

Examiners' Report
June 2012

GCE Chemistry 6CH04 01

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Introduction

The paper was accessible to all candidates, with section C proving to be the most challenging. There was no evidence that candidates were unable to complete the paper because of time constraints. It was pleasing that the graph drawing skills had measurably improved since the January sitting of this unit. However, the layout of many candidates' work in calculations was very untidy and made it very challenging to mark. A number of questions were testing concepts in a novel way and this presented a real challenge to large numbers of candidates as they failed to answer these questions. This was particularly the case with Q18(c)(i) and Q18(d).

Question 14(a)(i-ii)

Both parts (i) and (ii) were high-scoring with many candidates scoring maximum marks.

There were three main errors. The first was produced by a sizeable minority which was determining the pK_a rather than the pH because the candidate simply carried out a $-\log$ of K_a calculation. This was not acceptable and lost both marks. The second was to omit the square root in the determination of the hydrogen ion concentration. The second mark could still be awarded for a transferred error. The third error was a rounding error giving the pH as 2.53 from a calculated value of 2.535. This did require careful marking because if the hydrogen ion concentration had been earlier rounded up to 2.92×10^{-3} then a $pH = 2.53$ could be awarded both marks. Only if the candidate had clearly shown that this was their process could both marks be awarded.

SECTION B

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

14 In a pH titration, 30 cm^3 of sodium hydroxide solution was added, in 1 cm^3 portions, to 20 cm^3 of ethanoic acid solution, $\text{CH}_3\text{COOH}(\text{aq})$. The concentration of both solutions was 0.50 mol dm^{-3} . After the addition of each 1 cm^3 , the pH was recorded using a pH meter.

(a) (i) Write the K_a expression for ethanoic acid.

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad (1)$$

(ii) Using your answer to (i), calculate the pH of the 0.50 mol dm^{-3} ethanoic acid solution before the titration starts. Refer to page 18 of the data booklet.

$$K_a = 1.7 \times 10^{-5} \quad (2)$$
$$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$$
$$[\text{H}^+] = \sqrt{K_a \times [\text{CH}_3\text{COOH}]} = \sqrt{1.7 \times 10^{-5} \times 0.5}$$
$$= 2.915 \times 10^{-3}$$
$$pH = -\log(2.915 \times 10^{-3})$$
$$= 2.54 \quad (3\text{sf})$$



ResultsPlus Examiner Comments

Candidates should always be reminded to clearly set-out their working when doing calculations and then the marks can be easily awarded.



ResultsPlus Examiner Tip

This is a fine example of the lay-out which demonstrates to the examiner how the final answer is calculated and thus means that there is no hesitation in awarding maximum marks.

Question 14(a)(iii)

A very straight-forward question with the majority giving the correct answer, although a sizeable minority did give answers such as 15 cm^3 and 30 cm^3 .

Any units given were ignored unless a candidate had converted the volume into decimetres, which then meant that the units were essential. This was rarely seen however.

Question 14(a)(iv)

The answer to part (iii) was seen with the answer to part (iv) to allow candidates who had used their own value from part (iii), although incorrect, to arrive a pH value in part (iv) and to still score full marks. This was rarely seen but still an important principle to uphold. Consequently this did mean, on occasions, that despite a correct answer in part (iv), full marks were not awarded because it was not the correct 'follow-on' from the candidate's own answer to part (iii). However there were some candidates who very clearly demonstrated that they understood the situation, laid-out their answer and workings in full and who scored full marks in part (iv) from an answer that was not correct from their answer to part (iii) but was the true answer from the mark scheme. It showed that the candidate did grasp the question and had the ability to deduce the correct answer but that they really should have gone back and checked their answers to make them consistent.

