| Surname | | Other Names | |
|---|---|---|---|
| Centre Number | | | Candidate Number | | | | | |
| Candidate Signature | | | | | | | | |

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General Certificate of Education
January 2005
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

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

Tuesday 25 January 2005 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 $R = 8.31\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$
- 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 | | | |
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| Total (Column 1) → | | | |
| Total (Column 2) → | | | |
| TOTAL | | | |
| Examiner's Initials | | | |

## SECTION A

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

**1** (a) A solution with a pH of 3.25 was formed when 4.22 g of aluminium chloride, $AlCl_3$, were dissolved in water to make 1.00 $dm^3$ of solution.

(i) Calculate the concentration, in mol $dm^{-3}$, of aluminium chloride in this solution.

.....

.....

(ii) Calculate the concentration of hydrogen ions in this solution.

.....

.....

(iii) Identify the major aluminium-containing species present in this solution.

.....

(iv) Write an equation for the hydrolysis reaction which causes this solution to be acidic.

.....

(v) Use your answers from parts (i) and (ii) to calculate the percentage of aluminium ions which have been hydrolysed.

.....

.....

.....

*(8 marks)*

(b) State what is observed when sodium carbonate is added to an aqueous solution of aluminium chloride.

*Observation 1* .....

*Observation 2* .....

*(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 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 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

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

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

*Observation* .....

*Equation* .....

(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.

.....

.....

*(4 marks)*

(d) (i) State what is observed when concentrated sulphuric acid reacts with solid sodium chloride.

.....

(ii) Write an equation for the reaction occurring and state the role of sulphuric acid in this reaction.

*Equation* .....

*Role of concentrated sulphuric acid* .....

.....

*(3 marks)*

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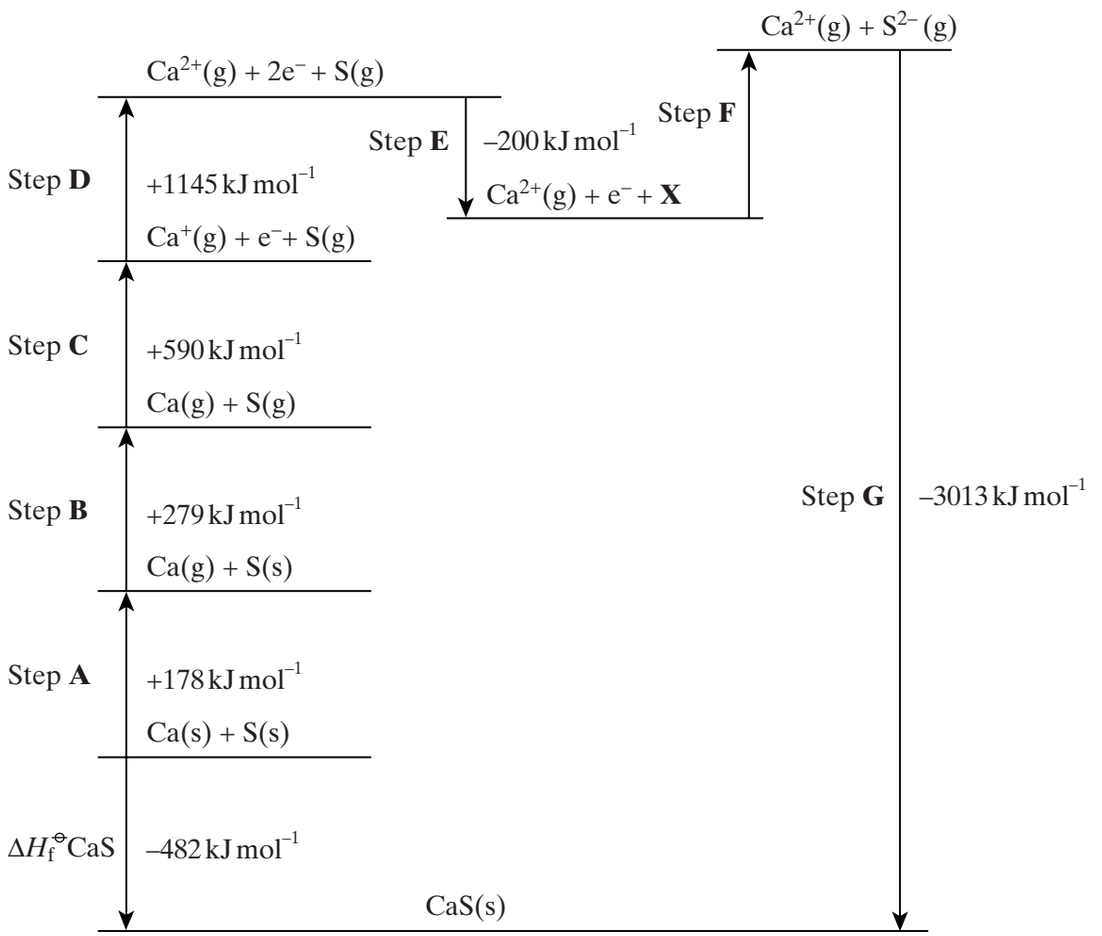
**TURN OVER FOR THE NEXT QUESTION**

**2** A Born–Haber cycle for the formation of calcium sulphide is shown below. The cycle includes enthalpy changes for all Steps except Step **F**. (The cycle is not drawn to scale.)




