2. Tollens' reagent
3. ethanoic acid, together with a small amount of concentrated sulphuric acid.

(a) Identify which of these three organic compounds would reduce acidified potassium dichromate(VI). Give the structures of the organic products formed. Write a half-equation for the reduction of dichromate(VI) ions in acidic solution. *(6 marks)*

(b) Identify which one of these three organic compounds would reduce Tollens' reagent. Give the structure of the organic product formed. Write a half-equation for the reduction of Tollens' reagent. *(3 marks)*

(c) Identify which of these three organic compounds would react with ethanoic acid in the presence of concentrated sulphuric acid. In each case, give the structure of the organic product formed. *(4 marks)*

(d) State the number of peaks in the proton n.m.r. spectra of $CH_3CH_2CH_2CH_2OH$ and of $(CH_3)_3COH$. (Analysis of peak splitting is not required.) *(2 marks)*

10 (a) Metal reactivity and required purity are important considerations when choosing the method of extracting a metal. Each of the following is a reduction process used in the industrial extraction of one or more metals from its ore.

Method 1 high temperature reaction between an oxide and carbon
Method 2 electrolysis of a molten compound
Method 3 displacement from a compound using a more reactive metal

(i) For each method of extraction, identify **one** metal which is extracted using this process and write an equation for the reaction in which the metal is formed.

(ii) Give **two** reasons why Method 3 is a very expensive extraction process.

(iii) When beryllium oxide is heated with carbon to a very high temperature, beryllium carbide, Be_2C, is formed. This carbide reacts with water to form beryllium hydroxide and methane. Write an equation for the reaction of beryllium carbide with water. *(10 marks)*

(b) Transition metals form complex ions. Using actual examples of complex ions formed by transition metal ions, give the formula of

- a linear complex ion,
- a tetrahedral complex ion and
- an octahedral complex ion formed by using a bidentate ligand. *(4 marks)*

END OF QUESTIONS