

Examiners' Report January 2007

GCE

GCE Chemistry Nuffield (8086/9086)

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Contents

Unit 6251/01	Page 1
Unit 6252 /01	Page 4
Unit 6254/01	Page 7
Appendix A (Statistics)	Page 10

Unit 6251/01

General

This paper contained some very accessible questions which were answered well by the vast majority of candidates. There were also some questions on unfamiliar material which proved within the capabilities of many candidates, although on occasions they did not use their wider knowledge and experience when trying to answer them.

Section A

In Q1(a) most candidates knew that the ion in acidic solutions is H^+ or H_3O^+ but a surprising number then failed to identify the two acids in (b). The two marks for this answer should have been a clue that there were more than one acid in the list. As all the substances contained hydrogen, perhaps selecting sodium hydroxide, NaOH , and/or ammonia, NH_3 , should not have been such a surprise.

Q2 was generally very well done, although a significant minority do not know the symbol for fluorine. Candidates were directed to the Periodic Table and if in any doubt they must be encouraged to use it rather than guess the symbol to be Fl .

Q3 was a real disappointment. Calculations involving gases remain a problem for many candidates, particularly when the balanced equation shows 3 moles of nitrogen and the question asked for the mass of sodium azide to make 2 moles of N_2 . However, the real surprise on the whole paper was the response to (b). Well over half the candidates thought that nitrogen would be the problem when disposing of the air bag rather than the sodium which was given in the equation as the other product. Their reasons for choosing nitrogen showed very little use of common sense and a lack of awareness of the reality of the situation. Common answers included that the nitrogen was flammable, toxic when breathed in, would react with oxygen in the air to form acidic nitrogen oxide gases including producing laughing gas, destroy the ozone layer and if the bag burst it would damage the hearing of the driver and passengers or change their voices. Candidates must be encouraged to think about their answers before moving on to the next question.

Section B

Question 4

This was very well answered by the vast majority of candidates even though the calculation in (a) was unfamiliar, using an ore of potassium which was a double salt. Any question involving ions remains a problem for a significant number of candidates although there are signs that this is an area which is gradually improving. Again the use of the Periodic Table should have prevented the formula of the magnesium ion being given as Mg^+ . It was acceptable to give the formulae of the ions present in water as well as the potassium, magnesium and chloride ions but not to think that there is the O^{2-} ion in water. Flame colours are generally well known although some candidates thought that the metal elements themselves were present and hence that magnesium would burn with a white flame.

Question 5

This question was very straightforward with many candidates scoring at least 9 out of 10. In (c)(ii) the question does suggest that candidates should show their working which is always a good idea so that method marks can be awarded even when a slip results in an incorrect final

answer. There are still a few candidates who confuse atomic mass and atomic number and thought that gallium has 70 electrons rather than the 31 given in the question. Poor handwriting cost some candidates a mark in (d)(i) when it became impossible to distinguish between the letter g and the letter s for the state symbols in the equation for the first ionisation energy of gallium.

Question 6

In (a) the items shown in the diagram were usually correctly named although some thought that item A was a conical flask. Candidates, from their practical experience, should realise that heating organic chemicals in quickfit apparatus is carried out in round-bottomed or pear-shaped flasks. Item C is best described as anti-bumping beads and candidates should be made aware of the reasons for using them although this was not asked on this occasion. When asked for three errors in the diagram, candidates should select those which are most significant and would lead to the experiment failing rather than comment on things which may be unnecessary or might differ from the actual apparatus that they used. There are still too many candidates who do not realise that in a condenser there must be an inner tube which separates the water jacket from the distillate inside the condenser. In (d) the (partial) oxidation was often not justified by using formulae as asked for in the question. Using OILRIG or oxidation numbers is much more difficult in organic chemistry than using either loss of hydrogen (as in this case) or gain of oxygen. In (f) the formula of ethanoic acid was frequently given in a rather strange way and did not show the carboxylic acid group. eg $C_2H_4O_2$, C_2H_3OOH , CH_3CHOO etc.

