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 23 January 2007 – 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 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 individual questions and the 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 account of your use of grammar, punctuation and spelling.

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

1. When barium nitrate is heated it decomposes as follows:

$$Ba(NO_3)_2(s) \longrightarrow BaO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H = +505.0\ kJ\ mol^{-1}$$

(a) Use the following data when answering this part of the question.

Substance	Standard entropy, $S^{\ominus}$/J mol^{-1} K^{-1}
$Ba(NO_3)_2(s)$	+ 213.8
$BaO(s)$	+ 70.4
$NO_2(g)$	+ 240.0
$O_2(g)$	+ 205.0

(i) Explain why:

- $S^{\ominus}$ [$NO_2(g)$] is greater than $S^{\ominus}$ [$BaO(s)$]

.....

.....

- $S^{\ominus}$ [$Ba(NO_3)_2(s)$] is greater than $S^{\ominus}$ [$BaO(s)$].

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(2)

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

(2)

(b) Calculate the entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings,}$ for the reaction at 298 K. Include a sign and units in your answer.

(2)

Leave blank

(c) Calculate $\Delta S^{\ominus}_{\text{total,}}$ and explain the significance of the sign for this value.

.....

(2)

(d) Calculate the minimum temperature at which the decomposition of barium nitrate should occur.

You can assume that ΔH and ΔS_{system} are **not** affected by a change in temperature.

(2)

Q1

(Total 10 marks)

Leave blank

2. This question is about butanal, $CH_3CH_2CH_2CHO$, and several related compounds.

(a) What would you **see** when Brady's reagent is added to a sample of butanal?

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(1)

(b) **F**, **G** and **H** are three isomers of butanal which are each tested with sodium, Benedict's reagent and Brady's reagent. The results are shown in the table below.

Key: ✓ = positive result
× = negative result

	Sodium	Benedict's reagent	Brady's reagent
F	×	✓	✓
G	×	×	✓
H	✓	×	×

Suggest structural formulae for **F**, **G** and **H**.

F

G

H

(3)

Leave blank

(c) An ester with the formula, $CH_3CH_2CH_2CO_2CH_2CH_3$, is heated under reflux with aqueous sodium hydroxide.

(i) Give ONE advantage of "heating under reflux", rather than simply boiling the two liquids together in a beaker.

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(1)

(ii) Name the **ester**.

.....

(1)

(iii) Name the TWO **products** of this reaction.

.....

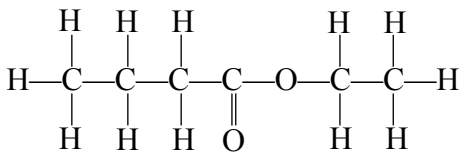
(2)

(iv) What type of reaction is taking place?

.....

(1)

(v) Which atom in the ester molecule is most likely to be attacked by hydroxide ions? Circle the atom on the displayed formula below.



Explain the choice you have made.

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(2)

Q2

(Total 11 marks)

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3. The reaction between peroxodisulphate and iodide ions occurs as follows:

$$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

Initial rates for this reaction can be determined by a method known as an 'iodine clock'.

A mixture of potassium iodide, sodium thiosulphate and starch is made up, and a clock started when a solution of potassium peroxodisulphate is added. When enough iodine has been formed to react with all the sodium thiosulphate, the excess iodine suddenly forms a blue-black complex with the starch. At this point the clock is stopped, and the time taken.

(a) In one particular experiment, the volumes of the reactants used were as follows:

Volume of $K_2S_2O_8(aq)$ / cm^3	Volume of KI(aq) / cm^3	Volume of $Na_2S_2O_3(aq)$ / cm^3	Volume of starch solution / cm^3	Volume of water / cm^3	Time taken / s
10.0	10.0	5.0	1.0	14.0	5

(i) The concentration of the sodium thiosulphate used was 0.010 mol dm^{-3}. Calculate the number of moles of thiosulphate ions, $S_2O_3^{2-}$, in the mixture.

