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

Paper Reference(s)

6245/01

Edexcel GCE

Chemistry

Advanced

Unit Test 5

(including synoptic assessment)

Wednesday 27 January 2010 – Morning

Time: 1 hour 30 minutes

Examiner's use only

Team Leader's use only

Question Number	Leave Blank
1	
2	
3	
4	
5	
6	
Total	

Materials required for examination	Items included with question papers
Nil	Nil

Candidates may use a calculator.

Instructions to Candidates

In the boxes above, write your centre number, candidate number, your surname, initial(s) and signature.
Check that you have the correct question paper. The paper reference is shown above.
Answer **ALL** the questions. Write your answers in the spaces provided in this question paper.
Do not use pencil. Use blue or black ink.
Show all the steps in any calculations and state the units.

Information for Candidates

The marks for individual questions and the parts of questions are shown in round brackets: e.g. **(2)**.
The total mark for this paper is 75. There are 24 pages in this question paper. Any blank pages are indicated.
A Periodic Table is printed on the back cover of this paper.

Advice to Candidates

You are reminded of the importance of clear English and careful presentation in your answers.
You will be assessed on your Quality of Written Communication in this paper.

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Turn over

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

1. The isomers of the halogenoalkane C_4H_9I can undergo nucleophilic substitution reactions by two different mechanisms, S_N1 or S_N2. The overall reaction with cyanide ions is represented by the equation below.

$$C_4H_9I + CN^- \rightarrow C_4H_9CN + I^-$$

Two rate equations are possible for this reaction.

Mechanism type	Rate equation
S_N1	Rate = $k_1[C_4H_9I]$
S_N2	Rate = $k_2[C_4H_9I]\ [CN^-]$

(a) Suggest the structural formula of the isomer of C_4H_9I that reacts almost entirely by the S_N1 mechanism and of the isomer that reacts almost entirely by the S_N2 mechanism.

S_N1

S_N2

(2)

Leave blank

(b) (i) Write the S_N1 mechanism for the reaction of cyanide ions with the isomer you have chosen in (a).

(3)

(ii) Write the S_N2 mechanism for the reaction of cyanide ions with the isomer you have chosen in (a).

(3)

Leave blank

(c) Complete the energy profile for each mechanism.

S_N1

S_N2

(2)

(d) State how the rate of the reaction would change if C_4H_9Cl was used in place of C_4H_9I. Justify your answer.

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(3)

Q1

(Total 13 marks)

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2. Solutions of hydrogen peroxide, H_2O_2, are generally supplied in bottles which have caps that allow gases to escape. This is because hydrogen peroxide tends to decompose slowly even at room temperature.

Hydrogen peroxide can act as a reducing agent or as an oxidising agent.

A $H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad E^{\ominus} = +1.77\ V$

B $O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \qquad E^{\ominus} = +0.68\ V$

(a) (i) In which half-equation, **A** or **B**, is hydrogen peroxide acting as a **reducing agent**? Justify your answer.

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(1)

(ii) Combine the two half-equations to write the overall equation for the decomposition of hydrogen peroxide.

(1)

(b) The rate equation for the decomposition of hydrogen peroxide is shown below.

$$\text{Rate} = k[H_2O_2]$$

(i) What is k?

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(1)

(ii) Give the unit of k.

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(1)

Leave blank

(iii) Why is the reaction described as **first order**?

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(1)

(c) The relationship between k, the activation energy, E_a, and the kelvin temperature, T, is given by the Arrhenius equation

$$\ln k = \text{constant} - \frac{E_a}{R}\left(\frac{1}{T}\right)$$

The rate of reaction is directly proportional to the value of k.

Use the Arrhenius equation to explain why the rate of a reaction increases when:

(i) the temperature is increased

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(2)

(ii) a catalyst is added.

