General Certificate of Education
June 2004
Advanced Extension Award

AQA

ASSESSMENT and
QUALIFICATIONS
ALLIANCE

CHEMISTRY   **6821**

Wednesday 30 June 2004   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**.

6821

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

Periodic Table

Key

Relative Atomic Mass → AA

E

Atomic Number → ZZ ← Element

Group 1	2		3	4	5	6	7	0
								4.0 He 2
1.0 H 1								
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
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
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
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
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
(223) Fr 87	226.0 Ra 88	** 89 - 103						

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

*	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

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

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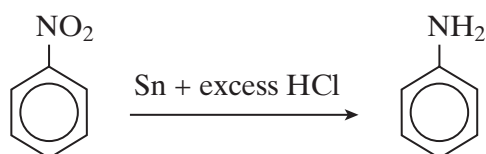
SECTION A

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

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

A laboratory preparation of phenylamine

Phenylamine can be prepared by the reduction of nitrobenzene using an excess of tin and hydrochloric acid.

In a typical experiment, hydrochloric acid is added slowly to a flask containing nitrobenzene and an excess of tin. When the initial vigorous reaction is over, the mixture is heated in an open flask to complete the reaction. Hydrochloric acid is then added to dissolve any remaining tin.

The reaction between tin and hydrochloric acid produces hydrogen and tin(II) chloride but, as the tin can be oxidised further, a hexachlorostannate(IV) complex ion, $[SnCl_6]^{2-}$, is formed.

At the end of the reduction, a salt is formed which contains phenylammonium ions and hexachlorostannate(IV) ions. Sodium hydroxide is added to this mixture and oily droplets of phenylamine are produced, together with a solution containing sodium ions and hexahydroxostannate(IV) ions.

Phenylamine is removed from this mixture by the process known as *steam distillation*. When steam is passed through this mixture, phenylamine and water distil off together. The composition of the distillate can be calculated using the relationship

$$\frac{\text{Moles of phenylamine}}{\text{Moles of water}} = \frac{\text{Partial pressure of phenylamine}}{\text{Partial pressure of water}}$$

In the vapour during distillation

    partial pressure of phenylamine + partial pressure of water = atmospheric pressure

Phenylamine and water form layers in the liquid distillate and can be separated using a tap funnel. The phenylamine layer can be dried by adding calcium oxide.

(a) Write a half-equation (ion-electron equation) for the reduction, in acidic solution, of nitrobenzene to phenylamine. *(1 mark)*

(b) Write a half-equation (ion-electron equation) for the oxidation, in the presence of an excess of hydrochloric acid, of tin(II) chloride to hexachlorostannate(IV) ions. *(2 marks)*

(c) Write equations for the reaction of phenylammonium ions and of hexachlorostannate(IV) ions with sodium hydroxide. *(3 marks)*

(d) During steam distillation at an atmospheric pressure of 100 kPa, the partial pressure of phenylamine is 8.0 kPa. Calculate the ratio, by mass, of water to phenylamine in the distillate. *(4 marks)*

(e) Explain how calcium oxide acts as a drying agent for this mixture. *(2 marks)*

(f) Explain why the boiling point of phenylamine, 457 K, is different from that of water. *(3 marks)*

TURN OVER FOR THE NEXT QUESTION

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*

Magnesium metal is manufactured by electrolysing molten magnesium chloride. The magnesium chloride can be obtained from sea-water. Magnesium hydroxide is precipitated and then converted into magnesium oxide by heating. The magnesium oxide is converted into anhydrous magnesium chloride.

(a)   The table below contains some enthalpy data.

