

General Certificate of Education
June 2006
Advanced Extension Award



CHEMISTRY

6821

Wednesday 28 June 2006 9.00 am to 12 noon

For this paper you must have:

- 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.
- The marks for part questions 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**.

This Periodic Table may be useful in answering some of the questions in the examination.

Periodic Table

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* in some elements the most abundant isotope is shown)
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Turn over for the first question

Turn over 

SECTION A

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

1

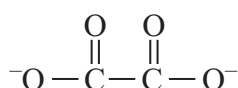
Total for this question: 10 marks

Cobalt is a typical transition metal; it is hard, fairly unreactive and is used in the production of special alloys. Cobalt has oxidation states of +2 and +3. The relative stability of these oxidation states in complexes depends on the coordinated ligands. With water as ligand the +2 state is the more stable, but the +3 state is the more stable when ammonia or nitrite ions, NO_2^- , are the ligands.

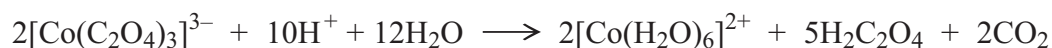
When cobalt metal, cobalt(II) oxide, cobalt(II) hydroxide or cobalt(II) carbonate are added to dilute acids, the pink octahedral hexaaquacobalt(II) ion, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, is formed in solution. This ion is also present in hydrated crystalline salts. Cobalt(II) forms octahedral and tetrahedral complex ions. A solution containing the blue tetrahedral tetrachlorocobaltate(II) ion is obtained by addition of an excess of chloride ions to an aqueous solution of a cobalt(II) salt.

The hexaaquacobalt(III) ion is not stable in aqueous solution because it oxidises water to oxygen. When an excess of sodium nitrite is added to an aqueous solution of a cobalt(II) salt in the presence of an acid, nitrite ions can act both as ligands and as an oxidising agent. Products of the reaction are the hexanitritocobaltate(III) ion, $[\text{Co}(\text{NO}_2)_6]^{3-}$, nitrogen monoxide and water. Sodium hexanitritocobaltate(III) is soluble in water. When a solution of this compound is added to an aqueous potassium salt, a yellow precipitate of potassium hexanitritocobaltate(III) is obtained. This reaction can be used as a test for the presence of potassium ions.

Another octahedral complex ion formed by cobalt(III) is the dark green ion $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$. The structure of the ethanedioate ion is shown below.



Each ethanedioate ion bonds to the cobalt ion in two adjacent positions. The complex ion is chiral and can exist in two different forms that are mirror images of each other. An acidic solution containing the dark green complex ion gradually turns to a pale pink solution which contains the hexaaquacobalt(II) ion. When the kinetics of this reaction are studied the reaction is found to be first order with respect to the complex ion. The overall equation can be written as



-
- (a) Write an equation for the reaction that occurs when an excess of chloride ions is added to an aqueous cobalt(II) salt. *(1 mark)*
- (b) Write an equation for the reaction between the hexaaquacobalt(II) ion and nitrite ions in acidic solution. *(1 mark)*
- (c) Suggest the unusual property of the compound potassium hexanitritocobaltate(III) that makes it suitable to show the presence of potassium ions. *(1 mark)*
- (d) Draw a diagram of the $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ ion which shows the three-dimensional structure of the complex ion.

Draw a second diagram to show the structure of the mirror image of the complex ion.

(3 marks)

- (e) Outline a laboratory method that could be used to follow the conversion of $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ into $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ in acidic solution and to show that the reaction is first order with respect to the complex ion. *(4 marks)*

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.

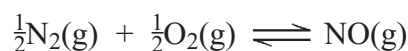
Each question carries 30 marks.

2

Total for this question: 30 marks

The gases sulphur dioxide and nitrogen monoxide cause atmospheric pollution and are responsible for the formation of acid rain.

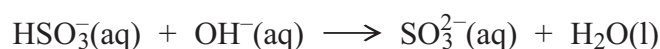
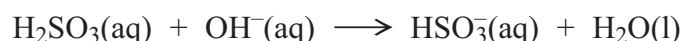
- (a) In thunderstorms, nitrogen from the air combines with oxygen forming nitrogen monoxide.



At a temperature of 3000 K, the equilibrium constant, K_c , for this reaction is 0.12.

