Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1095/01

CHEMISTRY CH5

P.M. TUESDAY, 19 June 2012

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

1095
010001

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a copy of the **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

You are reminded that marking will take into account the Quality of Written Communication in all written answers.

Examiner only

SECTION A

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

1. Potassium peroxodisulfate(VI) (persulfate) is a white crystalline compound of formula $K_2S_2O_8$. It is a powerful oxidising agent and has uses as a food additive, in hair dyes and as a nappy steriliser.

(a) Unusually for potassium compounds, it is not very soluble in water.

Temperature / °C	Solubility / g per 100 g H_2O
0	1.75
20	5.29

1 dm^3 of a saturated solution of potassium persulfate at 20 °C was cooled to 0 °C. Calculate the mass of solid potassium persulfate that crystallised from the solution. [2]

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(b) (i) A hot solution of potassium persulfate slowly decomposes, giving oxygen as one of the products.

$$2K_2S_2O_8(aq) + 2H_2O(l) \longrightarrow 4KHSO_4(aq) + O_2(g)$$

Calculate the maximum volume of oxygen gas that can be produced at 80 °C when a solution containing 0.100 mol of potassium persulfate decomposes as shown above. [2]

[At 80 °C 1 mol of oxygen has a volume of 29.0 dm^3]

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(ii) Suggest a way that the rate of decomposition of the potassium persulfate solution described in (i) could be measured. [1]

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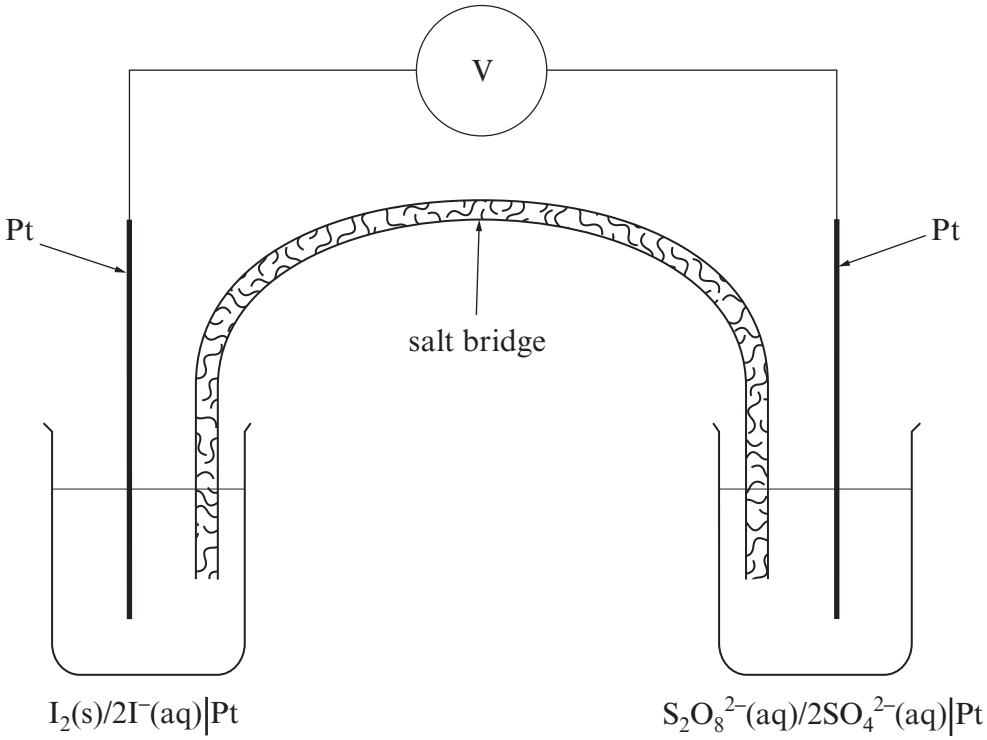
(c) The diagram below shows a cell that uses persulfate ions in aqueous solution.



