

General Certificate of Education
June 2008
Advanced Extension Award



CHEMISTRY

6821

Monday 23 June 2008 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

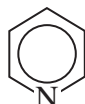
- You are advised to spend about 30 minutes on **Section A**, 2 hours on **Section B** and 30 minutes on **Section C**.

SECTION A

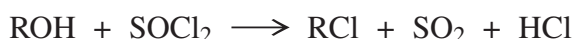
You are advised to spend about 30 minutes on this section.

There are 10 marks for this section.

- 1 Pyridine, C_5H_5N , is a cyclic amine. It has the same number of electrons as benzene. Electrons are delocalised around the ring in a similar way to benzene. The molecule can be represented as follows.

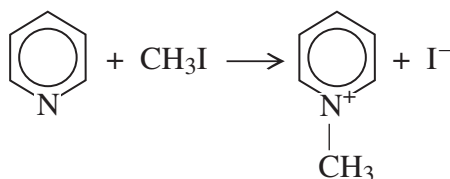


Pyridine is a weak base. It is soluble in water and reacts to form a small amount of the pyridinium ion, which can act as a weak acid with an acid dissociation constant, K_a , of $3.6 \times 10^{-6} \text{ mol dm}^{-3}$. Due to its basic nature, pyridine is often added to the reaction mixture in the preparation of a halogenoalkane from an alcohol and sulphur dichloride oxide, because it removes the hydrogen chloride.



The ring in pyridine is less reactive than that in benzene and only readily undergoes electrophilic substitution reactions if the ring of delocalised electrons is activated by the presence of an electron-donating group such as $-NH_2$. Treatment of pyridine with a mixture of concentrated sulphuric acid and concentrated nitric acid causes protonation of the nitrogen atom. The pyridinium ion formed is resistant to nitration. Electrophilic reagents attack the nitrogen atom rather than a carbon atom in the ring.

Like other amines, pyridine acts as a nucleophile in reactions with halogenoalkanes. When pyridine is added to a solution of iodomethane in methanol an exothermic reaction occurs.



On cooling the mixture, colourless crystals of the salt *N*-methylpyridinium iodide are formed. Pyridine also acts as a nucleophile in reactions with acyl chlorides such as ethanoyl chloride, CH_3COCl , and attacks the carbonyl group to form the *N*-ethanoylpyridinium ion. This ion reacts with alcohols to form esters.

Pyridine is widely used as a solvent in organic chemistry despite being toxic and having an unpleasant smell.

-
- (a) Suggest why pyridine dissolves in water. (1 mark)
- (b) Write equations to show how pyridine acts as a weak base in water and how the pyridinium ion acts as a weak acid when it reacts with water.
- Give the expression for the acid dissociation constant, K_a , for the pyridinium ion. (3 marks)
- (c) Explain how the presence of a nitrogen atom enables pyridine to have bonding similar to that of benzene and also enables it to act as a base. (4 marks)
- (d) (i) Draw the structure of the *N*-ethanoylpyridinium ion. (1 mark)
- (ii) Write an equation for the reaction between this ion and ethanol to form ethyl ethanoate. (1 mark)

Turn over for the next question

Turn over ►

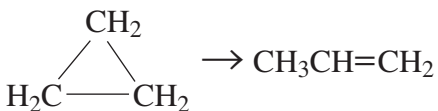
SECTION B

Answer **all** three questions.

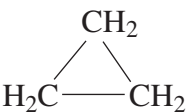
You are advised to spend about 40 minutes on each question.

There are 30 marks for each question.

- 2 (a) The equation below is for a gas phase isomerisation reaction that has a first-order rate equation. The rate constants k_1 and k_2 at 298 K and 773 K are shown next to the equation.

Equation	k_1 at 298 K/s ⁻¹	k_2 at 773 K/s ⁻¹
	3.14×10^{-33}	6.71×10^{-4}

Some thermodynamic data are also shown below.