Process	$\Delta H^{\ominus}/\text{kJ}\,\text{mol}^{-1}$
$Mg(s) \longrightarrow Mg(g)$	+150
$Mg(g) \longrightarrow Mg^+(g) + e^-$	+736
$Mg^+(g) \longrightarrow Mg^{2+}(g) + e^-$	+1450
$O_2(g) \longrightarrow 2O(g)$	+496
$O(g) + e^- \longrightarrow O^-(g)$	−142
$O^-(g) + e^- \longrightarrow O^{2-}(g)$	+844
$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$	−602

(i)   Suggest why the second ionisation enthalpy for magnesium is greater than the first.
(2 marks)

(ii)   Suggest why the oxygen atom has a negative electron affinity and why the electron affinity of the O^- ion has a positive value. *(3 marks)*

(iii)   Use the above data to calculate the lattice enthalpy of magnesium oxide. *(3 marks)*

(iv)   Suggest qualitatively how the magnitude of the lattice enthalpy of magnesium chloride compares with that of magnesium oxide. Explain your answer. *(4 marks)*

(b) Magnesium hydroxide is slightly soluble in water. An equilibrium is established when solid magnesium hydroxide is in contact with a saturated solution of magnesium and hydroxide ions.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

An equilibrium constant, K, for this reaction is

$$K = [Mg^{2+}(aq)][OH^-(aq)]^2 = 1.1 \times 10^{-11}\,mol^3\,dm^{-9}$$

(i) A sample of sea-water contains magnesium ions at a concentration of $2.0 \times 10^{-4}\,mol\,dm^{-3}$. Use the expression for K to calculate the pH at 298 K of a solution in which these magnesium ions are in equilibrium with aqueous hydroxide ions and solid magnesium hydroxide. ($K_w = 1.0 \times 10^{-14}\,mol^2\,dm^{-6}$ at 298 K)

Suggest what will happen in the solution if the pH is raised above this value and explain your answer. *(7 marks)*

(ii) The sample of sea-water also contains calcium ions at a concentration similar to that of magnesium ions. A similar equilibrium between the calcium ions, hydroxide ions and solid calcium hydroxide is reached at a pH of 12.30.

Suggest, qualitatively, what this information implies about the solubility of calcium hydroxide compared with that of magnesium hydroxide and explain your answer.

(If you have been unable to calculate an answer for part (b)(i), you may assume a pH value of 9.50 but that is not the correct value.)

Suggest a method for the separation of magnesium hydroxide, but not calcium hydroxide, from the sample of sea-water. Explain your reasoning. *(6 marks)*

QUESTION 2 CONTINUES ON THE NEXT PAGE

Turn over ▶

(c) The equation for the equilibrium established when magnesium oxide and chlorine react is given below.

$$MgO(s) + Cl_2(g) \rightleftharpoons MgCl_2(s) + \tfrac{1}{2}O_2(g)$$

The expression for the equilibrium constant, K_p, is

$$K_p = \frac{(pO_2)^{\frac{1}{2}}}{pCl_2}$$

At a given temperature and an overall pressure of 100 kPa, equilibrium is established when 50% of the chlorine is converted into magnesium chloride.

(i) Calculate the value of K_p under these conditions and state its units. *(5 marks)*

(ii) Calculate the overall pressure that would be necessary, at this temperature, in order to increase the amount of chlorine converted at equilibrium to 80%.

(If you have been unable to calculate an answer for part (c)(i), you may assume a numerical value of 0.13 for K_p but this is not the correct value.) *(4 marks)*

(iii) In practice, the yield of magnesium chloride from this reaction is improved by adding an excess of carbon to the mixture of magnesium oxide and chlorine. The carbon reacts as shown in the following equations.

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$
$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$
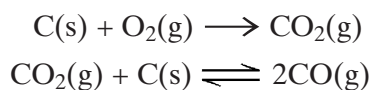
Explain why the yield of magnesium chloride is improved in the presence of carbon.