(iii) Deduce the volume of sodium hydroxide solution required to reach the end point. (1)

10 cm^3

(iv) Calculate the pH of the solution after all of the sodium hydroxide is added. (4)

$$K_a = \frac{[H^+][OH^-]}{[H_2O]}$$
$$K_a [H_2O] = [H^+][OH^-]$$
$$K_w = [H^+][OH^-]$$
$$1 \times 10^{-14} = [H^+][0.5]$$
$$2 \times 10^{-14} = H^+$$
$$-\log_{10} [2 \times 10^{-14}] = pH$$
$$pH = 13.69897$$
$$= \underline{\underline{13.70(2dp)}}$$


ResultsPlus Examiner Comments

Two marks out of four were awarded for this response and it illustrates the advantage of clearly showing how the final answer is arrived at. The hydrogen ion concentration, although incorrect, is determined in the right way from K_w and then the pH value from the hydrogen ion concentration. These two steps were given credit and 2 marks were the outcome.

(iii) Deduce the volume of sodium hydroxide solution required to reach the end point.

(1)

~~10 cm³~~ ~~10 cm³~~ 20 cm³

(iv) Calculate the pH of the solution after all of the sodium hydroxide is added.

(4)

moles of NaOH = 0.015

conc = ~~0.015~~ $\frac{0.015}{(50/1000)}$

= 0.3 mol dm⁻³

~~10 cm³~~ ~~10 cm³~~ $[H^+] = \frac{K_w}{[OH^-]}$

$[H^+] = \frac{1 \times 10^{-14}}{3.3 \times 10^{-14}}$

$pH = -\log[3.3 \times 10^{-14}] = 13.4771... = 13.5$



ResultsPlus

Examiner Comments

In this example, the number of moles of NaOH is incorrectly determined as 0.015 at the beginning. Thereafter the calculation is carried out correctly and so only 1 mark lost, resulting in this response scoring 3 out of 4.



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Examiner Tip

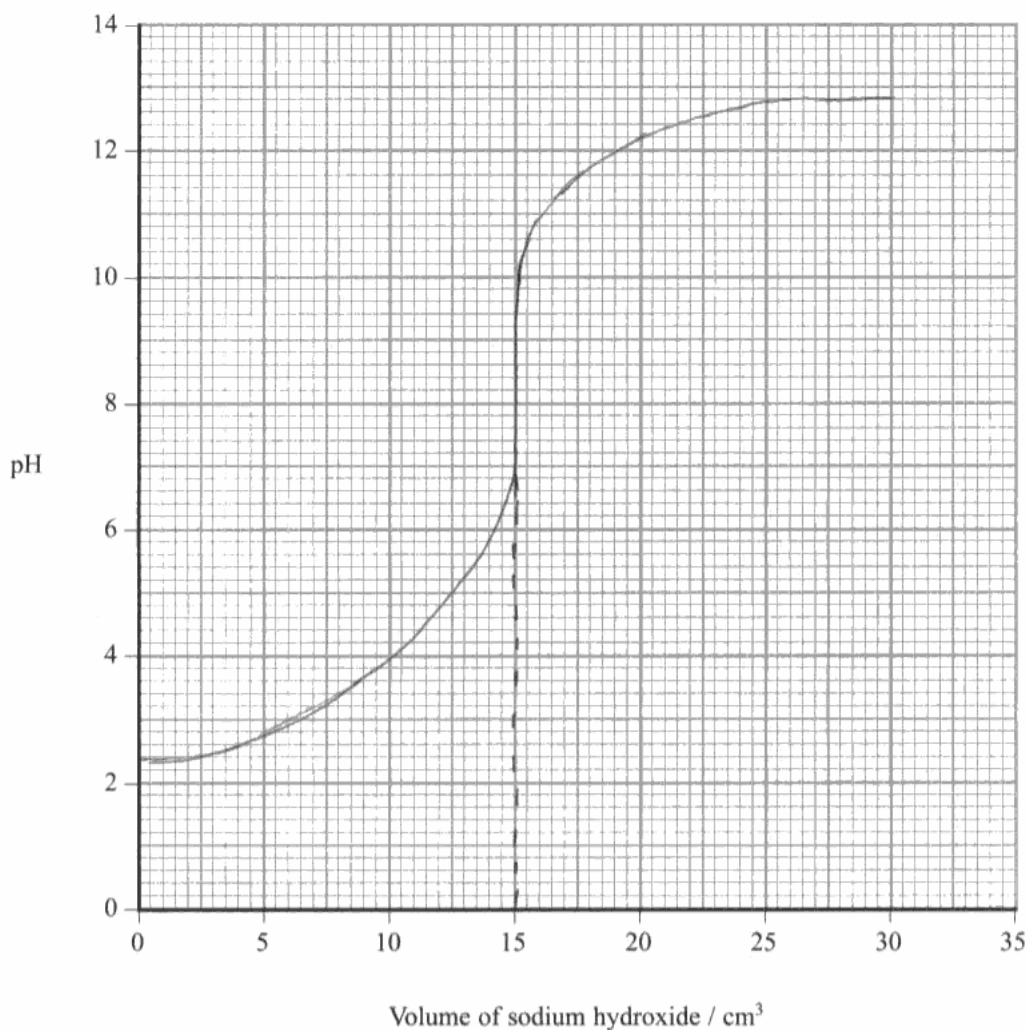
Within calculations marks are normally awarded after a mistake as a transferred error and so not all marks are lost. Thus a candidate should always show all of their working clearly.

