Centre No.						Paper Reference							Surname	Initial(s)
Candidate No.						6	2	5	4	/	0	1	Signature	

Paper Reference(s)

6254/01

Edexcel GCE

Chemistry (Nuffield)

Advanced

Unit Test 4

Tuesday 22 January 2008 – Morning

Time: 1 hour 30 minutes

Examiner's use only

Team Leader's use only

Question Number	Leave Blank
1	
2	
3	
4	
5	
Total	

Materials required for examination
Nil

Items included with question papers
Nil

A calculator may be used.

Instructions to Candidates

In the boxes above, write your centre number, candidate number, your surname, initial(s) and your signature.
Answer **ALL** the questions. Write your answers in the spaces provided in this question paper.
Final answers to calculations should be given to an appropriate number of significant figures.

Information for Candidates

A Periodic Table is printed on the back cover of this question paper.
The marks for the various parts of questions are shown in round brackets: e.g. **(2)**.
The total mark for this paper is 60. There are 16 pages in this paper. All blank pages are indicated.

Advice to Candidates

You are advised to show all steps in any calculations.
You will be assessed on your ability to organise and present information, ideas, descriptions and arguments clearly and logically, taking into account your use of grammar, punctuation and spelling.

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Answer ALL the questions. Write your answers in the spaces provided.

1. This question is about the reaction between barium hydroxide and ammonium chloride:

$Ba(OH)_2(s) + 2NH_4Cl(s) \rightarrow BaCl_2.2H_2O(s) + 2NH_3(g) \qquad \Delta H = +21.2\ kJ\ mol^{-1}$

(a) Standard entropies of the reactants and products are shown below:

Substance	Standard entropy, $S^{\ominus}$ / J mol^{-1} K^{-1}
$Ba(OH)_2(s)$	+ 99.7
$NH_4Cl(s)$	+ 94.6
$BaCl_2.2H_2O(s)$	+202.9
$NH_3(g)$	+192.3

Calculate the standard entropy change for the system, $\Delta S^{\ominus}_{system}$, for this reaction. Include a sign and units in your answer.

(2)

(b) Calculate the entropy change for the surroundings, $\Delta S^{\ominus}_{surroundings}$, at 298 K. Give your answer to **3** significant figures and include a sign and units in your answer.

(2)

Leave blank

(c) (i) Use your answers to (a) and (b) to explain why this reaction is spontaneous at 298 K.

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(1)

(ii) When these two solids are mixed together in a beaker, no reaction is observed. What explanation can be given for this, in view of the fact that the process is spontaneous?

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(1)

(iii) Apart from heating the mixture, suggest what might be done to encourage the reaction to take place. Explain why your suggestion is likely to work.

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(2) **Q1**

(Total 8 marks)

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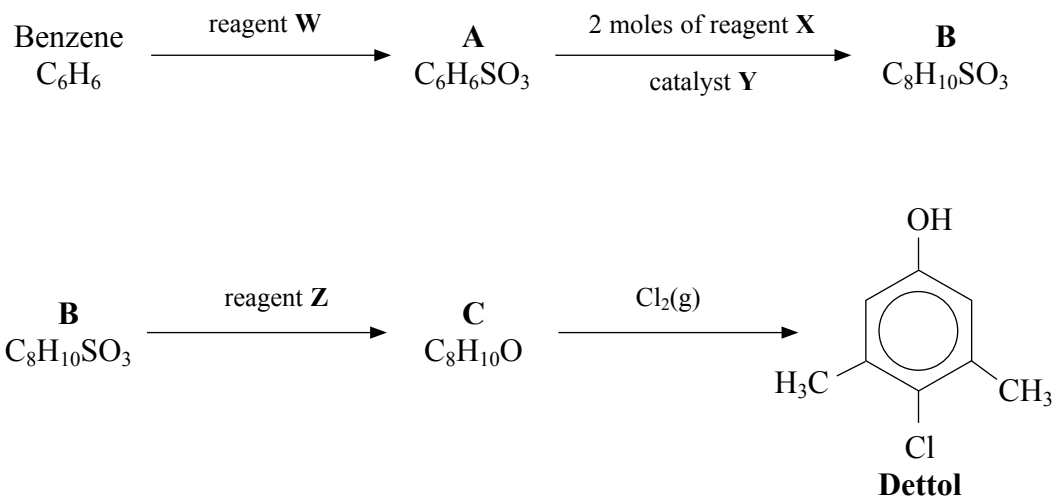
2. The reaction scheme below shows a synthesis of the antiseptic, Dettol, from benzene.



