Surname		Other Names	
Centre Number		Candidate Number	
Candidate Signature			

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General Certificate of Education
January 2003
Advanced Level Examination

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

Friday 24 January 2003 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.

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 $R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$
- 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			
4			
5			
6			
7			
8			
9			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

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

1 (a) At high temperatures, aluminium chloride exists in the vapour phase as the molecule $AlCl_3$. On cooling, two molecules of $AlCl_3$ combine by co-ordinate bonding to form molecules of Al_2Cl_6.

(i) State the shape of the $AlCl_3$ molecule and give the bond angle.

Shape ....

Bond angle ....

(ii) Sketch the structure of Al_2Cl_6 and mark on your sketch the value of **one** of the bond angles.

(iii) Explain how two $AlCl_3$ molecules are able to bond together.

....

....

(6 marks)

(b) (i) Describe what is observed when anhydrous $AlCl_3$ is added to an excess of water. Identify the major aluminium-containing species formed and predict the pH of the final solution.

Observation ....

Major aluminium-containing species ....

pH of final solution ....

(ii) Describe what you would observe when aqueous sodium carbonate is added to aqueous aluminium chloride. Write an equation for the reaction.

Observations ....

....

Equation ....

....

(7 marks)

13

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

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

LEAVE MARGIN BLANK

2 (a) Write equations for the reactions which occur when the following compounds are added separately to water. In each case, predict the approximate pH of the solution formed when one mole of each compound is added to 1 dm^3 of water.

Sodium oxide

Equation ....

pH of solution formed ....

Sulphur dioxide

Equation ....

pH of solution formed ....

(4 marks)

(b) When silicon dioxide and carbon are heated in a stream of chlorine gas, silicon tetrachloride and carbon monoxide are formed.

(i) Write an equation for this reaction.

....

(ii) State what is observed when silicon tetrachloride is added to water. Write an equation for the reaction which occurs.

Observations ....

....

Equation ....

(iii) Explain, in terms of their structure and bonding, why silicon tetrachloride has a lower melting point than phosphorus pentachloride.

....

....

....

....

(7 marks)

11

Turn over ▶

LEAVE MARGIN BLANK

3 Use the data in the table below to answer the questions which follow.

Substance	$Fe_2O_3(s)$	Fe(s)	C(s)	CO(g)	$CO_2(g)$
$\Delta H_f^\ominus$ / kJ mol^{-1}	−824.2	0	0	−110.5	−393.5
$S^\ominus$ / J K^{-1} mol^{-1}	87.4	27.3	5.7	197.6	213.6

(a) The following equation shows one of the reactions which can occur in the extraction of iron.

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$$

(i) Calculate the standard enthalpy change and the standard entropy change for this reaction.

Standard enthalpy change ....

....

....

....

....

....

Standard entropy change ....

....

....

....

....

(ii) Explain why this reaction is feasible at all temperatures.

....

....

....

(9 marks)

(b) The reaction shown by the following equation can also occur in the extraction of iron.

$$Fe_2O_3(s) + 3C(s) \longrightarrow 2Fe(s) + 3CO(g) \quad \Delta H^{\ominus} = +492.7 \text{ kJ mol}^{-1}$$

The standard entropy change, $\Delta S^{\ominus}$, for this reaction is +542.6 J K^{-1} mol^{-1}

Use this information to calculate the temperature at which this reaction becomes feasible.

....

....

....

(3 marks)

(c) Calculate the temperature at which the standard free-energy change, $\Delta G^{\ominus}$, has the same value for the reactions in parts (a) and (b).

....

....

....

....

(3 marks)

15

TURN OVER FOR THE NEXT QUESTION

Turn over ▶

4 Use the standard electrode potential data in the table below to answer the questions which follow.

	$E^\ominus/V$
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	+1.70
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	+0.17

(a) Name the standard reference electrode against which all other electrode potentials are measured.

....

(1 mark)

(b) When the standard electrode potential for $Fe^{3+}(aq)/Fe^{2+}(aq)$ is measured, a platinum electrode is required.

(i) What is the function of the platinum electrode?

....

(ii) What are the standard conditions which apply to $Fe^{3+}(aq)/Fe^{2+}(aq)$ when measuring this potential?

....

....

....

(3 marks)

(c) The cell represented below was set up under standard conditions.

$$Pt|H_2SO_3(aq), SO_4^{2-}(aq)||MnO_4^-(aq), Mn^{2+}(aq)|Pt$$

Calculate the e.m.f. of this cell and write an equation for the spontaneous cell reaction.

Cell e.m.f. ....

Equation ....

....

....

(3 marks)

(d) (i) Which one of the species given in the table is the strongest oxidising agent?

....

(ii) Which of the species in the table could convert $Fe^{2+}(aq)$ into $Fe^{3+}(aq)$ but could not convert $Mn^{2+}(aq)$ into $MnO_4^-(aq)$?

