Surname		Other Names	
Centre Number			Candidate Number									
Candidate Signature												

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General Certificate of Education
June 2002
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

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

Tuesday 25 June 2002 Morning Session

In addition to this paper you will require:
the AQA Periodic Table (Reference CHEM/PT/EX);
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.

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 mol^{-1} K^{-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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10			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

Answer **all** the questions in the spaces provided.
You are advised to spend about 1 hour on this section.

1 (a) The following reaction occurs in the high-temperature preparation of titanium(IV) chloride.

$$TiO_2(s) + C(s) + 2Cl_2(g) \longrightarrow TiCl_4(l) + CO_2(g)$$

(i) Use the data given below to calculate the standard enthalpy change and the standard entropy change for this reaction.

Substance	$TiO_2(s)$	C(s)	$Cl_2(g)$	$TiCl_4(l)$	$CO_2(g)$
$\Delta H_f^{\ominus}$/kJ mol^{-1}	–940	0	0	–804	–394
$S^{\ominus}$/J K^{-1} mol^{-1}	49.9	5.7	223	252	214

Standard enthalpy change .....

.....

.....

.....

.....

Standard entropy change .....

.....

.....

.....

(ii) Calculate the temperature at which this reaction ceases to be feasible.

.....

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.....

.....

(9 marks)

(b) In the industrial extraction of titanium, $TiCl_4$ is reduced to titanium in an inert atmosphere.

(i) Write an equation for this reduction process.

.....

(ii) Explain why it is essential to exclude air when this reduction takes place.

.....

.....

(3 marks)

(c) Write an equation for the reaction of $TiCl_4$ with water.

.....

(1 mark)

13

TURN OVER FOR THE NEXT QUESTION

2 Large blocks of magnesium are bolted onto the hulls of iron ships in an attempt to prevent the iron being converted into iron(II), one of the steps in the rusting process.

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

	$E^{\ominus}$/V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.37
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.44
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40

(a) Calculate the e.m.f. of the cell represented by $Mg(s)|Mg^{2+}(aq)||Fe^{2+}(aq)|Fe(s)$ under standard conditions. Write a half-equation for the reaction occurring at the negative electrode of this cell when a current is drawn.

Cell e.m.f. .....

Half-equation .....

(2 marks)

(b) Deduce how the e.m.f. of the cell $Mg(s)|Mg^{2+}(aq)||Fe^{2+}(aq)|Fe(s)$ changes when the concentration of Mg^{2+} is decreased. Explain your answer.

Change in e.m.f. .....

Explanation .....

.....

(3 marks)

(c) Calculate a value for the e.m.f. of the cell represented by $Pt(s)|OH^-(aq)|O_2(g)||Fe^{2+}(aq)|Fe(s)$ and use it to explain why iron corrodes when in contact with water which contains dissolved oxygen.

Cell e.m.f. .....

Explanation .....

.....

(2 marks)

7

3 (a) State the origin of the colour of transition-metal complexes.

.....

.....

(2 marks)

(b) Give **three** changes to a transition-metal complex which result in a change in colour.

Change 1 .....

Change 2 .....

Change 3 .....

(3 marks)

(c) You are provided with a 1.00 mol dm^{-3} solution of iron(III) ions and a visible-light spectrophotometer (colorimeter). Outline a plan for experiments using this solution and this apparatus which would enable you to determine the concentration of iron(III) ions in a solution of unknown concentration.

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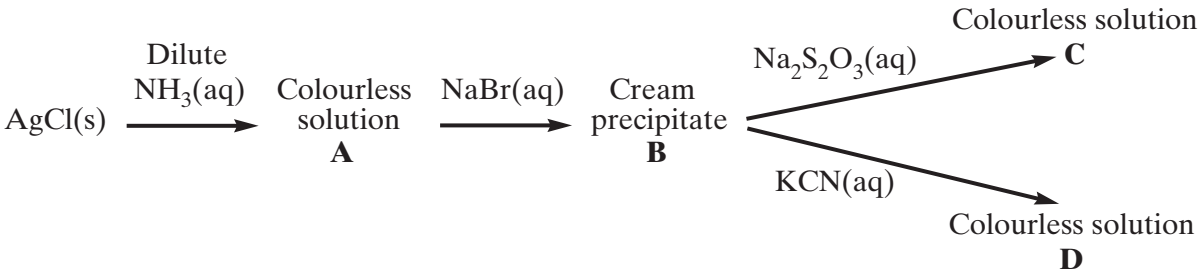
(5 marks)

10

4 Consider the reaction sequence below.



(a) Identify the silver-containing species in **A**, give its shape and state a use for it in organic chemistry.

Species .....

Shape .....

Use .....

.....

(3 marks)

(b) (i) Identify the cream precipitate **B** and the silver-containing species in **C**.

Precipitate B .....

*Silver-containing species in **C*** .....

(ii) Write an equation for the reaction in which the silver-containing species in **C** is formed from **B** and explain the use of this reaction in photographic processing.

Equation .....

Explanation .....

.....

(4 marks)

(c) Identify the silver-containing species in **D**, and state **one** use of solutions containing this species.

Species .....

Use .....

(2 marks)

(d) What can be deduced about the outer electronic configuration of silver in each of the species **A**, **C** and **D** from the fact that all the species are colourless?

.....

(1 mark)

10

5 (a) (i) Write an equation to show why aqueous chromium(III) chloride is acidic.

.....

(ii) Explain why aqueous chromium(III) chloride is more acidic than aqueous chromium(II) chloride.

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.....

.....

(3 marks)

(b) The addition of sodium hydroxide or of sodium carbonate to aqueous chromium(III) chloride results in the formation of the same green precipitate.

(i) Identify this green precipitate.

