General Certificate of Education
June 2002
Advanced Extension Award

ASSESSMENT and QUALIFICATIONS ALLIANCE

# CHEMISTRY 6821

Wednesday 26 June 2002 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.
- All working must be shown.
- 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 160.
- Mark allocations are shown in brackets.
- 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**.

# Periodic Table

| Group / Period | 1 | 2 | | | | | | | | | | | 3 | 4 | 5 | 6 | 7 | 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 | 58.9 Co 27 | 58.7 Ni 28 | 63.5 Cu 29 | 65.4 Zn 30 | 69.7 Ga 31 | 72.6 Ge 32 | 74.9 As 33 | 79.0 Se 34 | 79.9 Br 35 | 83.8 Kr 36 |
| 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) Tc 43 | 101.1 Ru 44 | 102.9 Rh 45 | 106.4 Pd 46 | 107.9 Ag 47 | 112.4 Cd 48 | 114.8 In 49 | 118.7 Sn 50 | 121.8 Sb 51 | 127.6 Te 52 | 126.9 I 53 | 131.3 Xe 54 |
| 6 | 132.9 Cs 55 | 137.3 Ba 56 | * 57 - 71 | 178.5 Hf 72 | 180.9 Ta 73 | 183.9 W 74 | 186.2 Re 75 | 190.2 Os 76 | 192.2 Ir 77 | 195.1 Pt 78 | 197.0 Au 79 | 200.6 Hg 80 | 204.4 Tl 81 | 207.2 Pb 82 | 209.0 Bi 83 | (209) Po 84 | (210) At 85 | (222) Rn 86 |
| 7 | (223) Fr 87 | 226.0 Ra 88 | ** 89 - 103 | | | | | | | | | | | | | | | |

**Key**

Relative Atomic Mass → AA E ← Element

Atomic Number → ZZ

Insert elements * 57 - 71 | Insert elements ** 89 - 103

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

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| * | 138.9 La 57 | 140.1 Ce 58 | 140.9 Pr 59 | 144.2 Nd 60 | (145) Pm 61 | 150.4 Sm 62 | 152.0 Eu 63 | 157.3 Gd 64 | 158.9 Tb 65 | 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 | 232.0 Th 90 | 231.0 Pa 91 | 238.0 U 92 | 237.0 Np 93 | (244) Pu 94 | (243) Am 95 | (247) Cm 96 | (247) Bk 97 | (251) Cf 98 | (252) Es 99 | (257) Fm 100 | (258) Md 101 | (259) No 102 | (260) Lr 103 |

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

**TURN OVER FOR THE FIRST QUESTION**

## SECTION A

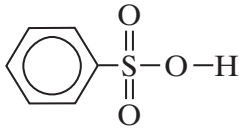
You are advised to spend about 30 minutes on this section.

**1** **Total for this question: *15 marks***

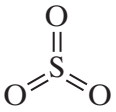
### Sulphonation

The incorporation of highly polar sulphonic acid groups into dyes is important in conferring water solubility. Sulphonic acid groups are also involved in the attachment of dyes to certain substrates, such as wool and nylon.

The structure of benzenesulphonic acid is shown below.



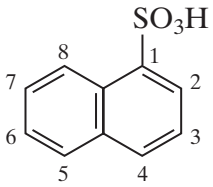
Benzenesulphonic acid can be made by the reaction of benzene with a solution of sulphur trioxide, $SO_3$, in concentrated sulphuric acid. In this reaction sulphur trioxide, which has the structure given below, acts as an electrophile.



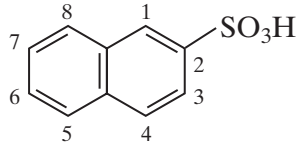
Unlike nitration, sulphonation is reversible and desulphonation takes place when sulphonic acids are heated in aqueous solution.

Some sulphonic acids are not obtained by direct sulphonation reactions. The important intermediate 4-aminobenzenesulphonic acid is manufactured by heating phenylammonium hydrogensulphate at about 200 °C for several hours.

Naphthalene, an aromatic compound, can be monosulphonated using concentrated sulphuric acid. The isomers shown below can form.