(1)

(ii) Iodine reacts with thiosulphate ions as shown below:

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Calculate the number of moles of iodine which had reacted when the clock was stopped.

(1)

(iii) Calculate the rate of formation of iodine in mol dm^{-3} s^{-1}.

(2)

Leave blank

(b) Further experiments were carried out and the results are shown below.

Experiment	$[S_2O_8^{2-}(aq)]$ / mol dm^{-3}	$[I^-(aq)]$ / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.0100	0.0200	2.74×10^{-5}
2	0.0100	0.0400	5.47×10^{-5}
3	0.0300	0.0800	3.28×10^{-4}

(i) What is the order of reaction with respect to iodide ions, I^-?

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(1)

(ii) Deduce the order of reaction with respect to peroxodisulphate ions, $S_2O_8^{2-}$.
Show how you arrived at your answer.

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(1)

(iii) Use your answers to (i) and (ii) to write an overall rate equation for the reaction.

(1)

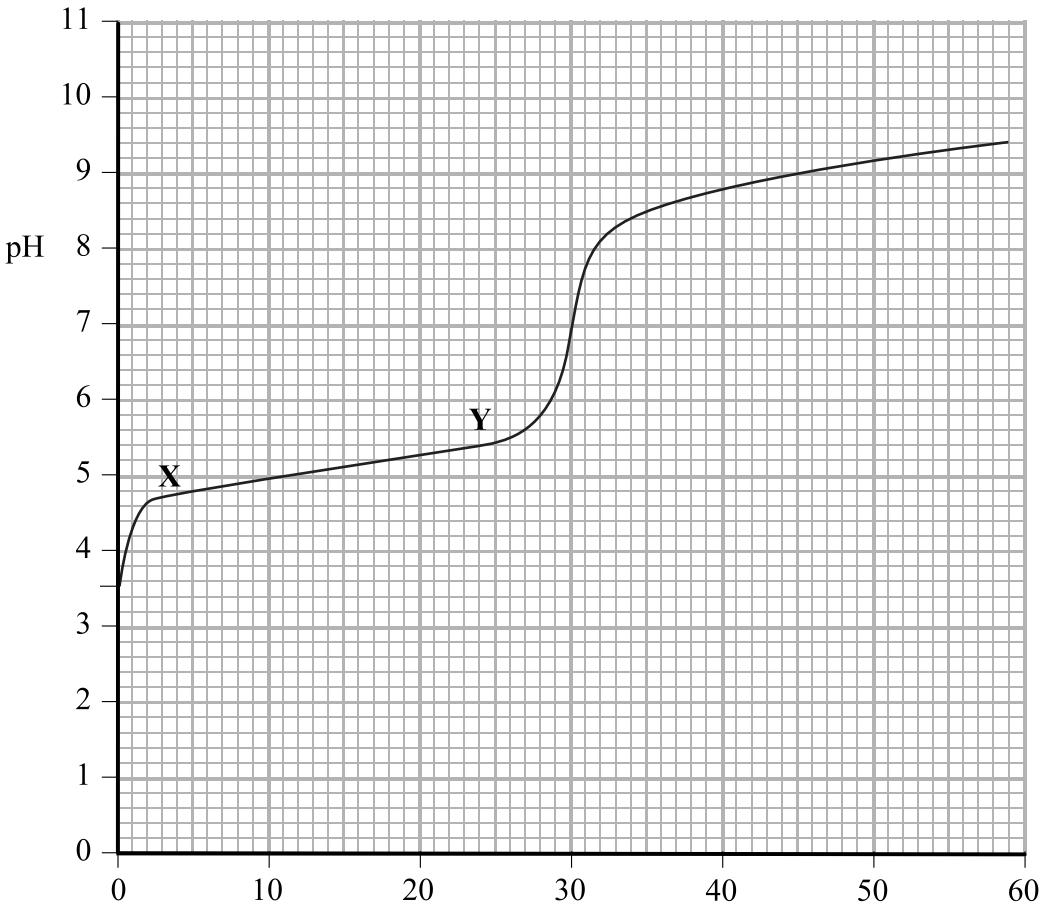
(iv) Use the data from **experiment 1** to calculate the rate constant for this reaction.
Give the units for the rate constant.

