



Examiners' Report January 2012

GCE Chemistry 6CH04 01

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Introduction

The paper was accessible to candidates of all abilities and there was no evidence that a shortage of time resulted in some candidates being unable to complete the paper. Any blank spaces that were evident on the paper appeared to be due to candidates not being able to answer those particular question parts. The use of significant figures seemed to be improved from the summer 2011 entry, as was the use of the data booklet, but it is important to continue to stress to candidates the need to note the clear instructions in the question. This is particularly so when a sign is requested, as otherwise marks are lost when they really should not be. There was evidence that the topic entropy was well understood but it was clear that candidates need further support to fully grasp the concepts behind nmr spectroscopy. A logical step-wise approach to answering questions is also to be recommended so that full marks can be awarded. This was clearly required in question 23b on the colour changes of the indicator in the bubble bath.

Centres are also reminded to use the most up-to-date published material from Edexcel.

The standard of graph drawing was often not to an acceptable standard, especially with regard to the choice of an appropriate scale. Likewise the reasoning behind the greater reactivity of acyl chlorides tended to be insufficient.

Question 17 (a)

The vast majority of candidates knew that a yellow or orange precipitate would be seen. The most common error was the omission of 'precipitate'. A number of candidates gave unnecessary explanations of the chemistry involved which would have used up precious time.

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

- 17 Two organic compounds, \mathbf{X} and \mathbf{Y} , both with the molecular formula C_4H_8O , contain a carbonyl group.
 - (a) Describe what you would see when 2,4-dinitrophenylhydrazine is added to either of these compounds.

(1)

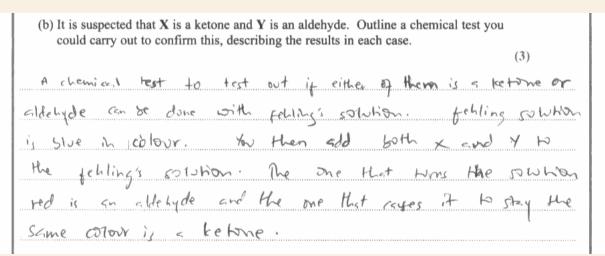
yellow/(orange) precipitate forms (ppt)



This candidate has suggested two colours for the possible precipitate observed. Either of which would have been acceptable.

Question 17 (b)

A very large proportion of candidates correctly understood how to distinguish between aldehydes and ketones with a simple chemical test. Tollens' reagent or Benedict's/Fehling's solution were popular choices but at times acidified dichromate was given. Occasionally two different tests were given for X and Y but the question clearly requests 'a chemical test'.





In order to score the mark for the test on the aldehyde with Bendict's or Fehling's solution, the colour change and the state were **both** required.



If the result of a chemical test is negative then do remember to clearly state, as this candidate has, that the colour stays the same or that there is no change.

Question 17 (c)

In 17c(i) most candidates were able to give structural formulae for the two aldehyde isomers. A sizeable number of responses had the aldehyde group incorrectly given as -COH and a very small number of candidates had the odd missing hydrogen from the chain.

In 17c(ii) a higher than expected proportion of candidates wrote crystallization or just filtration, neither of which were acceptable. The question clearly stated that the product had already been obtained but needed to be purified.

17c(iii) was very well answered with the most common error being to suggest that boiling temperature was the means to identify the hydrazone product.

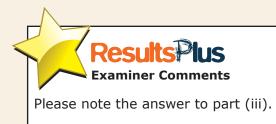
Please note the answer to part (iii).

(c) (i) Give the structural formulae of the two possible isomers of Y which are aldehydes.	
CH3 CH (CH3) CHO	(1)
CH3 CH2 CH2 CHO	
(ii) Name the technique you would use to purify the product of the test with 2,4-dinitrophenylhydrazine.	(1)
recrystalisation.	,
(iii) Other than by spectroscopic techniques, how would you use the purified proto identify compound Y? [Practical details are not required.]	duct (2)
recrystallisation and men	
determine meeting point and	
compare with possible applicatives	имичтиний придаваний поли



Parts (i) and (ii) are fine but in part (iii) the comparison to "possible derivatives" was felt to be too vague. How would this be done? The expected answer was comparison to a database of known values.