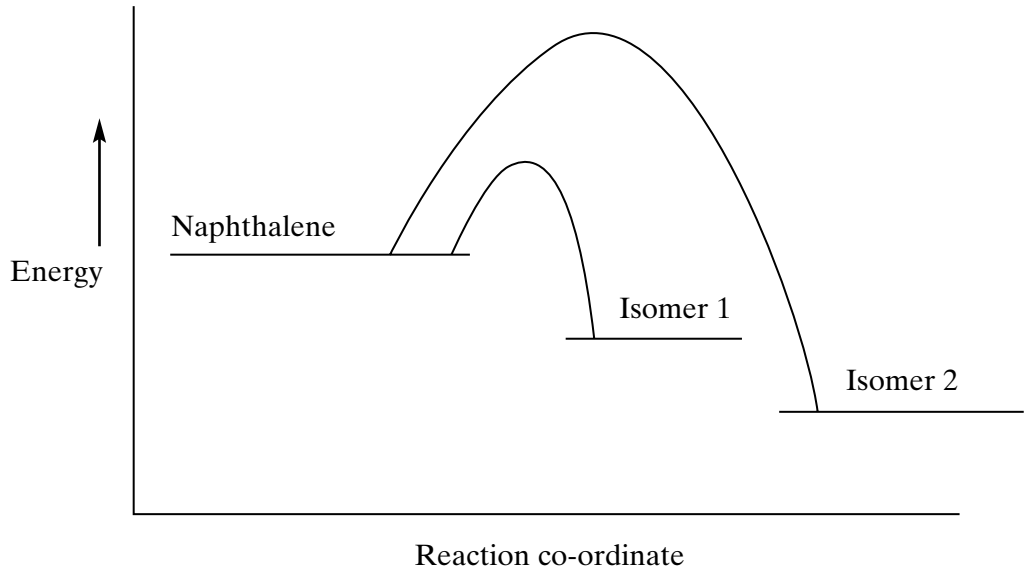
Isomer 1



Isomer 2

When naphthalene is sulphonated at 40 °C, approximately 95% of the product is Isomer 1. At 160 °C, the product contains approximately 85% of Isomer 2.

The reaction profiles for the formation of Isomers 1 and 2 are shown below.




The difference in thermodynamic stability of the two isomers can be attributed largely to the destabilising repulsion between the very bulky sulphonic acid group at the 1-position and the hydrogen atom at the adjacent 8-position. If Isomer 1 is heated with concentrated sulphuric acid, an equilibrium mixture with the 2-isomer is formed.

(a) (i) Write an equation for the formation of phenylammonium hydrogensulphate from phenylamine and sulphuric acid. *(1 mark)*

(ii) Write an equation for the formation of 4-aminobenzenesulphonic acid from phenylammonium hydrogensulphate showing clearly the structure of the reactant and the organic product. *(2 marks)*

(b) Suggest a mechanism for the sulphonation of benzene by the electrophile sulphur trioxide. *(4 marks)*

(c) Use the reaction profiles to explain why the monosulphonation of naphthalene forms a very high yield of Isomer 1 at 40 °C and a high yield of Isomer 2 at 160 °C. *(8 marks)*

## SECTION B

Answer all three questions in this section.

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

Each question carries 40 marks.

**2** **Total for this question: *40 marks***

(a) Le Chatelier's Principle states that if a constraint is applied to an equilibrium, the position of equilibrium moves so as to minimise the effect of that constraint.
Consider the following endothermic reaction in which $x$ mol of **X** are in equilibrium with $y$ mol of **Y**.

$$2\mathbf{X}(g) \rightleftharpoons \mathbf{Y}(g) \quad \Delta H \text{ is positive}$$

(i) Write an expression for $K_p$ in terms of $x$, $y$ and the overall pressure, $P$.
Use this expression to explain the effect on the position of equilibrium of changing the overall pressure.
Show that the effect on the equilibrium is consistent with that predicted using Le Chatelier's Principle. *(6 marks)*

(ii) The value of $K_p$ changes with temperature. At temperatures $T_1$ and $T_2$, $K_p$ has the values $K_1$ and $K_2$, respectively. The following equation shows how the value of $K_p$ changes with temperature.

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

Use this expression to explain qualitatively how the magnitude of $K_p$ changes as the temperature increases.
Show that this change is consistent with that predicted using Le Chatelier's principle. *(4 marks)*

(b) Ammonia is produced from nitrogen and hydrogen. In an experiment, nitrogen and hydrogen were placed in a sealed vessel in the molar ratio 1:3, respectively. At a temperature of 750 K and a pressure of 20 MPa, the system reached equilibrium when 20% of the nitrogen had been converted into ammonia.