Question 7

This was not only the longest question but also the most challenging. Clearly defining terms such as spectator ions proves surprisingly difficult. For example suggesting that a spectator ion does not change its oxidation number is true but does not define a spectator ion as in precipitation reactions the same thing applies. When asked for which apparatus to use, candidates should recall laboratory experience and consider the accuracy required. To measure out 50 cm^3 a volumetric flask is clearly not sensible and we did not allow it, although on this occasion we did accept a pipette or burette whereas a measuring cylinder is the most sensible piece of apparatus to choose.

In (c) most candidates realised that polystyrene is a much poorer conductor of heat than a metal container but did not also realise that it would absorb much less heat energy. In part (d)(i) many candidates who were able to correctly calculate the number of moles present in each of the reactants did not read the question carefully enough and did not suggest which reactant would be completely used up. This was required for the final calculation. It was also surprising that many candidates did not know the colour of copper(II) sulphate solution and there are still some who do not understand the difference between clear and colourless. As most metals are grey the error in the colour of zinc was also a surprise.

The type of graph in (e) has not been asked before but most candidates coped well with most of this question. At AS level candidates should be able to cope with any scale but quite a few could not plot the point at 90s plotting it at 100s instead. Part (e)(ii) proved beyond most candidates because they did not read the question carefully enough. They were asked to explain the shape of the graph but nearly everyone just described the shape and so could not score any marks. Candidates were expected to realise that the reaction was not instantaneous and so heat loss would occur to the surroundings resulting in the real maximum temperature being greater than $65\text{ }^\circ\text{C}$.

The calculation in (f)(i) resulted in some surprising errors. The mass of solution was taken as 1 g by some and others added in the mass of zinc to use 55 g instead of 50 g. The temperature rise was also not calculated by some who forgot to subtract the room temperature of $22\text{ }^\circ\text{C}$.

Hints for Revision

- Learn the formulae of simple ions and also how to deduce the charges on ions from the Periodic Table or from the formulae of compounds
- When carrying out calculations, clearly show your working so that method marks become available to you
- Understand the difference between the key words describe and explain
- When carrying out practical work, note down and learn the colours of the reactants and products
- When answering questions on the applications of chemistry, remember to draw on your experiences and knowledge and understanding of everyday life

Unit 6252/01

General

The paper was accessible to the majority of candidates, though both the first calculation in Q2 and the summary comprehension question proved to be demanding. The best answers on this paper were to Q1 on halogen chemistry and intermolecular forces, and Q3 on alkanes and equilibrium. The standard of written communication was sometimes disappointing and meant that marks were lost in questions where explanations had to be given.

Question 1

For most candidates this was the highest scoring question on the paper.

Part (a) (i) provided an easy start and only a small proportion failed to get 2 marks, either because they did not know the formula of sodium sulphate or because they thought sulphur dioxide was given off as well as hydrogen chloride. In (a)(ii) the response expected was “white fumes” or “white smoke”, but “steamy” and “misty” are the words used to describe hydrogen chloride, and these were not allowed. The fumes consist of fine particles of solid ammonium chloride, so “white solid” was also allowed, but not “a white precipitate” as the reaction did not involve solutions. Most candidates realised that hydrogen bromide and hydrogen iodide give the same result as hydrogen chloride.

The oxidation numbers in (b)(i) were usually given correctly. However in (b)(ii) few candidates showed how the changes in oxidation numbers related to the numbers given in the equation. They said that the oxidation number of sulphur goes from +6 to +4 while two bromide ions go from -1 to zero, though the equation shows that two moles of sulphuric acid react with two moles of bromide ions. A comment was required on the fact that one of the sulphur atoms in the equation did not change oxidation state.

The most common error in (c)(i) was to explain the increase in boiling point by the size or mass of the atom, or number of quantum shells, rather than referring to the number of electrons. Some candidates correctly said that the strength of van der Waals' forces increases, but then added incorrectly that dipole-dipole forces also become stronger going down the group. There were many good answers to (c)(ii), though weaker candidates either forgot about formation of hydrogen bonds in hydrogen fluoride, or did not make clear that these bonds are stronger than van der Waals' forces.