(i) State the role of the platinum electrodes in this cell. [1]

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(ii) Use the information given in the equations to state and explain the direction of electron flow in the external circuit. [2]

$$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq) \qquad E^{\ominus} = +2.01\ V$$

$$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq) \qquad E^{\ominus} = +0.54\ V$$

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(d) The reaction between persulfate ions and iodide ions in aqueous solution is

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

In an experiment to follow the rate of this reaction, the values below were obtained.

Experiment	Initial rate / mol $dm^{-3}s^{-1}$	Initial concentration of $S_2O_8^{2-}$ / mol dm^{-3}	Initial concentration of I^- / mol dm^{-3}
1	8.64×10^{-6}	0.0400	0.0100
2	3.46×10^{-5}	0.0800	0.0200

(i) The reaction is first order with respect to iodide ions. Use both the initial rate values and the concentrations to show that the order with respect to persulfate ions is also first order. [2]

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(ii) Write the rate equation for this reaction and use it to calculate the value of the rate constant, *k*, giving its units. [3]

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..... *Units* .....

(iii) It is suggested that this reaction occurs in two steps.

Step 1 $S_2O_8^{2-} + I^- + H_2O \longrightarrow 2SO_4^{2-} + HOI + H^+$

Step 2 $HOI + H^+ + I^- \longrightarrow H_2O + I_2$

State, using your answer to (ii), why Step 1 is the rate-determining step. [1]

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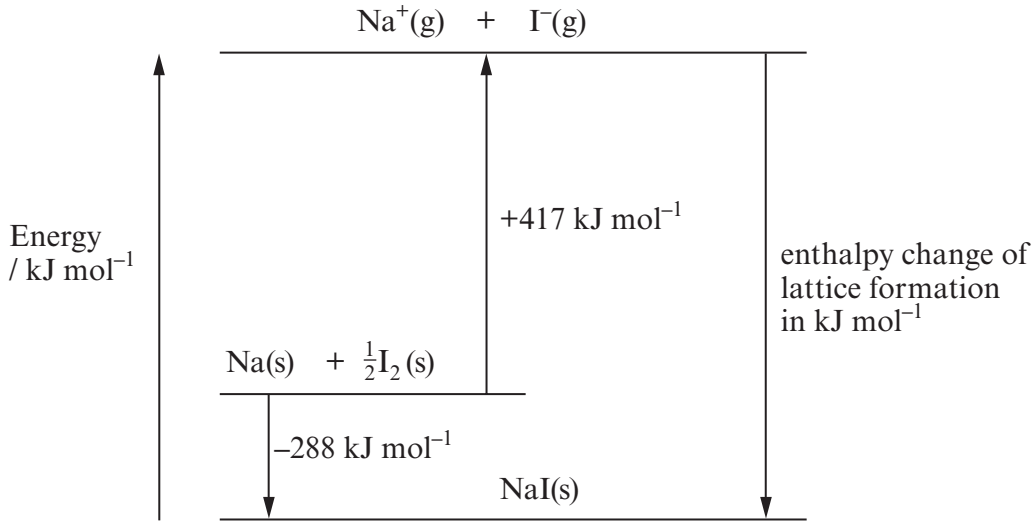
Total [14]

2. *(a)* The diagram shows an outline of the Born-Haber cycle for the formation of sodium iodide (NaI) from its elements.



Use the information given to calculate the enthalpy change of lattice formation (in kJ mol^{-1}) of sodium iodide. [2]

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(b) Sodium iodide is very soluble in water at room temperature.

(i) Complete the sentence below using the relevant enthalpy terms.

For a compound to be very soluble in water the value of the enthalpy of

..... will be greater than the enthalpy of .....

[1]

(ii) Aqueous solutions of sodium iodide become yellow in the presence of oxygen due to the slow production of iodine.
One suggested reason for this is that a low concentration of hydrogen ions in the solution produces iodine according to the equation below.

$$4H^+(aq) + 4I^-(aq) + O_2(aq) \rightleftharpoons 2I_2(aq) + 2H_2O(l)$$

Use Le Chatelier's principle to suggest a reagent that you could add, apart from water, to decrease the amount of yellow iodine present. Explain your choice. [2]

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(c) Sodium chloride and sodium iodide both react with concentrated sulfuric acid to give the corresponding hydrogen halide e.g.