Study this reaction scheme carefully before answering any of the questions below.

(a) (i) Give the structural formula of **A**.

(1)

(ii) Name reagent **W**.

.....

(1)

(iii) State the type of reaction and the mechanism for the conversion of benzene into **A**.

.....

(1)

(iv) Give the **formula** of the species which attacks benzene to form **A**.

.....

(1)

Leave blank

(b) (i) Suggest the structural formula of **B**. You may find it helpful to study the formula for Dettol, as well as your answer to (a)(i), when answering this question.

(1)

(ii) Give the formulae for reagent **X** and catalyst **Y**.

Reagent **X** ..... Catalyst **Y** .....

(2)

(iii) What gaseous inorganic compound will also be produced during the formation of **B**?

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(1)

(c) (i) Compound **C**, $C_8H_{10}O$, reacts with sodium and with sodium hydroxide. What does this tell you about its structure?

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(1)

(ii) Suggest a possible identity for reagent **Z**.

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(1)

(iii) The conversion of **C** into Dettol involves the use of chlorine in the dark.

Suggest the structural formula of ONE alternative product which may form if this reaction is carried out in sunlight.

(1)

Leave blank

(d) (i) Give the systematic name for Dettol.

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(1)

(ii) Suggest why Dettol does not mix well with water.

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(1)

Q2

(Total 13 marks)

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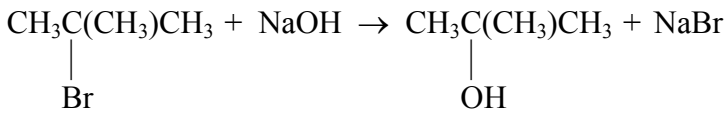
3. The principal reaction occurring when 2-bromo-2-methylpropane reacts with aqueous sodium hydroxide is as follows:



Several experiments were carried out in order to follow the kinetics of this alkaline hydrolysis.
A few drops of phenolphthalein were added to a sample of sodium hydroxide, and, after the addition of a measured amount of 2-bromo-2-methylpropane, the mixture was vigorously shaken and a clock was immediately started. The time was taken when the pink colour due to the indicator disappeared.
This experiment was repeated twice using different concentrations of the two reactants. All experiments were carried out at the same temperature.
The results are shown in the table below.

Experiment	2-bromo-2-methylpropane / mol dm^{-3}	Sodium hydroxide / mol dm^{-3}	Time /s
A	0.011	8.0×10^{-4}	33
B	0.022	8.0×10^{-4}	16
C	0.022	1.2×10^{-3}	24

(a) (i) Identify the attacking species responsible for this alkaline hydrolysis.

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(1)

(ii) Assuming that the final concentration of sodium hydroxide is zero, calculate the average rates of reaction in mol dm^{-3} s^{-1} for experiments **A** and **B**.

A ..... mol dm^{-3} s^{-1} **B** ..... mol dm^{-3} s^{-1}

(2)

(iii) Deduce the order of reaction with respect to 2-bromo-2-methylpropane. Justify your answer.

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(1)

Leave blank

(iv) By comparing the average rates of reaction between experiments **B** and **C**, deduce the order of reaction with respect to sodium hydroxide.

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(2)

(v) Write the rate equation for the reaction.

Rate =

(1)

(vi) From your rate equation, suggest how this reaction proceeds by giving a possible mechanism.