(c) (i)	Give the structural formulae of the twaldehydes.	o possible isomers of Y which are	
	CH3CH2CH2CHO	CH3CH(CH3)CH2CHO	
	Name the technique you would use to 2,4-dinitrophenylhydrazine.	(1)	
		product and mixing it with extend in	١ ۵
	Other than by spectroscopic technique to identify compound Y? [Practical d	es, how would you use the purified product letails are not required.]	
Find	the melting point a	f the purified somple and	
		a set list of temperature	
	and the compound.		h4F[k41,461)24+4130





Candidates should always double-check their structures in case they have made a simple mistake.

In this example of c(i) this response has an additional carbon in the branched aldehyde on the right. If the atoms had been counted up for both isomers then the obvious mistake would most likely have been spotted.

Question 18 (a)

This question seemed difficult for most candidates with few scoring all 4 marks so would be a worthwhile practice exercise for teachers with their students. At times the hazard was not clearly identified but the precaution was appropriate and so the mark was awarded. A worryingly high number of candidates thought that the reaction temperature of 50°C was high! The toxicity of methanol was not well known and there were a large number of candidates who gave insufficient information, such as NaOH would affect the skin but without giving the necessary detail of its corrosive nature.

18 Kits for manufacturing biodiesel from vegetable oils and methanol are sold for home use. The reaction which takes place may be represented by the following equation.
$3CH_{3}OH + CH_{2}OOCR \xrightarrow{NaOH(s)} CH_{2}OH + RCOOCH_{3}$ $CHOOCR' CHOH + R'COOCH_{3}$ $CH_{2}OOCR'' CH_{2}OH + R''COOCH_{3}$
*(a) Describe any two of the main hazards when carrying out this reaction. What precaution would you take to minimise the risk in each case? (4)
Hazard methanol is flam mobile
Precaution Mare of approprate fire retardants nearby.
Hazard The reaction is at a high temperature
Precaution House a cooling system nearby if the reaction goes wrong.

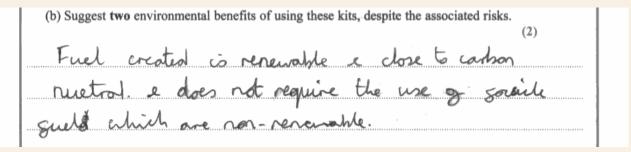


The flammability of the methanol is fine but the precaution is not. An electrical heat source or the avoiding of naked flames were the appropriate answers.

Question 18 (b)

Most candidates understood that biodiesel reduced the use of non-renewable fossil fuels. A small proportion of responses described the offsetting of CO_2 emissions by the growing plants taking in CO_2 . However, there were a sizeable number of candidates who felt that no CO_2 was given off by the combustion of biodiesel or gave vague comments about biodegrability or pollution.

It was disappointing that there were very few responses referring to the reuse or recycling of the waste vegetable oil which is a key point.





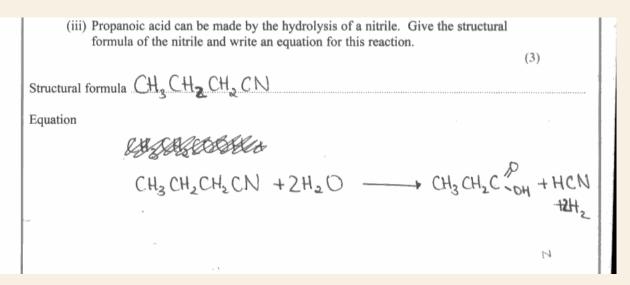
Although the resources to produce the fuel are renewable it was acceptable for the fuel to be described as renewable as in the answer here.