Question 2

Many candidates did not know how to use value for the heat capacity in (a)(i), and multiplied their answer by 0.500, the mass of propane. Looking at the units of heat capacity, which are $\text{kJ}^\circ\text{C}^{-1}$, might help candidates to deduce that the heat capacity indicates the number of kilojoules needed to raise the temperature by one degree. After an error in (a)(i) full marks could still be gained in (a)(ii) by using the correct method. There was little sense of the importance of precision in this calculation. Often the number of moles of propane, which has the value $0.500 / 44$, was taken as 0.01 while it could have been left in the calculator for the second stage of the calculation. The final answer was then given to more than the three significant figures required. In (a)(iii), the question said that this method of measuring an enthalpy change allowed for heat loss, but the most common answer was repetition of this information. Some candidates recognised that incomplete combustion occurred, but others said that “not all of the propane burnt” which is a different matter.

The calculation in (b)(i) was much more successful, and though there were errors in balancing the cycle with five oxygen molecules going to ten atoms, most were able to calculate ΔH_f and the final value. In (b)(ii) the phrase “mean bond energies were used”

appeared frequently, but it was much less common to see the explanation that bond energies of the substances in the reaction vary with their environment and differ from the mean. Another commonly used phrase was that “mean bond energies are inaccurate” which again does not actually explain the answer. In this question, candidates seemed to be quoting a phrase without thinking about it and actually relating it to the question.

It was surprising to see nucleophilic substitution suggested so often in (c)(i), especially as there were a lot of good answers suggesting the combination of two propyl radicals in a termination step to give hexane in (c)(ii). A lot of good detail of the mechanism was given here, which unfortunately exceeded the requirements of the question and could not gain extra marks.

The colours of the silver halide precipitates were well known, as was the equation for formation of silver iodide, but even the best candidates had trouble with (d) (iii). Nitro compounds were suggested regularly, and even if propanol was suggested it was rarely propan-2-ol.

Question 3

Part (a)(i) produced a range of incorrect answers, and it was not widely known that three identical groups should be shown by a tri- in the name, or that a number is shown twice if two identical groups are on the same carbon in a chain, in this case 2,2. The meaning of the term “empirical formula” in (a)(ii) was not well known either, and molecular and structural formulae were given. There was more success with (a)(iii) and (a)(iv), and about half of the equations in (a)(v) were correct. However the errors included production of hydrogen and carbon dioxide in incomplete combustion.

Questions on the effect on an equilibrium of changing conditions are asked regularly and (b)(i) was well answered, though there is a tendency to refer to the equilibrium moving, without answering the question and stating the effect on the yield. Most candidates realised that an increase in temperature would cause the increase in rate in (b)(ii), though a few wrote about how a catalyst works. There were also many correct answers to (b)(iv), but it surprised the examiners to see so many references to carbon dioxide as the least harmful of the gases, given the extent of current media discussion about it. In (b)(iv) most candidates showed the profile of a non-catalysed reaction above the original line. However marks were lost by those who labelled the maximum of the curve as the activation energy, rather than labelling the difference in energy level between the reactants and the maximum.

Many candidates were successful in drawing the dot and cross diagram of carbon dioxide in (c), but found carbon monoxide more difficult, even though they referred to its triple bond or dative covalent bond in the explanation. Some had the mistaken idea that lone pairs on oxygen were responsible for the bond lengths.

Question 4

This question proved difficult, and candidates often quoted phrases from the passage, rather than using their knowledge to provide explanations. In (a) the expected answer was the lack of reactivity or lack of solubility of polythene, but answers saying that polythene behaves like bone, or is similar to natural bone were often given. In (b) many answers referred to strong intermolecular forces without specifying the nature of the forces found in polythene, or why they are so strong. The most common answer to (c) was a circular argument which said that polythene is easier to turn to a liquid if its melting point is reduced, and only a small minority suggested that the intermolecular forces were weakened.

