Examiners' Report January 2008

GCE

GCE Chemistry Nuffield (8086/9086)

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6251/01

General

This paper proved demanding. It remains essential for candidates to read the questions carefully and make sure that they answer the question asked and not one from previous years. Candidates generally show a good understanding of calculations although this year it was particularly noticeable that they often had a lack of understanding of significant figures. However, the standard of English shows no sign of improving.

Section A

Question 1

This question proved more difficult than expected with only just over half able to name these two compounds. The functional group CHO was not recognised as an aldehyde and examiners had to look carefully at the handwriting to distinguish between methanal and methanol. In part (b) a significant minority of candidates thought that the OH group was on the second rather than the third carbon atom.

Question 2

This question proved even more challenging with under half the candidates able to answer any part correctly. Although most were able to draw a ketone rather than an aldehyde, they found it difficult to draw a branched chain and ensure that each carbon atom had four covalent bonds. Candidates who drew a straight chain ketone were able to score two marks out of three if they were able to name the ketone with the correct number for the position of the functional group. In part (d) describing the advantages of refluxing over distillation was poorly explained with many candidates confusing the different techniques for obtaining aldehydes and carboxylic acids with this experiment when the ketone cannot be further oxidised.

Section B

Question 3

Most candidates started this question with more confidence and, even though deuterium was unfamiliar to some, had no difficulty in identifying the number of protons, neutrons and electrons in one atom of deuterium. Part (a)(ii) was the occasion on the paper when a specific number of significant figures were asked for and candidates lost a mark for any number other than four.

Part (b) proved much more difficult. Very few candidates recognised reaction A as an acid-base reaction even though a hydrogen ion is clearly donated by the water to the ammonia. Quite a few candidates thought this was neutralisation but, as the product is ammonia solution which is hardly neutral, it meant this answer did not receive any credit. For B just reduction or oxidation on their own was not sufficient and redox was expected. Part (b)(ii) was much better answered with few candidates falling into the trap of thinking that because sodium gained hydrogen it was reduction but recognised that the sodium had lost an electron and so had been oxidised.

There were many good answers to part (c) although some candidates required more than the six lines given to explain their answer. It is no problem if they put part of their answer at the bottom of the page or on another page provided that they indicate in the space given that their answer continues elsewhere.

In (d)(i) surprisingly less than half the candidates could convert K to ^{0}C. Numbers given ranged from the tiny (2) to involving 285.8 the enthalpy change of combustion of hydrogen to a very large number obtained by multiplying a pair of numbers together.

Candidates also found it difficult to suggest advantages and disadvantages to the use of hydrogen as a fuel. The fact that hydrogen is flammable was often thought to be a disadvantage as was the fact that it burnt in an exothermic way. The production of water as the only product was also thought to be a problem by some leading to flooding and slippery roads.

Question 4

Able candidates found this the easiest question on the paper often scoring eight or nine out of nine. Part (b) proved to be the easiest question on the paper although only just over half the candidates realised that chromium was responsible for the colour in the reactants and products with some candidates giving chromate rather than the element as asked for in the question.

Good candidates had no difficulties with part (d)(i) although units caught some out as they gave their answer in dm^3 and then put the decimal point in the wrong place or gave the index as a negative number. There are still too many candidates who do not read the question carefully enough and seeing that they are required to prepare crystals give the pre-prepared answer of ‘drive off some water leaving some for water of crystallisation, cool, filter off the crystals and dry between filter papers’. This answer would only score one mark out of a maximum of four. The formula of KCl shows that there is no water of crystallisation and so all the water could be driven off. But more importantly many candidates failed to realise that ‘the resulting mixture’ as stated in the question would contain solid barium chromate which had to be removed first by filtering.