....

(3 marks)

(e) Use data from the table of standard electrode potentials to deduce the cell which would have a standard e.m.f. of 0.93 V. Represent this cell using the convention shown in part (c).

....

(2 marks)

12

TURN OVER FOR THE NEXT QUESTION

LEAVE MARGIN BLANK

5 (a) Give **one** example of a bidentate ligand.

....

(1 mark)

(b) Give **one** example of a linear complex ion formed by a transition metal.

....

(1 mark)

(c) Write an equation for a substitution reaction in which the complete replacement of ligands in a complex ion occurs with a change in **both** the co-ordination number and the overall charge of the complex ion.

....

(2 marks)

(d) Write an equation for a substitution reaction in which the complete replacement of ligands in a complex ion occurs without a change in either the co-ordination number or the overall charge of the complex ion.

....

(2 marks)

(e) When a solution containing $[Co(H_2O)_6]^{2+}$ ions is treated with a solution containing $EDTA^{4-}$ ions, a more stable complex is formed. Write an equation for this reaction and explain why the complex is more stable.

Equation ....

Explanation ....

....

(3 marks)

9

SECTION B

Answer **all** questions in the space provided on pages 13 to 20 of this booklet.

6 (a) Water, copper(II) ions and nitrogen dioxide are formed when copper metal reacts with concentrated nitric acid.

Write half-equations for the reactions occurring and use these to construct an overall ionic equation for the reaction. *(3 marks)*

(b) When copper reacts with dilute nitric acid, gaseous nitrogen monoxide is formed as shown by the following equation.

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

Calculate the volume of nitrogen monoxide, measured at 330 K and 98.0 kPa, which is formed when 1.25 g of copper metal reacts completely with an excess of dilute nitric acid. *(6 marks)*

(c) When copper(II) chloride dissolves in concentrated hydrochloric acid, a yellow-green copper-containing complex is formed.
When an excess of copper metal is added to this solution and the mixture is warmed, the complex species $[CuCl_4]^{3-}$ is formed.
When the solution containing the complex $[CuCl_4]^{3-}$ is poured into water, CuCl is formed as a white solid.

Identify the yellow-green copper-containing complex, write an equation for the reaction in which $[CuCl_4]^{3-}$ is formed and deduce the role of copper in this reaction.
Explain why CuCl is not coloured. *(6 marks)*

7 (a) "The strength of adsorption onto the active sites on the surface of a heterogeneous catalyst helps to determine the activity of the catalyst."

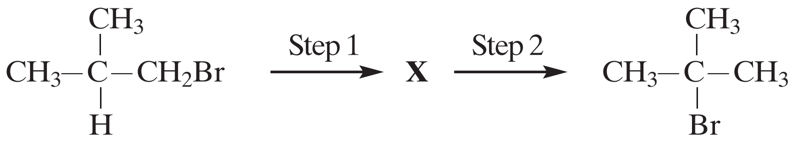
Explain how heterogeneous catalysts work, give **one** example of a reaction catalysed in this way and discuss why different catalysts have different activities. *(8 marks)*

(b) Outline a plan of an experiment to determine the percentage of iron present as iron(III) in a solution containing Fe^{3+}(aq) and Fe^{2+}(aq) ions. You are provided with zinc, a standard solution of potassium dichromate(VI) and dilute sulphuric acid. Zinc can reduce Fe^{3+}(aq) to Fe^{2+}(aq).

Write equations for all the reactions that occur. Explain how you would use the zinc and how you would calculate the final answer. *(7 marks)*

Turn over ▶

8 The conversion of compound **A** into compound **B** can be achieved in two steps as shown below.



A **B**

The intermediate compound, **X**, has an absorption at 1650 cm^{-1} in its infra-red spectrum.

(a) Identify compound **X**. Explain your answer. *(2 marks)*

(b) For each step in this conversion, give the reagents and essential conditions required and outline a mechanism. *(11 marks)*

(c) Show how the number of peaks in their proton n.m.r. spectra would enable you to distinguish between compounds **A** and **B**. *(2 marks)*

9 (a) The lone pair of electrons on the nitrogen atom is involved in the separate reactions of ammonia with hydrogen chloride, silver chloride and ethanoyl chloride.

Write equations for the reaction of ammonia with each of these compounds. State the role of ammonia in each of these reactions. *(7 marks)*

(b) Explain, in terms of the forces between particles, why the following compounds, which have similar relative molecular masses, have different melting points.

Compound	Formula	M_r	Melting point/K
Pentane	$CH_3(CH_2)_3CH_3$	72	143
Butanone	$CH_3CH_2COCH_3$	72	187
Propanoic acid	$CH_3CH_2CO_2H$	74	252

(8 marks)

END OF QUESTIONS