Surname		Other Names	
Centre Number			Candidate Number					
Candidate Signature								

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General Certificate of Education
June 2005
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

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

Tuesday 28 June 2005 Morning 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.

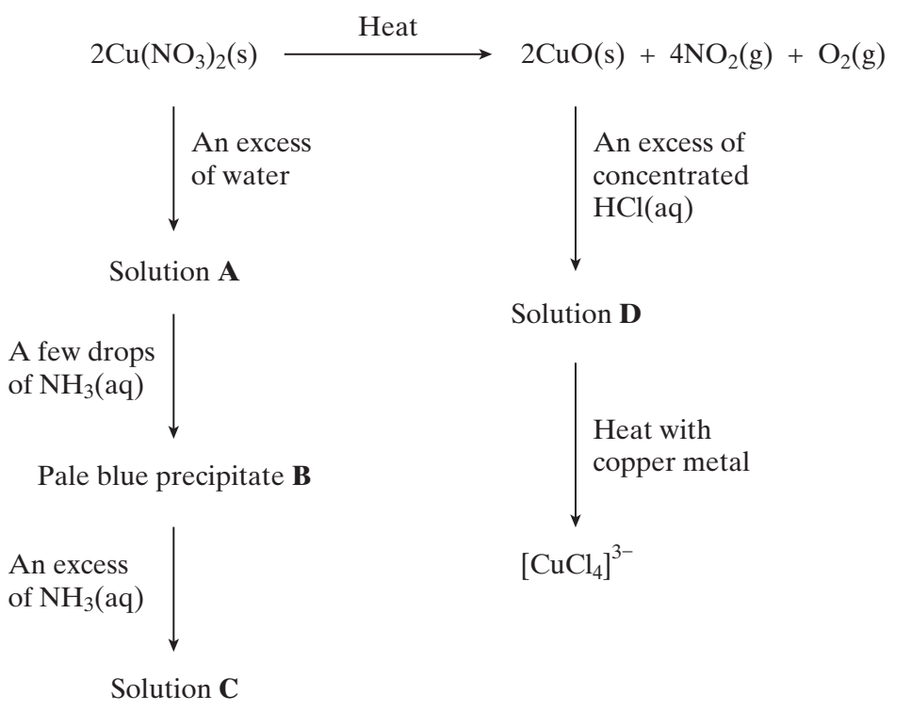
Advice
- You are advised to spend about 1 hour on **Section A** and about 1 hour on **Section B**.

For Examiner's Use			
Number	Mark	Number	Mark
1			
2			
3			
4			
5			
6			
7			
8			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

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

1 Consider the reaction scheme below and answer the questions which follow.



(a) A redox reaction occurs when $Cu(NO_3)_2$ is decomposed by heat. Deduce the oxidation state of nitrogen in $Cu(NO_3)_2$ and in NO_2 and identify the product formed by oxidation in this decomposition.

Oxidation state of nitrogen in $Cu(NO_3)_2$ .....

Oxidation state of nitrogen in NO_2 .....

Oxidation product .....

(3 marks)

(b) Identify and state the shape of the copper-containing species present in solution **A**.

Copper-containing species .....

Shape .....

(2 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
																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

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) (i) Identify the pale blue precipitate **B** and write an equation, or equations, to show how **B** is formed from the copper-containing species in solution **A**.

*Identity of precipitate **B*** .....

Equation(s) .....

.....

(ii) In what way does the NH_3 behave as a Brønsted–Lowry base?

.....

(3 marks)

(d) (i) Identify the copper-containing species present in solution **C**. State the colour of this copper-containing species and write an equation for its formation from precipitate **B**.

Identity .....

Colour .....

Equation .....

.....

(ii) In what way does the NH_3 behave as a Lewis base?

.....

(4 marks)

(e) Identify the copper-containing species present in solution **D**. State the colour and shape of this copper-containing species.

Identity .....

Colour .....

Shape .....

(3 marks)

(f) The oxidation state of copper in $[CuCl_4]^{3-}$ is +1.

(i) Give the electron arrangement of a Cu^+ ion.

.....