The standard enthalpies of formation of carbon dioxide and carbon monoxide are

$CO_2\ \Delta H_f^{\ominus} = -395\,kJ\,mol^{-1}$;
$CO\ \Delta H_f^{\ominus} = -137\,kJ\,mol^{-1}$

Use these data to explain the effect of increasing the reaction temperature on the relative amounts of CO_2 and CO present in the equilibrium mixture. *(6 marks)*
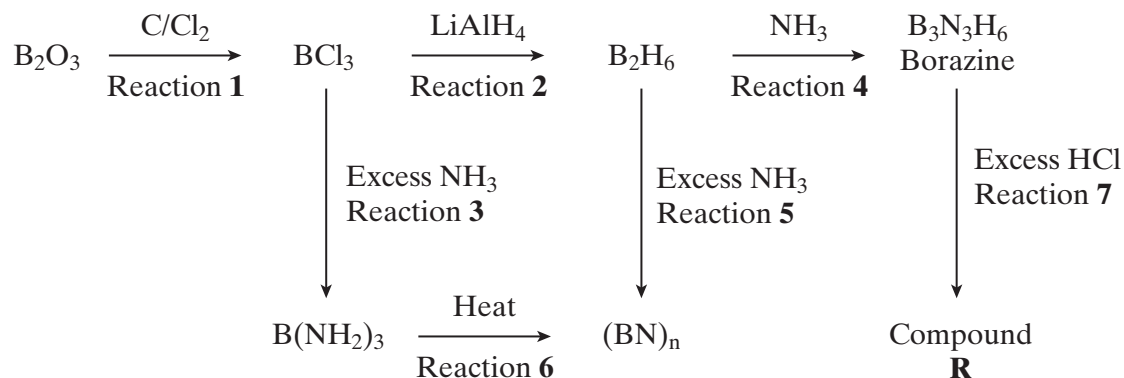
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TURN OVER FOR THE NEXT QUESTION

Turn over ▶

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

(a) Consider the reaction scheme shown below.

$$B_2O_3 \xrightarrow[\text{Reaction } \mathbf{1}]{C/Cl_2} BCl_3 \xrightarrow[\text{Reaction } \mathbf{2}]{LiAlH_4} B_2H_6 \xrightarrow[\text{Reaction } \mathbf{4}]{NH_3} \begin{array}{c} B_3N_3H_6 \\ \text{Borazine} \end{array}$$

BCl₃ — Excess NH₃ Reaction **3** → B(NH₂)₃

B₂H₆ — Excess NH₃ Reaction **5** → (BN)ₙ

Borazine — Excess HCl Reaction **7** → Compound **R**

$$B(NH_2)_3 \xrightarrow[\text{Reaction } \mathbf{6}]{\text{Heat}} (BN)_n$$

(i) Write equations for the reactions **1** and **3**. Reaction **1** is a redox reaction; identify the reducing agent and the oxidising agent in this reaction. Justify your answer by reference to the oxidation states of the elements involved.   *(8 marks)*
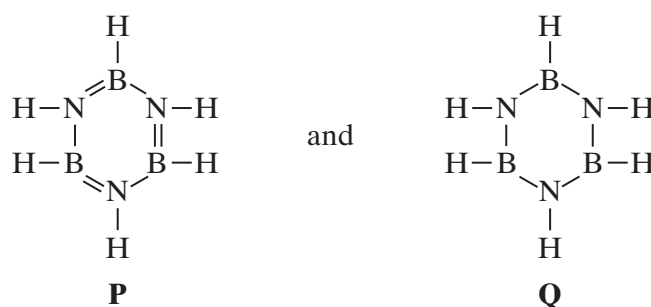
(ii) Boron nitride, $(BN)_n$, exists in two structural forms. One form has a layer structure similar to that of graphite.

Draw a diagram to represent one layer of this structure.

The other structural form is obtained as small crystals, harder than diamond, when the layer structure is subjected to high temperature and pressure.

Suggest why these conditions are needed for this conversion and why the crystals are harder than diamond.   *(5 marks)*

(iii) Two possible structures of borazine are shown below.


```
        H                              H
        |                              |
        B                              B
      //  \                          /   \
  H—N      N—H        and       H—N       N—H
     |      ||                      |       |
  H—B      B—H                   H—B       B—H
      \\  /                          \   /
        N                              N
        |                              |
        H                              H
        P                              Q
```

Explain how the involvement of the lone pairs of electrons on the nitrogen atoms produces the bonding shown in structure **P**.