$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI$$

However, the reaction with sodium iodide continues, giving hydrogen sulfide and iodine as two of the products. This further type of reaction does not occur when sodium chloride is used in place of sodium iodide.

(i) Describe what is **seen** when solid sodium iodide is added to concentrated sulfuric acid. [2]

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(ii) The following equations show the standard electrode potentials for the Cl_2/Cl^- and I_2/I^- systems.

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \qquad E^{\ominus} = +1.36\,V$$

$$I_2 + 2e^- \rightleftharpoons 2I^- \qquad E^{\ominus} = +0.54\,V$$

Use these values to explain why only hydrogen iodide (represented as I^- in the equation) is able to further react with concentrated sulfuric acid in this way. [2]

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(d) The reaction of chlorine with sodium hydroxide solution gives aqueous sodium chlorate(I) as one of the chlorine-containing products.

(i) Give the equation for this reaction. [1]

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(ii) State **one** use for a solution of sodium chlorate(I). [1]

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Total [11]

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3. *Read the passage below and then answer the questions (a) to (e) in the spaces provided.*

Copper – an essential element

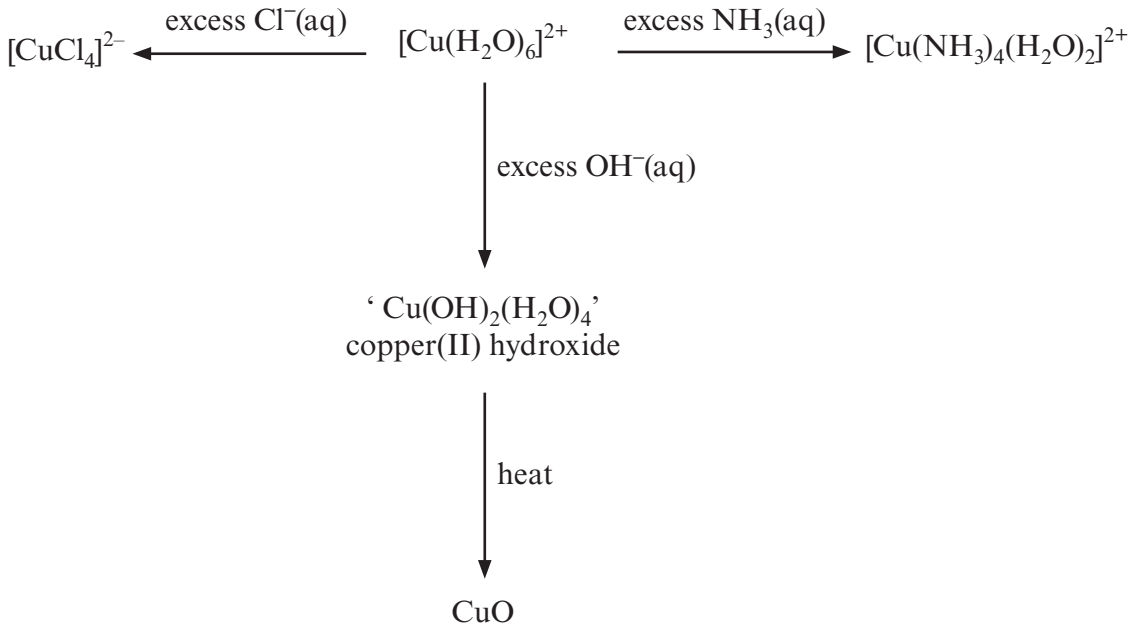
There is an ever-increasing world demand for copper and this has driven its cost upwards. This has led to the extraction of copper from sources once thought to be uneconomic. One such source of copper is the spoil heaps from old mines. The spoil heap material is crushed and then sprayed with acidified water in the presence of the bacterium *Thiobacillus ferrooxidans*. These bacteria convert any iron present to aqueous iron(III) ions, which then oxidise sulfide ions to aqueous sulfate(VI) ions, SO_4^{2-}. A solution containing copper(II) sulfate is produced that is then treated with iron to leave copper.

