

Examiners' Report

Summer 2013

GCE Chemistry (6CH05) Paper 01R General Principles of Chemistry II



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General

This paper produced a wide spread of marks with many questions where the all students could provide acceptable answers and with others more challenging which stretched the most able. A significant number of students scored over 70 out of 90 as their raw mark and in the highest scoring scripts students were able to demonstrate their depth of knowledge and understanding of this unit. Answers to a small number of questions lacked precision in the explanations offered e.g. when comparing the strengths of bases in organic amines students often did not refer to 'the lone pair of electrons on the nitrogen atom'.

Question 20

Question 20(a)(i) - Most students gained credit and knew at least two correct formulae for the chromium entities. Many stated the correct formula Cr^{3+} and a minority gave the more precise formula for the hexaaqua ion and a small minority incorporated sulfate or an odd species. The identities of **A** and **B** given were generally correct, although a minority gave oddly balanced species, either in terms of charge e.g. $Cr(OH)_6^{3+}$ or numbers e.g. $[Cr(H_2O)_5(OH)_2]^-$. The chromate (VI) ion sometimes appeared incorrectly for **C**, with a significant number giving a single negative charge and a minority stating the dichromate (VI) ion.

Question 20(a)(ii) - Students demonstrated a good understanding of the half equation for the reduction of hydrogen peroxide, with most showing that two electrons and two hydroxide ions are required to balance the equation.

Question 20(a)(iii) -The majority identified a 'suitable' acid, most commonly sulphuric acid, although a significant minority did not and just stated 'an acid' or gave ' H^+ '.

Question 20(a)(iv) -The ionic equation for conversion of **C** into $Na_2Cr_2O_7$ proved challenging although a significant percentage gave fully correct answers. Similarly a significant number of students included extraneous species e.g. e-, O_2 and a small proportion gained no credit in this question. There were some answers where odd spectator 'species' appeared, which were clearly not ions.

Question 20(b) - Where students identified the correct half equations, calculations usually followed through to a correct conclusion regarding the disproportionation of chromium (III) in aqueous solution. Problems arose when different oxidation states for chromium were chosen. A significant number of students calculated the cell emf incorrectly by mixing up the half cells. However, some of those who did this still demonstrated that they understood the principle of cell emf, charge and feasibility of reaction.

Question 21

Question 21(a) - The large majority of students used the Data Booklet effectively to obtain the correct standard enthalpy change of formation of water.

Question 21(b)(i) - Many students tried to use either the acid fuel cell equations, rather than those involved in an alkaline fuel cell, or a combination of one of each. In addition a significant number of students gave incorrect equations e.g. unbalanced or with no electrons. Only a minority scored 3 marks for this question and state symbols were often omitted. The mark scheme awarded much good chemistry. However, the majority of studentss struggled with an unfamiliarity of alkaline conditions.

Question 21(b)(ii) - The key word 'electrolyte' was often omitted and the answer frequently given was a description of the role of the alkali, in the fuel cell, as a 'catalyst'. Movement of electrons rather than ions was a common error, as was inadequate reference to the solvent or medium conducting electricity. A minority gave the correct idea of ion movement and often students referred to the role as an 'electrolyte', indicating a clear understanding of how the process works.

Question 21(b)(iii) - Many students clearly understood the similarities in the two processes where platinum acts as a catalyst, but a significant number of students misinterpreted the question and gave answers simply explaining what all catalysts do. Many unrewarded responses made reference to the heterogeneous nature of the catalysis and surface reactions or there being an alternative route of lower activation energy. Adsorption of reactant gases on to catalyst surface, with a weakening of the bonds within hydrogen and oxygen molecules, were among the more common correct answers and the existence of active sites was also referred to in a number of cases. Occasionally absorption was given incorrectly. Some students made comments about increasing the rate of reaction, but there were fewer references as to how this is achieved, indicating a misinterpretation of the question.

Question 21(c)(i) - A significant number of candidates did not answer the question fully enough. Many answers focussed on energy efficiency and hydrogen being eco-friendly. The word **only** was frequently omitted even when water was given and other answers referred incorrectly to less carbon emissions/oxides of carbon rather than **none**. A common misconception was that water is not a greenhouse gas e.g. "the combustion of hydrogen does not release any greenhouse gases" was stated by a number of students.

Question 21(c)(ii) - Very few students mentioned the important point that fuel cells produce electricity directly. The majority scored only 1 mark, for stating that the fuel cell is "more efficient", but many did not show a clear understanding of what they meant by efficiency in this context. Reference to

"less heat loss" was rarely stated and other answers that referred to safety issues or a fuel cell having lower or higher energy input gained no credit. Many students missed the point of the question and discussed pressure, noise, hazardous hydrogen or pollution, for example.

Question 221(c)(iii) - The high cost of making a fuel cell or the fact that the catalyst is expensive were among the most common answers. Students often referred to storage and/or less energy output. Many missed the point and referred to the explosive nature of hydrogen and had not appreciated the both processes involved hydrogen. A relatively common mistake was to refer to the catalyst without the context of cost e.g. "a platinum catalyst is required".