Suggest and explain any differences in the three-dimensional shapes of **P** and **Q**.   *(6 marks)*

(iv) Borazine reacts with HCl gas, in reaction **7**, forming a covalently bonded product, **R**, of molecular formula $B_3N_3H_9Cl_3$.

Draw the structure of a molecule of **R** that is formed from borazine. Explain how and why the reaction between borazine and an excess of HCl occurs.   *(4 marks)*

(b) (i) Sodium dichromate(VI), $Na_2Cr_2O_7$, can be prepared from the ore 'chromite' which is a mixed oxide of formula $FeO \cdot Cr_2O_3$. Heating powdered chromite with aqueous sodium hydroxide in the presence of an excess of oxygen produces a solution of sodium chromate(VI), Na_2CrO_4, and a brown precipitate. The sodium chromate(VI) is then converted into sodium dichromate(VI) by the addition of aqueous acid.

Identify the brown precipitate and deduce the half-equations for the two oxidation processes and the one reduction process occurring.

Write an ionic equation for the conversion of chromate(VI) ions into dichromate(VI) ions.   *(6 marks)*

(ii) The addition of concentrated sulphuric acid to a mixture of sodium dichromate(VI) and sodium chloride produced compound **Z** as a red vapour. When **Z** was passed into concentrated aqueous sodium chloride, a salt of formula $NaCrO_3Cl$ was formed.

The composition of **Z** was found to be Cr, 33.55 %; O, 20.65 %; Cl, 45.81 % by mass. A sample of **Z** of mass 1.37 g occupied a volume of 291 cm^3 at 101 kPa and 400 K.

Deduce the empirical and molecular formulae of compound **Z**. Draw a diagram to show the shape of and the bonding in a molecule of **Z**. Write ionic equations for the formation of **Z** and for its reaction with aqueous chloride ions.
(The gas constant $R = 8.31 \, J \, K^{-1} mol^{-1}$. The Gas Molar Volume = 32.9 dm^3 at 400 K and 101 kPa.)   *(11 marks)*

TURN OVER FOR THE NEXT QUESTION

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

(a)   This question concerns the acid strengths of organic compounds.

pK_a is used as a measure of acid strength; strong acids have lower pK_a values than weak acids.
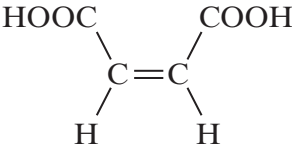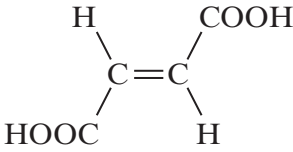
The ability of an organic compound containing the OH group to act as an acid depends on the strength of the O—H bond in the particular compound and also on the stability of the anion formed by loss of a proton.

(i)   Explain why ethanoic acid (pK_a = 4.76) is a much stronger acid than ethanol (pK_a = 16.0).   *(6 marks)*

(ii)   Discuss the variation in strength of the following monoprotic carboxylic acids.

Name	*Formula*	pK_a
methanoic acid	HCOOH	3.75
propanoic acid	CH_3CH_2COOH	4.87
2-chloropropanoic acid	$CH_3CHClCOOH$	2.83
3-chloropropanoic acid	$ClCH_2CH_2COOH$	4.10
3-fluoropropanoic acid	FCH_2CH_2COOH	3.90

(6 marks)

(iii)   Discuss the variation in strength of the following diprotic carboxylic acids.

	pK_{a1}	pK_{a2}
cis-butenedioic acid	1.92	6.23
trans-butenedioic acid	3.02	4.38

```
          HOOC        COOH
             \        /
              C = C
             /        \
            H          H
```

```
          H          COOH
           \          /
            C = C
           /          \
        HOOC           H
```
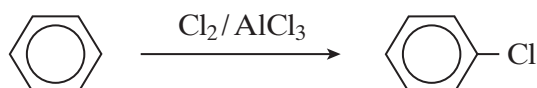
(2 marks)

(b) This question concerns substitution in aromatic rings.