Question 5

Part (a) was generally well answered by over 75% of the candidates. However, part (b) was not understood by most. Only a fifth of candidates knew that the arrows used to represent electrons indicated that the electrons were spinning in opposite directions on their axis with many thinking that the electrons orbited the nucleus in opposite directions. Others thought that the ‘up’ arrows indicated that the electron would be promoted to higher energy levels and that the ‘down’ arrows indicated the electron was going to fall back to a lower energy level. The energy change when a sodium atom ionises was also not shown correctly with many candidates thinking that the first electron to be lost would be from the n=1 energy level rather than from the n=3 energy level. The existence of sub-levels, 2s and 2p, was also not realised by many candidates who thought either that all electrons in an energy level would have the same energy or that the energies would change as more and more electrons were removed. Whilst this is true, it is not the correct answer to the question as asked. In part (iv) although most candidates knew that potassium would have more electrons than sodium, they did not include enough detail to get the mark.

Many good descriptions of the flame test were seen with few candidates trying out other ways of distinguishing between sodium and potassium chloride. The commonest ways for losing a mark here was not to know the colour of the potassium flame (lilac) or to state that the chlorides would burn in the flame rather than colour the flame. Part (d) did not prove to be as easy as expected with only a few words being sufficient to obtain both marks.

Question 6

The unfamiliar format with four parts to the Hess cycle rather than three did put off the weaker candidate although it was possible to score marks with transferred errors if the candidate was prepared to keep going.

In part (a) many candidates who correctly balanced the first box failed to do the same in the second box. Again poor writing lost some candidates a mark when it was impossible to tell whether the state symbol was a g for gas or an s for solid.

In part (b)(i) a surprisingly large number of candidates thought that it was acceptable to give 0.100/24 as 0.004 thinking that this was to three significant figures or 0.00416 rather than 0.00417. This resulted in the examiners having to resort to their calculators on many occasions to allow for transferred errors throughout the rest of the question. In part (ii) although candidates could calculate how many moles of hydrochloric acid was present at the start, few realised that the equation showed that twice as many moles of hydrochloric acid would react as magnesium and so lost at least one of the three marks for this part. In part (b)(iii) the graph was not drawn as well as you would expect for AS candidates. Many thought that you had to start the vertical axis at zero and so the values were cramped into little more than a sixth of the graph paper resulting in the loss of one of the two marks for drawing the graph. Also it was not uncommon to see the first two points (when nothing is happening) to be connected with a curve rather than a straight line.

In Part (b)(iv) too many candidates added the mass of the magnesium to the 100g of the hydrochloric acid giving a mass of 100.1g. We continue to have difficulty in presenting this equation but our current method of quoting the equation, stating that the candidate should include the mass of the solution and stating that 1 cm^3 of the solution has a mass of 1 g ought to make it clear and be technically correct. Even though in part (b)(v) we reminded candidates to include a sign and units, too large a number did not include a sign and did not realise that the reaction was exothermic and so should have a negative sign.

In part (b)(vi) there were a few good answers from candidates who realised that between one and two minutes the temperature might have risen above 25.3 with some heat being lost or used their graph to show this heat loss the majority of candidates thought that 4.3 had been rounded up to 4.5 or that the thermometer could only read to the nearest 0.5 of a degree.

In part (c) most candidates were able to calculate the mass of one mole of magnesium carbonate but again their understanding of significant figures was poor with 0.0262 being corrected to either 0.03 or even worse 0.02.

A good number of candidates were able to show how to apply Hess's law to the four-membered cycle and insert their values and so obtain full marks for this part. Part (e) proved to be the hardest question on the paper with few candidates realising that you cannot get magnesium, carbon and oxygen to combine together to make magnesium carbonate and so it would be impossible to measure the enthalpy change of formation directly.

Hints for revision

- Ensure you fully understand how to calculate and use significant figures in calculations
- When looking at past papers and mark schemes, do not learn the answers off by heart but ensure that you can apply these answers to the actual question asked
- In calculations think carefully about the appropriate units such as cm^3 , dm^3 , dm^{-3} and J or kJ and how to convert K to ^0C

6252/01

General

The overall performance of candidates in this paper was variable. There were clearly many able candidates who were able to apply the underlying principles of bonding and bond energies from Topic 7 to unfamiliar situations. At the same time many did not have the necessary knowledge of organic chemistry from Topics 8 and 10, and inorganic chemistry from Topic 6.