$$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$$

The concentration of copper in this copper(II) sulfate solution can be found by a variety of methods, which include

- precipitating the copper and weighing it
- reacting the solution with an excess of iodide ions and titrating the liberated iodine with aqueous sodium thiosulfate
- titrating the copper(II) ions with ethylenediaminetetra-acetic acid (EDTA)
- using instrumental methods such as atomic absorption and X-ray fluorescence spectroscopy

Copper(II) sulfate continues to be a familiar and commonly used substance in schools and colleges and its reactions are typical of many transition metal compounds. For example, in aqueous solution the copper ions are present as the complex cation, $[Cu(H_2O)_6]^{2+}$. The water molecules in this complex ion can be replaced by other ligands.



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Copper is a relatively unreactive metal and is easy to obtain by the smelting of its ores, as was carried out in the Bronze Age. Small quantities of many transition metals can be produced by strongly heating the oxide with aluminium or magnesium. One application of this is the reaction of aluminium with iron(III) oxide to give molten iron that can be used to weld together lengths of railway track. A similar reaction occurs when magnesium is strongly heated with copper(II) oxide.

$$Mg(s) + CuO(s) \longrightarrow Cu(l) + MgO(s) \qquad \Delta H = -431\,kJ\,mol^{-1}$$

Transition metals also have important uses as catalysts and copper can be used as an economical catalyst in a number of organic processes, for example in the production of methanal.

$$CH_3OH \xrightarrow[600\ K]{Cu} \begin{matrix} H \\ \diagdown \\ C{=}O \\ \diagup \\ H \end{matrix}$$

- End of passage -

(a) The percentage of copper in a sample from a spoil heap was found by a titration using ethylenediaminetetra-acetic acid (EDTA).
19.20 cm^3 of an EDTA solution of concentration 0.010 mol dm^{-3} reacted with 50.00 cm^3 of a solution containing copper(II) ions.
EDTA reacts with copper(II) ions in a 1:1 mole ratio.

(i) Calculate the number of moles of EDTA solution used in the titration. [1]

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(ii) State the number of moles of copper(II) ions present in 50.00 cm^3 of the copper-containing solution. [1]

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(iii) Calculate the concentration of copper in the solution in **g dm^{-3}**. [2]

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(iv) The mass of the copper-containing sample was 11.56 g. All the copper in this sample was present in a solution of volume 1.00 dm^3.
Calculate the percentage of copper in the sample. [1]

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(b) Both copper and zinc are d-block elements. Explain, using electron configurations, why copper is described as a transition metal and zinc (whose compounds contain Zn^{2+} ions) is not. [2]
(QWC) [1]

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(c) The passage shows the formulae of some copper-containing species formed by ligand exchange *(line 20)*.
Complete the table below, stating the approximate shape and colour of the complex ions shown. [2]

Complex ion	Shape	Colour
$[CuCl_4]^{2-}$		
$[Cu(NH_3)_4(H_2O)_2]^{2+}$		

(d) Standard enthalpy of formation values, $\Delta H_f^{\ominus}$, can be used to calculate enthalpy changes, such as the reduction of copper(II) oxide by magnesium, described in the article *(line 27)*.
Some $\Delta H_f^{\ominus}$ values are given in the table below.

Metal oxide	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
CuO	–157
PbO	–217

State and explain how the $\Delta H_f^{\ominus}$ values for these two oxides give an indication of their relative stability. [2]

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Examiner only

(e) Many transition metals and their compounds act as catalysts. The article describes copper acting as a catalyst in the oxidation of methanol *(line 30)*.

(i) Give **two** reasons why transition metals and their compounds can act as catalysts. [2]

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(ii) Give a reason, in terms of Green Chemistry, why scientists often seek new catalysts for established chemical processes. [1]

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Total [15]

Total Section A [40]

Turn over.

SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* In the reaction below carbon monoxide is acting as a reducing agent.

$$5CO + I_2O_5 \longrightarrow 5CO_2 + I_2$$

Use oxidation states (numbers) to show that carbon monoxide is acting as a reducing agent in this reaction. [2]

(b) State how the stabilities of the +II and +IV oxidation states vary down Group 4. [1]

(c) You are given two solutions. One contains aqueous aluminium ions, Al^{3+}, and the other contains aqueous lead(II) ions, Pb^{2+}.

(i) Describe a reaction to show that both of these ions exhibit amphoteric behaviour. Your answer should state the reagent(s) used, the names of any precipitates and any relevant observations. *Chemical equations are not required.* [4]
QWC [1]

(ii) Describe what is **seen** when iodide ions are added to an aqueous solution of Pb^{2+} ions. Give the **ionic** equation for the reaction that occurs. [2]

(d) Monomeric aluminium chloride is described as containing an electron-deficient species.

(i) Explain, using monomeric covalent aluminium chloride, what is meant by *electron deficient* and why this leads to the ready formation of the Al_2Cl_6 dimer.
You should show the structure of this dimer as part of your answer. [3]

(ii) The electron-deficient nature of the aluminium chloride monomer results in the compound having an affinity for chlorine-containing species. This is important in catalysis and also in the production of specialised solvents.
Give **one** example of the use of the monomer in either of these ways. [1]

(iii) On heating, gaseous dimeric aluminium chloride molecules dissociate into the monomer.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

I State **one** reason why the entropy of this gaseous system is increasing. [1]

II Use the equation

$$\Delta G = \Delta H - T\Delta S$$

to calculate the temperature at which the dissociation of gaseous Al_2Cl_6 molecules into gaseous $AlCl_3$ molecules just occurs spontaneously.
The entropy change for this reaction, ΔS, is 88 J mol^{-1} K^{-1} and the enthalpy change, ΔH, is 60 kJ mol^{-1}. [2]

(e) Solutions containing aqueous aluminium ions are weakly acidic because of the dissociation of one of the coordinated water molecules.

$$[Al(H_2O)_6]^{3+}(aq) \quad \rightleftharpoons \quad [Al(H_2O)_5(OH)]^{2+}(aq) \quad + \quad H^+(aq)$$

The acidity of this solution has been used to stop bleeding from minor cuts.

The expression for the equilibrium constant, in terms of concentrations, for the above system is shown below.

$$K_c \quad = \quad \frac{\left[\,[Al(H_2O)_5(OH)\,]^{2+}(aq)\right]\left[H^+(aq)\right]}{\left[\,[Al(H_2O)_6]^{3+}(aq)\right]}$$

Use this expression to calculate the pH of a solution of aluminium ions of concentration 0.10 mol dm^{-3}. The equilibrium constant, K_c, for this system is 1.26×10^{-5} mol dm^{-3}. [3]

Total [20]

Turn over.

5. *(a)* A student obtained some measurements of the partial pressures of reactants and products for the reaction between sulfur(IV) oxide and nitrogen(IV) oxide.