In (b) candidates had to think about how many electrons are around the phosphorus atom, and whether any lone pairs are present. Every common bond angle, and a few others, were suggested. The reasons given did not always match the suggested angle in terms of realising that there were four bonding pairs but no lone pairs present. It is easy to draw the structure of addition polymers such as the one in (c)(i) if the monomer is drawn with four groups attached to a central C=C bond. The resulting polymers should then be no more difficult to draw than poly(ethene), and the groups round the C=C will be the groups attached to the carbon backbone of the polymer. This approach should prevent errors such as putting the carboxylic acid group into the polymer chain. In (c) (ii), comparison of the formulae of lactic acid and propenoic acid would have shown that they differed by one water molecule so that hydration had occurred.

The summary exercise was demanding, and the full quota of six key points was rarely achieved. The passage referred to four materials used for repairing bone damage: metals, two different polymer composites, and biodegradable implants. The meaning of the word “composite” may not have been understood, as polythene and hydroxyapatite were sometimes suggested as two materials which could be used separately. Supercritical carbon dioxide is used in mixing and shaping composites, but some thought it was a material which was implanted. A significant number of candidates gave detailed descriptions of the shaping process using supercritical carbon dioxide and lasers, and therefore exceeded the word total. A number of high word totals were stated to be 110 words, and candidates are not helping themselves by doing this as word totals are checked. If the limit is exceeded then they need to look again at the requirements of the question and do some editing! There was not much evidence of planning, by first selecting the materials which are used, and then looking for their advantages or disadvantages. The usual format was to write a summary of each of the original paragraphs and this is what led to the use of excess words.

Hints for revision

- When you are deciding what factors affect boiling point, think about the types of intermolecular force that may be present. There may be more than one.
- Electronegativity differences make a bond within a molecule polar, but you cannot explain boiling points only on the basis of electronegativity.
- Make sure you know the meaning of heat capacity, which you use in Experiment 7.6 in the *Students Book*. If you don't remember the meaning, look at the units, which are $\text{kJ}^\circ\text{C}^{-1}$. The units tell you that it is the number of kilojoules which raise temperature by one degree.
- Learn the difference between using “mono”, “di” and “tri” in a name and the numbers 1,2 and 3. “Di” refers to two groups eg two methyl or two chlorine, but the number 2 shows that these groups are attached to the second carbon in a chain.
- To predict a bond angle, count up the number of bonding pairs and lone pairs of electrons round a central atom. Assume a dative covalent bond is equivalent to a normal covalent bond, and ignore lone pairs on other atoms in the molecule.
- When working out the formula of an addition polymer, draw a displayed formula of ethene and substitute the hydrogen atoms with whatever groups are present in the monomer. The polymer will then consist of a series of these units linked together, with the C=C bond broken.

Unit 6254/01

General

Examiners were generally pleased with the quality of answers seen, particularly in the calculations and questions testing factual recall. They were less impressed with answers involving descriptions and explanations, both with regard to the quality of written communication and to the appropriate use of technical vocabulary.

Question 1

The first part of this question covered familiar ground and was handled extremely well by the majority of candidates. A missing sign in the entropy of the system in (a)(ii), and giving the entropy of the surroundings to more than four significant figures in (b), were the commonest faults. Part (d) was handled impressively well by the majority, even though this type of question has rarely been asked before.

Question 2

The majority knew the observation associated with a positive result for Brady's Test in (a), but in (b) a surprising number gave butanal itself as the formula for **F**, even though the question referred to "**isomers** of butanal". However, the formula for **G** was almost always given correctly, and candidates came up with some interesting possible formulae for **H**, including enols, cyclobutanol and branched cyclopropanols.

In (c) examiners were looking for a well-expressed explanation, comparing "heating under reflux" with "boiling in a beaker", but good answers were rarely encountered. Common responses, which scored no credit, included "to stop the liquids escaping" or "to keep the chemicals in the flask", without any reference to the reactants or products, or to the processes of volatilisation or condensing. In (c)(ii), the name for the ester - ethyl butanoate - was usually given, but the hydrolysis products often included butanoic acid rather than sodium butanoate. Answers giving butyl ethanoate, followed by butanol and sodium ethanoate in (c)(iii), were marked sympathetically. A surprising number were unable to give "hydrolysis" as the name for this type of reaction, yet saponification - a perfectly acceptable alternative name - was seen on a number of occasions.