Calculate the percentage equilibrium-yield of nitrogen monoxide at this temperature, starting from equimolar amounts of nitrogen and oxygen. (5 marks)

- (b) In the presence of air, nitrogen monoxide reacts to form nitrogen dioxide, NO_2 . This then reacts with water, forming a mixture of the acids HNO_2 and HNO_3 . Write an equation for this reaction of NO_2 . Predict the arrangement of electrons round nitrogen in NO_2 and hence suggest why NO_2 is a reactive molecule. (3 marks)
- (c) When sulphur dioxide dissolves in water, it forms the dibasic acid H_2SO_3 . This acid can be neutralised by sodium hydroxide in two stages as shown below. The first stage goes to completion before the second stage begins.



An aqueous solution of sulphur dioxide was formed by dissolving 0.100 mol of SO_2 in water and making up to 1.00 dm^3 of solution. A 20.0 cm^3 sample of this solution was titrated with a $0.200 \text{ mol dm}^{-3}$ solution of sodium hydroxide.

- (i) A $0.100 \text{ mol dm}^{-3}$ solution of sulphur dioxide has a pH of 1.54. Calculate the value of K_a for the following dissociation of H_2SO_3 .

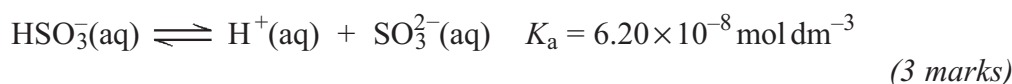


In your calculation, you should ignore any dissociation of HSO_3^- . (4 marks)

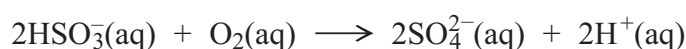
- (ii) Calculate the pH of the solution after the addition of 6.00 cm^3 of the sodium hydroxide solution. (6 marks)

[If you have been unable to calculate a value for K_a in part (c)(i) you may assume a value of $1.50 \times 10^{-3} \text{ mol dm}^{-3}$ although this is not the correct answer.]

- (iii) Using the value of K_a given below, calculate the pH of the solution after the addition of 10.00 cm^3 of the sodium hydroxide solution.



- (d) Hydrogensulphite ions, HSO_3^- , in aqueous solution are slowly oxidised by dissolved oxygen, forming sulphate ions and hydrogen ions.



The rate of this reaction was studied at different pH values and different initial concentrations of oxygen and hydrogensulphite ions. The results are shown in the table.

pH	$[\text{O}_2(\text{aq})]/\text{mol dm}^{-3}$	$[\text{HSO}_3^-(\text{aq})]/\text{mol dm}^{-3}$	Initial reaction rate $/\text{mol dm}^{-3} \text{ s}^{-1}$
5.00	1.0×10^{-4}	1.0×10^{-4}	4.0×10^{-12}
5.00	0.50×10^{-4}	1.0×10^{-4}	4.0×10^{-12}
5.00	2.0×10^{-4}	3.0×10^{-4}	3.6×10^{-11}
5.60	2.0×10^{-4}	2.0×10^{-4}	1.0×10^{-12}

- (i) For the reaction, deduce the order with respect to O_2 , to HSO_3^- and to H^+ . In each case give a reason for your answer.

Comment on the function of the H^+ ions in this reaction.

Suggest what the order with respect to oxygen indicates about the involvement of oxygen in this reaction. (6 marks)

- (ii) Write the rate equation for the reaction, calculate a value for the rate constant and state its units. (3 marks)

Turn over 

- (a) A Brønsted–Lowry acid is a proton donor; a Brønsted–Lowry base is a proton acceptor.
- (i) In liquid water, some water molecules dissociate. They do this by proton transfer.

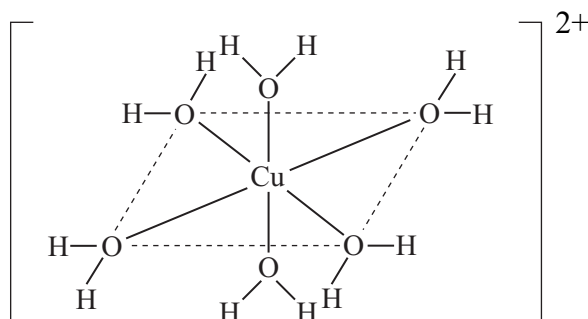


Explain how, in the liquid state, water acts both as a Brønsted–Lowry acid and as a Brønsted–Lowry base. (2 marks)