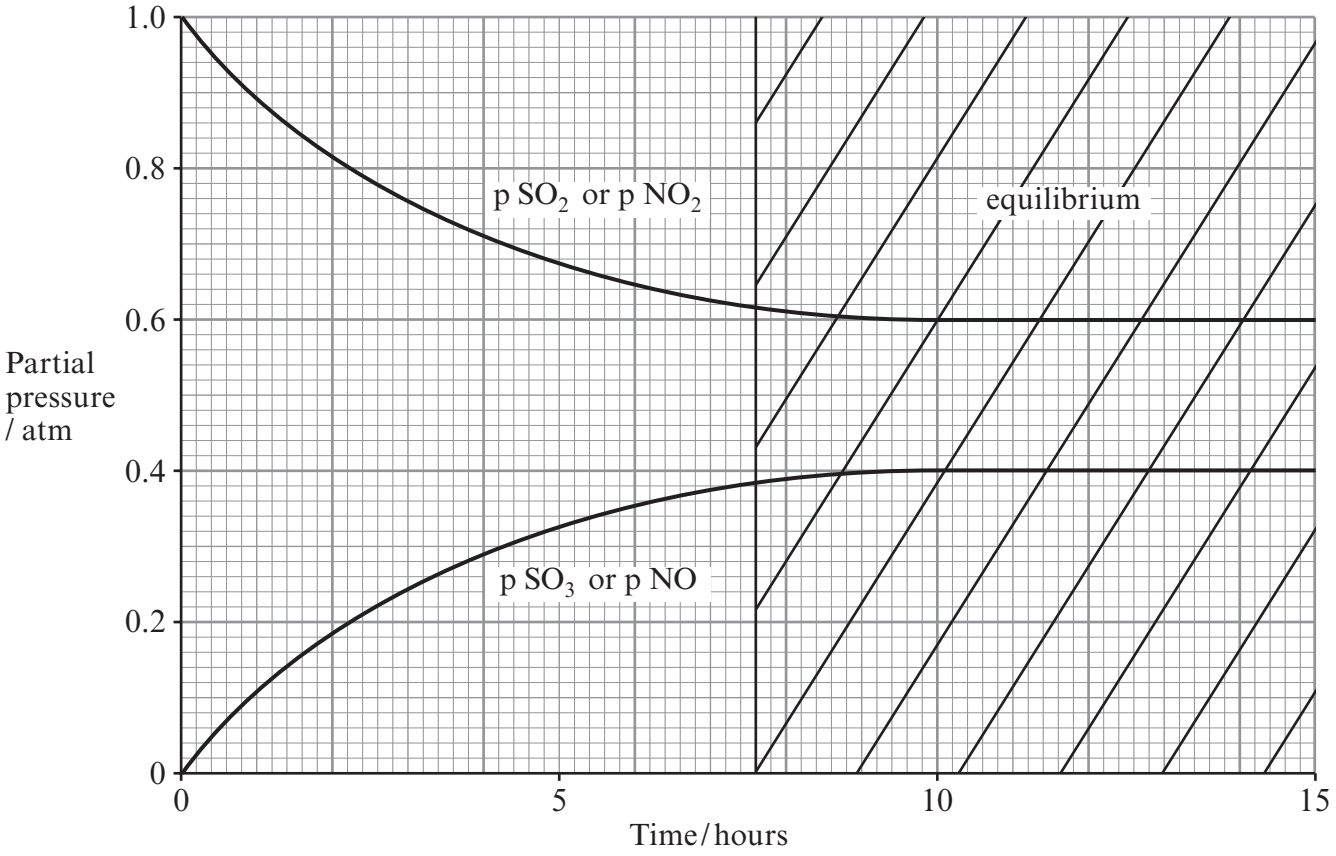
$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

The numerical value of K_p for this reaction is 2.5.

(i) Give the expression for the equilibrium constant in terms of partial pressures, K_p, stating its units (if any). [2]