(i) Calculate the value of the equilibrium constant $K_p$ for this reaction at 750 K. *(7 marks)*

(ii) Use your value of $K_p$ to calculate the pressure required to increase the equilibrium yield of ammonia to 50% at 750 K.
(If you were unable to calculate a value for $K_p$ in part (b)(i) you may use a value of 0.002 in your calculation but this is not the correct value.) *(6 marks)*

(iii) Suggest, with reasons, which of the two pressures in parts (b)(i) and (b)(ii) above is more likely to be used in the industrial synthesis of ammonia. *(4 marks)*

(c) Ammonia is used in the synthesis of fertilisers such as ammonium nitrate, $NH_4NO_3$, although pure ammonia can be used directly as a fertiliser.

Use the following data to answer the questions below.

For the ammonium ion, $K_a = 5.6 \times 10^{-10}$ mol dm$^{-3}$.
The ionic product of water, $K_w = 1.0 \times 10^{-14}$ mol$^2$ dm$^{-6}$.

(i) Write an equation to show that the solution containing ammonium ions formed by dissolving ammonium nitrate in water is acidic.
Calculate the pH of a 0.010 mol dm$^{-3}$ aqueous solution of ammonium nitrate.
Explain any approximations that you need to make. *(6 marks)*

(ii) Write an equation to show that an aqueous solution of ammonia is alkaline.
Calculate the pH of a 0.010 mol dm$^{-3}$ aqueous solution of ammonia.
Explain any approximations that you need to make. *(7 marks)*

**TURN OVER FOR THE NEXT QUESTION**

**3** **Total for this question: *40 marks***

(a) A student was provided with four bottles, each containing an aqueous solution of one of the following compounds. Unfortunately, the labels had been removed from the bottles.

$HCl$ $Na_2CO_3$ $BaCl_2$ $CuSO_4$

Using the above solutions ONLY, devise a plan by which you could identify each substance. In each case, describe fully the observations you would make. Negative results should be quoted but they should not be used as the sole evidence for the identity of any of the substances. Write equations for each reaction. *(12 marks)*

(b) (i) When a solution containing potassium manganate(VII) and potassium hydroxide is heated, a green solution of potassium manganate(VI), $K_2MnO_4$, is formed and oxygen gas is evolved.

Identify the oxidising agent in the reaction between potassium manganate(VII) and potassium hydroxide. Write half-equations for the oxidation and reduction processes and an overall equation for the reaction. *(4 marks)*

(ii) On cooling the green solution formed in (b)(i), green crystals of potassium manganate(VI) are produced. On addition of an excess of dilute sulphuric acid to the green crystals, solid manganese(IV) oxide is formed together with a purple solution.

Identify the ion responsible for the purple colour in the final solution. Write an equation for the reaction of $MnO_4^{2-}$ ions in an excess of acid. *(3 marks)*

(c) Sodium metal reacted with oxygen to form a compound, **X**, of composition Na, 59.0%, O, 41.0% by mass which has a molar mass of 78.0 g $mol^{-1}$. On dissolving in water, compound **X** reacted with water to form a solution, **Y**, which contained two products, one of which was $H_2O_2$.

(i) Deduce the formula of compound **X** and write an equation for its reaction with water. *(4 marks)*

(ii) Compound **X** reacts with carbon dioxide to form sodium carbonate and a colourless gas. Write an equation for this reaction and suggest why compound **X** is used in air purifiers such as those found in submarines. *(3 marks)*

(iii) A sample of **X** was dissolved in water. The $H_2O_2$ produced was determined by titration with a solution containing cerium(IV) ions. In this reaction, hydrogen peroxide was converted into oxygen and the cerium(IV) ions became cerium(III) ions.

The solution reacted with exactly 18.2 $cm^3$ of a 0.102 mol $dm^{-3}$ solution of cerium(IV) ions.

Calculate the mass of **X** used. *(8 marks)*

(d) Consider the following information and answer the questions below.

Phosphorus trifluoride reacts with chlorine to produce a gas, **B**, of formula $PF_3Cl_2$. On heating, **B** reacts to form two phosphorus pentahalides, each containing only two elements. On standing, **B** slowly transforms into an ionic solid, **C**, containing one cation and one anion. Compound **C** has the empirical formula $PF_3Cl_2$ and $M_r$ of 318. When reacted with sodium fluoride, **C** forms two products, $PCl_4F$ and $NaPF_6$.