Note that two statements are given but they are the same marking point and so only score 1 mark.

Question 19 (a) (iii)

This was a question which discriminated between the ability of the candidates and the more able often score well. However, the structure of nitriles was not well known and oftentimes amides, amines and hydroxynitriles/cyanohydrins were given. Credit was given to those who realised that hydrolysis required both water and acid or who could give a correctly balanced equation from the amide.





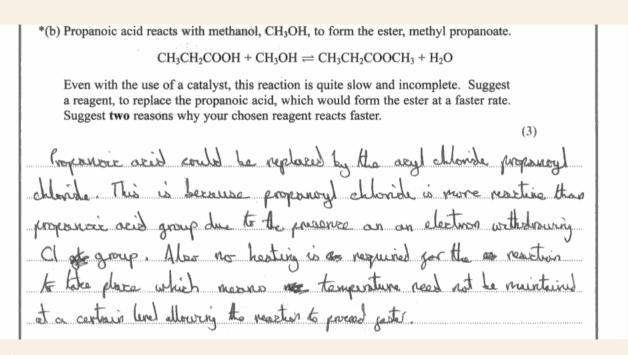
The use of an incorrect nitrile would have lost the first mark but the remaining marks could have been awarded if the equation had been correct. However, in this example the products are clearly wrong and although the equation does balance for atoms it does not score.



A reminder once again to check the number of carbons in the chemical stated. The nitrile group does have a carbon and it does count!

Question 19 (b)

Most candidates knew that propanoyl chloride would react faster and scored the reagent mark. However, only the more able could correctly give suitable reasons **why** the acyl chloride reacts faster. The weaker nature of the C-Cl bond was the most common correct reason given. Confusion between rate of reaction and equilibrium was common.





The question requests reasons for the faster reaction with the proposed reagent. Note the examiner tip on this response.



In this response the lack of heating is unlikely to result in a faster reaction. The simple statement that the Cl is an electron-withdrawing group is insufficient to be given credit as more explanation is required.

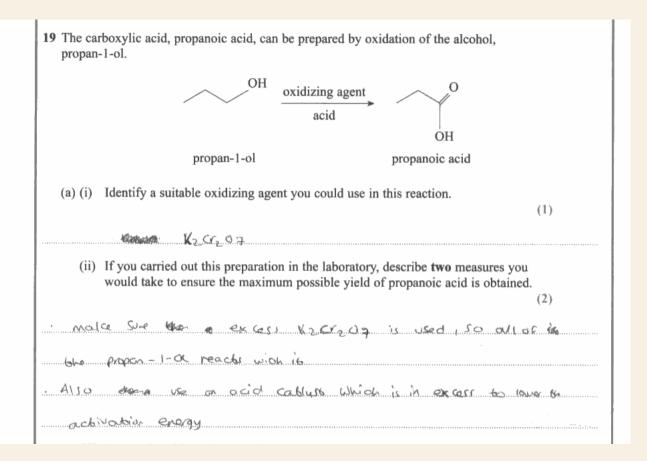
Question 19 (c) (i)

The vast majority of candidates correctly knew that "radio waves" was the correct type of radiation for nmr.

Question 19 (a) (i-ii)

Excellent knowledge of oxidising agents was shown. However, this was occasionally spoilt by the use of the wrong oxidation number. Candidates should be reminded not to add information which might negate their otherwise correct response.

In part (ii) the use of reflux was extremely common but the use of excess oxidising agent was less so and could be accompanied with excess alcohol which obviously undermined the correct point.





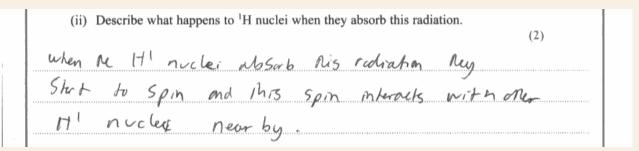
Read the answer that the student gives to part (ii) and then note the examiner tip.