(a) Give the full electronic arrangement of the ion $S^{2-}$

.....

*(1 mark)*

(b) Identify the species **X** formed in Step **E**.

.....

*(1 mark)*

(c) Suggest why Step **F** is an endothermic process.

.....

.....

*(2 marks)*

(d) Name the enthalpy change for each of the following steps.

(i) Step **B** .....

(ii) Step **D** .....

(iii) Step **F** .....

*(3 marks)*

(e) Explain why the enthalpy change for Step **D** is larger than that for Step **C**.

.....

.....

*(2 marks)*

(f) Use the data shown in the cycle to calculate a value for the enthalpy change for Step **F**.

.....

.....

.....

*(2 marks)*

11

**TURN OVER FOR THE NEXT QUESTION**

**3** Use the standard electrode potential data given in the table below, where appropriate, to answer the questions which follow.

| | $E^{\ominus}$/V |
|---|---|
| $V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$ | –0.26 |
| $SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow H_2SO_3(aq) + H_2O$ | +0.17 |
| $VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$ | +0.34 |
| $O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$ | +0.68 |
| $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ | +0.77 |
| $VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$ | +1.00 |
| $2IO_3^-(aq) + 12H^+(aq) + 10e^- \rightarrow I_2(aq) + 6H_2O(l)$ | +1.19 |
| $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ | +1.52 |

Each of the above can be reversed under suitable conditions.

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

$$Pt\,|\,H_2SO_3(aq), SO_4^{2-}(aq)\,||\,Fe^{3+}(aq), Fe^{2+}(aq)\,|\,Pt$$

(i) Calculate the e.m.f. of this cell.

.....

(ii) Write a half-equation for the oxidation process occurring at the negative electrode of this cell.

.....

*(2 marks)*

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

$$Pt\,|\,H_2O_2(aq), O_2(g)\,\|\,IO_3^-(aq), I_2(aq)\,|\,Pt$$

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

.....

.....

.....

(ii) Give **one** reason why the e.m.f. of this cell changes when the electrodes are connected and a current flows.

.....

(iii) State how, if at all, the e.m.f. of this standard cell will change if the surface area of each platinum electrode is doubled.

.....

(iv) State how, if at all, the e.m.f. of this cell will change if the concentration of $IO_3^-$ ions is increased. Explain your answer.

*Change, if any, in e.m.f. of cell* .....

*Explanation* .....

.....

*(7 marks)*

(c) An excess of acidified potassium manganate(VII) was added to a solution containing $V^{2+}(aq)$ ions. Use the data given in the table to determine the vanadium species present in the solution at the end of this reaction. State the oxidation state of vanadium in this species and write a half-equation for its formation from $V^{2+}(aq)$.

*Vanadium species present at end of reaction* .....

*Oxidation state of vanadium in final species* .....

*Half-equation* .....

*(3 marks)*

12

**Turn over ▶**

**4** (a) The Period 3 elements, Na, Mg, Al, Si, P and S, all form oxides when the elements are burned in an excess of oxygen.

(i) Give the formula of an oxide of **one** of these elements in which the element is not in its highest oxidation state. Give the oxidation state of the element in this oxide.

*Formula of oxide* .....

*Oxidation state of element* .....

(ii) Write an equation for the reaction in which phosphorus(V) oxide is formed from phosphorus and oxygen.

.....

*(3 marks)*

(b) The melting points of some of the oxides formed by Period 3 elements are given in a random order below.

| Oxide | **A** | **B** | **C** | **D** | **E** |
|---|---|---|---|---|---|
| $T_m$/°C | 2852 | −73 | 1610 | 1275 | 300 |

(i) Using the letters **A** to **E**, give **two** oxides which have simple molecular structures. Explain your answer.

*Oxide 1* .....

*Oxide 2* .....

*Explanation* .....

.....

(ii) Give a simple chemical test which could be used to show which of the oxides in the table is sodium oxide. State the observation you would make.