(3)

(b) Explain briefly why 1-bromobutane, an isomer of 2-bromo-2-methylpropane, reacts by a different mechanism when it is hydrolysed.

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(2)

Q3

(Total 12 marks)

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4. The equation below shows the equilibrium existing between nitrogen, oxygen and nitrogen monoxide.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

The equilibrium constant, K_p, at 298 K is 5.0×10^{-31}

(a) (i) Write an expression for the equilibrium constant, K_p, in terms of the partial pressures of the three gases.

(1)

(ii) Why does the value for K_p have no units?

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(1)

(b) An equilibrium mixture of these three gases was found to contain nitrogen, at a partial pressure of 0.87 atm, and oxygen, at a partial pressure of 0.23 atm.

(i) Calculate the partial pressure exerted by the nitrogen monoxide.

(2)

(ii) Deduce the value of the total pressure of the equilibrium mixture of gases.

(1)

Leave blank

(iii) Assuming that the total pressure on the mixture of gases is doubled, what, if any, would be the effect on the

- partial pressure of nitrogen monoxide

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- equilibrium constant, K_p?

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(2)

(c) Inside a car engine, air (a mixture of nitrogen and oxygen) is drawn in and, under the high temperatures operating, the value of K_p increases dramatically.

This increase is also accompanied by an increase in the value of ΔS_{total}. Typical values of K_p and ΔS_{total} are shown in the table below.

Temperature / K	K_p	ΔS_{total} / J mol^{-1} K^{-1}
298	5.0×10^{-31}	–580
1500	1.0×10^{-5}	– 96

Although the value of ΔS_{system} is unlikely to alter very much, the value for $\Delta S_{surroundings}$ will change significantly.

(i) At a temperature of 1500 K, ΔS_{total} is negative.

Does this mean that the reaction between nitrogen and oxygen cannot occur at this temperature? Explain your reasoning.

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(1)

(ii) Why is the value for ΔS_{system} for this equilibrium approximately constant when the temperature rises above 298 K?

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(1)

Leave blank

(iii) What is the sign of $\Delta S_{surroundings}$ for an **endothermic** reaction? Justify your answer.

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(1)

(iv) Explain why an endothermic reaction results in an increase in the value of ΔS_{total} as the temperature increases.

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(1)

(d) A student used the value for K_p at 1500 K to calculate the partial pressure of nitrogen monoxide inside a working car engine.

Why might the actual partial pressure be lower than the calculated answer?

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(1)

Q4

(Total 12 marks)

Leave blank

5. This question is about benzoic acid, $C_6H_5CO_2H$, and some of its derivatives.

(a) (i) Give the structural formula of the carbonyl compound which can be oxidised to benzoic acid.

(1)

(ii) Give the names of the TWO reagents which together could be used to carry out this oxidation.

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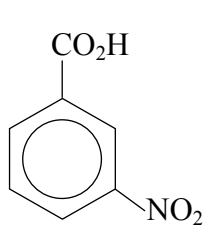
(2)

(b) The compound below can be prepared by heating together a mixture of benzoic acid, concentrated nitric acid and concentrated sulphuric acid.



This nitration process is a slow one, despite the use of such vigorous conditions.

Suggest why benzoic acid is less reactive than benzene towards reagents of this type.

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(2)

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(c) Benzoic acid can be converted into the salt sodium benzoate, $C_6H_5CO_2Na$, and also into the ester, methyl benzoate, $C_6H_5CO_2CH_3$.

(i) Give the names of suitable substances needed to convert benzoic acid to these two compounds.

$C_6H_5CO_2Na$

.....

$C_6H_5CO_2CH_3$

..... and .....

(3)

(ii) Give ONE difference in physical properties between sodium benzoate and methyl benzoate.

Explain this difference in terms of the bonding present.

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(2)

(iii) In sodium benzoate the two carbon oxygen bonds are of the same length, whereas in methyl benzoate these lengths are different.

Suggest why this is the case, illustrating your answer with appropriate diagrams.