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(2)

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(2)

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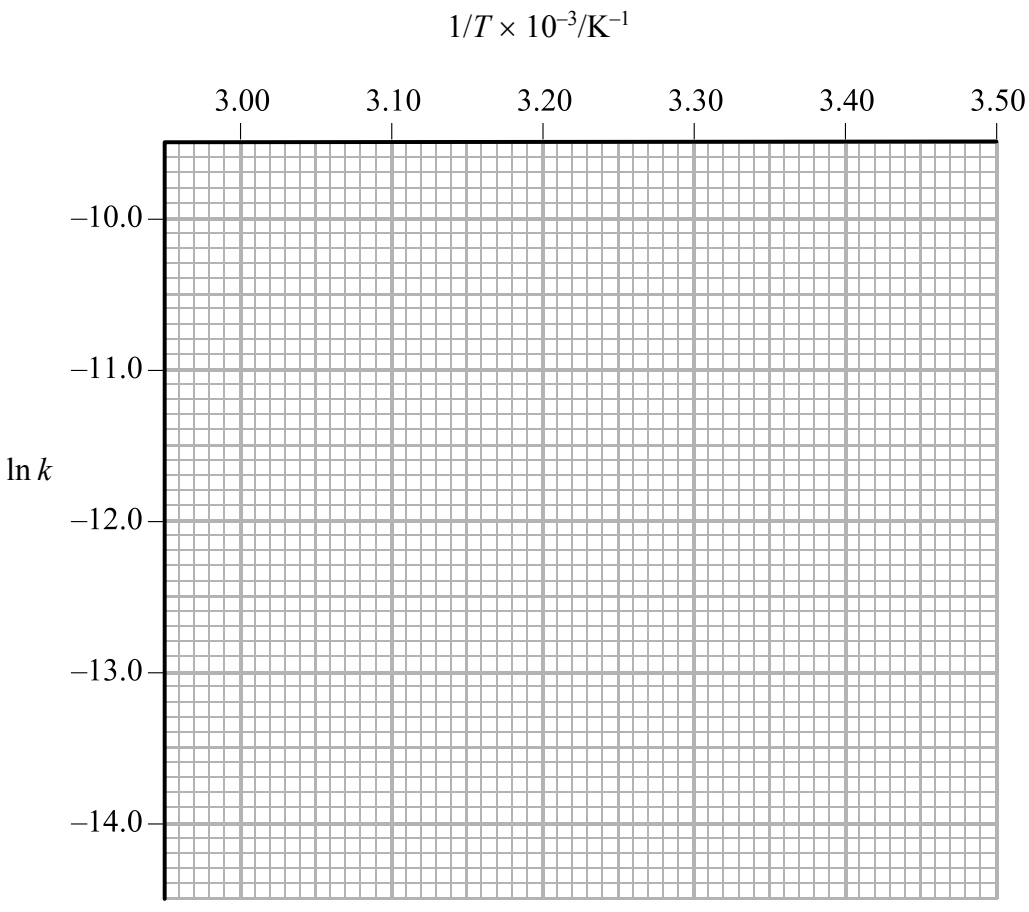
(d) In an investigation to find the value of the activation energy for the decomposition of a solution of hydrogen peroxide, the values of k were found at different temperatures.

$$\ln k = \text{constant} - \frac{E_a}{R}\left(\frac{1}{T}\right)$$

The gas constant, R, is 8.31 J $K^{-1}mol^{-1}$.

T /K	$1/T$ /K^{-1}	$\ln k$
293	3.41×10^{-3}	–13.3
302	3.31×10^{-3}	–12.4
314	3.19×10^{-3}	–11.1
323	3.10×10^{-3}	–10.3

(i) Plot a graph of $\ln k$ against $1/T$ on the axes below.



(2)

Leave blank

(ii) Calculate the slope (gradient) of the straight line and hence calculate the value of the activation energy, E_a, for the reaction. Include a sign and units in your answer.

(3)

Q2

(Total 14 marks)

Turn over

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3. The data below are required to answer this question.

	$E^{\ominus}$ /V
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.27
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52

Oxidation number	Ion	Colour
+5	VO_2^+	yellow
+4	VO^{2+}	blue
+3	V^{3+}	green
+2	V^{2+}	violet

(a) Zinc metal powder is added to an acidified solution of ammonium vanadate(V), which contains the VO_2^+ ion. The following successive colour changes seen as the reaction proceeds are

yellow → green → blue → green → violet

(i) Use the numerical data above to explain why zinc can reduce the VO_2^+ ion all the way down to V^{2+}. You are **not** required to write the equations for the reactions taking place.

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(3)

(ii) Suggest the formulae of the vanadium ions present in the **first** green solution.

