

General Certificate of Education
June 2005
Advanced Extension Award



CHEMISTRY

6821

Wednesday 29 June 2005 9.00 am to 12 noon

In addition to this paper you will require:

- a calculator,
- a 16-page answer book.

Time allowed: 3 hours

Instructions

- Use blue or black ink or ball-point pen.
- Write the information required on the front of your answer book. The **Examining Body** for this paper is AQA. The **Paper Reference** is 6821.
- Answer **all** questions.
- Show **all** your working.
- Do all rough work in the answer 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.
- Quality of Written Communication will be assessed in your answers to Question 5. You will be awarded a mark out of 3 which will take into account: the breadth and balance of examples chosen, the overall structure of the essay (organisation, avoidance of repetition), the correct use of chemical terms, and the appropriate use of equations, mechanisms, diagrams.
- You are expected to use a calculator where appropriate.
- A Periodic Table is provided on page 2 of this paper.

Advice

- You are advised to spend about 30 minutes on **Section A**, 2 hours on **Section B** and 30 minutes on **Section C**.

TURN OVER FOR THE FIRST QUESTION

Turn over ►

SECTION A

You are advised to spend about 30 minutes on this section.

1**Total for this question: 10 marks**

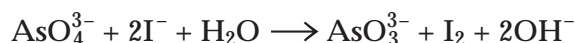
The toxicity of compounds containing arsenic and antimony has been known for a very long time. Arsenic(III) oxide, As_2O_3 , is described as an amphoteric oxide because it reacts with both acids and bases. For centuries, before analytical techniques were developed, the colourless and odourless solution of arsenic(III) oxide in water was a commonly used poison. Compounds of antimony are less poisonous than those of arsenic. Antimony potassium tartrate was for many years used to induce vomiting although too large a dose could prove fatal.

Small amounts of either arsenic or antimony present in any compound in body tissue can be detected using zinc in the presence of an acid. Arsenic compounds form arsine, AsH_3 , and antimony compounds form stibine, SbH_3 . Both hydrides are gases at room temperature.

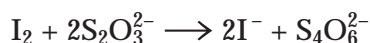
Both arsine and stibine decompose into their elements when heated. A film of arsenic or antimony can form on a weighed cool glass surface thus enabling the mass of the element produced to be determined. Stibine decomposes at a lower temperature than arsine.

The two elements, arsenic and antimony, can be distinguished by adding aqueous sodium chlorate(I). Arsenic reacts to form a solution which contains arsenate(V) ions, AsO_4^{3-} , and chloride ions. Antimony does not react with aqueous sodium chlorate(I), a property which shows the greater metallic character of antimony compared to arsenic.

In aqueous solution, arsenate(V) ions oxidise iodide ions to iodine as shown by the equation:



The iodine produced can be titrated against sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$. Thiosulphate ions reduce iodine to iodide as shown by the equation



Poisoning by arsenic continues to be a problem today. Ground water used for drinking and irrigation in Bangladesh and West Bengal is contaminated by arsenic compounds derived from sedimentary rock. The process by which water becomes contaminated with arsenic compounds is complex. Laboratory experiments suggest that arsenate(V) ions, AsO_4^{3-} , normally strongly adsorbed onto hydrated iron(III) oxide, are released when the iron(III) oxide is reduced to iron(II) oxide. Ethanoate ions, present in the water, act as the reducing agent in this reaction. The ethanoate ions are oxidised to carbon dioxide; hydrogen ions are also produced in the reaction.

-
- (a) Write equations for **two** reactions which illustrate the *amphoteric* nature of As_4O_6 . (2 marks)
- (b) Write an equation for the formation of AsH_3 by the reaction of As_4O_6 with zinc in the presence of hydrogen ions. (1 mark)
- (c) Suggest why stibine decomposes at a lower temperature than arsine. (3 marks)
- (d) The sodium arsenate(V) present in a sample of body tissue was extracted using water. The solution obtained was treated with an excess of potassium iodide. The liberated iodine reacted with 18.5 cm^3 of a $0.0500 \text{ mol dm}^{-3}$ solution of sodium thiosulphate. Calculate the mass of arsenic present in the sample. (3 marks)
- (e) Write a half-equation for the oxidation of ethanoate ions in aqueous solution to carbon dioxide and hydrogen ions. (1 mark)

TURN OVER FOR THE NEXT QUESTION

Turn over ►

SECTION B

Answer all three questions in this section.