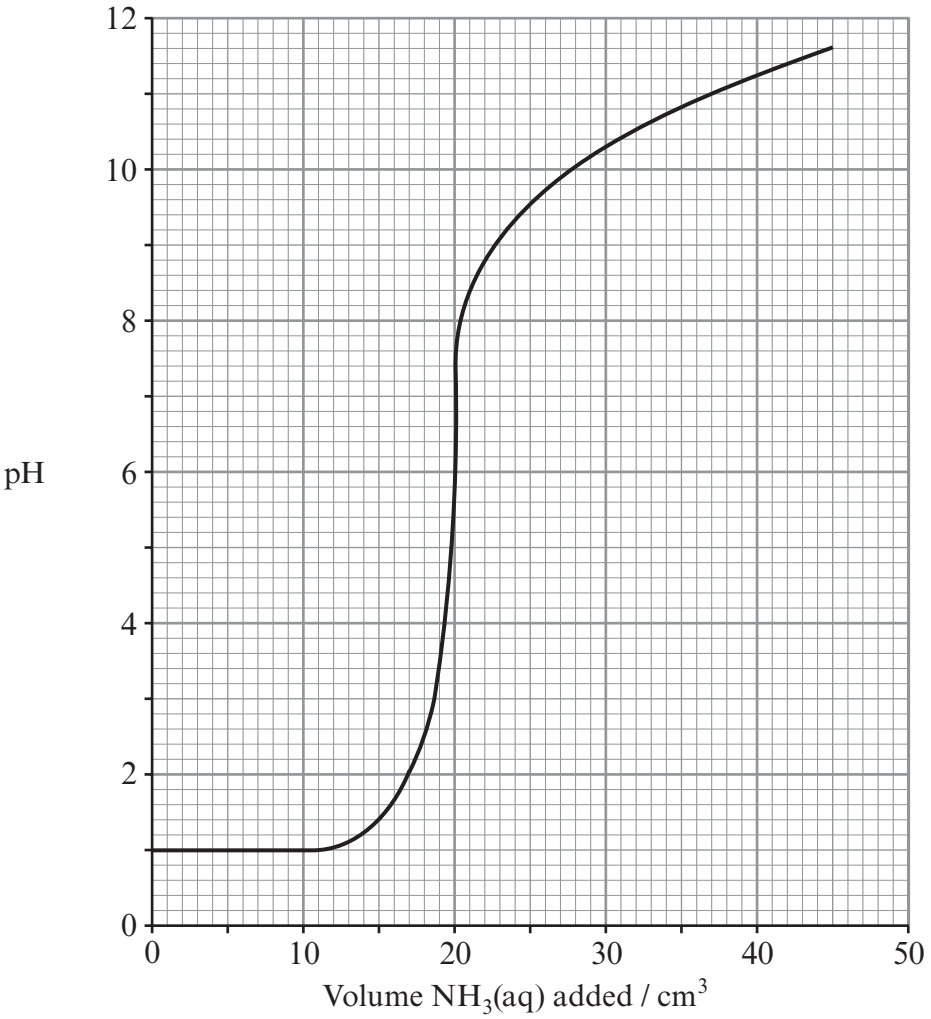
(ii) He decided to present his results in the form of the diagram below.

State the **two** things that are wrong with this diagram, explaining your answer. [4]



(iii) The enthalpy change for this reaction is –41 kJ mol^{-1}. State and explain how the value of the equilibrium constant would change (if at all) when the reaction is run at a higher temperature. [2]

(b) The acid-base titration curve for the reaction between aqueous solutions of nitric acid, HNO_3, and ammonia, both of concentration 0.100 mol dm^{-3}, is shown in the diagram. In this strong acid-weak base system, aqueous ammonia was added to 20.0 cm^3 of aqueous nitric acid.



(i) Describe and explain the shape of the curve obtained when aqueous ammonia is added to the aqueous nitric acid. [3]
QWC [1]

(ii) Deduce, using information obtained from the graph, the mole ratio of the two reactants in this titration. Explain your reasoning. [2]

(iii) I Explain why the pH of a solution of ammonium nitrate is not 7. [1]
II Use the graph to state the pH of the ammonium nitrate solution obtained at the equivalence point. [1]

Turn over.

(iv) Use your answer to (iii) to state the colour obtained if a few drops of the acid-base indicator bromophenol blue are added to the ammonium nitrate solution, giving the reason for your answer. [1]

pH	Colour
$\leqslant 2.8$	yellow
$\geqslant 4.7$	blue

(c) Ammonium nitrate ($M_r = 80$) is used in 'cold packs' to give a cooling effect for sports injuries. The solid crystals are added to water producing an endothermic reaction.

A typical 'cold pack' contains 40 g of ammonium nitrate that is dissolved in water to make 200 g of the solution. Calculate the molar concentration of the ammonium nitrate solution and hence the drop in temperature that occurs when this pack is used.

[1 mole of ammonium nitrate dissolved in water to make 1 kg of solution produces a drop in temperature of 6.2 °C] [3]

Total [20]

Total Section B [40]

GCE A level

1095/01-A

CHEMISTRY – PERIODIC TABLE
FOR USE WITH CH5

P.M. TUESDAY, 19 June 2012

THE PERIODIC TABLE