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(1)

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(b) Solutions containing the VO_2^+ ion can be reduced in acid solution using either excess zinc metal or sulphur dioxide, SO_2. The oxidation state of vanadium in the resulting solutions can be found by measuring the volume of acidified potassium manganate(VII) needed to re-oxidise the product back to VO_2^+.

Titration Data

Volume of solution containing VO_2^+ ions	25.0 cm^3
Concentration of VO_2^+ ions	0.0500 mol dm^{-3}
Concentration of potassium manganate(VII)	0.0200 mol dm^{-3}
Volume of potassium manganate(VII) solution required	
after reduction with zinc	37.5 cm^3
after reduction with sulphur dioxide	12.5 cm^3

(i) Use the titration data to confirm that the oxidation state of vanadium after reduction with **zinc** is +2.

(4)

(ii) Use the titration data to deduce the actual final oxidation state of vanadium after reduction with sulphur dioxide.

(2)

(iii) Analysis of the $E^{\ominus}$ data would suggest that acidified sulphur dioxide would reduce VO_2^+ to V^{3+}.

Suggest why the final oxidation state found by titration is different from that predicted from $E^{\ominus}$ values.

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(1)

(Total 11 marks)

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Q3

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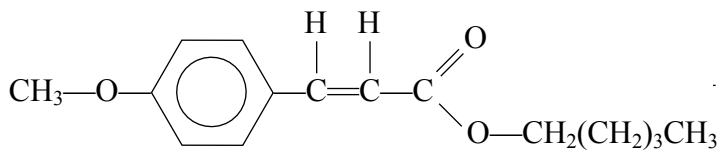
4. The compound 1-pentyl-4-methoxycinnamate can act as a sunscreen. It has the formula



(a) Give a chemical test and its result that would show the presence of the alkene group in this molecule.

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(1)

(b) (i) The addition of one molecule of hydrogen bromide, HBr, to this molecule could result in two **structural** isomers as products.

Draw the structural formulae of the two isomers. You may use C_5H_{11} to represent the pentyl group.

(2)

Leave blank

(ii) Both the isomers in (i) have chiral centres. Circle the chiral centre on ONE of the isomers you have drawn in (b)(i).

Explain, in terms of the mechanism, why the product of this reaction is a racemic mixture.

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(3)

(c) Give the structural formulae of the products formed when 1-pentyl-4-methoxycinnamate is boiled with sodium hydroxide solution and excess acid is then added to the mixture.

(2)

Leave blank

(d) Suggest the reagents and conditions necessary to convert 1-pentyl-4-methoxycinnamate into 4-methoxybenzoic acid, $CH_3OC_6H_4COOH$.

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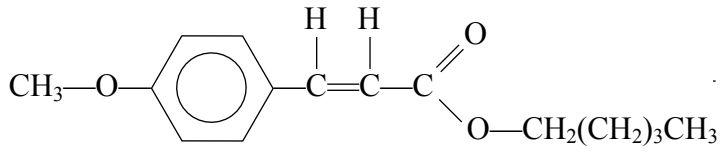
(2)

(e) When hydrogen, in the presence of a nickel catalyst, is reacted with 1-pentyl-4-methoxycinnamate,



both the alkene group and the benzene ring react with the hydrogen.

Infra-red spectroscopy data

Bond	Functional group	Wavenumber / cm^{-1}
C—O	Esters	1200 – 1150
C=O	Esters	1750 – 1735
C—H	Alkanes	3000 – 2850
C—H	Alkenes and arenes	3100 – 3000
C=C	Arenes	1700 – 1650
C=C	Alkenes	1650 – 1450

Suggest how the data above could be used to show that this reaction is complete.