Strong oxidation of any alkylbenzene leads to benzenecarboxylic acid as shown below.
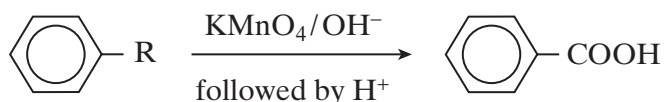
Reaction of benzene with chlorine in the presence of $AlCl_3$ forms chlorobenzene as shown below.


When monosubstituted aromatic compounds undergo further substitution, the position in the aromatic ring where the new substituent enters is determined mainly by the nature of the original substituent.

Use the data in the table below to answer the questions which follow.

Original substituent in position 1	Position(s) to which new substituent is directed
$-CH_3$	2 and 4
$-NH_2$	2 and 4
$-Cl$	2 and 4
$-NO_2$	3
$-COOH$	3
$-COOCH_3$	3

 (i) Draw the structure of the major organic product formed when benzenecarboxylic acid is mononitrated and outline a mechanism for the reaction.   *(4 marks)*

 (ii) Draw the structure of the two isomers formed when 1 mol of methylbenzene is treated with 1 mol of Cl_2 in the presence of $AlCl_3$. Suggest which isomer will be formed in the larger amount.   *(3 marks)*

 (iii) Suggest, by giving reagents and conditions, how you might prepare the following compounds from the given starting materials. (Ignore mixtures of isomers.)
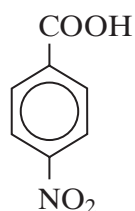
starting from methylbenzene
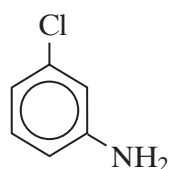
starting from benzene

(6 marks)

QUESTION 4 CONTINUES ON THE NEXT PAGE   **Turn over ▶**

(c)   Six different compounds, **A** – **F**, are isomers with the molecular formula $C_5H_{10}O$.

The infra-red spectra of **A**, **B** and **C** all contain absorptions at about $1700\,cm^{-1}$.

The infra-red spectra of **D** and **E** both contain absorptions at about $3400\,cm^{-1}$.

The infra-red spectrum of **D** also contains an absorption at $1650\,cm^{-1}$ but that of **E** does not.

The infra-red spectrum of **F** does not contain any of the absorptions mentioned above.

Reduction of **A** followed by dehydration of the product forms only one alkene, which can exist as a pair of geometrical (*cis-trans*) isomers.

B has only two peaks in its proton n.m.r. spectrum.

C exists as a pair of optical isomers.

D has a branched carbon chain and exists as a pair of geometrical (*cis-trans*) isomers.

Use the information above and the table of data below to suggest a structure for each of the compounds **A** – **F** and explain your working.

Table of infra-red absorption data

Bond	Wavenumber/cm^{-1}
C—H	2850–3300
C—C	750–1100
C=C	1620–1680
C=O	1680–1750
C—O	1000–1300
O—H (alcohols)	3230–3550
O—H (acids)	2500–3000

(13 marks)

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 how changes in reaction conditions affect

  (i) the rate of a chemical reaction and the rate constant for the reaction; *(15 marks)*

  (ii) the position of equilibrium in a homogeneous reaction and the equilibrium constant for the reaction. *(10 marks)*

OR

(b) (i) Discuss, using examples of your own choice, isomerism in organic chemistry.
  (12 marks)

  (ii) Complex ions are formed when transition metal ions react with ligands. Common complex ion shapes include octahedral and tetrahedral. The ligands H_2O, CN^-, Cl^- and NH_3, which attach to just one position on the transition metal ion, are said to be unidentate. The ligand ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$, 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.

  Transition metal ions can form a wide range of isomeric complex ions, some of which are geometrical isomers whilst others are optical isomers.

  Using your knowledge and understanding of isomerism in organic chemistry, deduce which types of isomers of the complexes with octahedral and tetrahedral shapes are formed by these ligands.

  Suggest examples in each case. *(13 marks)*

END OF QUESTIONS

THERE ARE NO QUESTIONS PRINTED ON THIS PAGE