(i) Write a balanced equation for the conversion of compound **B** into two phosphorus pentahalides. *(2 marks)*

(ii) Use the above information to identify compound **C**. *(2 marks)*

(iii) Sketch the shapes of the ions present in solid **C**. *(2 marks)*

**TURN OVER FOR THE NEXT QUESTION**

**4** **Total for this question: *40 marks***

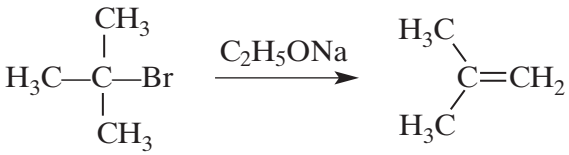
(a) Ethanol reacts with sodium to form sodium ethoxide, $C_2H_5ONa$.
When sodium ethoxide reacts with 2-bromopropane, both substitution and elimination reactions occur.

(i) Write an equation for the reaction of sodium with ethanol and state the role of sodium in this reaction. *(2 marks)*

(ii) Write a mechanism for the substitution reaction of sodium ethoxide with 2-bromopropane and state the role of sodium ethoxide in this reaction.
Suggest why sodium ethoxide causes elimination from 2-bromopropane and write an equation for this reaction. *(6 marks)*

(iii) Comment on the yields shown for the following reactions and suggest reasons for the differences.

$$CH_3CH_2Br \xrightarrow{C_2H_5ONa} \underset{90\%}{CH_3CH_2OCH_2CH_3} + \underset{10\%}{CH_2{=}CH_2}$$



100% *(4 marks)*

(b) Compound **A** ($C_5H_{10}O_3$) has an unbranched carbon skeleton and effervesces with sodium hydrogencarbonate solution. When heated under reflux with acidified potassium dichromate(VI), **A** forms compound **B** ($C_5H_8O_4$).

In a titration, 1.98 g of **B** reacts exactly with 60.0 $cm^3$ of a 0.50 mol $dm^{-3}$ solution of sodium hydroxide.

When **B** is heated, it eliminates water to form a cyclic compound **C** ($C_5H_6O_3$).

The action of heat on **A** forms another cyclic compound **D** ($C_5H_8O_2$).

Reaction of **B** with a diol **E** forms a polymeric compound **F** which contains 55.8% of carbon and 7.0% of hydrogen by mass.

Calculate the empirical formula for **F**. Deduce structural formulae for compounds **A** to **E** and name the type of compound to which **D** belongs. Deduce the repeating unit of the polymer. *(15 marks)*

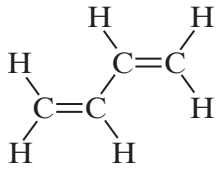
(c) (i) Why are the carbon–carbon bonds in benzene all the same length? *(1 mark)*

(ii) The enthalpy of hydrogenation of but-1-ene is –126.9 kJ $mol^{-1}$ and that of buta-1,3-diene is –238.8 kJ $mol^{-1}$.

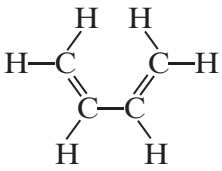
Suggest why the value for buta-1,3-diene is not twice that for but-1-ene.

Predict how the carbon–carbon bond lengths in buta-1,3-diene differ from those in but-1-ene. *(5 marks)*

(iii) Buta-1,3-diene can exist as the following two isomers at low temperatures.



I



II

Why can isomers I and II both exist? Suggest why isomer I is more stable. *(2 marks)*

(iv) Using the carbon skeleton in isomer I, draw the stereoisomers of 1,4-dichlorobuta-1,3-diene. *(3 marks)*

(v) When hydrogen bromide reacts with buta-1,3-diene, 2,3-dibromobutane is formed. Suggest **two** possible stereoisomers of 2,3-dibromobutane. *(2 marks)*

**TURN OVER FOR THE NEXT QUESTION**

## SECTION C

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

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

**5** **EITHER** (a) Discuss the factors which determine the melting/boiling points of organic compounds. Illustrate your answer by reference to four different types of bonding interaction.

*(25 marks)*

**OR** (b) Discuss the use of redox reactions in inorganic, organic and industrial chemistry.

*(25 marks)*

**END OF QUESTIONS**