		CH ₃ CH=CH ₂
ΔH_f^\ominus /kJ mol ⁻¹	+53.3	+20.4
	C=C	C-C
Mean bond enthalpy /kJ mol ⁻¹	612	345

- (i) Write the rate equation for this isomerisation reaction of cyclopropane and use it to calculate the initial rate of reaction of a 0.50 mol dm⁻³ sample of cyclopropane at 773 K. (2 marks)
- (ii) Calculate the factor by which the rate constant for this isomerisation changes as the temperature increases from 298 K to 773 K and suggest a reason for this change. (2 marks)
- (iii) The mean kinetic energy of gaseous molecules can be obtained from the following expression.

$$\text{mean kinetic energy} = \frac{3RT}{2}$$

Use this expression to calculate a value for the mean kinetic energy of one mole of cyclopropane molecules at 773 K. (The gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)

The rate constant for a chemical reaction changes with temperature as shown by the following expression.

$$\log_{10} \left(\frac{k_1}{k_2} \right) = \frac{-E_a}{2.30R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Use this expression and the data given to calculate a value for the activation energy, E_a , for the isomerisation of cyclopropane.

Comment on your answer compared with the mean kinetic energy of cyclopropane molecules and explain how it is possible for all the cyclopropane molecules to isomerise when the temperature is maintained at 773 K. (6 marks)

- (iv) Use the enthalpy of formation data to calculate a value for the enthalpy change for the isomerisation reaction of cyclopropane.

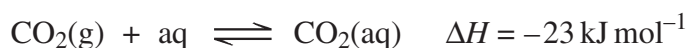
Use the bond enthalpy data to calculate a value for the enthalpy change for this reaction.

Identify which of these two values is likely to be closer to the true value.

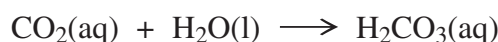
Suggest, in terms of structure and bonding, why the two values are different.

(5 marks)

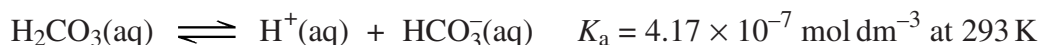
- (b) The solubility of carbon dioxide in a given volume of water at a fixed temperature is directly proportional to the partial pressure of the carbon dioxide. When a sample of pure carbon dioxide gas at a temperature of 293 K and a pressure of 100 kPa is placed in contact with water, the mass of carbon dioxide that dissolves in 1.00 dm³ of water is 1.69 g.



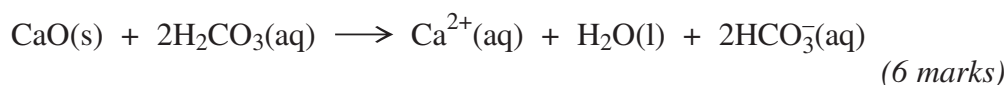
You should assume that all of the dissolved carbon dioxide reacts completely in water as shown in the equation below.



The H₂CO₃ then partially ionises.



- (i) When air at 293 K and 100 kPa is placed in contact with water some of the carbon dioxide from the air dissolves. Calculate the maximum amount, in moles, of carbon dioxide that will dissolve in 1.0 dm³ of water at 293 K, assuming that the proportion of carbon dioxide in the air is maintained at 0.030%. (2 marks)
- (ii) Calculate an approximate value for the pH of the solution formed in part (b)(i). Mention any approximation that you have used in your calculation. (If you have been unable to calculate an answer to part (b)(i), you may assume that the amount of carbon dioxide is 1.56×10^{-6} mol, but this is not the correct answer.) (4 marks)
- (iii) In a sample of 1.0 dm³ of water at 293 K, the amount of dissolved carbon dioxide is 2.5×10^{-4} mol and the pH of the solution is 5.00. Calculate the mass of calcium oxide (quicklime) that must be added to the water in order to raise the pH to a value of 6.00. Assume that the CaO reacts as follows.