Most knew which atom to ring in the formula for the ester in (c)(v), and there were some excellent answers justifying this choice. However, several candidates ruined their work by referring to the carbon being attached to oxygen "molecules". In general, however, terms such as "electrophilic", "electron deficient" and "electronegative" were used in the correct context, and it is perhaps regrettable that the explanation in (c)(v) was worth only one, rather than two marks.

Question 3

The straightforward calculations in (a)(i) and (a)(ii) were usually answered correctly, but the calculation of the rate of formation of iodine in (a)(iii) was beyond the abilities of most. Although many candidates realised that their answers to (a)(ii) had to be divided by 5 to calculate a rate, the majority failed to appreciate that since the total volume of solution was 40 cm^3 , the values needed to be scaled up by $(1000/40)$ to convert to the correct units of $\text{mol dm}^{-3} \text{ s}^{-1}$. There were some very impressive answers in (b)(ii), in which candidates had to predict the order of reaction with respect to peroxodisulphate ions. The information required was not immediately obvious from the rates table, yet the majority spotted the relevant trends and were able to express their reasoning with

pleasing clarity, using numerical evidence from the table appropriately. The rate equation was given correctly by most candidates, and it was pleasing to note that very few lost the mark through a failure to include the rate constant. In (b)(iv), most candidates deduced the appropriate units for a second order reaction and many calculated the value correctly as well. Full consequential marking was applied in (b), so that the candidate who gave a rate equation with an overall order of 7 was given full credit for a consistent response in (b)(iv), horrendous though the units turned out to be.

Question 4

Most candidates read off an appropriate value for the initial pH from the graph (between 3.5 and 3.6) and the calculation of $[H^+]$ in (a)(i) was usually carried out correctly. The expression for K_a was generally quoted properly, but a significant minority gave the one for propanoic acid instead, or wrote the reciprocal of the correct expression. In (a)(iii), those who had previously rounded their answers to $3.2 \times 10^{-4} \text{ mol dm}^{-3}$ in (a)(i) should have used the more precise answer when calculating the value for K_a , and there were several who lost credit through a failure to quote answers to two significant figures, as required by the question.

Examiners were dismayed that very few knew the correct equation for the neutralisation process in (b)(i), in which butanamide, or even butylamine were given as products, rather than ammonium butanoate. Those who gave a proper equation, and then the correct names for the compounds present between points X and Y on the curve, usually realised that this solution was a buffer, before verifying from the graph that the pH rise was relatively small compared with the volume of base added. Part (iv) was answered disappointingly, most candidates simply pointing out that titrations between weak acids and weak bases cannot be carried out using an indicator. In other answers candidates displayed a complete lack of understanding as to how indicators operate, simply stating that no indicator could operate over the pH range in question, when it is evident here, that at the end-point, no such "range" exists. Despite the help given in (b)(v) many interpreted the requirement to read off the end-point as a need to measure the pH, and, by giving a value of 9.4, revealed a complete lack of understanding as to what was going on. Those who correctly used the point of inflexion as indicating the correct end-point and who read off the volume as 30 cm^3 , generally knew exactly what to do to calculate $[NH_3]$ subsequently.

Question 5

This question produced answers with a wide range of marks. The majority knew the factual material in (a) well enough, though a surprising number of candidates described the formation of a sulphonic acid as an addition process. Part (b) was answered well by many, and though the test for phenols using $FeCl_3$ is not in the specification, it was the one quoted by the majority, so it is evident that the relevant practical work is being carried out. Although it was decided to give a maximum of 1 mark out of 2 for a simple pH test on a solution of vanillin, candidates need to be reminded that a **chemical** test must involve a **chemical** reaction. Tests using bromine water and dilute nitric acid, which are essentially properties of the arene ring, were only given 1 mark (providing that both the test and the appropriate observation were described) on the basis that both the phenol and the methoxy groups activate the arene ring. As a consequence, to gain full credit, candidates needed to point out that the reaction with the phenol was relatively rapid, rather than stating or implying that nothing happened with 2-methoxybenzene.