Question 21(c)(iv) - Students showed a good understanding of the advantages of ethanol rather than hydrogen as a fuel. Many students thought that they had given two advantages but they had actually just expanded the first marking point. Some responses gave "less pressure needed for ethanol", rather than the no pressure required and the efficiency of ethanol was often referred to. Students often used the word 'easier' to cover a range of meanings and many responses referred to energy density and failed to score.

Question 22

Question 22(a)(i) - Most students knew that the suitable reagent used as a source of sulphur trioxide is fuming sulfuric acid or oleum. Those who lost marks often gave just the name or formula for sulfuric acid or stated that it was concentrated. The were some unusual answers such as HNO_3 , $Na_2S_2O_3$ or NaOH.

Question 22(a)(ii) - The majority of students knew how to represent the partial charges on the sulphur trioxide molecule, but it was not uncommon to see full rather than partial charges and oxidation states (6+ and 2-) on the diagrams. Whilst most students gave correct partial charges, fewer referred to the higher electronegativity of oxygen or that oxygen is more electronegative. Many mentioned the oxygen atom attracting electrons without referring to electronegativity.

Question 22(a)(iii) - This question was well answered generally, but the main mistake students made was that students referred to the sulfur atom as being "positively charged" rather than having a large partial positive charge.

Question 22(b)(i) - Most students understood the electron movement from the benzene ring to the sulfur atom, but a significant number did not show a second curly arrow correctly going from the S=O bond to the O atom. Often the second curly arrow drawn was the arrow from the C-H bond which is part of the second step.

Question 22(b)(ii) - The second and third steps of the electrophilic substitution were well understood by most students. There were very good responses provided by the higher ability students and weaker answers often had the first curly arrow starting from H atom rather than the C-H bond. The intermediate anion structure was represented accurately in the majority of answers, but the final curly arrow to the H⁺ ion or H atom within H_2SO_4 was often omitted or shown in the wrong direction. In some answers the final curly arrow from the $-O^-$ of the intermediate anion was shown going to the H atom on the tetrahedral C of the Wheland intermediate, which is acceptable for one of the last two marks. Many either omitted the final curly arrow to the H⁺ or drew it in the wrong direction. Half arrows were rare occurrences.

Question 22(c)(i) - For the production of phenol from benzenesulfonic acid, few students gave a correct first equation, but many provided one of the three acceptable alternatives for the second equation. The main problem in the first equation was achieving correct balancing, so 2NaOH on the reactants' side was very common. A significant number of ionic equations had ions missing or incorrect products appeared on the right hand side such as Cl_2 , H_2 , HCl. A few students thought the first stage simply neutralised the sulfonic acid, with HCl as an electrophile in the second stage attacking the benzene ring, so a number of answers showed a carbocation linking both stages.

Question 22(c)(ii) - Among some excellent answers students made all four alternative marking points. Many students knew that the Hock process is only one step or involves fewer steps, with a high atom economy, but only a small percentage referred to it as a continuous rather than a batch process. A significant number referred to less "by-products" rather than "waste products". References to yield or safety due to the chemicals involved were often stated and other unacceptable answers emphasised that the Hock process is cheaper.

Question 23

Question 23(a)(i) - The majority understood that the feature of amine molecules than causes them to be alkaline is the lone pair of electrons on the nitrogen atom. Some students associated the idea of the amine group or nitrogen atom being a proton acceptor or producing hydroxide ion, without the lone pair being mentioned.

Question 23(a)(ii) - This question was accessible to all but the weakest students and was very well answered by most. A number of students made a careless omission of the positive charge on the butylammonium ion or the negative charge on the hydroxide ion.

Question 23(a)(iii) - Many students made reference to the extra butyl or alkyl group in dibutylamine along with the resulting additional electron donating effect. Among the best answers students made all three marking points, even though only two were required. The increased lone pair availability and other alternatives linked to the lone pair were less well expressed however e.g. some students stated that nitrogen becomes more electronegative. There were also some references to longer alkyl chains or methyl groups rather than the extra butyl group. Some answers stated that nitrogen was often negative rather than partially negative. A minority said that two amine groups were present in dibutylamine or that it had two methyl groups. Some made reference to butylamine being able to attract H⁺ ions, the carbon chain length doubling or there being more electrons in butylamine. There were also inadequate explanations or comments about producing less hydrogen ions or hydroxide ions, less hydrogen bonding or just stating the two compounds were primary and secondary amines.

Question 23(a)(iv) - The majority of students explained the lone pair of electrons on the nitrogen atom being pulled into the ring or interacting with the 'pi' or delocalised electrons of the ring. The reduction of the lone pair availability due to this was less well expressed as were the alternative answers which required students to refer to the nitrogen atom having a lower electron density or the amine group being less able to accept protons. An example of an unacceptable answer read "decreases the ability of phenylamine to attract the proton".