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(ii) State the role shown by both sodium hydroxide and sodium carbonate in the formation of this green precipitate.

.....

(iii) Identify the gas evolved when carbonate ions react with aqueous chromium(III) ions and write an equation for the reaction occurring.

Gas evolved .....

Equation .....

.....

.....

(4 marks)

(c) State the reagents which could be used to convert aqueous chromium(III) ions into chromate(VI) ions.

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.....

(2 marks)

9

6 (a) State what is meant by the term *co-ordinate bond*.

.....

.....

(2 marks)

(b) Define the terms *Brønsted–Lowry acid* and *Lewis acid*.

Brønsted–Lowry acid .....

Lewis acid .....

(2 marks)

(c) State what is meant by the term *bidentate ligand*.

.....

.....

(2 marks)

(d) State how the co-ordination number of cobalt(II) ions in aqueous solution changes when an excess of chloride ions is added. Give a reason for the change.

Change in co-ordination number .....

Reason for change .....

.....

(2 marks)

(e) Suggest why the enthalpy change for the following reaction is close to zero.

$[Co(NH_3)_6]^{2+} + 3NH_2CH_2CH_2NH_2 \rightarrow [Co(NH_2CH_2CH_2NH_2)_3]^{2+} + 6NH_3$

.....

.....

(2 marks)

(f) Deduce the formula of the compound formed when ethane-1,2-diamine is treated with an excess of hydrochloric acid.

.....

(1 mark)

11

SECTION B

Answer **all** of the questions below in the space provided on pages 11 to 20 of this booklet.

7 A 4.54 g sample of PCl_5 was heated in a sealed flask at 525 K. Partial decomposition occurred as shown by the equation below.

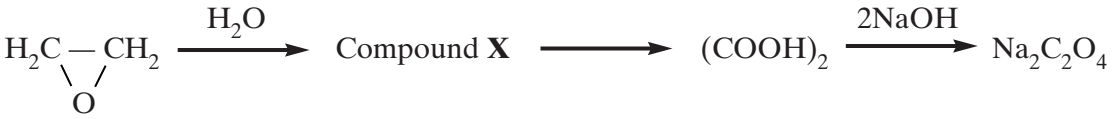
$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

At equilibrium, 45.0% of the PCl_5 had dissociated and the total pressure in the flask was 91.9 kPa.

(a) Calculate a value for the equilibrium constant K_p of this reaction at 525 K. *(9 marks)*

(b) In the gaseous state, both PCl_3 and PCl_5 exist as molecules. In the solid state, PCl_5 is ionic and made up of two species both of which contain phosphorus. Sketch and name the shape of the PCl_3 molecule and that of the PCl_5 molecule. Suggest a formula and a shape for each of the two ionic species present in solid PCl_5 *(6 marks)*

8 The reaction scheme below shows the conversion of epoxyethane into sodium ethanedioate.



(a) Identify compound **X**. State the reageants and conditions required to convert **X** into ethanedioic acid. Draw the structure of the anion in sodium ethanedioate. *(4 marks)*

(b) The addition of sodium ethanedioate to an aqueous solution containing $[Co(H_2O)_6]^{2+}$ ions results in the formation of a more stable complex ion. Draw the structure of the complex ion formed and explain, in thermodynamic terms, why this substitution reaction occurs. *(4 marks)*

(c) (i) Sketch the pH curve for the titration of ethanedioic acid with aqueous sodium hydroxide. Write equations for the reactions which occur during this titration.

(ii) A 25.0 cm^3 sample of a solution of ethanedioic acid was found to react with exactly 18.2 cm^3 of a 0.145 mol dm^{-3} solution of sodium hydroxide. Calculate the concentration of the ethanedioic acid solution.

What volume of sodium hydroxide solution would have been required if the solution titrated had been sodium hydrogenethanedioate, $NaHC_2O_4$, of the same concentration rather than ethanedioic acid? *(7 marks)*

Turn over ▶

9 (a) The reaction between aqueous persulphate ions, $S_2O_8^{2-}(aq)$, and iodide ions, $I^-(aq)$, is catalysed by $Fe^{2+}(aq)$ ions. Suggest why this reaction has a high activation energy. Write equations to explain the catalytic action of $Fe^{2+}(aq)$ ions.
Suggest why $V^{3+}(aq)$ ions will also act as a catalyst for this reaction but $Mg^{2+}(aq)$ ions will not. *(6 marks)*

(b) Outline a mechanism for the reaction between benzene and ethanoyl chloride and explain why $AlCl_3$ acts as a Lewis acid catalyst for this reaction. Predict, with an explanation in each case, the suitability of $FeCl_3$ and of NH_4Cl to act as a catalyst for this reaction. *(9 marks)*

10 (a) **P** and **Q** are oxides of Period 3 elements.

Oxide **P** is a solid with a high melting point. It does not conduct electricity when solid but does conduct when molten or when dissolved in water. Oxide **P** reacts with water forming a solution with a high pH.

Oxide **Q** is a colourless gas at room temperature. It dissolves in water to give a solution with a low pH.

(i) Identify **P**. State the type of bonding present in **P** and explain its electrical conductivity. Write an equation for the reaction of **P** with water.

(ii) Identify **Q**. State the type of bonding present in **Q** and explain why it is a gas at room temperature. Write an equation for the reaction of **Q** with water.
(9 marks)

(b) **R** is a hydroxide of a Period 3 element. It is insoluble in water but dissolves in both aqueous sodium hydroxide and aqueous sulphuric acid.

(i) Give the name used to describe this behaviour of the hydroxide.

(ii) Write equations for the reactions occurring.

(iii) Suggest why **R** is insoluble in water. *(6 marks)*

END OF QUESTIONS

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