In (c)(i), working out the correct molecular formula for vanillin proved to be a straightforward enough task, but many inexplicably gave an answer of $C_8H_8O_2$. In (c)(ii), hydrogen bonding was correctly given as the intermolecular force operating

between molecules of vanillin and water, but the diagrams drawn often displayed this type of bonding inappropriately. Some drew the bonding between two molecules of vanillin, and many wrongly introduced “hydrogen bonding” with the hydrogen atoms of the methoxy or aldehyde groups. Examiners were surprised to see several answers showing water as **O-H-O**, and those in which the **hydrogen** atom of water was hydrogen-bonded to one of the eligible **hydrogen** atoms of vanillin. As perhaps expected, the **hydroxide**, alcohol or aldehyde groups were often wrongly quoted as being responsible for the acidity in vanillin. The equation proved to be a straightforward one for those who knew the properties of phenols.

The first part of (d) was very disappointingly handled, though questions on recrystallisation are repeatedly set in Unit 4 papers. Examiners are sure that most candidates will have carried out recrystallisations in the laboratory - perhaps of aspirin – but they do not appear to have queried why, for example, the “**minimum** volume of hot solvent” is used. Far too many answers in (d)(i) such as, “to make a more concentrated solution”, were given. Candidates fared little better in (d)(ii), and even those who possibly knew what was going on failed to make it clear which filtration removed the **insoluble** impurities, or compounded their omissions and mistakes by writing that the soluble impurities were filtered off and washed with water. Centres are urged to ensure that candidates gain a better understanding of this important practical technique, even though it is appreciated that the principles underlying the process of recrystallisation are not clearly set out in the Students’ Guide. Determining the purity of a covalent solid via a melting point determination was widely known, but there are still many candidates who believe that a boiling point test is feasible, when it should be clear that a temperature high enough to boil a substance which is solid at room temperature, is likely to be so high as to decompose or burn it in the process.

In (e), candidates were presented with a novel situation, which was intended to make them think about how infra-red spectra are used in qualitative analysis. Though many appreciated that the fundamental difference between 2-methoxyphenol and vanillin was the presence of an aldehyde group, the question clearly asked for the use of **evidence** (from the spectra). The hope was that candidates would then study the table, realise that the C=O stretching vibration for an aldehyde should show up at $1740-1720\text{ cm}^{-1}$ in one spectrum but not the other - which then turned out to be the case. The best candidates knew exactly what to do, but the majority wasted a great deal of time giving superfluous information which did not address the terms of the question.

Hints for revision

- Make sure you know exactly how to calculate hydrogen ion concentrations from a pH value, using the 10^x button on a scientific calculator.
- Once a numerical value has been calculated, remember to check three things. Has a sign been given, is the value quoted to an appropriate number of significant figures and have the correct units been included?
- Many marks are lost in multi-stage calculations through “premature rounding errors”. When carrying out a string of calculations, remember to use the raw calculator answer at each step, even if values to fewer significant figures have to be quoted at intermediate stages
- Ensure that you know exactly why indicators operate and, in particular, **why** they cannot be used for titrations involving weak acids with weak bases.
- Make sure that you fully understand **why** recrystallisation helps to purify a product at the expense of yield.

Appendix A – Statistics

6251/01

Grade	Max. Mark	A	B	C	D	E
Raw boundary mark	60	48	44	40	36	32
Uniform boundary mark	90	72	63	54	45	36

6252/01

Grade	Max. Mark	A	B	C	D	E
Raw boundary mark	60	42	37	32	27	23
Uniform boundary mark	120	96	84	72	60	48

6254/01

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

Notes

Maximum Mark (Raw): the mark corresponding to the sum total of 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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