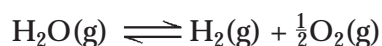
You are advised to spend about 40 minutes on each question.

Each question carries 30 marks.

2**Total for this question: 30 marks**

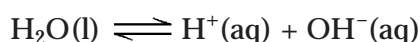
This question is about the chemistry of water.

- (a) Water can be formed by the exothermic reaction between hydrogen and oxygen. This reaction can be reversed and the following equilibrium established.



At a temperature of 3000 K and an overall pressure of 115 kPa (1.14 atm), 5.0% of the water is converted into hydrogen and oxygen.

- (i) Calculate the value of K_p for this equilibrium under these conditions. (6 marks)
- (ii) Comment on how you would expect this value of K_p to change with an increase in the temperature and how K_p would change with an increase in the overall pressure. (3 marks)
- (iii) Suggest, with a reason, whether or not this reaction would be a suitable method for the industrial manufacture of hydrogen. (1 mark)
- (b) In the liquid state, at 298 K, water dissociates slightly.

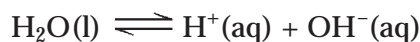


The forward reaction is first order with respect to water and has a rate constant $k_1 = 2.50 \times 10^{-5} \text{ s}^{-1}$

The reverse reaction is second order overall. It is first order with respect to $\text{H}^+(\text{aq})$ ions and also with respect to $\text{OH}^-(\text{aq})$ ions. This reverse reaction has a rate constant $k_2 = 1.39 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

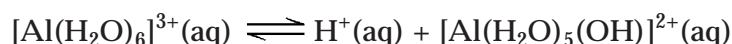
- (i) In terms of activation energies, suggest an explanation for the relative magnitudes of the rate constants k_1 and k_2 . (3 marks)

- (ii) Write rate equations for the forward and reverse reactions. Write an expression for the equilibrium constant K_c for the following equilibrium. Your expression for K_c must include a term for the concentration of water, $[\text{H}_2\text{O}(\text{l})]$.



Use this expression and the rate equations to calculate a value for K_c . (4 marks)
(You must calculate a value for $[\text{H}_2\text{O}(\text{l})]$ in mol dm^{-3} .)

- (iii) Explain why the expression $K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$ has a constant value at a fixed temperature and use your answer to part (b) (ii) to show that the value of K_w at 298 K is $1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. (3 marks)
- (iv) Calculate the percentage of water molecules converted into $\text{H}^+(\text{aq})$ ions at 298 K. (2 marks)
- (c) Water also releases $\text{H}^+(\text{aq})$ ions when it is bonded to metal ions. For example, consider the hydrated aluminium ion



For this dissociation the $\text{p}K_a$ value is 4.90

- (i) Calculate the percentage of bonded water molecules converted into $\text{H}^+(\text{aq})$ ions. In your calculation you may assume that the original concentration of the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ion is 1.00 mol dm^{-3} . Suggest, in terms of bonding, why your answer is different from your answer to part (b) (iv). (4 marks)
- (ii) Calculate the pH of a buffer solution formed by adding 20 cm^3 of a 1.0 mol dm^{-3} aqueous solution of sodium hydroxide to 80 cm^3 of a 1.0 mol dm^{-3} aqueous solution of aluminium ions. You may assume that the only aluminium-containing ions in the solution are $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ and $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}(\text{aq})$. (4 marks)

