

Report on WCH04, January 2017

Introduction

The paper was accessible with a mix of straightforward and more challenging questions. In most scripts all of the questions were attempted but, when parts were left blank, they were most often in Question 24. Many candidates were well prepared for the calculation questions on acids, equilibrium and entropy, but the activation energy graph and calculation proved to be demanding. The questions which asked candidates for an explanation about buffer function, equilibrium and entropy required good quality written communication and were the most discriminating.

Question 21

In (a)(i) many candidates found it difficult to express the answer clearly. Some candidates were confused by the fact that crystal violet is an indicator and thought that it was being used as such.

The relatively high concentration of sodium hydroxide meant that its concentration was almost constant during the reaction, and the rate was therefore dependent on the concentration of crystal violet only. The phrase “limiting factor” appeared quite regularly, but was often used wrongly by candidates who thought that, unless the sodium hydroxide was in excess, all of the crystal violet would not react. The answer should make clear that the high concentration of sodium hydroxide would not limit the rate.

Colorimetry was the most usual answer given in (a)(ii). “Calorimetry” was not allowed; a pH meter would not detect a change in the presence of excess sodium hydroxide, and methods such as titration do not allow continuous monitoring so did not score.

Most candidates scored one mark in (a)(iii) by correctly measuring one half-life as 7.5 minutes. Many gave the second half-life as 15 minutes despite drawing suitable lines on the graph to measure it. Answers given as 7.5 and 15 seconds were not penalised on this occasion.

Most candidates identified the order in (a)(iv) to be first, possibly from the shape of the graph. A mark for the correct order was allowed even if it was followed by the meaningless statement that half-lives of 7.5 and 15 minutes were constant.

Completing the table in (b)(i) should have been a very simple task. Sometimes it was not attempted, perhaps because candidates did not have a calculator. It was disappointing that some candidates at this level could not round numbers correctly, and rounded 3.367 to 3.36.

When marking (b)(ii), examiners gained the impression that some candidates had never plotted points on an Arrhenius graph before, nor calculated the gradient. The choice of odd scales hampered many candidates leading to imprecise plotting and consequent loss of a mark. Lack of a unit on the x axis was a common error. Candidates also seemed to struggle with giving more negative values down the vertical axis. Well drawn graphs were very rare.

The gradient was most often calculated from the data in the table. This was allowed, as the points on the graph were all on a straight line. Many scored the first mark in (b)(iii) for correctly multiplying their gradient by 8.31, but lost the second mark because they did not include units, wrote incorrect units or gave more than two significant figures.

Question 22

Most candidates found the first three parts of the question straightforward, and many scored both marks in (a). However if their choice of reagent was wrong they lost both marks. The most common error was to miss the observation that a precipitate formed, and only to give the colour. In (b) the most common error was missing the requirement that the product to be identified is the one which is observed, iodoform, and not the other product. Quite a few answers gave the product as $(\text{CH}_3)_2\text{CHCOO}^-$, as if these candidates did not class iodoform as 'organic'.

The name required in (c) was often given correctly, though pentanol was seen on some occasions.

The question on nmr spectra in (d) proved to be very discriminating. The number of peaks in the low resolution spectrum equals the number of different hydrogen environments, but many different numbers were given, suggesting that candidates did not understand the principles involved. The peaks with greatest area are the peaks with most hydrogen atoms in the same environment, and again many different answers were seen. The answers expected for the splitting patterns were doublet and triplet, but on this occasion the numbers 2 and 3 were accepted as this followed the style of the rest of the table. Again, answers suggested a lack of understanding of the features of the spectra.

Few candidates scored full marks for the mechanism in (e)(i) and it discriminated well. Candidates found it hard to apply their knowledge when using an unfamiliar starting molecule. The errors seen frequently on this question were lack of a dipole on $\text{C}=\text{O}$, no lone pair on the carbon of the attacking cyanide ion, arrows from the N on the CN^- instead of from the lone pair on the C atom, missing the negative sign on the oxygen in the intermediate, hydrogen cyanide being shown as fully ionised, arrows from the H in hydrogen cyanide to the intermediate, and arrows to NaCN instead of HCN in the final stage.

By contrast, (e)(ii) was straightforward. Some candidates thought that water alone would be suitable, probably knowing the reaction was hydrolysis, but to score they had to give a strong acid, or an alkali followed by an acid. Adding alkali and acid at the same time was not allowed, and the disappointingly frequent combination of potassium dichromate(VI) and an acid came from candidates who had no idea about the reaction involved.

Drawing the polymer required in (e)(iii) proved a challenge for many. Most candidates scored the first mark for the correct displayed ester linkage. A few other links were seen. However many lost the second mark for the rest of the structure, with incorrect bonding on the C_2H_5 groups, missing or extra oxygens at each end, or missing extension bonds.

Question 23

Giving the IUPAC name for lactic acid in (a) proved more difficult than naming the organic product in question 22(c). Credit was not given for “hydroxide” or “hydroxo” in place of “hydroxy”. “Propanic” was not allowed for “propanoic”.

Few candidates scored all three marks in (b). Most often, only one OH was substituted by Cl as candidates did not realise the significance of phosphorus(V) chloride being in excess. Unfortunately, the minority of candidates who realised that both OH groups would be substituted then failed to balance the equation. Some seemed to struggle with OH being replaced by Cl and only substituted the H, leaving an extra O on either the hydroxyl or carboxylic acid group. It was not unusual to see water as a product, though it would react with PCl_5 .

Answers to (c)(i) were often correct. A few gave the equation for dissociation of the acid instead of the expression for K_a , and others gave the approximation used in calculating pH.