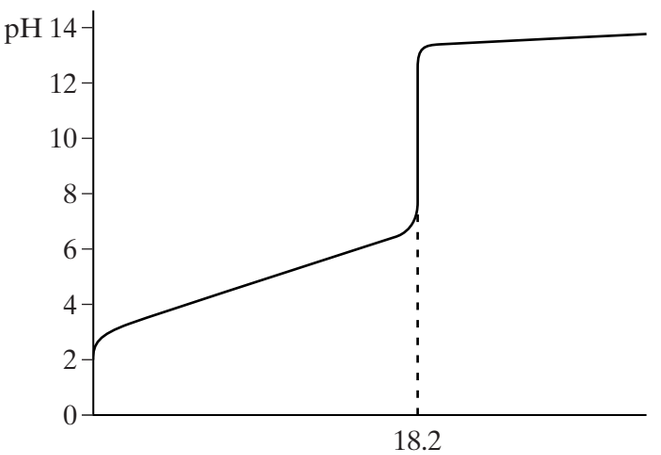
(ii) Deduce the role of copper metal in the formation of $[CuCl_4]^{3-}$ from the copper-containing species in solution **D**.

.....

(2 marks)

17

2 The pH curve shown below was obtained when a 0.150 mol dm^{-3} solution of sodium hydroxide was added to 25.0 cm^3 of an aqueous solution of a weak monoprotic acid, HA.



(a) Use the information given to calculate the concentration of the acid.

.....

.....

.....

(2 marks)

(b) (i) Write an expression for the acid dissociation constant, K_a, for HA.

.....

(ii) Write an expression for pK_a

.....

(iii) Using your answers to parts (b)(i) and (b)(ii), show that when sufficient sodium hydroxide has been added to neutralise half of the acid,

pH of the solution = pK_a for the acid HA

.....

.....

.....

(4 marks)

(c) Explain why dilution with a small volume of water does not affect the pH of a buffer solution.

.....

.....

(2 marks)

(d) (i) Calculate the change in pH when 0.250 mol dm^{-3} hydrochloric acid is diluted with water to produce 0.150 mol dm^{-3} hydrochloric acid.

.....

.....

.....

(ii) Calculate the volume of water which must be added to 30.0 cm^3 of 0.250 mol dm^{-3} hydrochloric acid in order to reduce its concentration to 0.150 mol dm^{-3}.

.....

.....

.....

(4 marks)

12

TURN OVER FOR THE NEXT QUESTION

3 (a) (i) The addition of aqueous silver nitrate, followed by concentrated aqueous ammonia, can be used to distinguish between separate aqueous solutions of sodium bromide and sodium iodide.
Record what is observed in the table below.

	The addition of $AgNO_3(aq)$	followed by the addition of concentrated $NH_3(aq)$
Observation with NaBr(aq)		
Observation with NaI(aq)		

(ii) Explain why it is not possible to distinguish between separate solutions of sodium nitrate and sodium fluoride by the addition of silver nitrate solution.

.....

(5 marks)

(b) When aqueous sodium thiosulphate is added to solid silver bromide a reaction occurs and a colourless solution is formed.

(i) Identify the silver-containing species present in the colourless solution.

.....

(ii) Write an equation for this reaction.

.....

(iii) Give **one** use of this reaction.

.....

(3 marks)

(c) Aqueous silver nitrate can be used to distinguish between chloroethanoic acid and ethanoyl chloride.

(i) Draw the structure of ethanoyl chloride. Predict what, if anything, you would observe when ethanoyl chloride is added to aqueous silver nitrate.

Structure of ethanoyl chloride

Observation .....

.....

(ii) Draw the structure of chloroethanoic acid. Predict what, if anything, you would observe when chloroethanoic acid is added to aqueous silver nitrate.

Structure of chloroethanoic acid

Observation .....

.....

(4 marks)

(d) (i) Tollens' reagent is formed by the addition of aqueous ammonia to aqueous silver nitrate. Identify the silver-containing complex present in Tollens' reagent and state its shape.

Silver-containing complex .....

Shape .....

(ii) Draw the structure of methanoic acid. By reference to this structure, suggest why a silver mirror is formed when this acid reacts with Tollens' reagent.

Structure .....

Explanation .....

(iii) Deduce the identity of a carbon-containing species formed when methanoic acid reacts with Tollens' reagent.

.....

(5 marks)

17

4 Where appropriate, use the standard electrode potential data in the table below to answer the questions which follow.

	$E^{\ominus}$/V
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$	–0.26
$SO_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightarrow SO_3^{2-}(aq) + H_2O(l)$	+0.17
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$	+0.34
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$	+1.00
$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36

(a) From the table above select the species which is the most powerful reducing agent.