Question 1

Responses to Question 1 clearly demonstrated the problem of lack of knowledge. Part (a) required the recall of four reactions of the alkenes. Very few candidates were able to answer part (i). There was much confusion with the oxidation of alcohols. The most common wrong response was 'acidified sodium dichromate(VI)'. Precision was needed in answering parts (ii) and (iii). Common errors were the omission of the numbers 1,2, or 'di'. Weaker responses retained the 'e' as in 1,2-dibromobut**e**ne. The addition of hydrogen bromide was better known in part (iv), though bromine was a popular incorrect response. Parts (b), (c) and (d) required candidates to explain terms in the context of organic reactions and once again candidates were let down by their lack of knowledge. The key to part (b)(i) was the idea of two reactants producing one product. The common way to achieve the mark in (c)(i) was to offer 'an electron deficient species', though good candidates referred to entities with a vacancy available for a pair of electrons to form a covalent bond. Wrong answers to (b)(ii) were usually Br_2 or Br^-. In (d)(ii) many candidates just trotted out 'oxidation is loss of electrons', when a little thought about the reaction would suggest that 'oxygen is added' or 'carbon increases in oxidation number' are more accurate. The little synthesis in (e) proved easy to most candidates in part (i), but again the detailed knowledge required in parts (ii) and (iii) was lacking.

Question 2

Question 2(a) was generally well done. Candidates applied the principles of bonding well to the three unfamiliar molecules. There were some problems with three dimensional diagrams. At this level the 'saw tooth' convention should be known. Weaker candidates omitted to consider the non-bonding electrons. The slightly unusual Hess calculation in (b) was also well done. A few candidates omitted multiples either of the Si-Cl bonds or the enthalpy of atomisation of chlorine. Weaker candidates were unable to apply Hess. Part (c) was more demanding. The affect of temperature was usually well justified, but the affect of pressure justification often lacked reference to the number of **gaseous** molecules. Answers consistent with part (i) were needed in part (ii). Part (iii) was probably the easiest question on the paper. A small number of candidates confused it with the distribution of molecular energies graphs. Most candidates gained a mark for the correct bonding electrons in (d), but found the final tally of electrons more difficult. Weak candidates omitted the non-bonding electrons.

Question 3

Part (a) examined intermolecular forces. Part (i) proved straightforward to most candidates, except those who tried to explain in terms of permanent dipole–permanent dipole forces. Part (ii) was more demanding. The common confusion was to refer to ease of molecular packing which increases melting point, but decreases boiling point. Part (iii) was answered correctly by the majority of candidates. The opposite was the case for part (b)(i). Similarly, few candidates were able to identify 1-chlorobutane as the slowest to react with hot silver nitrate solution, and even fewer were able to relate this to the strength of the carbon–halogen bond. Only weak candidates gave the hydrox**ide** group or OH^- in (iii). The equation in (iv) was also well done, though some gave an incorrect state symbol like AgCl(**aq**). About two thirds of candidates answered (v) correctly. Part (c) was back to detailed knowledge of organic chemistry and therefore very demanding. The problems were identifying the correct organic formula, realising that hydrogen iodide reacts with ammonia (Topic 6), and naming the organic product. Many thought ammonium iodide was the organic product.

Question 4

The comprehension/summary question was challenging, requiring candidates to think and apply their knowledge of chemistry. Good candidates realised the enormous currents would generate heat in (a)(i), weaker candidates just answered 'because cells operate at 90^oC'. Weaker candidates concentrated on rate, rather than the fact that the melt would solidify if it got too cold in (ii).The first oxidation number was fairly easy in (b), but +10 was a frequent response for the second. Failure to answer the question and 'identify the reaction' was the main problem in (c). In (d) the key was to write two good, well justified points. 'For – power stations, against – bombs' was the common weaker response, where good candidates gave detail like 'nuclear power stations which do not lead to carbon dioxide emissions' or 'nuclear weapons which lead to indiscriminate loss of civilian life'. Other good answers referred to the difficulty of disposing of nuclear waste as a disadvantage. In the summary key points 2, 4 and 7 were most frequently given, followed by 1, 3 and 6, then 8 and finally least frequent was 5. Again candidates need reminding that accurate selection of key points is essential. Fluorine forming in key point 6 was often missed because either the anode, or the impurity, hydrogen fluoride, were missed. There were more word penalties than usual. Candidates are foolish to allow themselves to exceed the word limit – it is better to work well within it say five words less than the limit to allow for failure to count some things – here it was probably the units that were forgotten. Many lost a mark because they cannot spell; 'flourine', 'flouride' and 'pottassium' were the common chemical examples. Ideally a single paragraph is usually appropriate and bullet points should be avoided.