(2) **Q3**

(Total 9 marks)

Leave blank

4. 10.0 cm^3 of a solution of butanoic acid, $CH_3CH_2CH_2CO_2H$, of concentration 0.00660 mol dm^{-3}, was titrated with a solution of aqueous ammonia using a pH probe. The pH was recorded throughout, and the results were plotted as shown below.



(a) (i) Using the pH of butanoic acid from the graph, calculate the initial hydrogen ion concentration.

(2)

(ii) Write the expression for the acid dissociation constant, K_a, for an aqueous solution of butanoic acid.

(1)

Leave blank

(iii) Calculate the value of K_a making the usual assumptions. Give your answer to **two** significant figures.

(2)

(b) (i) Write an equation for the reaction between butanoic acid and ammonia. State symbols are **not** required.

(1)

(ii) Name the **two** compounds, apart from water, which are present in the mixture between **X** and **Y** shown on the graph.

.....

(2)

(iii) What **type** of mixture is present between **X** and **Y**? What evidence is there for your answer by reference to the graph?

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(2)

(iv) Explain why it is **not** possible to carry out this titration using an indicator.

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(1)

(v) Use the graph to estimate the end-point of the titration. Hence calculate the concentration of the ammonia solution.

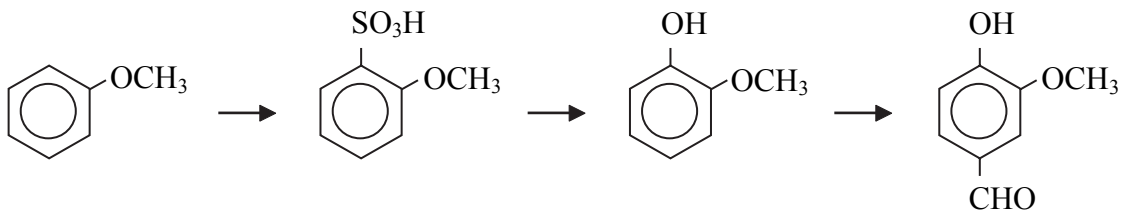
(2)

Q4

(Total 13 marks)

Leave blank

5. Vanillin, the main ingredient of vanilla essence, is one of the commonest flavouring ingredients found in foods. Synthetic vanillin, which is identical to natural vanillin, can be manufactured from methoxybenzene. One synthetic route is shown below:



methoxybenzene — 2-methoxybenzene sulphonic acid — 2-methoxyphenol — vanillin

(a) (i) Name the reagent which converts methoxybenzene to 2-methoxybenzene sulphonic acid.

.....

(1)

(ii) Name the type of reaction which occurs and its mechanism.

.....

(2)

(b) Describe a chemical test which would enable you to distinguish between methoxybenzene and 2-methoxyphenol. Give the observations you would make.

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(2)

(c) Vanillin is a white solid, and is slightly soluble in water, giving a solution which is mildly acidic.

(i) Write the molecular formula for vanillin.

(1)

Leave blank

(ii) What is the strongest type of intermolecular force which can exist between molecules of vanillin and water? Illustrate your answer with a diagram.

.....

(2)

(iii) Which functional group in vanillin is responsible for its acidity? Give an equation to support your answer.

.....

(2)

(d) After the final stage, in which 2-methoxyphenol is converted to vanillin, the impure product can be purified by recrystallisation. In this process the solid is dissolved in the minimum volume of hot water. The mixture is then filtered whilst still hot. The filtrate is cooled in an ice bath to produce crystals of vanillin. These can be removed by filtration and dried.

(i) Why is the "minimum volume of hot water" used?

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(1)

(ii) The impure vanillin may contain soluble and insoluble impurities. Describe how each of these is removed during recrystallisation.

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(2)

Leave blank

(iii) How would you check the purity of the vanillin after recrystallisation, other than by using an infrared spectrometer.