- (iv) Discuss qualitatively the effect that global warming will have on the pH of water that is acidic due to dissolved carbon dioxide. In your answer you should assume that the temperature of the water has risen and that the amount of carbon dioxide in the atmosphere has increased. You should assume that the value of K_{a} remains constant as the temperature changes. (3 marks)

Turn over ►

3 The questions below concern the properties and chemistry of uranium and its compounds.

- (a) A sample of uranium (relative atomic mass, $A_r = 238.0$) contained the three isotopes ^{234}U , ^{235}U and ^{238}U .
- (i) State what can be deduced about the composition of this sample from the A_r value given. (1 mark)
- (ii) State and explain whether there are any differences in the chemistry of these isotopes. (2 marks)
- (b) (i) Aqueous solutions containing $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ ions, such as $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ions, are acidic. Write an equation to show how $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ions form an acidic solution. (1 mark)
- (ii) Suggest, with an explanation, whether the acidity of $[\text{U}(\text{H}_2\text{O})_6]^{3+}$ would be greater or less than that of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. Explain why $[\text{U}(\text{H}_2\text{O})_6]^{4+}$ produces a more acidic solution than $[\text{U}(\text{H}_2\text{O})_6]^{3+}$. (3 marks)
- (c) Transition metals and their ions readily form complexes, the shapes of which depend on the number of ligand–metal bonds. For example, six bonds give an octahedral (square-based bipyramidal) shape. The $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ complex has eight ligand–metal bonds and has a hexagonal bipyramidal shape. The nitrate ions are trigonal and each forms two ligand–metal bonds. The UO_2 group is linear and the complex is symmetrical.
- (i) Sketch a diagram to show the three-dimensional shape of the $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ complex. You should use arrows to represent the ligand–metal bonds. (3 marks)
- (ii) Mark on your diagram three different O–U–O bond angles. (2 marks)
- (d) (i) The unstable ion, UO_2^+ , forms when UCl_5 reacts with water. Write an equation for this reaction. (1 mark)
- (ii) A disproportionation reaction is a redox reaction in which an element in a single species is both oxidised and reduced.
- The UO_2^+ ion formed in part (d)(i) readily disproportionates in acidic solution to form U^{4+} and UO_2^{2+} ions. Write half-equations, and an overall equation, for this disproportionation reaction. Explain, using oxidation states, why this reaction is a disproportionation reaction. (4 marks)

- (e) Photographic printing involves the use of paper coated with a light-sensitive salt. In the 19th century, 'uranyl nitrate', $\text{UO}_2(\text{NO}_3)_2$, was used as a light-sensitive salt.

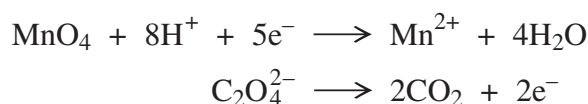
When light is shone through a photographic negative onto paper coated with $\text{UO}_2(\text{NO}_3)_2$ a reaction occurs in which U^{4+} ions are formed on the surface of the paper.

The paper is then placed in a solution containing AuCl_4^- ions, which react with U^{4+} ions producing UO_2^{2+} ions and depositing gold atoms on the paper. The gold atoms form the dark areas of the photographic print.

- (i) Write an overall equation for the reaction between U^{4+} and AuCl_4^- ions. (2 marks)
- (ii) Suggest, in chemical terms, why a photographic print obtained by this method has light and dark areas. (2 marks)
- (f) The reaction of sodium uranyl(VI) methanoate, $\text{NaUO}_2(\text{HCOO})_3$ with an excess of ethanedioic acid produces a compound, **X**, which is uranyl(IV) ethanedioate hexahydrate, $\text{UO}(\text{C}_2\text{O}_4).6\text{H}_2\text{O}$ ($M_r = 450$).

