

General Certificate of Education
June 2007
Advanced Extension Award



CHEMISTRY

6821

Wednesday 27 June 2007 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 to be 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 12 of this paper.

Advice

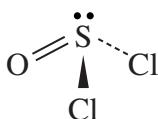
- You are advised to spend about 30 minutes on **Section A**, 2 hours on **Section B** and 30 minutes on **Section C**.

SECTION A

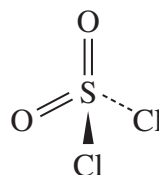
You are advised to spend about 30 minutes on this section.

There are 10 marks for this question.

- 1 Sulphur forms the oxochlorides thionyl chloride (sulphur dichloride oxide), SOCl_2 , and sulphuryl chloride (sulphur dichloride dioxide), SO_2Cl_2 .

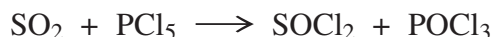


Thionyl chloride

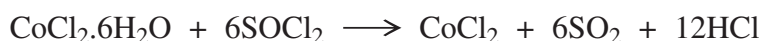


Sulphuryl chloride

Thionyl chloride is prepared by the reaction of sulphur dioxide with phosphorus pentachloride.



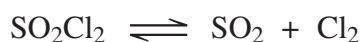
The thionyl chloride (b.p. 80°C) can be separated from the phosphorus trichloride oxide (b.p. 105°C) by fractional distillation. Thionyl chloride is a colourless liquid that fumes in moist air because of rapid hydrolysis, forming sulphur dioxide and hydrogen chloride. A similar hydrolysis reaction occurs with water in solid hydrated metal salts. Thionyl chloride can be used to prepare anhydrous metal salts from hydrated metal salts, e.g.



Anhydrous metal chlorides are also formed when thionyl chloride reacts with metal hydroxides.

Thionyl chloride and phosphorus pentachloride can both be used as chlorinating agents in organic chemistry to prepare chloroalkanes from alcohols. When thionyl chloride is used, sulphur dioxide and hydrogen chloride are the other products; when phosphorus pentachloride is used, phosphorus trichloride oxide and hydrogen chloride are the other products.

Sulphuryl chloride is prepared by the reaction of chlorine with sulphur dioxide in the presence of a catalyst such as iron(III) chloride. Sulphuryl chloride is stable up to 300°C but above this temperature it begins to decompose to reform chlorine and sulphur dioxide. The extent of decomposition increases as the temperature increases.



Sulphuryl chloride is a colourless liquid (b.p. 69°C). It fumes in moist air and is hydrolysed fairly rapidly forming sulphuric acid and hydrogen chloride. Sulphuryl chloride can also be used as a chlorinating agent in organic chemistry.

-
- (a) Write equations for the reaction of thionyl chloride and of phosphorus pentachloride with propan-1-ol. Hence, suggest why it may be an advantage to use thionyl chloride rather than phosphorus pentachloride when preparing 1-chloropropane (b.p. 47 °C). (3 marks)
- (b) Write an equation for the reaction of thionyl chloride with cobalt(II) hydroxide tetrahydrate. (1 mark)
- (c) Suggest why thionyl chloride has a higher boiling point than sulphuryl chloride. (3 marks)
- (d) Write the equation for the hydrolysis of sulphuryl chloride. (1 mark)
- (e) Deduce whether the formation of sulphuryl chloride from sulphur dioxide and chlorine is exothermic or endothermic. Explain your answer. (2 marks)

Turn over for the next question

Turn over ►

SECTION B

Answer **all** questions in this section.

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

There are 30 marks for each question.

2 Fluorine is a very reactive element that forms very stable compounds. This question is about the chemistry of fluorine, hydrogen fluoride and sodium fluoride.

- (a) Fluorine and chlorine react with methane by a similar mechanism although the rates of reaction are very different. Write an equation for the reaction between equimolar amounts of fluorine and methane. Suggest why fluorine reacts rapidly with methane at room temperature and also why a mixture of chlorine and methane requires heat or light before any reaction occurs. (4 marks)
- (b) (i) Suggest why hydrogen fluoride, in aqueous solution, is a much weaker acid than hydrogen chloride. (1 mark)
- (ii) Calculate the pH of a $0.200 \text{ mol dm}^{-3}$ aqueous solution of HF at 298 K. State any **one** assumption that you make.
(For HF, $K_a = 5.62 \times 10^{-4} \text{ mol dm}^{-3}$ at 298 K.) (4 marks)
- (iii) Calculate the pH of 100 cm^3 of a $0.200 \text{ mol dm}^{-3}$ aqueous solution of HF after the addition of 50.0 cm^3 of a $0.100 \text{ mol dm}^{-3}$ aqueous solution of sodium hydroxide. (4 marks)
- (iv) Calculate the pH of the solution formed by addition of 5.00 cm^3 of a $0.100 \text{ mol dm}^{-3}$ solution of hydrochloric acid to the final solution from part (b)(iii). Comment briefly on the difference between your answers to parts (b)(iii) and (b)(iv). (4 marks)
- (c) Sodium fluoride forms a weakly alkaline solution in water.