Turn over ►

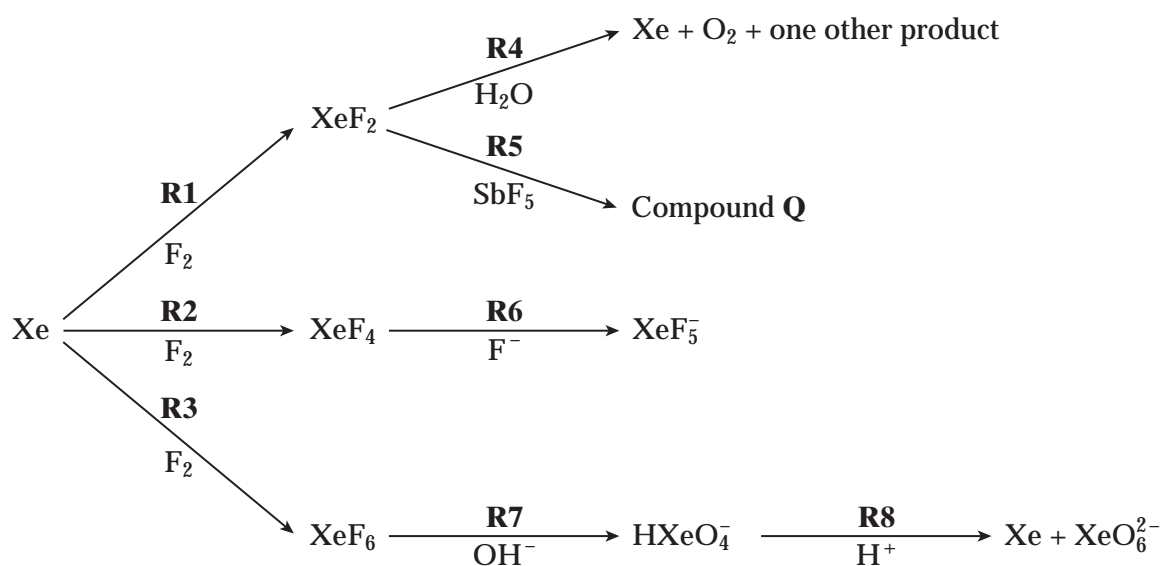
3

Total for this question: 30 marks

- (a) In transition metal complexes, Cl^- ions attach to just one position on the transition metal ion and are said to be unidentate. The ligand ethane-1,2-diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, which can attach to a transition metal ion in two adjacent positions using the lone pairs on the nitrogen atoms, is said to be bidentate.

The complex ion $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^+$ has both geometrical and optical isomers. Draw the structures of these isomers. (4 marks)

- (b) Xenon reacts with fluorine under different conditions to form different xenon fluorides. Consider the reaction scheme shown below.



- (i) Reaction **R1** occurs in sunlight; suggest a free-radical mechanism for this reaction. (3 marks)
- (ii) Write an equation for reaction **R4**. (1 mark)
- (iii) The ion formed in reaction **R6**, XeF_5^- , is planar.

Draw diagrams, showing all the outer shell lone pair electrons on the central Xe atom for XeF_2 , XeF_4 and XeF_5^- . Deduce the bond angle in XeF_5^- . (6 marks)

- (iv) In reaction **R5**, XeF_2 reacts in a 1 : 1 ratio with SbF_5 to form an ionic compound, **Q**, in which xenon is present only in the cation.

Deduce the formulae of the ions present in **Q** and give a 'curly arrow' mechanism for the formation of **Q** by this reaction. (3 marks)

- (v) Write an equation for the formation of HXeO_4^- in reaction **R7**. (1 mark)

- (vi) A redox reaction in which the same species is both oxidised and reduced is known as a disproportionation reaction. Reaction **R8** is the disproportionation, in acidic solution, of HXeO_4^- .

Write half-equations for the oxidation and reduction processes involved in this disproportionation reaction, and write an overall equation for the reaction. (3 marks)

- (c) In acidified aqueous solution, the hydroxylammonium ion, $(\text{NH}_3\text{OH})^+$, reduces Fe^{3+} ions to Fe^{2+} ions. The hydroxylammonium ion is oxidised, forming a gaseous oxide of nitrogen as the only nitrogen-containing product.

A sample of hydroxylammonium sulphate, $(\text{NH}_3\text{OH})_2\text{SO}_4$, of mass 0.711 g was dissolved in water and the solution was made up to 100 cm^3 in a volumetric flask. A 10.0 cm^3 sample of this solution was mixed with an excess of acidified aqueous Fe^{3+} ions. Some of the Fe^{3+} ions were reduced to Fe^{2+} ions by the $(\text{NH}_3\text{OH})^+$ ions. It was found that this mixture required 17.35 cm^3 of $0.0200\text{ mol dm}^{-3}$ aqueous potassium manganate(VII) to oxidise all these Fe^{2+} ions back to Fe^{3+} ions.

Calculate the reacting mole ratio of $(\text{NH}_3\text{OH})^+ : \text{Fe}^{3+}$ in this reaction.

Deduce the oxidation state of nitrogen in $(\text{NH}_3\text{OH})^+$ and in the final nitrogen oxide and hence identify the nitrogen oxide formed.