- (i) When 585 mg of **X** were left in a vacuum desiccator for 48 hours, some water of crystallisation was removed and a new hydrate, of mass 538 mg, was formed. Deduce the formula of this new hydrate. (3 marks)
- (ii) A 300 mg sample of **X** was dissolved in hot dilute sulphuric acid and titrated with $0.500 \text{ mol dm}^{-3}$ potassium manganate(VII) solution. The end-point was obtained after the addition of 10.70 cm^3 of the KMnO_4 solution. In this titration, the KMnO_4 oxidised both the $\text{C}_2\text{O}_4^{2-}$ ions and the uranyl(IV) ions.

Use these data to calculate the change in oxidation state of the uranium and hence deduce the final oxidation state of the uranium.



(6 marks)

Turn over for the next question

Turn over ►

4 Lithium tetrahydridoaluminate(III), LiAlH_4 , is a powerful reducing agent which reduces all carbonyl groups but not aromatic rings or simple alkenes.

- (a) Esters are reduced to primary alcohols and acid amides are reduced to amines, as shown in the conversions below.



Write equations to illustrate the reduction of methyl benzenecarboxylate (methyl benzoate) and *N*-methylethanamide by LiAlH_4 . In your answer show the structures of the products and use [H] to represent the reducing agent. (2 marks)

- (b) The reduction of the ester RCOOR' by LiAlH_4 involves several steps.

In the first step, a hydride ion, H^- , adds to the carbonyl of the ester group.

In the second step, the aldehyde RCHO is produced when the carbonyl group re-forms with the simultaneous elimination of an alkoxide ion.

In the third step, hydride ions add to the aldehyde so formed to give a primary alkoxide ion, RCH_2O^- , which subsequently forms the alcohol when treated with water or dilute acid.

- (i) Explain why LiAlH_4 reduces carbonyl groups but does not reduce aromatic rings or simple alkenes. (3 marks)
- (ii) Use this information to suggest a mechanism for the reaction of LiAlH_4 with ethyl ethanoate to give ethanol as the organic product. (7 marks)
- (c) Water is added carefully at the completion of reductions using LiAlH_4 to destroy the excess of LiAlH_4 . The products are hydrogen and the metal hydroxides.

Deduce the equation for the complete reaction of LiAlH_4 with an excess of water and hence suggest a practical difficulty of working with the reagent. (2 marks)

- (d) There are two stereoisomers of hex-4-en-2-one. The alkene and carbonyl groups can be reduced selectively by different reagents.

- (i) Draw the **two** stereoisomers of hex-4-en-2-one. (2 marks)
- (ii) In the reduction of either of the two isomers of hex-4-en-2-one to hex-4-en-2-ol by LiAlH_4 the alcohol formed is an equimolar mixture of two enantiomers. Draw the **two** enantiomers of the alcohol and suggest why they are formed in a 1:1 ratio. (4 marks)

- (e) **A**, **B** and **C** are three structural isomers of molecular formula $C_6H_{10}O$. They are all cyclic. Isomers **A** and **B** have strong infra-red absorptions, **A** at 1720 cm^{-1} and **B** at 1780 cm^{-1} ; **C** has an absorption at 1650 cm^{-1} and a broad absorption between 3230 and 3550 cm^{-1} .

In the proton n.m.r. spectrum **A** has three peaks (signals) with areas in the ratio 2:2:1 whereas **B** has two peaks in the ratio 3:2; **C** has 4 peaks with areas in the ratio 1:2:3:4.

C reacts readily with bromine water; **A** and **B** do not. None of the three isomers can be oxidised by acidified potassium dichromate(VI).

Suggest structures for **A**, **B** and **C**, explaining your reasoning.

(10 marks)

Table of infra-red absorption data

Bond	Wavenumber / cm^{-1}
C-H	2850–3300
C-C	750–1100
C=C	1620–1680
C=O	1680–1800
C-O	1000–1300
O-H (alcohols)	3230–3550
O-H (acids)	2500–3000

Turn over for the next question

Turn over ►

SECTION C

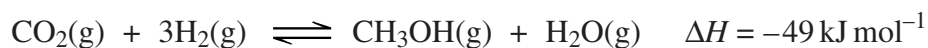
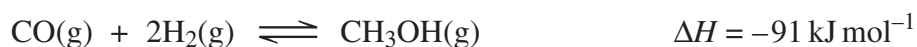
Answer **EITHER** Question 5(a) **OR** Question 5(b).