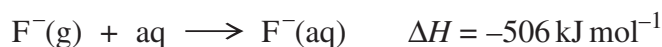
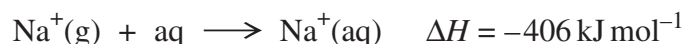


In this solution it may be assumed that the concentrations of HF(aq) and OH⁻(aq) are equal.

Using this assumption and the values for K_a and for K_w , calculate the pH of a $0.500 \text{ mol dm}^{-3}$ solution of sodium fluoride.

($K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K.) (4 marks)

- (d) The lattice enthalpy of sodium fluoride has the value -902 kJ mol^{-1} . Values for the hydration enthalpies of the Na^+ and F^- ions are given below.



Calculate the enthalpy change when one mole of sodium fluoride dissolves in an excess of water. (2 marks)

- (e) In a saturated solution of sodium fluoride the following equilibrium exists.



The equilibrium constant expression shown below can be written for the reaction. The solid NaF does not appear in the expression because its concentration can be regarded as constant; it remains as a solid in a different phase from the ions.

$$K_s = [\text{Na}^+(\text{aq})][\text{F}^-(\text{aq})]$$

The solubility of NaF in water at 293 K is 4.00 g per 100 cm^3 of solution. Use this information to calculate a value for K_s at 293 K. (3 marks)

- (f) The following expression shows how the value of an equilibrium constant, K_1 , changes to a different value, K_2 , as the temperature changes from T_1 to T_2 . In this expression, the unit of temperature is the kelvin, ΔH is expressed in J mol^{-1} and R is the gas constant, $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

$$\log_{10}K_1 - \log_{10}K_2 = \frac{-\Delta H}{2.3R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Use this expression and your answers to parts (d) and (e) to calculate a value for K_s at 60°C . Hence, calculate the solubility of sodium fluoride in water at 60°C . Express your answer in g per 100 cm^3 of solution.

(If you have been unable to obtain values for K_s in part (e) and ΔH in part (d), you may assume that $K_s = 1.20 \text{ mol}^2 \text{ dm}^{-6}$ and $\Delta H = -15 \text{ kJ mol}^{-1}$. These are not the correct values.) (4 marks)

Turn over ►

- 3 (a)
- Aqueous barium chloride is a common laboratory reagent and is kept in containers labelled with a 'toxic' symbol.
 - In 50 % of cases a lethal dose of BaCl_2 for an adult is approximately 20 g.
 - Hydrochloric acid is present in the stomach to aid digestion.

A suspension of barium sulphate in water is used when making an X-ray examination of the digestive system. A patient swallows this suspension, as a 'barium meal', a little while before the X-ray examination is made.

If a suspension of barium carbonate were used instead of barium sulphate, the patient may die of barium poisoning.

Suggest an explanation for the difference in toxicity of barium sulphate and barium carbonate. Write an equation for any reaction which occurs. (4 marks)

- (b) Silicon tetrachloride dissolves in ethoxyethane, an inert solvent. If the ethoxyethane is contaminated with a little water, a partial hydrolysis occurs and two compounds **A** and **B** are formed. The formula of **A** is Si_2OCl_6 and that of **B** is $\text{Si}_3\text{O}_2\text{Cl}_8$
- (i) Compound **B** is a symmetrical molecule in which the arrangement of atoms around each silicon atom is tetrahedral. Draw the structural formula of compound **B**, showing all the bonds. (1 mark)
- (ii) When a 0.100 g sample of one of the compounds **A** or **B** reacted with an excess of water, all the chlorine present was converted into chloride ions. Titration of this solution with aqueous silver nitrate, in the presence of a suitable indicator, required 42.10 cm^3 of $0.0500 \text{ mol dm}^{-3}$ aqueous silver nitrate for complete precipitation of silver chloride.

