Examiners' Report
Principal Examiner Feedback

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Pearson Edexcel International Advance Subsidiary Level
In Chemistry (WCH14)
Paper 01 Rates, Equilibria and Further Organic Chemistry

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Introduction

Overall, the paper seemed accessible across the ability range with little evidence that students ran short of time. Calculations such as those involving entropy and Born-Haber cycles were a particular strength and students were clearly well prepared for familiar contexts, such as the chemistry of buffer solutions and comparison of theoretical and experimental lattice energies. The quality of graphs in the Arrhenius questions was more variable, with a number of inappropriate scales used and the use of novel contexts to test ideas such as the pH calculation in 20(a)(iii) proved discriminating.

The mean mark for the paper was 56.

Section A

The mean mark for the multiple-choice questions was 15. The most challenging questions were 4 (reaction of a dicarboxylic acid with sodium hydroxide), 10 (comparing two acidic solutions), 13(a) (interpreting data from an equilibrium experiment) and 13(b) (practical procedures involved in an equilibrium experiment). Questions 6 (preparation of ethanoyl chloride) and 12 (estimating pH of a sodium hydroxide solution) proved to be the most accessible questions with over 90% of students getting them correct.

Section B

Question 16
(a)(i)
Many students could identify the hydrogen atoms responsible for each peak, with around 70% scoring 2 marks. Common errors included the reversal of x and y or w and z, or the inclusion of the carbonyl groups when circling parts of the displayed formula. Some labelling was borderline, for instance using letters next to the carbon atoms of the appropriate group. In this context, students were given the benefit of the doubt due to the phrasing of the question, but students should be careful to make the distinction between ^{13}C and ^{1}H nmr spectra.

(a)(ii)
Students were well prepared for this type of question, with clear links made to the 'n+1' rule and hydrogen atoms on adjacent carbons. Occasionally students used phraseology such as '4 splits' for quartets, which is acceptable. A small number of responses failed to refer explicitly to each peak but were able to score a rescue mark for evidence of understanding of the 'n+1' rule.

(a)(iii)
This question discriminated well among the more able students. However, some students ignored the guidance in the question and drew the structures of a variety of functional groups, the most common being an ester. Others did not appreciate the concept that the number of peaks is equivalent to the number of carbon environments, and structures with more than four unique environments were common.

(b)(i)
This question highlighted the lack of practical experience of some students. Although the baseline was often shown, the position of the solvent front was sometimes absent or unclear due to the student drawing freehand lines that were not straight. It was expected that students' use the R_f value in the question to show the spot at an appropriate position on the chromatogram. Even with a relatively generous tolerance, a number of students did not score this mark, often showing the spot far too close to the solvent front. Some drew several spots but did not indicate which one was the ethyl-3-oxobutanoate, so could not score the third mark.

(b)(ii)
The most accurate answers here were often the simplest and were based on a comparison of the polarity of hexane and ethyl-3-oxobutanoate, and the subsequent solubility.   A number of students considered the solubility of ethoxyethane in hexane, which wasn't relevant to the question. Others simply based their answer on the mathematical expression for R_f but gave no justification for the idea that the spot due to ester was a shorter distance from the baseline.

Question 17
The mean mark was 4 out of 6, and most students took care to use the structure in the stem to frame their answers. The chemistry of the carbonyl groups was well known.

It was rare to see students unaware of the precipitate formed with 2,4-dinitrophenylhydrazine, though a few thought the reaction was unique to aldehydes. Similarly, most were aware of lithium tetrahydridoaluminate, the formula being far more commonly given than the name. Sometimes less was more when discussing the reduction products, for instance when formulae and names of the alcohols contradicted each other. As a general rule, if students give both the name and formula in an answer, both need to be correct.

The most common suggested oxidising agent was acidified potassium dichromate(VI), though missing out 'acidified' prevented the award of the mark. Many students used structural formulae to represent propanal in the equation. A number of students used CH_3CH_2COH, which could be confused for an alcohol. Others thought water was an additional product, perhaps confusing their answer with the equation for complete oxidation.

Additional erroneous chemistry meant a significant minority lost a reasoning mark, most commonly for incorrectly balancing reduction equations.

Question 18
(a)(i)-(iii)
The vast majority of students could complete the table successfully, with a small number failing to model their answer to match the precision of the data in the table. These responses tended to quote '6.4' though '6.400', 3 decimal places, rather than 3 significant figures was also noted. In part (ii), the graphs varied in quality, often being discriminating marks. The more able students have drawn graphs with care, with a scale that ensured the points plotted covered over half the available space.
Other responses tended to spread the $1 / T$ data across quite a narrow range, missing out on the second mark and a small but noticeable number of students ignored the advice in the stem of (ii) and plotted $1 / T$ against $\ln k$. Others plotted the data the wrong way around (e.g. staring the y axis at -11 or x axis at 1.4×10^{-3}) and as a consequence made it harder for themselves to process the data in (iii). There was evidence of missing units, incorrect units added to the $\ln k$ axis and incorrectly plotted data. Once again in (iii), a number ignored the stem and tried to calculate E_a by inputting data into the Arrhenius Equation and attempting to then re-arrange it. However, many students could calculate the gradient and subsequently E_a, though attempts to deduce the units for the gradient were infrequent.

(b)
Few students showed the ability to think critically about the two values for E_a and were unable to recall a suitable response. Many students simply pointed out that their calculated **value** was larger than $+ 50$ kJ mol^{-1} but made no effort to link this to the concept of the activation energy and bond breaking in reactants. A few did realise that a high activation energy is likely to lead to a slow reaction, with the phrase 'kinetically stable' being used to emphasise this point.