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

There are 20 marks for this section.

5 EITHER

- (a) Methanol is manufactured from synthesis gas, which is a mixture of carbon monoxide, carbon dioxide and hydrogen. The reactions occurring may be represented by the equations



The operating conditions used in the process are

- a temperature of about 250 °C
- a pressure of about 70 atmospheres
- a heterogeneous copper-based catalyst.

Use of these conditions results in approximately 10 % conversion into methanol.

Discuss the choice of the operating temperature and pressure. You should include, where appropriate, reference to the equilibrium constants, the rate of production of methanol and the yield.

Explain why a catalyst is used and its effect on the rate and yield of the process. Suggest how the catalyst in this process works.

(17 marks)

(QWC 3 marks)

OR

- (b) The properties of elements and of their oxides vary across a period and down a group in the Periodic Table, and are related to their bonding and the inter-particle attractions.

Suggest explanations for each of the following statements.

- The melting point of sulphur is higher than that of chlorine but both melting points are much lower than that of silicon.
- The magnitude, found using a Born–Haber cycle, for the lattice enthalpy of magnesium oxide is greater than that of sodium oxide but smaller than that of beryllium oxide. For magnesium oxide there is good agreement between this value and the value calculated on a purely ionic model. For beryllium oxide the agreement is not good.
- The acid–base characteristics of sodium oxide, aluminium oxide and sulphur dioxide illustrate a trend across a period. This trend can be used to show the change in the metal–nonmetal character of the elements across the period.

(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	2	<div style="border: 1px solid black; padding: 5px; margin: 0 auto; width: 80%;"> <p>Key</p> <p>Relative Atomic Mass → AA</p> <p>Atomic Number → ZZ</p> <p style="text-align: center;">E ← Element</p> </div>					0
1	1.0 H 1							4.0 He 2
2	6.9 Li 3	9.0 Be 4	10.8 B 5	12.0 C 6	14.0 N 7	16.0 O 8	19.0 F 9	20.2 Ne 10
3	23.0 Na 11	24.3 Mg 12	27.0 Al 13	28.1 Si 14	31.0 P 15	32.1 S 16	35.5 Cl 17	39.9 Ar 18
4	39.1 K 19	40.1 Ca 20	45.0 Sc 21	47.9 Ti 22	50.9 V 23	52.0 Cr 24	54.9 Mn 25	55.8 Fe 26
5	85.5 Rb 37	87.6 Sr 38	88.9 Y 39	91.2 Zr 40	92.9 Nb 41	95.9 Mo 42	98 (98) Tc 43	101.1 Ru 44
6	132.9 Cs 55	137.3 Ba 56	178.5 Hf 72	180.9 Ta 73	183.9 W 74	186.2 Re 75	190.2 Os 76	192.2 Ir 77
7	(223) Fr 87	226.0 Ra 88	* 57 - 71	*	*	** 89 - 103	**	**
			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 (210) At 85	(222) Rn 86
			158.9 Tb 65	157.3 Gd 64	152.0 Eu 63	150.4 Sm 62	145 (145) Pm 61	138.9 La 57
			162.5 Dy 66	164.9 Ho 67	167.3 Er 68	168.9 Tm 69	173.0 Yb 70	175.0 Lu 71
			227.0 Ac 89	231.0 Th 90	238.0 Pa 91	237.0 U 92	244 (244) Pu 94	243 (243) Am 95
			251 (251) Cf 98	252 (252) Es 99	257 (257) Fm 100	258 (258) Md 101	259 (259) No 102	260 (260) Lr 103

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