Deduce which of the compounds, **A** or **B**, was present in the 0.100 g sample. (3 marks)

- (c) A gaseous mixture of ammonia and chlorine reacts to form nitrogen and solid ammonium chloride. This reaction may be considered to occur in two stages. The role of ammonia in the first stage is that of a reducing agent, while in the second stage it acts as a base.

Write separate equations for these two stages, and an overall equation for the reaction. (3 marks)

- (d) When phosphorus(V) chloride and ammonium chloride are heated together in an inert solvent, hydrogen chloride is evolved and a solid compound **C** ($M_r = 464$) is formed. This compound is cyclic and contains 26.7% of phosphorus and 12.1% of nitrogen by mass, the remainder being chlorine. All of the chlorine atoms are bonded to phosphorus atoms.

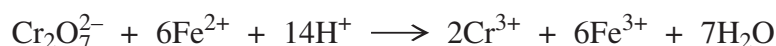
In a similar manner to compounds containing ^1H atoms, compounds containing ^{31}P atoms may be investigated using n.m.r. spectroscopy. From the ^{31}P n.m.r. spectrum of **C** it can be deduced that all of the phosphorus atoms are in the same chemical environment.

- (i) Calculate the empirical and molecular formulae of **C**.
Write an equation for the preparation of **C** from PCl_5 and NH_4Cl .
Suggest, with an explanation, a precaution which should be taken when carrying out this reaction in the laboratory. (4 marks)
- (ii) By using your understanding of ^1H n.m.r. spectroscopy, suggest what feature of the ^{31}P n.m.r. spectrum of **C** would show that all the phosphorus atoms are in the same chemical environment.

Draw a possible structure for the molecule.

Name the shape formed by the atoms around each phosphorus atom in a molecule of **C**. (4 marks)

- (e) (i) The gas SO_2 is bubbled into an aqueous solution containing ClO_3^- ions. The ClO_3^- ions are reduced to Cl^- ions and the SO_2 is oxidised to SO_4^{2-} ions.
Write half-equations to represent the reduction and oxidation processes in the reaction between SO_2 and ClO_3^- and hence deduce the overall equation for this reaction. (3 marks)
- (ii) An excess of SO_2 was bubbled into a 100 cm^3 sample of aqueous KClO_3 (solution **D**), so that all the ClO_3^- was converted into Cl^- . The solution was boiled to remove excess SO_2 and then treated with an excess of silver nitrate solution. The precipitate of silver chloride was collected, washed and dried, and was found to weigh 0.414 g. Calculate the concentration of ClO_3^- ions in solution **D**. (2 marks)
- (iii) Solution **E** contains FeSO_4 of concentration 0.210 mol dm^{-3} . A 30.00 cm^3 sample of solution **D** was mixed with 30.00 cm^3 of solution **E** and the mixture was acidified. When the reaction was complete, the excess Fe^{2+} required 8.20 cm^3 of $0.0225\text{ mol dm}^{-3}$ aqueous $\text{K}_2\text{Cr}_2\text{O}_7$



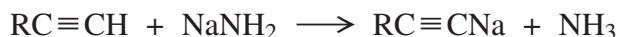
Calculate the number of moles of Fe^{2+} which have reacted with one mole of ClO_3^- and, hence, deduce an equation for the reaction between ClO_3^- and Fe^{2+}

(6 marks)

Turn over ►

- 4 Alkynes contain a carbon–carbon triple bond ($C \equiv C$). They are versatile reagents in organic synthesis.
- (a) When ethyne, $HC \equiv CH$, is passed through a red-hot tube in the absence of air, a colourless liquid, **Q**, is formed containing 92.3% by mass of carbon. The mass spectrum of **Q** has a molecular ion peak at $m/z = 78$. The proton n.m.r. spectrum of **Q** has only one peak. Reaction of **Q** with chloroethane in the presence of aluminium chloride gives **R** ($M_r = 106$). Reaction of **R** with a mixture of concentrated nitric acid and concentrated sulphuric acid gives a mixture of isomers **S**, **T** and **U** ($M_r = 151$).
- (i) Draw structures for the compounds **Q**, **R**, **S**, **T** and **U**. Explain how you have used the data to deduce their identities. (10 marks)
- (ii) Ethyne forms two straight-chain addition polymers, **V** and **W**. The repeat unit of polymer **V** has a different stereochemistry from that of polymer **W**. Draw the structure of the repeat unit of each polymer and state the type of stereoisomerism shown. (3 marks)
- (b) (i) The addition of one mole of hydrogen bromide to one mole of propyne, $CH_3C \equiv CH$, forms 2-bromopropene. Suggest a mechanism for this reaction. (3 marks)
- (ii) The addition of hydrogen bromide to 2-bromopropene gives a mixture of structural isomers **X** and **Y**. Isomer **X** shows stereoisomerism. Draw the stereoisomers of **X**, showing their relationship. Give the structural formula of **Y**. (3 marks)