(c)
This question tested ideas that have regularly been assessed. However, the slight change of context, bringing in the link to the rate constant, meant an increase in challenge. As a result, the responses discriminated across all ability ranges. Most could state that as T increases k increases, having the data in the stem to refer to if necessary. The justifications then provided the discrimination. A surprising number of students confused rate constant with equilibrium constant and tried to use Le Chatelier's Principle or $\Delta S_{total} = RT\ln K$ to justify their answer. Others presented their justification as mathematical proofs by restating the Arrhenius Equation with little or no attempt to discuss the increase in rate, and hence $k,$ at a particulate level. The most accurate answers simply linked the increase in temperature to the energy of the particles compared to E_a.

Question 19

(a)

Students were familiar with part (i) and many were able to score at least 4 marks. However, it was common to the calculated value for ΔS_{total} given to 4 or more significant figures, despite the fact that the temperature and the value for the standard molar entropy if silicon carbide were both given to 3 significant figures.

In part (ii) many students deduced that $\Delta S_{surroundings}$ would be less positive and so ΔS_{total} would be smaller, but only a small proportion linked this to yield, which is relevant in the industrial context. A small number of students appreciated that the change in temperature may have a negligible effect on $\Delta S_{surroundings}$ due to its large value, which was a creditworthy approach. Most students realised that a high temperature in industry is used to increase the rate, and then spent time explaining this in terms of collision theory. Reading the question with more care may have prevented this as the command was to **justify the use** of this temperature, not explain the outcome. The equation in (iii) was remembered by many, and most could process the data effectively. A small number did not score due to their inability to find k from $\ln k$.

(b)

In (i), only a few students failed to link the appropriate energy changes to the diagram, though omissions such as arrowheads or the need to multiply E by 2 prevented them from gaining marks. The calculation in (ii) was very well answered, with only a very small number unable to re-arrange the cycle to deduce a value for the enthalpy change of formation. In fact, overall in parts (i) and (ii), over 30% of students scored 5 marks. Part (iii) revealed that most students appreciated the difference in lattice energies was linked to polarisation and were able to justify why the iodide ion was polarized to a greater extent than the fluoride ion, by the calcium cation. Care with terminology has to be emphasised here, with some answers discussing polarisation of the iod**ine** or fluor**ine** or using phrasing that implies they believe the compound as a whole is polarised, e.g. 'the calcium iodide is polarised more than the calcium fluoride'. Many students linked the difference in values for calcium iodide to a degree of covalent character, but far fewer explicitly made an attempt to link the similar values for calcium fluoride to a near 100% ionic model.

(c)

This three mark question was discriminating as all but the more able students tended to lose either the first or second mark. Misunderstanding the idea that electron affinity is exothermic hindered some in the first mark, whilst other used imprecise language, such as 'larger' or 'higher' which in this context was not enough on its own. Others lost the second mark by discussing the relative sizes of the ions, rather than the atoms, which confusion between chlor**ide** and chlor**ine** evident as in (b)(iii).

Question 20

(a)

The systematic naming of isoamylacetate in (i) provided a significant level of challenge, and in general was only accessible to the more able students. Some did not appreciate the importance of the functional group to determine the direction of counting, so suggested 2-methylbutyl ethanoate whilst others named the CH_3COO group as methanoate. However, the wide variety of incorrect names suggested many students found it difficult to interpret a structural formula. Over 50% of students could correctly calculate the % of ester present in part (ii). A number of students struggled because they calculated the mass of sodium hydroxide that reacted with the ester, not using the balanced equation to deduce the moles, and hence mass, of ester that reacted. Others could not determine the molar mass of the ester, once again suggesting that some students found it difficult to interpret a structural formula. Part (iii) revealed that most students could determine the pH of an alkaline solution, with many using the relationship pH = 14 – pOH.   Unfortunately, it was common to see responses that neglected to take into account the hydroxide ions / sodium hydroxide used up in the hydrolysis reaction, leading to an answer of 13.99. There was a number of low scoring answers to part (iv). Many students assumed the titration was between sodium hydroxide and a weak acid, despite the clear reference to hydrochloric acid in the stem of the question. As a result, by far the most common suggestion was that student B was correct.   Others seemed to confuse 'either' with 'neither' so claimed student C was correct but with a justification based on the idea that no indicator was suitable. In part (v), the majority of students recognised the need for an acid. The main source of error was the failure to suggest the name or formula of a suitable acid and simply give a generic response such as 'acid hydrolysis'.

(b)

In part (i), a large number of students showed they were familiar with this common format of buffer calculation, with over 40% of the students scoring 5 marks. Common errors included assuming all the initial ethanoic acid was present in the buffer and ignoring the presence of the salt and assuming that $[H^+] = [CH_3COO^-]$. A number of students relied on recall of the Henderson-Hasselbalch equation and made mistakes with the format, getting [acid] / [salt] the wrong way around, depending on the version of the equation they were attempting to use. Lots of excellent answers were seen in part (ii), with most students familiar with reactions involved in buffer solutions.

Paper Summary

The content assessed in this unit is very similar to that examined in WCH04 from the previous specification, and it was evident that many students were familiar with the types of questions seen on past papers.

Based on the performance in this paper students should:

- read the question carefully to ensure that their answers match the requirements of the question, especially when the stem describes a practical procedure

- practice balancing equations for organic oxidation and reduction reactions

- use the IUPAC system to name a wider range of organic compounds

- make sure they can interpret structural formulae, translating them to displayed or skeletal if necessary

- take care to distinguish between the rate constant, k, and the equilibrium constant, K.

- look at all the data in a question to help deduce an appropriate number of significant figures