Write an overall equation for the reaction. (9 marks)

TURN OVER FOR THE NEXT QUESTION

Turn over ►

4

Total for this question: 30 marks

- (a) (i) Outline a mechanism for the reaction of butane with chlorine to form 2-chlorobutane. State a necessary condition for the reaction. (4 marks)
- (ii) Draw the other structural isomer of chlorobutane formed in this reaction. Predict the mole ratio of these isomers of chlorobutane in the product mixture and give a reason for your answer. (2 marks)
- (iii) The sample of 2-chlorobutane obtained consists of a mixture of two optical isomers. Suggest why this mixture is formed. (2 marks)
- (iv) Further reaction of 2-chlorobutane with chlorine leads to the formation of 2,3-dichlorobutane. Each molecule of 2,3-dichlorobutane contains two identical chiral centres. Explain why only three stereoisomers of 2,3-dichlorobutane exist. (2 marks)
- (b) Bromoethane reacts with magnesium in dry ethoxyethane as solvent to form ethylmagnesium bromide, $\text{CH}_3\text{CH}_2\text{MgBr}$. This can act as a source of CH_3CH_2^- ions which react with molecules containing a $\text{C}=\text{O}$ group to form ions with new $\text{C}-\text{C}$ bonds. Reactions of these new ions with dilute acid give products which contain an OH group.
- (i) Outline a possible mechanism for the reaction of CH_3CH_2^- with propanone and the subsequent reaction with dilute acid. (3 marks)
- (ii) Draw the structure of the organic product of the reaction of carbon dioxide with ethylmagnesium bromide followed by acidification. (1 mark)
- (iii) By stating reagents and intermediates, suggest a synthesis of 3-methylpentan-3-ol using ethylmagnesium bromide and ethanal as starting materials. (4 marks)
- (iv) Suggest why ethylmagnesium bromide reacts with water and give the molecular formula of the organic product formed. (2 marks)

- (c) Ten different compounds **A** to **J** are structural isomers with molecular formula $C_5H_8O_2$

Use the information below to suggest a structure for each of the compounds **A** to **J**.

A to **D** all react with sodium hydrogencarbonate to produce a colourless gas.

All four compounds contain a branched carbon chain and none shows geometrical isomerism. **A** exists as a pair of optical isomers.

E to **J** do not react with sodium hydrogencarbonate.

E shows geometrical isomerism and reacts with aqueous sodium hydroxide to form methanol as one of the products.

F does not show geometrical isomerism and reacts with aqueous sodium hydroxide to form sodium ethanoate.

G can be hydrolysed to form a compound which is oxidised by acidified potassium dichromate(VI) giving pentanedioic acid.

H, **I** and **J** all have only two peaks in their proton n.m.r. spectra.

The areas under the peaks in the spectra of **H** and of **I** are in the ratio 3 : 1.

H reacts with acidified potassium dichromate(VI) but **I** does not.

The areas under the peaks in the spectrum of **J** are in the ratio 1 : 1.

(10 marks)

TURN OVER FOR THE NEXT QUESTION

Turn over ►

SECTION C

Answer **EITHER** Question 5(a) **OR** Question 5(b).

You are advised to spend about 30 minutes on this section.

In addition to the chemical content of your answer, up to 3 marks will be awarded for Quality of Written Communication.

5 EITHER

- (a) The melting and boiling points of many substances are determined by the strength of one, or more, of the following interactions.

ion–ion attraction
covalent bonding
dipole–dipole attraction
van der Waals' (instantaneous dipole-induced dipole) forces of attraction
hydrogen bonding.

By reference to these interactions, explain why

- magnesium fluoride has a higher melting point than sodium chloride
- diamond has a higher melting point than silicon
- 1-chlorobutane has a higher boiling point than bromomethane
- water has a higher boiling point than ethanol.

(17 marks)

(QWC 3 marks)

OR

- (b) Explain the following facts.

- Alkenes react readily with electrophiles but benzene only reacts in the presence of a catalyst. Neither alkenes nor benzene react with nucleophiles.
- When dissolved in water, ethanoic acid behaves as a weak Brønsted–Lowry acid. When dissolved in anhydrous liquid ammonia, ethanoic acid behaves as a strong acid.
- When tetrachlorosilane, SiCl_4 , reacts with water it initially forms Si(OH)_4 . Si(OH)_4 then undergoes condensation polymerisation. When dichlorodimethylsilane, $(\text{CH}_3)_2\text{SiCl}_2$, reacts with water a polymeric silicone oil is formed. The viscosity of this oil is increased when small amounts of tetrachlorosilane are added to the dichlorodimethylsilane before water is added.

(17 marks)

(QWC 3 marks)

END OF QUESTIONS