Part (ii) requests **two** measures that need to be taken to maximize yield. These need to be different. In this response the second statement really refers to the first statement as the acid catalyst would have no affect without the oxidising agent. Make sure that two **different** suggestions are made.

Question 19 (c) (ii)

The responses seen to this question demonstrated that many candidates do not understand the concepts behind nmr. There was confusion between how infrared affects bonds and how nmr affects the spin state of the nucleus. There were also a considerable number who referred to electrons and their excitation. Only the more able candidates were confidently able to express the ideas correctly and to score both marks.





This response illustrates the misunderstanding that some candidates seem to have because the nuclei do not start to spin but they always have this state. Hence this response did not score.

Question 19 (c) (iii)

This was a high scoring question, with the spin-splitting patterns being well known and the data booklet being used effectively.

(2)

(iii) Complete the table to show values for the chemical shift of the different ¹H nuclei in methyl propanoate and their splitting pattern. Page 7 of the data booklet gives information about chemical shifts.

¹ H environment	Chemical shift, δ / ppm	Splitting pattern
CH ₃ O-	3.7	Singlet
-CH ₂	2.3	quadruplet.
-CH ₃	1	Triplet



Alternative spellings of quartet were given credit.



Although this response did score both marks candidates should be reminded to use the same number of significant figures as are used elsewhere in the table.

Question 20 (a)

Most candidates could correctly refer to the shift in the equilibrium to the right due to the molar ratios. However the comments on the disadvantages of increased pressure were generally insufficient. For example, the reason for the increase in cost was required for the second mark.

20 The exothermic reaction between carbon monoxide and hydrogen can be used industrially to make methanol. The process is carried out at 250 °C and be 100 atm.	
$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$	
(a) Explain why increasing the pressure increases the yield of methanol. Go disadvantage of increasing the pressure. Higher Increasing pressure shifts the	(2)
fo the side with Ferrer miles of gas who product side is more products are a gield. Increasing the pressure has a high	bomed Ligle



A simple reference to cost is unlikely to be given credit at A2 level.

Question 20 (b)

Parts (i) and (ii) were well answered by most candidates, demonstrating an excellent understanding of how temperature affects the entropy change of the surroundings.

Question 20 (c)

Candidates were largely able to explain how to maximise atom economy by the removal of the product but fewer responses correctly referred to the recycling of unreacted reactants. Instead addition of more reactants or the use of a catalyst were common incorrect suggestions. A small minority of candidates were confused by the question and stated that the atom economy was already 100% which may demonstrate that they had learnt the formula for atom economy but not the concept.

(c) Given that the reaction is an equilibrium, suggest two ways in which the atom economy of this process could be maximised without changing the temperature or pressure.

(2)

. Remove product continuously . Have a high Concestration of reactants.



Atom economy is not improved by addition of more reactants but the removal of the product will score one mark.

Question 21 (a)

This calculation was generally well carried out with many gaining the maximum marks. However, relatively common errors in part (i) were to use 4 significant figures instead of the 3 requested, or to give incorrect units. Transferred errors were allowed in part (ii) where the only mistake seen tended to show issues with the use of powers of ten.

- 21 This question is about the kinetics of the reaction between bromoethane and aqueous hydroxide ions.
 - (a) The results of an experiment to find the initial rate of the reaction are shown in the table below.