Hints for revision

- Learn the organic chemistry: three reactions of the alkanes; six reactions of the alkenes; three reactions of the halogenoalkanes

- Be familiar with and able to define terms used in organic reactions like: nucleophile; electrophile; free radical; addition; substitution; oxidation; reduction.

- Practise and develop summary and comprehension skills.

- In the summary remember to work within the word limit and that a number with a unit counts as two words.

6254/01

General

Examiners were generally pleased with the quality of answers to the calculations and routine questions, but were less impressed by answers to those involving descriptions and explanations. Technical words were frequently used out of context and it was therefore often difficult to understand what points were being made. However, the majority of candidates were able to score well on questions of a more familiar type, and a sizable minority produced extremely impressive answers to those which were more testing and discriminating.

Question 1

This question scored well overall, with the majority knowing how to calculate the standard entropy changes of the system and surroundings during the reaction between barium hydroxide and ammonium chloride. It was hoped in (c)(ii) that, having found that the reaction was spontaneous, candidates would appreciate that this in itself gave no indication as to how fast it would proceed. Other good answers concentrated on the difficulties involved in interacting two solids. In (c)(iii) there were some excellent answers, but many suggested adding a catalyst as a matter of course, without applying their understanding to this particular situation. Others referred to using a reduction in pressure, without realising that this particular process is irreversible and that the application of Le Chatelier's Principle would be irrelevant.

Question 2

Most knew the structural formula for benzene sulphonic acid, but a significant minority gave "$C_6H_5SO_3$", perhaps being over-influenced by the molecular formula given in the question. There was also some careless placing of the bond between the benzene ring and the sulphonic acid group and occasional juggling of the atoms, eg HSO_3, instead of SO_3H. The rest of (a) was answered well by the majority for whom this was very familiar chemistry. However, SO_3^+, and even SO_3^-, were often given as the formula for the attacking species. There were some good answers to (b)(i), and this was marked consequentially on what the candidate had given in (a)(i). The reagents for the Friedel Craft reaction were usually quoted accurately, but it is unfortunate that many gave names rather than the **formulae** asked for. In this case, answers from other candidates showed that a correct formula was often not known, so it was thought fair not to allow full marks for someone who had written two correct names instead. Hydrochloric acid was often incorrectly given as a by-product of the process.

Part (c)(i) was answered surprisingly poorly with only a few concluding that compound **C** was probably a phenol. Many correctly suggested water as a suitable reagent for converting the sulphonic acid to a phenol in (c)(ii), and since a sulphonic acid grouping had been substituted by a hydroxyl group it was decided to allow any metal hydroxide as a perfectly sensible alternative answer, even if in reality a phenoxide ion would have been formed instead. $LiAlH_4$ cropped up frequently as an answer to this question. Most candidates were stumped by (c)(iii), though many gave 1,2,3,4,5,6-hexachlorocyclohexane, so they obviously knew how (free radical) addition would take place with benzene, but were unable to apply this knowledge to the corresponding addition with 3,5-dimethylphenol. A few gave an acceptable alternative product involving substitution of the methyl hydrogen atoms.

The systematic name for Dettol in (d)(i) was given by the majority, but a common mistake was to give 4-chloro-3,5-methylphenol instead of 4-chloro-3,5-**di**methylphenol.

The most disappointingly answered question on the paper was (d)(ii), with most referring to hydrophilic and hydrophobic parts of the molecule, without mentioning any specific type of intermolecular bond whatsoever. Only a handful of candidates compared the energy involved in breaking the relatively large van der Waals forces in Dettol or the considerable hydrogen bonding in pure water with the relatively small energy which would be released in forming hydrogen bonds between the hydroxyl group in Dettol and that in water. Full credit was given for half of this full answer, however, but only a minority even gave this. Many were side-tracked into discussing the activating effect of the hydroxyl group on the benzene ring and the influence that this would have on the strength of the hydrogen bonds formed between Dettol and water.