Question 23(b) - Many students showed a good understanding and knowledge of the formulae of the correct copper entities, even if equations were unbalanced. The second equation was commonly correct even when students were unable to gain any credit for the first equation. However it was not uncommon to see the amine as the ligand in the first equation or ammonia in both equations. Other common errors were incorrect or no charges on the copper entities. Six amine ligands were seen is some answers, even though only four appear on the left hand side of the second equation. Water, completely omitted, was seen on occasions.

Question 23(c) - The large majority of students understood that water behaves as a nucleophile when reacting with the diazonium ion and where nucleophilic substitution is taking place. Many students then made reference to the more common reaction for benzene compounds being electrophilic substitution. Fewer mentioned the high electron density on the benzene ring repelling nucleophiles. In some less good answers students referred to nucleophilic addition. Some students who could give nucleophilic substitution couldn't explain why this is unusual and went on to comment on decomposition above 10° C.

Question 24

Question 24(a)(i) - The majority of students did not give a very accurate explanation on why the presence of a second carboxylic acid group increases the extent of the first dissociation. The electron withdrawing effect of the extra -COOH group was rarely stated. Many students referred to oxygen being very electronegative, or that the second -COOH group makes the oxygen more electronegative or makes the acid stronger. Many answered question 24(a)(ii) here and discussed the equilibrium and in other answers dimers and H-bonds were mentioned. Those who did refer to the electron withdrawing effect of the extra -COOH group often referred correctly to the weakening of the O-H bond and some stated that the O-H bond/group becomes more polar, which gained no credit. Few students mentioned the increased stability of the hydrogenethandioate ion, an alternative acceptable answer.

Question 24(a)(ii) - Students demonstrated a good understanding that the second dissociation of a dibasic acid is suppressed by the formation of hydrogen ions from the first dissociation, so the equilibrium moves to the left. Students who failed to gain credit here often did not make any reference to the hydrogen ions.

Question 24(b)(i) - A significant number of students knew that the colour change in the ethandioic acid and potassium manganate (VII) titration was from colourless to pink (or purple), but many gave the colour change in reverse.

Question 24(b)(ii) - This calculation was well carried out by most students. A small proportion of students used an incorrect mole ratio (usually 2:5 rather than 5:2) but by far the most common single loss of marks was the use of an incorrect Mr for oxalic acid, where 88 instead of 90 was seen. Students often failed to give their final answer to at least two significant figures, having carried out all earlier steps correctly.

Question 24(c)(i) - The vast majority of students defined a bidentate ligand satisfactorily. Covalent rather than dative bonds were sometimes referred to and misspellings also led to loss of the mark e.g. "forms to dative bonds", "has too lone pairs to make dative bond"

Question 24(c)(ii) - Students found this question challenging, but the minority of very good answers demonstrated an excellent understanding by the more able. Many answers did not make the overall charge of zero very clear, many students drew wedges in such a way that square planarity was undermined, others used only one of the two ligands and a high proportion of (even otherwise fully correct) answers did not show dative bonds. The ligands shown in the structure were often incorrect with some students, however, still able to represent two dative bonds arising from two separate nitrogen and two separate oxygen atoms of the ligands given. There were some instances of dative bonds arising from doubly bonded oxygen atoms.

Question 24(d)(i) - Many fully correct answers were provided reflecting a good knowledge and understanding of the reagents and conditions required for the conversion of ethene into ethandioic acid. Some students appeared to think that reaction with hydroxide ions converts ethene to ethan-1,2-diol and it was not uncommon for students to completely omit reagents and use [O] for both steps. Sometimes the acid was omitted when sodium dichromate (VI) was used for the second step. In cases where students did not understand the chemistry involved they knew that the diol was the intermediate compound formed and even where its full proper name was not given, students were able to gain credit by showing its correct structural formula.

Question 24(d)(ii) - The vast majority of students understood that either ethandioic acid can be obtained from carbohydrates/glucose which are renewable resources or ethene is derived from non-renewable resources i.e. fossil fuels or both.

Question 24(d)(iii) - Students answered this question well overall, with a significant number of fully correct answers and most students making reference to the appropriate number of peaks and correct splitting patterns for each acid. However, a small, but significant proportion of students stated that ethandioic acid has two singlet peaks. The intensity ratio of 3:2:1 was often expressed in terms of the numbers of correct proton type being associated with the related peak.

Hints for revision

- Try to practise as many of the different types of calculation question found in this Unit e.g. the calculation of E^{e}_{cell} from standard electrode potentials of half equations for transition metal ions and calculations based on titration results for redox reactions.
- Study the equations (both half-equations and the overall equation) that are involved in both alkaline and acid fuel cells, where hydrogen and oxygen react to produce electricity and explore the advantages and disadvantages of the hydrogen fuel cell, compared to direct combustion of hydrogen or the ethanol fuel cell.
- Learn and understand the chemical concepts which explain why organic amines have different strengths as bases.
- Revise and learn the formulae and equations involved for the different type of copper entities that can form when aqueous amines are added to copper (II) ions in excess.
- Study the NMR spectra for monobasic and dibasic carboxylic acids including the splitting patterns and intensity ratios of the peaks.

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