[CH ₃ CH ₂ Br]	[OH ⁻]	Initial rate
/ mol dm ⁻³	/ mol dm ⁻³	/ mol dm ⁻³ s ⁻¹
0.100	0.150	

The rate equation for the reaction is

rate =
$$k[CH_3CH_2Br][OH^-]$$

(i) Calculate the value of k. Give your answer to three significant figures and include units.

$$K = \frac{r_{3} + c}{c_{0} + c_{0} + c_{0}}$$

$$= (1.54 \times 10^{-6}) \qquad \text{unib} = \frac{moldon^{3} s^{-1}}{(moldon^{-3} moldon^{-3} moldon^{-3} moldon^{-3} moldon^{-3} moldon^{-3})}$$

$$K = 1.03 \times 10^{-4} \text{ mol}^{-1} \text{dm}^{3} s^{-1}$$
(3)

(ii) Calculate the initial rate if the concentrations of both reactants were changed to 0.020 mol dm⁻³.

$$124e = k \ \mathbb{C} C U_{3} C U_{2} B r \ \mathbb{T} \ \mathbb{E} O U^{-1}$$

$$= (1.03 \times 10^{-4}) \times 0.02 \times 0.02$$

$$rate = 4.12 \times 10^{-8} \quad \text{Molecum}^{3} \text{s.i.}$$
(1)



An example of a good answer, clearly laid out.

Question 21 (b) (i)

The occasional 'first order' was seen but most candidates knew that the overall reaction order was second.

Question 21 (b) (ii)

Fully correct transition states were in the minority. Omission of the overall negative charge was fairly common and the orientation of the in-coming -OH group and out-going -Br atom was often incorrect. A significant number gave the reaction mechanism rather than the requested transition state.

(b) (i)	State the order of the reaction.	(1)
	2nd order	
(ii)	The mechanism for this reaction can be inferred from the rate equation. Draw the transition state formed in the reaction between bromoethane and hydroxide ions.	
	H³C H	(2)
	HOC+B-	



The charges given in this response illustrate some confusion between the different mechanisms for halogenoalkanes. The central carbon does not become positively charged as shown in $S_{\rm N}2$ reactions.

Question 21 (c) (i)

Although 3 x 10^{-3} was acceptable, candidates should be guided by the number of significant figures already used in the table and have given 3.00 x 10^{-3} . However, the majority of candidates did give the figures correctly.

Question 21 (c) (ii)

This question illustrates the need for candidates to have more practice with drawing graphs. It was very common to see a poor choice of scale, particularly for the y axis, and so less than half of the graph paper was used. The attempts at calculating E_A were better but frequent errors were the inclusion of K^{-1} in the units and/or a negative sign. The omission of 10^{-3} from the graph also caused some candidates problems.

Temperature (T) / K	1/Temperature (1/T) / K ⁻¹	Rate constant, k	ln k
293	3.41 × 10 ⁻³	5.83×10^{-5}	-9.75
303	3.30×10^{-3}	1.67 × 10 ⁻⁴	-8.70
313	3.19 × 10 ⁻³	5.26 × 10 ⁻⁴	-7.55
323	3.10×10^{-3}	1.36 × 10 ⁻³	-6.60
333	3.00 810-3	3.77×10^{-3}	-5.58

(i) Complete the missing values in the table.

(2)

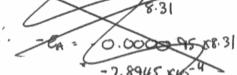
(ii) Plot a graph of $\ln k$ against 1/T. Calculate the gradient of your graph and use this to calculate the activation energy, $E_{\rm A}$. The Arrhenius equation can be expressed as

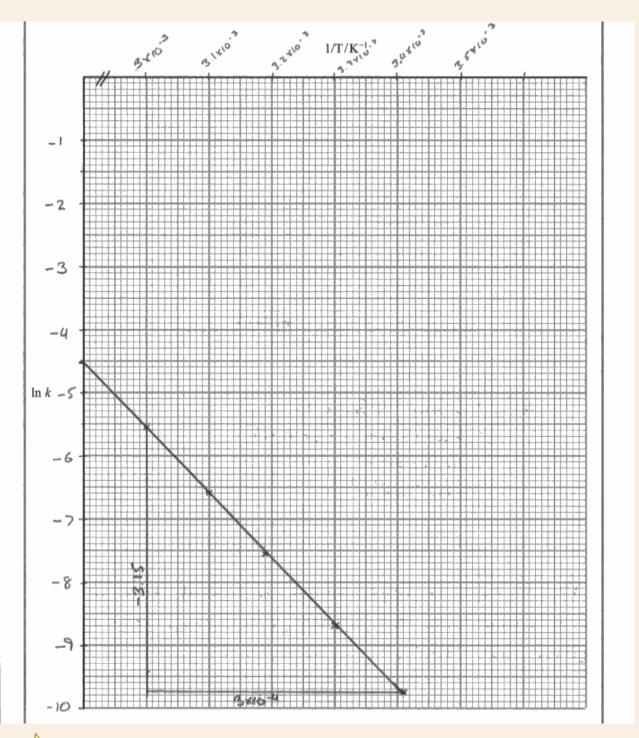
$$\ln k = \frac{-E_{\rm A}}{\rm R} \times \left(\frac{1}{\rm T}\right) + \text{a constant}$$