Question 3

This question produced the greatest range of marks on the paper. Although it was based on Case Study C in the course, and the stem clearly explained how the experiment was carried out, many candidates divided [2-bromo-2-methylpropane] by the time, instead of using [NaOH]. Candidates in any case should have been able to deduce that it was the NaOH that had been used up if the phenolphthalein had lost its pink colour when the time was taken, or that the concentration of the halogenoalkane was at least ten times greater than that of the alkali, so that the former was bound to remain in excess by the end of the process.

Fortunately an error in (a)(ii) did not necessarily affect a correct answer in (a)(iii), since the majority simply used the fact that the doubling of [2-bromo-2-methylpropane] approximately halved the time taken for the reaction to complete when [NaOH] remained constant. In (a)(iv) many failed to answer the question fully and did not calculate a rate for experiment **C** before going on to deduce that the reaction was zero order with respect to NaOH. The rate equation in (a)(v) was usually given correctly, with the commonest mistake being a failure to include the rate constant, ***k***. Full consequential marking was applied to equations based on incorrect answers to (a)(iii) and (a)(iv). When it came to answering (a)(vi), consequential marking was again adopted, and there were some excellent answers from those who had already deduced S_N1 kinetics. Some carelessly forgot to identify the rate-determining step, and others placed the carbocation's positive charge in the wrong place, without using any brackets to show delocalisation. There were also many who lost a mark by using NaOH rather than OH^- in the nucleophilic attack involved in the second step. Those who had at this stage predicted an S_N2 process were given credit for producing an appropriate mechanism. Several enterprising candidates whose rate equation showed that the reaction was second order with respect to 2-bromo-2-methylpropane and zero order with respect to NaOH produced a perfectly compatible mechanism with the two halogenoalkane molecules colliding to form a halogenoalkane molecule, a carbocation and a bromide ion, and continued thereafter as for a conventional S_N1 mechanism.

In (b) many were able to classify the two halogenoalkanes correctly, but were unable to suggest why S_N1 kinetics should predominate with one and S_N2 with the other. However, excellent answers were seen, some referring to the relative stabilities of the carbocations and others discussing potential steric hindrance with the S_N2 mechanism for a tertiary halogenoalkane. In many cases it was clear that these answers were generated from a good understanding of the mechanisms rather than from rote learning, and such accounts were often extremely impressive.

Question 4

Most knew how to construct a correct expression for K_p and why the value is dimensionless in this case. Most also managed to calculate a value for the partial pressure of nitrogen monoxide in (b)(i), and virtually all were able to add the partial pressures to obtain a value for the total pressure in (b)(ii). A small number of candidates incorrectly doubled the partial pressure of nitrogen monoxide before adding it to that of the other two gases. Most candidates were able to predict the effect of doubling the total pressure on the partial pressure of nitrogen monoxide and on the value for K_p in (b)(iii).

There were some good answers to part (c), although many candidates appear to be unaware of the entropy changes occurring during the establishing of an equilibrium, and that a negative value for the total entropy change simply indicates that the position of equilibrium lies over to the left. Accordingly, in this particular case, a little nitrogen and oxygen **will** react to form nitrogen monoxide. Many answering (c)(ii) spent their time mentioning the number of moles on each side of the equation without appreciating that the constancy in ΔS_{system} with a rise in temperature has nothing to do with this, but with the fact that none of the components of the mixture changes state on heating. There were far too many answers such as "temperature has no effect on the entropies of the reactants or products", which shows a serious misunderstanding of the concept of entropy. There were many good answers to (c)(iii), the majority using $-\Delta H/T$ to explain why the value for $\Delta S_{surroundings}$ is negative for an endothermic reaction. Many alternatively referred to the loss of energy in the surroundings and equated this to a loss in disorder or entropy. In (c)(iv) it was necessary first to explain the effect on the entropy of the surroundings caused by an increase in temperature, and most did so successfully by explaining that as T increases, the value of $-\Delta H/T$ becomes less negative. The problem with negative numbers is that "greater" and "smaller" are ambiguous expressions, so candidates are strongly advised in future to use "less negative" or "more negative" which makes things much clearer. The purpose of asking (c)(ii)-(c)(iv) was to take candidates through the steps needed to explain why the yield of product in an endothermic equilibrium can be increased by a rise in temperature, and its explanation in terms of entropy rather than by the often misquoted, and usually badly explained Le Chatelier's Principle.