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(2)

(e) In order to establish whether or not vanillin had been formed, two infrared spectra were obtained: a sample of pure 2-methoxyphenol and a sample of the product.

Study the spectra and data on page 13.

Comment as to whether any vanillin is likely to have been formed during the process. Support your answer with relevant evidence.

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(2)

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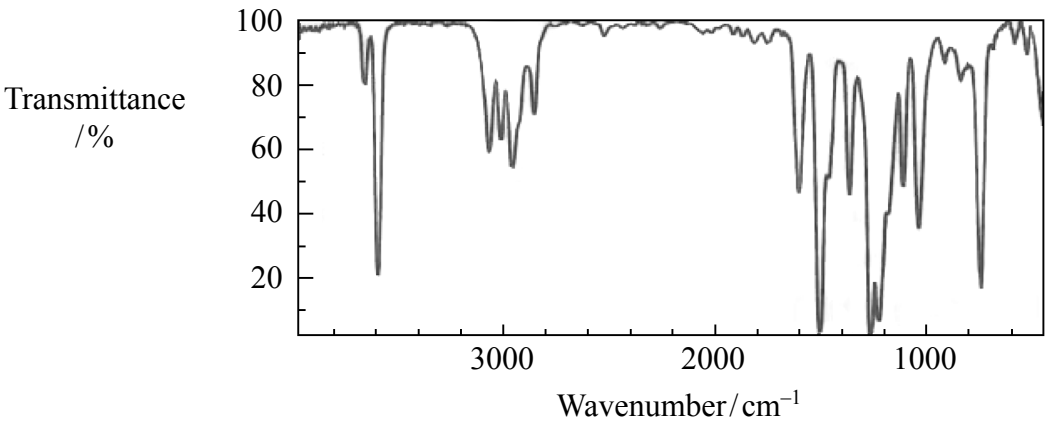
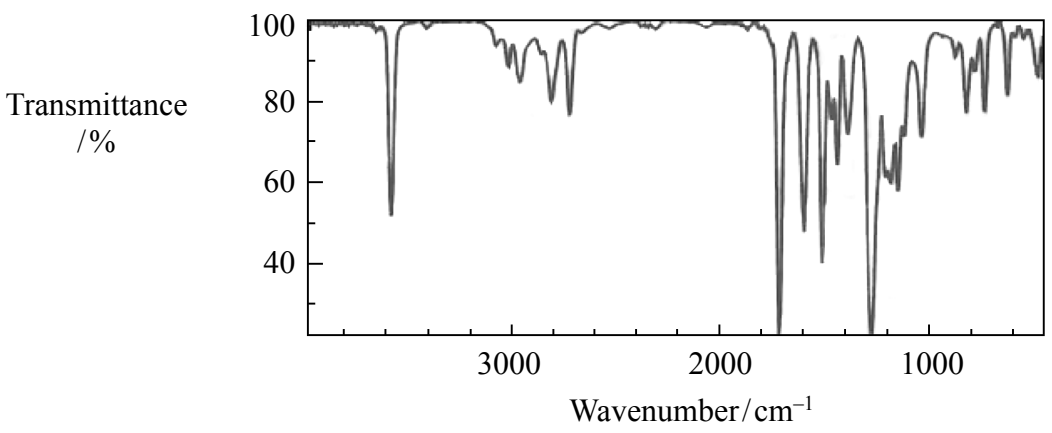
Infrared Spectrum of 2-Methoxyphenol



Infrared Spectrum of Product



		Wavenumber/cm^{-1}
C═C Stretching Vibrations	Arene	1600 – 1450
C—H Stretching Vibrations	Arene	3030
O—H Stretching Vibrations	Alcohols and phenols	3750 – 3200
C═O Stretching Vibrations	Aldehydes Ketones Carboxylic acids Esters	1740 – 1720 1700 – 1680 1725 – 1680 1750 – 1735

Q5

(Total 17 marks)

TOTAL FOR PAPER: 60 MARKS

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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 Radius (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)