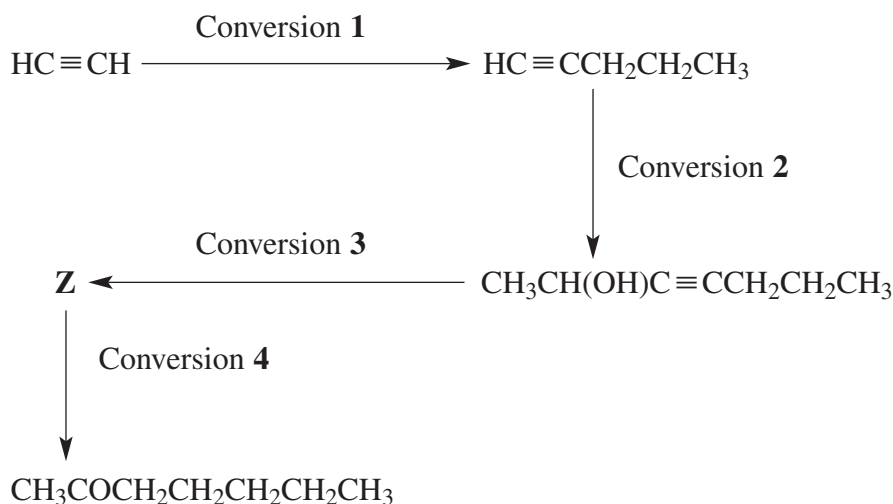
- (c) In an alkyne, the hydrogen atom attached to a carbon of the $C\equiv C$ is acidic. Thus alkynes react with the base sodium amide, $NaNH_2$, to give a salt. For example



The sodium salt, $RC\equiv CNa$, contains the $RC\equiv C^-$ anion which reacts as a nucleophile with halogenoalkanes and with the carbonyl group.

Alkynes can be reduced to alkanes by the same reagents used to reduce alkenes.

- (i) The sodium salt, $HC\equiv CNa$, can be converted in two steps into the alcohol $HC\equiv CCH_2OH$. In the first step, $HC\equiv C^-$ reacts with methanal to give an anionic intermediate. In the second step, acidification with dilute sulphuric acid gives the alcohol.
Give a mechanism for this conversion, showing clearly the structure of the anionic intermediate. (4 marks)
- (ii) Heptan-2-one can be synthesised from ethyne as shown in the scheme below.



Suggest reagents for each of the conversions and give the structural formula of **Z**. (7 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) Titanium is a transition metal which shows the typical characteristic of variable oxidation states, +3 and +4 being the most common.

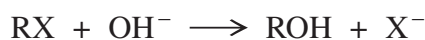
- With reference to the electronic configurations of titanium in oxidation states +3 and +4, suggest why titanium(III) compounds are easily oxidised to titanium(IV) compounds and identify **one** change in characteristic property that would indicate that the oxidation had occurred. Explain your answer.
- Suggest another characteristic property of transition metals, other than catalysis, shown by titanium in the +3 oxidation state. Explain why this property arises.
- Titanium(IV) chloride shows some similarities to Group IV chlorides such as silicon tetrachloride. Describe the bonding in titanium(IV) chloride and state and explain the shape of the molecule. Explain why titanium(IV) chloride fumes in moist air.
- Titanium(IV) chloride is one component in a catalyst for the conversion of propene into poly(propene).

Classify the type of reaction undergone by propene and write an equation for the process, clearly showing the structure of the reactant and the structure of the repeat unit of the polymer.

(17 marks)

OR

- (b) When a halogenoalkane is warmed with aqueous sodium hydroxide, a substitution reaction occurs which can be represented by the equation



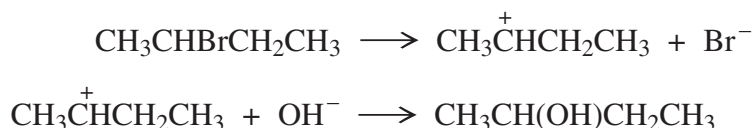
The reaction can take place by two possible mechanisms, one involving one step and the other involving two steps.

- The rate equation for the one-step reaction between 1-bromopropane and sodium hydroxide is

$$\text{Rate} = k[\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}][\text{OH}^-]$$

Describe fully a laboratory method to follow the reaction and explain how you would use the results to show that it is first order with respect to the hydroxide ion.