[Gas constant, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$]



=> Y= Mx+c







An example of the wrong use of units in the answer and the poor choice of scale, both of which resulted in the loss of a mark.

Question 22 (a) (i)

Excellent use of the data booklet was seen throughout the paper as evidenced in the responses to this question.

Question 22 (a) (ii-v)

Parts (ii) to (v) again serve as a reminder to candidates to carefully read the question and to answer exactly as they are requested. In part (ii) a sign is clearly asked for and while the vast majority did give the correct sign there were a significant minority that omitted one. In part (iv) a sign and units are requested and a similar type of candidate response to part (ii) was seen.

However, this was a high-scoring question with many candidates achieving high marks. The most common other errors were the omission of gas in part (ii) and the failure to use zero for the total entropy change in the calculation in part (v).

Hydrocarbon	S [⊕] / J mol ⁻¹ K ⁻¹
C ₄ H ₁₀ (g)	+310.1
C ₃ H ₆ (g)	+266.9
CH ₄ (g)	+186.2

(ii) Calculate the standard entropy change of the system, $\Delta S_{\text{system}}^{\ominus}$, for this reaction. Include a sign in your answer.

$$\Delta S_{syst} = \Delta \text{ products - reactants}$$

$$= (186.2 + 266.9) - (+310.1)$$

$$= 453.1 - 310.1$$

$$= + 1435 \text{ mol}^{-1} \text{ k}^{-1}$$

(iii) Was the sign for your answer as you expected? Fully justify your answer.

Yes because more molecules or gos have been produced which can have more arrangements and thus more dissorder.

(2)

(iv) Calculate the entropy change of the surroundings, $\Delta S_{\text{surroundings}}$, at 700 K.

Include a sign and units in your answer.

Use this value and your answer to (ii) to explain why butane cracks into propene and methane at this temperature.

AStotal = 143+-102.7 = +40.3. The positive AStotal show means the reaction is spontaneous at this temperature

(v) Calculate the minimum temperature needed for this reaction to be thermodynamically feasible.

(3)



For some reason the value for the total entropy change used in the calculation in part (v) was -200. Clearly this is incorrect but there were marks for the method of the calculation which thereafter was done correctly.

Question 22 (b)

A very high scoring question with the vast majority scoring all 3 marks. If there was an issue, it was that the state of the catalyst was compared to the reactants **and** the products instead of simply the reactants.

(b) The aluminium oxide behaves as a heterogeneous catalyst. Explain both what is meant by the term heterogeneous and how, in terms of activation energy, the catalyst is able to speed up the reaction.

(3)

4 different States, gas; liquid; solid and aqueous solution by use a catalyst that is in a different states of a catalyst that is in a different state.

State to that of a catalyst to are different state.

Using a catalyst in a reaction laws advation energy, because it uses len energy to get it uses len energy to get it to start the ceaching without bound used up.



No credit was given for the statement that a catalyst is not used up but a mark was given for the lowering of the activation energy.