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(2)

(Total 12 marks)

Q4

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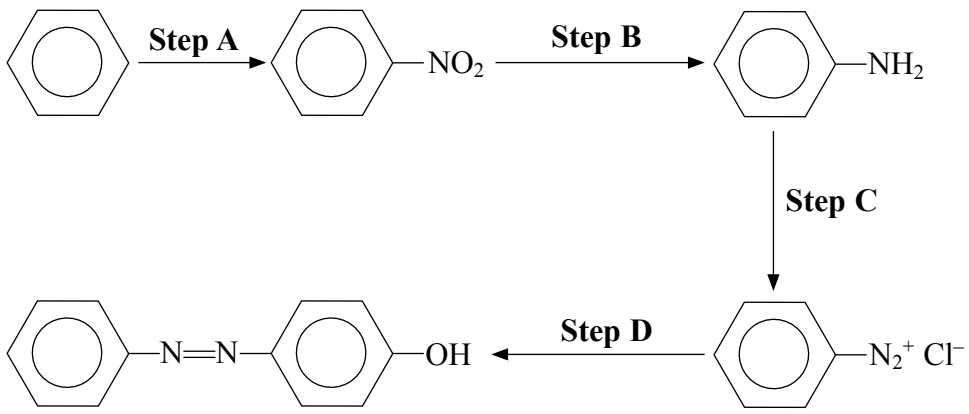
5. The compound 4-hydroxyazobenzene, an azo dye, can be synthesised from benzene as shown below.



4-hydroxyazobenzene

(a) The reagent for **step A** is a mixture of concentrated nitric and sulphuric acids. Write equations to show the formation of the electrophile NO_2^+.

(2)

(b) Write the mechanism for the electrophilic substitution reaction in **step A**.

(3)

Leave blank

(c) (i) Classify the type of reaction taking place in **step B** and state the reagents needed.

Type of reaction.....

Reagents.....

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(3)

(ii) State the reagents used in **step C**.

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(2)

(iii) Explain why the reaction in **step C** must be carried out with the reactants at a temperature below 10 °C **and** above 0 °C.

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(2)

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(d) The azo dye produced by the synthesis is impure. It is to be purified by recrystallisation using a solvent which is flammable.

The impure dye contains some impurities which are soluble in the solvent and some which are insoluble in the solvent.

Describe how a pure, dry sample of the dye can be obtained by recrystallisation. In your answer, explain any safety precautions you would take and explain how the steps involved lead to a pure product.

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(7)

Q5

(Total 19 marks)

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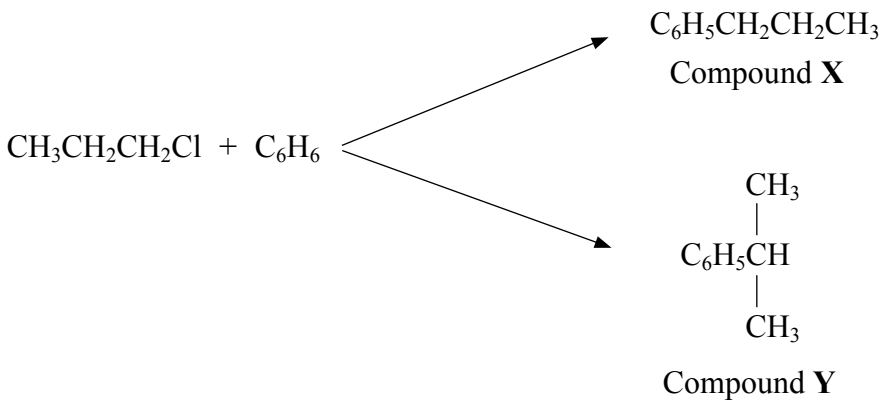
6. (a) Propanoic acid, CH_3CH_2COOH, can be used to prepare 1-chloropropane, $CH_3CH_2CH_2Cl$. Outline how this can be done, identifying the reagents for each step and the intermediate compound formed.

(3)

(b) When 1-chloropropane is reacted with benzene in the presence of a catalyst of anhydrous aluminium chloride, two isomers are possible as the organic product.



State ONE way in which the nmr spectra of **X** and **Y** differ.

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(1)

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(c) The actual product can also be analysed by mass spectroscopy. The spectrum has a line corresponding to the molecular ion at *m/e* value of 120 and a line with *m/e* value of 15 but no line at *m/e* of 29.

(i) Identify the species that causes a line at *m/e* of 15.

(1)

(ii) Use the fact that no line is found at *m/e* of 29 to deduce which of the two isomers is produced. Justify your answer.

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(1) **Q6**

(Total 6 marks)

TOTAL FOR PAPER: 75 MARKS

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THE PERIODIC TABLE

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

Key

Molar mass g mol^{-1}

Symbol

Name

Atomic number

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