- (ii) In liquid ammonia, some ammonia molecules dissociate, by a reaction involving the transfer of a proton, to form a cation and an anion.
- Write an equation for the dissociation of ammonia molecules in liquid ammonia.
 - Ethanoic acid, when dissolved in liquid ammonia, acts as a strong acid whereas, in water, ethanoic acid is a weak acid. Write an equation for the reaction between ammonia and ethanoic acid in liquid ammonia. Explain why the use of ammonia as solvent increases the acid strength of ethanoic acid. (4 marks)

- (b) Another theory of acid–base behaviour was proposed by G N Lewis. This theory defines an acid as an electron pair acceptor and a base as an electron pair donor.

- (i) When aqueous ammonia is added dropwise, with shaking, to aqueous copper(II) sulphate, which contains hexaaquacopper(II) ions, a pale blue precipitate is formed. On the addition of an excess of aqueous ammonia a dark blue solution is formed. The colour of this solution is due to the presence of dark blue copper-containing complex ions.
- Write an equation for a reaction between the hexaaquacopper(II) ions and ammonia molecules which results in the formation of the pale blue precipitate.
 - The original copper-containing complex ion has the structure shown below.



Using this structure, outline a ‘curly arrow’ mechanism for the reaction between this copper(II) complex ion and **one** ammonia molecule.

- Draw the structure of the dark blue copper-containing complex ion. By reference to both the Brønsted–Lowry and Lewis acid–base theories, compare the role of ammonia in the formation of this complex ion with its role in the formation of the pale blue precipitate. (6 marks)

- (ii) In liquid sulphur dioxide, some SO_2 molecules dissociate as shown in the following equation.



Identify the Lewis base in the **reverse** reaction and give a reason for your choice. In liquid sulphur dioxide, SOCl_2 and Na_2SO_3 react together in a Lewis acid–base reaction. A white precipitate is formed. Write a full equation for this acid–base reaction and identify the white precipitate formed. (3 marks)

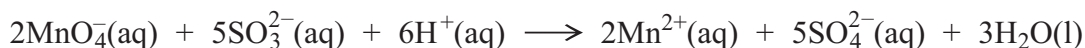
- (c) (i) When H_2S is bubbled through an aqueous solution of Na_2SO_3 a reaction occurs in which elemental sulphur is the only sulphur-containing product.

Write separate half-equations for the reactions undergone by SO_3^{2-} and H_2S , use oxidation states to deduce the role of SO_3^{2-} in this reaction and write an overall equation for the reaction. (5 marks)

- (ii) When aqueous KMnO_4 is mixed with an alkaline solution of Na_2SO_3 a reaction occurs in which a brown precipitate of MnO_2 is formed.

Write separate half-equations for the reactions undergone by SO_3^{2-} and MnO_4^- , use oxidation states to deduce the role of SO_3^{2-} in this reaction and write an overall equation for the reaction. (5 marks)

- (d) In acidic conditions, KMnO_4 reacts with SO_3^{2-} ions as shown in the equation below.



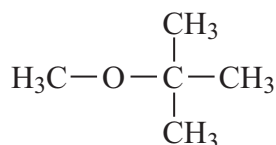
A 1.05 g sample of a pure anhydrous metal sulphite, M_2SO_3 , was dissolved in water and made up to 250 cm^3 in a volumetric flask. A 25.0 cm^3 portion of this solution was acidified and required the addition of 22.35 cm^3 of $0.0200 \text{ mol dm}^{-3}$ aqueous KMnO_4 for complete reaction. Use this information to deduce the identity of metal **M**.

(5 marks)

In petrol engines, the vaporised petrol–air mixture is compressed before it is sparked. Some hydrocarbons with a low octane rating, however, ignite under pressure before sparking so that pre-ignition, called knocking, occurs which causes the engine to run unevenly. The octane rating is based on a scale on which 2,2,4-trimethylpentane has an octane rating of 100.

One way to reduce knocking and improve the octane rating is to add tetraethyllead, $\text{Pb}(\text{C}_2\text{H}_5)_4$ (TEL), and 1,2-dibromoethane. During the combustion, TEL reacts with oxygen and 1,2-dibromoethane to form a mixture of products including lead(II) bromide. Use of TEL is limited in Britain because of the danger to health of lead compounds in the exhaust gases being released into the atmosphere.