Question 23 (a) (i)

Candidates of all abilities were able to score on this question. It was only 'careless' slips such as the omission of a charge that meant the mark was lost

- 23 The bubble bath 'Colour Change Matey' has amongst its ingredients the weak acid benzoic acid, as well as the indicator bromocresol green. When it is added to bath water, its colour changes from yellow to blue.
 - (a) (i) Write the K_a expression for the dissociation of benzoic acid, C₆H₅COOH.

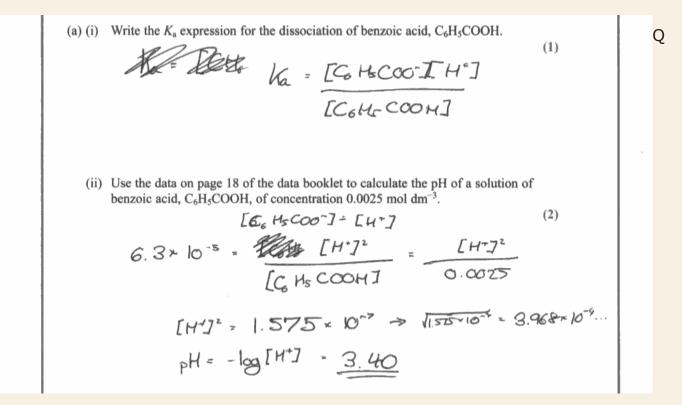
 $k_{a} = \frac{\left[C_{6}H_{5}C00\right]\left[H^{*}\right]}{\left[C_{6}H_{5}C00H\right]}$ (1)



An example of a correct response.

Question 23 (a) (ii)

Most candidates were correctly able to calculate pH and to score 2 marks. The occasional arithmetical error was seen.





Question 23 (b)

Only the more able candidates could correctly describe why the colour changes occurred. Most responses did include the requested pH range for the indicator and then state the addition of bath water diluted the acid so that the concentration of the H⁺ ions decreased. A logical stepwise approach to this type of question is always recommended. The colour is yellow to begin with because of the low pH from part a(ii) which is below the pH range of the indicator. Then the colour changes to blue when the pH goes above the range (5.4). References to green were not given credit because the colour changes in the question were from yellow to blue.

(ii) Use the data on page 18 of the data booklet to calculate the pH of a solution of benzoic acid, C₆H₅COOH, of concentration 0.0025 mol dm⁻³.

$$6.3 \times 10^{-5} = \frac{[H^{+}]^{2}}{0.0025}$$

$$-\log [H^{+}] = \beta H$$

$$6.3 \times 10^{-5} \times 0.0025 = [H^{+}]^{2}$$

$$1.575 \times 10^{-7} = [H^{+}]^{2}$$

$$[H^{+}] = 3.97 \times 10^{-4}$$

*(b) Use the data on page 19 of the data booklet, and your answer to (a)(ii), to suggest why the bubble bath changes colour when it is diluted by being added to the bath water.

changes colour because the range of the indicator used is between 3.8 - 5.4 this range covers the rectach height of pH range of the equivalence point of this reaction and therefore changes from yellow to blue when water 13 added and the benzoic acid is neutralized.

(4)



A reminder to make sure that a response includes the 'easy' mark. Here the question requests the data from page 19 of the booklet and this candidate has stated this first to be sure of that mark. There is nothing else worthy of credit here.

Page Summary

Questions 21a(i), 22a(iii) and (iv) clearly asked for either signs, a specific number of significant figures and/or units. Candidates need to always be reminded to answer exactly as requested. Practice at graph drawing would be useful to many, with particular emphasis on the appropriate choice of scale. When reasons are requested then the responses need to be clear and to refer to different reasons if full marks are to be awarded. Additional support to candidates on the concepts behind nmr and why acyl chlorides have greater reactivity than carboxylic acids would better help candidates.

Grade Boundaries

Grade boundaries for this, and all other papers, can be found on the website on this link:

http://www.edexcel.com/iwantto/Pages/grade-boundaries.aspx