The instruction in (c)(ii) was to quote data in the answer. However many answers simply made a statement about the relative strength of the acids without giving data on either K_a or pK_a . A significant number of answers correctly gave the K_a of ethanoic acid as 1.7×10^{-5} but then said that this number was greater than 1.38×10^{-4} , presumably because they did not look carefully at the power of 10 in the value.

Many candidates were familiar with how to calculate the pH of a weak acid in (c)(iii), though some did not read the question carefully and lost the second mark as they did not give their pH value to 2 decimal places. Some used the wrong K_a value in their calculation, but were allowed one of the marks if their calculation method was correct. The assumptions on which the calculation was based were generally well known.

The calculation in (c)(iv) can be carried out in two different ways. The expression for K_a can be rearranged to find the lactate concentration. Some candidates thought that the concentrations of hydrogen ions and lactate ions are equal which is not true in the buffer solution. Candidates could score a mark by calculating the hydrogen ion concentration from the pH, but many lost marks by thinking that the concentration of lactate ions was $0.150 \text{ mol dm}^{-3}$, which is actually the concentration of the lactic acid.

A significant minority of candidates used Method 2 in the mark scheme, but not many arrived at the correct answer. They made errors when trying to rearrange the expression or evaluate the logs.

In (c)(v) there were many irrelevant answers which appeared to be responses to past questions which had been learnt by rote. There was little understanding that a reservoir of lactate ions was necessary to react with added hydrogen ions. Reference to a reservoir of sodium lactate does not make this clear, and there had to be specific mention of the ions. Addition of hydrogen ions reduces the ionisation of lactic acid, but most of the buffering capacity is due to reaction with the lactate ions, and therefore the equation for the dissociation of the acid was not accepted. Some answers said that the concentrations of the acid and the conjugate base remained unchanged but the third mark was not given unless it referred to the ratio of these concentrations.

Question 24

Most candidates gave a correct expression for K_c in (a)(i). A few lost the mark by giving the expression for K_p . Others put a + sign on the top line, or wrote $[2\text{NO}]$ instead of $[\text{NO}]^2$.

The stage where most errors occurred in the calculation in (a)(ii) was finding the number of moles present at equilibrium, particularly for NOCl which was often given as 1.67 due to subtracting the number of moles of both products from the starting number. The next stage should have been to calculate the concentrations but this was often missed out, or else an attempt was made to calculate mole fractions. There were errors in calculating the K_c values when they were substituted into the expression; these candidates had failed to check their arithmetic. Candidates who set out their answers clearly were generally more successful than those who just wrote numbers without stating what they referred to, and then were confused. Many did manage to give the correct units.

Good written communication was important in (a)(iii). Candidates had to justify their answers and not just state how K_c and the number of moles of NO might change. Many thought wrongly that a change in volume would mean a change in K_c due to a change in concentration. However, as the temperature is constant K_c is unchanged, and the drop in pressure would cause the reaction to go to the side

with more gas molecules. A few candidates proved this by substituting “ n/V ” for concentration in the K_c expression and showing that as volume increases the number of moles of product must increase.

Most candidates scored only one mark in (b)(i) for correctly writing down the enthalpy change of formation and molar entropy for NO. Very few realised that the enthalpy change of formation for Cl_2 was zero and the most common value seen was for atomisation of chlorine. In (b)(ii) the most common error was to omit the factors of two for NO and NOCl. The wording of the question in (b)(iii) provided a hint, by asking why the total entropy change becomes less negative. Answers had to use the expression relating $\Delta S_{\text{surroundings}}$ to ΔH and show that this term becomes less negative as temperature increases. $\Delta S_{\text{surroundings}}$ is a negative number, and answers which referred to it becoming smaller or decreasing were ambiguous and were not allowed.

The expression $\Delta S_{\text{total}} = R \ln K$ was required in (b)(iv) and some candidates forgot the Δ sign. This expression, and the fact that the total entropy change becomes less negative as temperature increases, had to be used together for the second mark. It was not enough just to say that as the temperature increased the equilibrium constant increased, with no reasoning. Alternatively, if candidates had shown that the reaction was endothermic in (b)(ii) they could explain that the equilibrium moves to the right as the temperature increases.

In (c)(i) many candidates stated that the greater molar entropy values were due to more disorder. However some candidates could not access this mark as they had not explained that the energy of each particle was greater. A surprising number of answers missed the point and discussed activation energy, collision theory and rates.

The calculation in (c)(ii) was straightforward, but marks were lost by forgetting to use the factor of two for NO and NOCl, for omitting the sign and for giving incorrect units.

The final calculation was most often done by calculating $\Delta S_{\text{surroundings}}$, adding the value to ΔS_{system} and showing that the total was negative, meaning that the reaction would not be spontaneous. Care was needed with units so that numbers in $J \text{ mol}^{-1} \text{ K}^{-1}$ were not added to values in $kJ \text{ mol}^{-1} \text{ K}^{-1}$. A small number of candidates calculated the temperature at which ΔS_{total} would be zero, and showed that this was above 800K. Some candidates had been taught the relationship between ΔG and ΔS_{system} and were awarded full marks if they did the calculation showing that ΔG is negative at 800K.

Advice to candidates

Read questions carefully and at least twice. This piece of advice is given in every paper and is the most important one!

Read and check answers for errors, e.g. missed words, or writing the opposite of what was intended, before moving onto the next question.

Include units in the answer to a calculation and check whether a sign or a particular number of significant figures is required.

Set out calculations carefully so that you can earn intermediate marks if errors are made.

Practice drawing graphs to find activation energy, and choose scales which are easy to use.

