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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

<b>In addition to this paper you will require:</b> a calculator.
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For Examiner's Use			
Number	Mark	Number	Mark
1			
2			
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4			
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10			
Total (Column 1)	→		
Total (Column 2)	→		
TOTAL			
Examiner's Initials			

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  $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
- 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**.

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

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



- (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 <sub>2</sub> (g)	Cl <sub>2</sub> (g)	H <sub>2</sub> O(g)
$\Delta H_f^\ominus/\text{kJ mol}^{-1}$	-92	0	0	-242
$S^\ominus/\text{J K}^{-1}\text{mol}^{-1}$	187	205	223	189

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

.....

.....

.....

.....

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

.....

.....

.....

.....

(6 marks)



**Table 1**  
Proton n.m.r chemical shift data

Type of proton	$\delta/\text{ppm}$
$\text{RCH}_3$	0.7–1.2
$\text{R}_2\text{CH}_2$	1.2–1.4
$\text{R}_3\text{CH}$	1.4–1.6
$\text{RCOCH}_3$	2.1–2.6
$\text{ROCH}_3$	3.1–3.9
$\text{RCOOCH}_3$	3.7–4.1
$\text{ROH}$	0.5–5.0

**Table 2**  
Infra-red absorption data

Bond	Wavenumber/ $\text{cm}^{-1}$
$\text{C—H}$	2850–3300
$\text{C—C}$	750–1100
$\text{C=C}$	1620–1680
$\text{C=O}$	1680–1750
$\text{C—O}$	1000–1300
$\text{O—H}$ (alcohols)	3230–3550
$\text{O—H}$ (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**

Turn over 

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)

- 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**

Turn over 

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

Standard electrode potentials	$E^\ominus/V$
$2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$	0.00
$\text{Br}_2(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Br}^-(\text{aq})$	+1.09
$2\text{BrO}_3^-(\text{aq}) + 12\text{H}^+(\text{aq}) + 10\text{e}^- \longrightarrow \text{Br}_2(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$	+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* .....

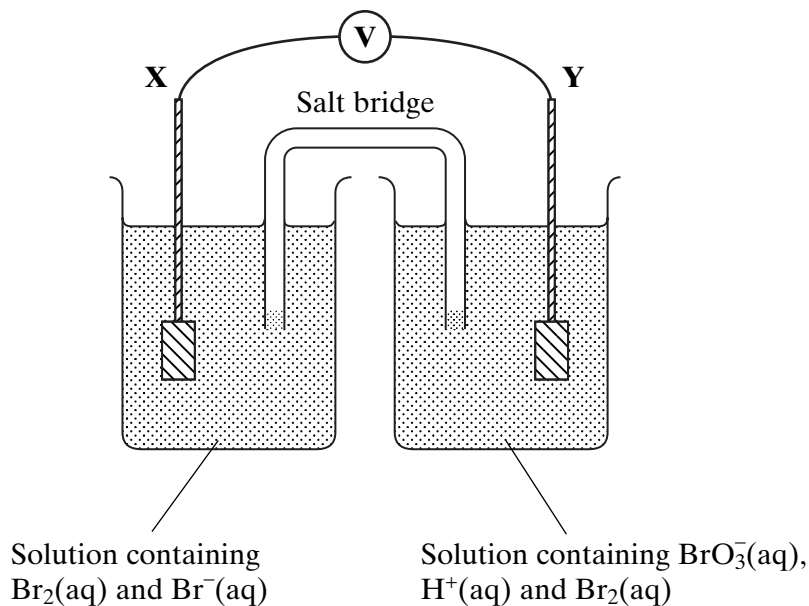
.....

*Change in electrode potential* .....

(3 marks)



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



(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

- 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  $1.0 \text{ mol dm}^{-3}$  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<sup>3</sup> of a 1.00 mol dm<sup>-3</sup> solution of ethanoic acid. The acid dissociation constant,  $K_a$ , for ethanoic acid is  $1.70 \times 10^{-5}$  mol dm<sup>-3</sup> at 298 K.

.....

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

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(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

**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,  $\text{CH}_3\text{CHClCH}_3$ , 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  $\text{VO}_2^+$  ions in this solution. When an excess of zinc was added to this solution, the  $\text{VO}_2^+$  ions were reduced to  $\text{V}^{2+}$  ions and the zinc was oxidised to  $\text{Zn}^{2+}$  ions.

After the unreacted zinc had been removed, the solution was titrated against a  $0.0200 \text{ mol dm}^{-3}$  solution of potassium manganate(VII). In the titration,  $38.5 \text{ cm}^3$  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  $\text{VO}_2^+$  to  $\text{V}^{2+}$  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  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ,  $(\text{CH}_3)_3\text{COH}$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$  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  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  and of  $(\text{CH}_3)_3\text{COH}$ . (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,  $\text{Be}_2\text{C}$ , 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