- The reaction between 2-bromobutane and sodium hydroxide can take place in two steps.



The intermediate is planar around the positive carbon.

If a single optical isomer of 2-bromobutane is reacted with sodium hydroxide, the final product mixture is not optically active.

Explain why 2-bromobutane can show optical isomerism and state how this can be detected. Explain why optical activity is lost during the two-step reaction with sodium hydroxide.

- Suggest and explain the trend in the rate of the substitution reactions for 1-chloropentane, 1-bromopentane and 1-iodopentane with aqueous sodium hydroxide.
- Suggest, with reference to the bonding present, why halogenoarenes, such as bromobenzene, do not undergo a substitution reaction with aqueous sodium hydroxide under normal laboratory conditions.

(17 marks)

(QWC 3 marks)

END OF QUESTIONS

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

Periodic Table

Group	1	2	3	4	5	6	7	0						
Period	1.0							4.0						
1	H 1							He 2						
2	6.9 Li 3	9.0 Be 4						19.0 F 9						
3	23.0 Na 11	24.3 Mg 12						20.2 Ne 10						
4	39.1 K 19	40.1 Ca 20						35.5 Cl 17						
5	85.5 Rb 37	87.6 Sr 38						39.9 Ar 18						
6	132.9 Cs 55	137.3 Ba 56						83.8 Kr 36						
7	(223) Fr 87	226.0 Ra 88						131.3 Xe 54						
<table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <tr> <td colspan="2" rowspan="2" style="width: 50%; vertical-align: middle;"> Key Relative Atomic Mass → AA Atomic Number → ZZ </td> <td colspan="2" rowspan="2" style="width: 50%; vertical-align: middle;"> ← Element E </td> </tr> <tr> <td colspan="2" style="text-align: left;"> Insert elements * 57 - 71 Insert elements ** 89 - 103 </td> </tr> </table>									Key Relative Atomic Mass → AA Atomic Number → ZZ		← Element E		Insert elements * 57 - 71 Insert elements ** 89 - 103	
Key Relative Atomic Mass → AA Atomic Number → ZZ		← Element E												
				Insert elements * 57 - 71 Insert elements ** 89 - 103										
			10.8 B 5	12.0 C 6	14.0 N 7	16.0 O 8	19.0 F 9	20.2 Ne 10						
			27.0 Al 13	28.1 Si 14	31.0 P 15	32.1 S 16	35.5 Cl 17	39.9 Ar 18						
			69.7 Ga 31	72.6 Ge 32	74.9 As 33	79.0 Se 34	79.9 Br 35	83.8 Kr 36						
			114.8 In 49	118.7 Sn 50	121.8 Sb 51	127.6 Te 52	126.9 I 53	131.3 Xe 54						
			204.4 Tl 81	207.2 Pb 82	209.0 Bi 83	209.0 Po 84	210 At 85	(222) Rn 86						
				65.4 Zn 30	63.5 Cu 29	58.7 Ni 28	58.9 Co 27							
				112.4 Cd 48	107.9 Ag 47	106.4 Pd 46	102.9 Rh 45							
				200.6 Hg 80	197.0 Au 79	195.1 Pt 78	192.2 Ir 77							
				190.2 Os 76	190.2 Re 75	186.2 W 74	183.9 Ta 73							
				178.5 Hf 72	180.9 Zr 40	183.9 Nb 41	180.9 Mo 42							
				45.0 Sc 21	47.9 Ti 22	50.9 V 23	52.0 Cr 24							
				88.9 Y 39	89.9 Sr 38	91.2 Zr 40	95.9 Nb 41							
				137.3 Ba 56	138.9 La 57	140.9 Ce 58	144.2 Pr 59							
				226.0 Ra 88	227.0 Ac 89	232.0 Th 90	231.0 Pa 91							
						140.1 La 57	140.9 Ce 58							
						150.4 Sm 62	157.3 Gd 64							
						158.9 Tb 65	167.3 Er 68							
						168.9 Tm 69	173.0 Yb 70							
						175.0 Lu 71								
						227.0 Ac 89	237.0 Np 93							
						238.0 Th 90	243 Am 95							
						231.0 Pa 91	243 Pu 94							
						238.0 U 92	244 Pu 94							
						237.0 Np 93	247 Cm 96							
						251 Cf 98	257 Fm 100							
						258 Md 101	259 No 102							
						260 Lr 103								

(Note - in some elements the most abundant isotope is shown)