There were some good answers to (d), the commonest being a reference to the fact that an actual car engine might well be operating at a lower temperature than 1500K. Other acceptable answers included a reason for the total pressure possibly being lower than the one used in the calculation, that there are other gases in the air apart from nitrogen and oxygen, or that other gases produced by the combustion process would lower the partial pressure of nitrogen monoxide considerably. Very few suggested that the equilibrium might not have been reached in the very short time the gases were present in the combustion chamber, which was another acceptable response.

Question 5

In (a), although a carbonyl compound was asked for, many gave phenylmethanol, $C_6H_5CH_2OH$, and others gave "C_6H_5COH", which is not a conventional means of representing the aldehyde group in benzaldehyde. The reagents for the oxidation process were well known, but there are still many who quote an incorrect oxidation number for chromium, often IV or VII.

Part (b) was answered extremely well by some, which is all the more impressive since this question was set to find out whether candidates could work things out for themselves. Many realised that, unlike the hydroxyl group in phenol, the carboxyl group must withdraw electrons from the benzene ring, making the latter less nucleophilic, or negative, towards incoming electrophiles, and this was all that was needed to score the two marks. Many enterprisingly and impressively went on to explain why the carboxyl group might withdraw electrons from the ring, rather than to supply them, but some lost some credit though an inappropriate use of the word "electronegative", in situations where "electron-rich" or perhaps "nucleophilic" would have been more appropriate. In a few cases there was much vagueness and confusion between the ring and the carboxyl side chain, with some answers referring to a reaction between the side chain and the mixture of concentrated acids used in the reaction. In other cases, answers were spoilt by the ambiguous use of "it" where there was no reference to the benzene ring whatsoever, eg "the carboxyl group draws electrons towards itself, making it less reactive towards electrophiles", or "the carboxyl group has made the electron cloud less dense making it less negative, so electrons are not drawn to it so easily".

In (c)(i) the reagents needed to prepare samples of sodium benzoate and methyl benzoate were widely known, but in (c)(ii) many scored only 1 mark because they failed to give a physical property at all, or, if they gave one, failed to provide the comparison for which the question asked. Most knew that there was ionic bonding in one but not the other. In (c)(iii) the delocalisation of electrons occurring in the benzoate ion was widely known, but answers were frequently spoilt by poor diagrams, in which the carbon oxygen bonds were still shown as double and single in the delocalised structure. The buffer calculation in (d) was generally carried out successfully by the majority. The exercise involved was a little trickier than usual since the acid and salt were of unequal concentrations and were not being mixed in a 1:1 volume ratio. Those who simply divided the two concentrations together to give an $^{[acid]}/_{[base]}$ ratio of 1:2, but who calculated everything else correctly, obtained a pH of 4.5 and lost only 1 mark.

Hints for revision

- When giving the structural formula for an aldehyde, always use –CHO, rather than –COH, since the latter implies that there is an OH group and that you are referring to an alcohol or phenol.
- Show full working in calculations.
- When comparing the relative magnitude of negative numbers, do not write "smaller" or "greater", but use "more negative" or less negative" instead. This makes everything much clearer.
- Do not use a highlighter in your answers. They often render your writing underneath illegible.

Appendix A: Statistics

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Grade	Max. Mark	A	B	C	D	E
Raw boundary mark	60	41	36	31	26	22
Uniform boundary mark	90	72	63	54	45	36

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Grade	Max. Mark	A	B	C	D	E
Raw boundary mark	60	43	38	33	29	25
Uniform boundary mark	120	96	84	72	60	48

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Grade	Max. Mark	A	B	C	D	E
Raw boundary mark	60	40	36	32	28	24
Uniform boundary mark	90	72	63	54	45	36

Maximum Mark (Raw): the mark corresponding to the sum total of the marks shown on the mark scheme.
Boundary Mark: the minimum mark required by a candidate to qualify for a given grade.

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