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(2)

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(d) Calculate the pH of the buffer solution formed by mixing 10 cm^3 of aqueous benzoic acid of concentration 0.010 mol dm^{-3} with 40 cm^3 of aqueous sodium benzoate of concentration 0.020 mol dm^{-3}.

For benzoic acid, the acid dissociation constant, K_a, is 6.3×10^{-5} mol dm^{-3}.

You may find it helpful to use the relationship $\text{pH} = -\log K_a - \log \dfrac{[\text{acid}]}{[\text{base}]}$

(3)

Q5

(Total 15 marks)

TOTAL FOR PAPER: 60 MARKS

END

THE PERIODIC TABLE

Period	1	2	Group										3	4	5	6	7	0
1	1 H Hydrogen 1																	2 He Helium 4
2	3 Li Lithium 7	4 Be Beryllium 9											5 B Boron 11	6 C Carbon 12	7 N Nitrogen 14	8 O Oxygen 16	9 F Fluorine 19	10 Ne Neon 20
3	11 Na Sodium 23	12 Mg Magnesium 24											13 Al Aluminium 27	14 Si Silicon 28	15 P Phosphorus 31	16 S Sulphur 32	17 Cl Chlorine 35.5	18 Ar Argon 40
4	19 K Potassium 39	20 Ca Calcium 40	21 Sc Scandium 45	22 Ti Titanium 48	23 V Vanadium 51	24 Cr Chromium 52	25 Mn Manganese 55	26 Fe Iron 56	27 Co Cobalt 59	28 Ni Nickel 59	29 Cu Copper 63.5	30 Zn Zinc 65.4	31 Ga Gallium 70	32 Ge Germanium 73	33 As Arsenic 75	34 Se Selenium 79	35 Br Bromine 80	36 Kr Krypton 84
5	37 Rb Rubidium 85	38 Sr Strontium 88	39 Y Yttrium 89	40 Zr Zirconium 91	41 Nb Niobium 93	42 Mo Molybdenum 96	43 Tc Technetium (99)	44 Ru Ruthenium 101	45 Rh Rhodium 103	46 Pd Palladium 106	47 Ag Silver 108	48 Cd Cadmium 112	49 In Indium 115	50 Sn Tin 119	51 Sb Antimony 122	52 Te Tellurium 128	53 I Iodine 127	54 Xe Xenon 131
6	55 Cs Caesium 133	56 Ba Barium 137	57 ► La Lanthanum 139	72 Hf Hafnium 178	73 Ta Tantalum 181	74 W Tungsten 184	75 Re Rhenium 186	76 Os Osmium 190	77 Ir Iridium 192	78 Pt Platinum 195	79 Au Gold 197	80 Hg Mercury 201	81 Tl Thallium 204	82 Pb Lead 207	83 Bi Bismuth 209	84 Po Polonium (210)	85 At Astatine (210)	86 Rn Radon (222)
7	87 Fr Francium (223)	88 Ra Radium (226)	89 ►► Ac Actinium (227)	104 Unq Unnil-quadium (261)	105 Unp Unnil-pentium (262)	106 Unh Unnil-hexium (263)												

Key

Atomic Number
Symbol
Name
Molar mass in g mol^{-1}

► Lanthanide elements	58 Ce Cerium 140	59 Pr Praseo-dymium 141	60 Nd Neodymium 144	61 Pm Promethium (147)	62 Sm Samarium 150	63 Eu Europium 152	64 Gd Gadolinium 157	65 Tb Terbium 159	66 Dy Dysprosium 163	67 Ho Holmium 165	68 Er Erbium 167	69 Tm Thulium 169	70 Yb Ytterbium 173	71 Lu Lutetium 175
►► Actinide elements	90 Th Thorium 232	91 Pa Protactinium (231)	92 U Uranium 238	93 Np Neptunium (237)	94 Pu Plutonium (242)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (245)	98 Cf Californium (251)	99 Es Einsteinium (254)	100 Fm Fermium (253)	101 Md Mendelevium (256)	102 No Nobelium (254)	103 Lr Lawrencium (257)