- (a) Using molecular formulae, write equations for
- the complete combustion of 2,2,4-trimethylpentane; (1 mark)
 - the complete combustion of TEL in the presence of 1,2-dibromoethane to form a mixture of products. Assume that all the bromine and lead combine to form lead(II) bromide. (2 marks)
- (b) Identify other gaseous pollutants formed in an engine during the combustion of sulphur-free petrol vapour. Write equations to show how these substances are removed using a catalytic converter. (3 marks)
- (c) Another way to improve the octane rating of petrol is to add compounds such as ethers or alcohols. The ether functional group is R-O-R. The most commonly used ether is methyl tertiary butyl ether (MTBE)



MTBE is produced by the reaction between 2-methylpropene and methanol in the presence of an acid catalyst.

- Give the number of peaks in the proton n.m.r. spectrum of MTBE and the relative areas under the peaks. (2 marks)
- Explain why the ether MTBE is more volatile than its isomeric alcohols. (3 marks)
- Suggest a mechanism, using curly arrows, to show the acid-catalysed formation of MTBE from 2-methylpropene and methanol. The first step involves the protonation of 2-methylpropene. (3 marks)

- (d) Ethers can also be synthesised by the reaction of alkoxide salts with bromoalkanes. Alkoxide salts, RO^-Na^+ , are formed by the reaction of sodium with alcohols.
- (i) Write an equation for the formation of sodium ethoxide from ethanol and sodium. (1 mark)
- (ii) Write an equation for the formation of the ether $\text{CH}_3\text{CH}_2\text{OCH}(\text{CH}_3)_2$ from sodium ethoxide and a bromoalkane. Outline a possible mechanism, using curly arrows, for this reaction. Name this type of mechanism. (4 marks)
- (iii) Suggest a different type of reaction which could occur when sodium ethoxide is added to the bromoalkane and draw the structures of the organic products formed. (3 marks)
- (e) Compounds **A** – **E** are isomers of MTBE and all are alcohols.
- A** and **B** each exist as pairs of optical isomers. **A** and **B** can both be oxidised by acidified potassium dichromate(VI). **A** forms a carboxylic acid but **B** does not.
- C** cannot be dehydrated to form an alkene when reacted with concentrated sulphuric acid. Reaction of an excess of **C** with concentrated sulphuric acid forms an ether **X**, with molecular formula $\text{C}_{10}\text{H}_{22}\text{O}$, in a dehydration reaction.
- D**, which has an unbranched carbon chain, can be oxidised to form compound **Y** which has only two peaks in its proton n.m.r. spectrum.
- Dehydration of **E** forms only one product, **Z**, which has at least five peaks in its proton n.m.r. spectrum.
- Use the information above to draw the structures of isomers **A** to **E** and compounds **X**, **Y** and **Z**. (8 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.

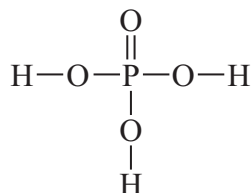
In addition to the chemical content of your answer, up to 3 marks will be awarded for Quality of Written Communication.

5 EITHER

- (a) This question is about some compounds of silicon and phosphorus, adjacent elements in Period 3.

Explain each of the following statements.

- Silicon(IV) oxide has a very high melting point (about 1700 °C) while that of phosphorus(III) oxide is much lower (24 °C).
- Silicon tetrachloride and phosphorus trichloride react with water forming acidic solutions. The reactions occur by similar mechanisms.
- Phosphoric acid, which has the structure shown below,



is a solid with a melting point of 42 °C.

A concentrated aqueous solution of phosphoric acid is very viscous and becomes gradually less viscous as the solution is diluted with water.

Phosphoric acid molecules can undergo condensation to form triphosphoric acid, which can be obtained in linear and cyclic forms.

(17 marks)

(QWC 3 marks)

OR

(b) This question is about the weak unsaturated acid $\text{CH}_3(\text{CH})_4\text{COOH}$.

- Outline a quantitative experiment that could be carried out to confirm that the acid has two carbon–carbon double bonds per molecule, using a solution of bromine of known concentration.
- Explain why this acid shows geometric isomerism. Include clear reference to the number of, and the structures of, the geometric isomers of this acid.
- A mixture of the acid and its potassium salt is used in foodstuffs to act as a buffer. Explain how the mixture can act as a buffer.

(17 marks)

(QWC 3 marks)

END OF QUESTIONS

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