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General Certificate of Education (A-level)
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Chemistry CHEM4

(Specification 2420)

Unit 4: Kinetics, Equilibria and Organic Chemistry

Report on the Examination

General Comments

The paper was found to be very slightly harder than that of the previous year but there were many very pleasing performances across the whole range of questions and the paper discriminated well. The general performance in the organic sections was better than in previous papers, most notably in the question about amino acids. An unfortunate number of candidates still lost marks in calculations because of their inability to rearrange mathematical expressions correctly or to use numbers involving powers of ten correctly in their calculators. The unstructured *stretch and challenge* questions discriminated well and elicited some impressively clear and concise answers although weaker candidates inevitably struggled here.

Question 1

Most parts of this question were answered well. The ester was named correctly by over two thirds of the candidates but a surprising number attempted to write a stoichiometric equation in part (a)(ii) rather than a rate equation. Part (a)(iii) was answered very well but in part (a)(iv) the effect of dilution on the concentration of both reagents was missed by a large majority. However, when the exact concentrations were given in part (a)(v) most candidates were able to calculate the new rate of reaction correctly. The effect on the rate constant of lowering the temperature was well known in part (a)(vi), but few candidates were able to give a correct explanation and many offered a mathematical rather than a kinetic explanation. In part (b), the requirement to use the rate equation to identify the rate determining step proved difficult for the majority.

Question 2

The early parts of this question were answered well, although in part (a)(iii), about a third of the candidates did not realise that adding water had no effect on the number of moles of acid present. Over two thirds of the candidates scored full marks in part 2(b); a common error for the others was to rearrange the expression for K_a incorrectly. In part 2(c), many answers stated general properties of a buffer solution, without giving any explanation specific to this situation.

It was pleasing to see that over 44% of the candidates gained full marks in part (d)(i). Many of the rest thought that addition of the salt to the solution of the acid changed the amount of acid present. Part (d)(ii) discriminated well and only the better candidates were able to calculate the amounts in moles of acid and of salt present in the solution after the addition of sodium hydroxide and then use these values correctly.

Question 3

In part (a), just over half the entry was able to use the mole ratio in the equation correctly and calculate the number of moles of methanol and of hydrogen. The expression for K_c was answered well in part (b) and half the candidates gained three or four marks in the calculation. The most common error was to confuse the number of moles of each gas with its concentration and forget to divide by the volume. Also, a considerable proportion ended up with the wrong answer due to incorrect use of their calculator. Only half of the candidates knew that K_c was unaffected by adding more hydrogen. In part (c), most candidates correctly deduced that T_1 was the higher temperature – although it was sometimes difficult to decipher whether the number written was 1 or 2. Many lost a mark in the explanation for giving a generic explanation such as “the equilibrium shifts to oppose the change” rather than explaining specifically that if the temperature is lowered, the equilibrium moves in the exothermic direction to oppose the lowering of the temperature or to increase the temperature. In part (d), most candidates were able correctly to link the process to produce hydrogen with an environmental problem but in part (e) fewer than a third of the candidates could write the correct formula for a methyl ester of one of the long chain carboxylic acids.

Question 4

Part (a) was answered well by two thirds of the candidates. In part (b)(i), half gave a correct structure; many wrong answers showed too many repeating units or included an extra oxygen atom. The type of polymerisation in part (b)(ii) and the required bond in part (c)(i) were both very well known. In part (c)(ii) the answer was required as a displayed formula, ie it must show **all** the bonds. Many candidates have still not realised that **all** includes the O–H bond. Part (d) was correctly answered by fewer than a fifth of the candidates. Many simply drew 2-aminobutanoic acid rather than its zwitterion. In parts (e)(i) and (e)(ii), many candidates did not recognise that both acid groups in glutamic acid would react. Two thirds of candidates answered part (e)(i) correctly, but parts (e)(ii) and (e)(iii) were found more difficult. In part (f), some candidates explained clearly how column chromatography worked and just under a third gained full marks in this section. Others described paper chromatography or were obviously unfamiliar with the topic.

Question 5

This question presented the usual range of difficulties for candidates when asked about n.m.r. spectroscopy. The amine functional group labelled **K** was recognised by most candidates, but the amide group labelled **J** was less well known. The range in part (b) was answered well but the splitting of the peak into a doublet was less well known. In part (c)(i), the presence of a hydrogen atom in $CHCl_3$ was recognised by most as interfering in the proton n.m.r. spectrum. However, part (c)(ii) was answered correctly by only a quarter of the candidates. Other answers showed confusion between the polarity of a bond and the overall polarity of a molecule with many suggesting incorrectly that CCl_4 is a polar molecule. The number of peaks in the ^{13}C spectrum of atenolol was deduced correctly only by the better candidates whereas all but the weakest could identify the standard substance and draw its formula correctly in part (e). The δ value of the required peak was fairly well answered in part (e)(ii) and over four fifths of the candidates identified the correct CH_2 group in part (e)(iii). Many were able to give a correct reducing agent in part (f)(i), although potassium dichromate(VI) was a surprisingly frequent answer, and three fifths of the candidates correctly identified the asymmetric carbon in part (f)(ii). Parts (f)(iii) and (iv) were answered quite well and in both cases two fifths of candidates gained full marks. Advantages offered in part (f)(iv) were often in terms of reduced cost but without any supporting reason. However, candidates were better at identifying suitable disadvantages.

Question 6

As is usual, mechanism questions such as this discriminate well. In part (a)(i), 13% of the candidates gained all five marks whereas a similar number scored only one mark. Many candidates omitted the name of the product in an otherwise perfect answer. In part (a)(ii), two fifths of the candidates gained full marks.

In part (b)(i), a number of candidates lost a mark because they gave the formula of the aldehyde propanal as CH_3CH_2COH rather than as CH_3CH_2CHO. For clarification of acceptable formulae styles, candidates and teachers are advised to consult the document "General principles applied to marking CHEM4 papers by CMI+ January 2011" which is available with the Mark Scheme for this paper.

The mechanism in part (b)(ii) was well known and two fifths of candidates gained full marks. Part (b)(iii) was a *How Science Works* question where candidates were not required to know the answer, but were expected to apply understanding gained from other areas of the specification. The inductive effect of alkyl groups is part of the explanation of the relative stability of carbocations. A similar effect using two alkyl groups will reduce the δ+ nature of the carbonyl carbon in propanone more than the single alkyl group does for the carbonyl carbon in propanal. Hence it can be predicted that the nucleophile will attack propanal more easily than propanone. About a third of the candidates gained both marks; most of these gave an answer based on inductive effects as above, but others correctly discussed steric effects and this answer was also accepted.

Question 7

Although diethylamine was the expected answer in part (a), several alternative names were allowed for the secondary amine. Candidates struggled to name the compounds correctly in part (b) and there were many incidences of incorrect naming of proposed compounds F and G, with ethanamide often being suggested when the candidate quite clearly meant ethylamine. Parts (b) and (c) involved a three-step synthesis and together made up a less structured *stretch and challenge* question. The very best candidates gained the available eight marks with splendidly clear and concise answers. Although one route was preferred, other less efficient routes were allowed and candidates were rewarded for demonstrating knowledge of correct chemistry even if their overall synthesis would not have worked. In part (d) just under half of the candidates realised that further substitution of the secondary amine could occur. Over half of these correctly identified a tertiary amine or a quaternary ammonium salt as the impurity.

Mark Ranges and Award of Grades

Grade boundaries and cumulative percentage grades are available on the Results statistics page of the AQA Website.