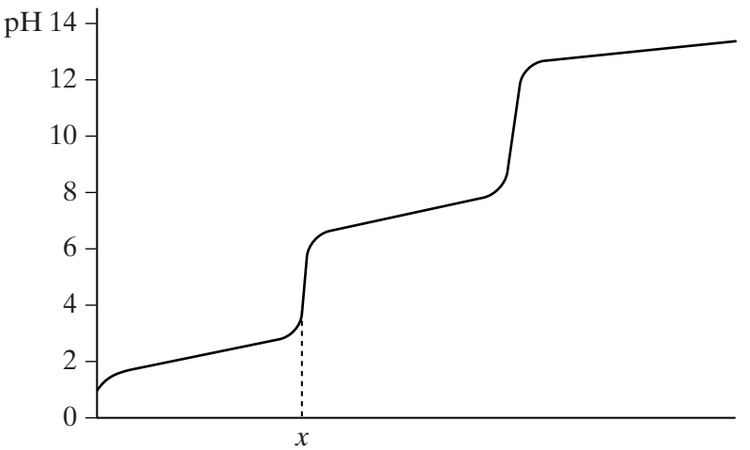
*Chemical test* .....

.....

*Observation* .....

*(6 marks)*

(c) The pH curve for the titration of the weak diprotic acid $H_2SO_3$ with aqueous sodium hydroxide is shown below.




(i) Identify the sodium salt formed from $H_2SO_3$ when $x\,cm^3$ of NaOH have been added.

.....

(ii) Write an equation for the reaction that occurs between the two end-points (equivalence points).

.....

(iii) Name an indicator which could be used to determine the second end-point (equivalence point).

.....

*(3 marks)*

12

**5** (a) Complete the electronic arrangement of the $Co^{2+}$ ion.

[Ar] .....

*(1 mark)*

(b) Give the formula of the cobalt complex present in an aqueous solution of cobalt(II) sulphate and state its colour.

*Formula of cobalt complex* .....

*Colour of cobalt complex* .....

*(2 marks)*

(c) (i) When a large excess of concentrated aqueous ammonia is added to an aqueous solution of cobalt(II) sulphate, a new cobalt(II) complex is formed. Give the formula of the new cobalt(II) complex and state its colour.

*Formula of new cobalt(II) complex* .....

*Colour of new cobalt(II) complex* .....

(ii) Write an equation for the formation of this new complex.

.....

*(3 marks)*

(d) When hydrogen peroxide is added to the mixture formed in part (c), the colour of the solution darkens due to the formation of a different cobalt complex. Identify this different cobalt complex and state the role of hydrogen peroxide in its formation.

*Cobalt complex formed*.....

*Role of hydrogen peroxide* .....

*(2 marks)*

8

## SECTION B

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

**6** (a) Octahedral and tetrahedral complex ions are produced by the reaction of transition metal ions with ligands which form co-ordinate bonds with the transition metal ion. Define the term *ligand* and explain what is meant by the term *co-ordinate bond*.

*(3 marks)*

(b) (i) Some complex ions can undergo a ligand substitution reaction in which both the co-ordination number of the metal and the colour change in the reaction. Write an equation for one such reaction and state the colours of the complex ions involved.

(ii) Bidentate ligands replace unidentate ligands in a metal complex by a ligand substitution reaction. Write an equation for such a reaction and explain why this reaction occurs.

*(8 marks)*

(c) The frequency, $v$, of light absorbed by a transition metal complex ion can be determined using the relationship $\Delta E = hv$. State what is meant by the symbols $\Delta E$ and $h$. Give **three** factors which result in a change in the frequency of light absorbed as a result of the reaction of a complex ion.

*(5 marks)*

**7** (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)*

(b) A 1.27 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 19.6 $cm^3$ of a 0.0220 mol $dm^{-3}$ solution of potassium manganate(VII).

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

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

(iii) Calculate the volume of hydrogen evolved, measured in $cm^3$, at 295 K and 98 kPa. (If you have been unable to complete the calculation in part (i) above assume that the sample contained $1.82 \times 10^{-2}$ mol of iron. This is not the correct value.)

*(11 marks)*

**Turn over ▶**

**8** (a) Addition reactions to both alkenes and carbonyl compounds can result in the formation of isomeric compounds.

(i) Choose an alkene with molecular formula $C_4H_8$ which 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.

(ii) 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.

*(14 marks)*

(b) Explain why ethanoyl chloride reacts readily with nucleophiles.
Write an equation for one nucleophilic addition–elimination reaction of ethanoyl chloride. (A mechanism is not required.)

*(4 marks)*

**9** (a) In the Haber Process for the manufacture of ammonia, the following equilibrium is established in the presence of a heterogeneous catalyst.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Identify the heterogeneous catalyst used in this process and state what is meant by the term *heterogeneous*.

A heterogeneous catalyst can become poisoned by impurities in the reactants. Give one substance which poisons the heterogeneous catalyst used in the Haber Process and explain how this substance poisons the catalyst.

*(5 marks)*

(b) State what is observed when an excess of aqueous ammonia reacts with an aqueous iron(II) salt. Write an equation for this reaction.

*(4 marks)*

**END OF QUESTIONS**

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*LEAVE MARGIN BLANK*

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