.....

(1 mark)

(b) From the table above select

(i) a species which, in acidic solution, will reduce $VO_2^+(aq)$ to $VO^{2+}(aq)$ but will **not** reduce $VO^{2+}(aq)$ to $V^{3+}(aq)$,

.....

(ii) a species which, in acidic solution, will oxidise $VO^{2+}(aq)$ to $VO_2^+(aq)$.

.....

(2 marks)

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

$Pt|Fe^{2+}(aq), Fe^{3+}(aq)||Tl^{3+}(aq), Tl^+(aq)|Pt$ Cell e.m.f. = + 0.48 V

(i) Deduce the standard electrode potential for the following half-reaction.

$$Tl^{3+}(aq) + 2e^- \rightarrow Tl^+(aq)$$

.....

.....

(ii) Write an equation for the spontaneous cell reaction.

.....

(3 marks)

(d) After acidification, 25.0 cm^3 of a solution of hydrogen peroxide reacted exactly with 16.2 cm^3 of a 0.0200 mol dm^{-3} solution of potassium manganate(VII). The overall equation for the reaction is given below.

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

(i) Use the equation for this reaction to determine the concentration, in g dm^{-3}, of the hydrogen peroxide solution.

.....

.....

.....

.....

.....

.....

(ii) Calculate the maximum volume of oxygen, measured at a pressure of 98 kPa and a temperature of 298 K, which would be evolved in this reaction.

.....

.....

.....

.....

.....

(8 marks)

14

NO QUESTIONS APPEAR ON THIS PAGE

SECTION B

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

5 (a) State and explain the effect of a catalyst on the rate and on the equilibrium yield in a reversible reaction. *(5 marks)*

(b) Explain the terms *heterogeneous* and *active sites* as applied to a catalyst. Give **two** reasons why a ceramic support is used for the catalyst in catalytic converters in cars. Explain how lead poisons this catalyst. *(7 marks)*

(c) In aqueous solution, Fe^{2+} ions act as a homogeneous catalyst in the reaction between I^- and $S_2O_8^{2-}$ ions. Give **one** reason why the reaction is slow in the absence of a catalyst. Write equations to show how Fe^{2+} ions act as a catalyst for this reaction. *(5 marks)*

6 Most elements can be extracted from one of their naturally-occurring compounds by one of the following methods:

electrolysis of a molten chloride or oxide
reduction of the oxide with carbon
displacement of the element from its compound by a more reactive element.

(a) Aluminium is extracted by the electrolysis of aluminium oxide which has been dissolved in molten cryolite.
Suggest why aluminium is not extracted by electrolysis of aluminium chloride.
(2 marks)

(b) Use the information given below to calculate the minimum temperature at which the following carbon reduction process is feasible.

$$Al_2O_3(s) + 3C(s) \longrightarrow 2Al(s) + 3CO(g)$$

	$Al_2O_3(s)$	Al(s)	CO(g)	C(s)
$\Delta H_f^{\ominus}$/kJ mol^{-1}	−1676	0	−111	0
$S^{\ominus}$/J K^{-1} mol^{-1}	51	28	198	6

(8 marks)

(c) (i) State why fluorine cannot be prepared by displacement from one of its compounds by another halogen.

(ii) Identify a fluorine-containing product formed when solid sodium fluoride reacts with concentrated sulphuric acid. Write an equation for the reaction which occurs.
(3 marks)

Turn over ▶

7 (a) By a consideration of the structure of and the bonding in each compound, explain why magnesium chloride has a high melting point and why silicon(IV) chloride has a low boiling point. *(6 marks)*

(b) State what is observed when separate samples of sodium oxide and phosphorus(V) oxide are added to water. Write equations for the reactions which occur and, in each case, state the approximate pH of the solution formed. *(6 marks)*

8 (a) Identify a reagent which reacts with ethanal by a nucleophilic addition reaction to form a racemic mixture. Write an equation for the reaction occurring. Explain why a racemic mixture is obtained. *(4 marks)*

(b) Identify a reagent which undergoes an addition reaction with propene to form a mixture of isomers. Outline a mechanism for the reaction occurring. Explain why isomers are obtained. *(7 marks)*

(c) Identify a reagent which reacts with 2-bromobutane to form a mixture of isomers by an elimination reaction. Outline a mechanism for this reaction, and draw the structures of the isomers obtained. *(7 marks)*

END OF QUESTIONS

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