Question 14(a)(v)

This question was generally answered well with the vast majority scoring at least one mark. The initial and final pH values were important for the first mark and this was the most common scoring point. Generally an 's-shaped' curve was drawn but the vertical section should only be between 3 and 5 units in length, otherwise a strong acid-strong base curve is suggested. This was the marking point most often lost. The vertical section needed to be seen at 20 cm³ and this was often awarded.

(v) On the axes below sketch a graph to show how the pH changes during the titration.

(3)



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Examiner Comments

One mark is lost for an incorrect vertical section at 15 cm³. However marks were awarded for the start and beginning points being within the suitable ranges expected and the vertical section was within 3-5 units in length.



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Examiner Tip

Care obviously does need to be taken when drawing a sketch, especially under the stress of an examination. One mark is nearly lost here because at the start of the curve on the left hand side it almost decreases in pH. A decrease would have been penalised but this was given the benefit of the doubt.

Question 14(b)

In part (i) there were two possible approaches to answering the question, one using the K_a equation and the other using the pK_a equation. Both were seen although the K_a route was much more common. Full marks were scored using either method and this question generated the full range of marks depending on the ability of the candidate to answer this type of calculation.

In part (ii) the marking point for the reaction of hydroxide ions with the ethanoic acid to make ethanoate ions and water was by far the most common scored. A sizeable minority appreciated that there was a need to state that the buffer contains a reservoir of ethanoic acid molecules but it was rare to see a statement that the concentrations of ethanoic acid and ethanoate remain (almost) constant. This has been examined before on a number of occasions and so should not have been a surprise to candidates.

~~CH₃COOH~~ + CH₃COO⁻Na⁺

(b) An acidic buffer solution can be made by mixing together a solution of ethanoic acid and solid sodium ethanoate.

(i) Calculate the mass of solid sodium ethanoate (molar mass = 82 g mol⁻¹) that would be added to 500 cm³ of ethanoic acid, concentration 1.0 mol dm⁻³, in order to make a buffer solution of pH = 4.70. (4)

pH = 4.70
-log [H⁺] = 4.70
[H⁺] = 1.995 × 10⁻⁵ mol dm⁻³

* (ii) Explain how this buffer solution resists a change in pH when a few drops of sodium hydroxide are added. (3)

When OH⁻ is added, H⁺ ions ~~are~~ combine with OH⁻ to form water which leads to the dissociation of ethanoic acid to form H⁺ ions.



ResultsPlus

Examiner Comments

One mark was gained in both parts of the question. In part (ii) the mark is gained for a description of the combination of the hydroxide ions with hydrogen ions to make water and then the further dissociation of the ethanoic acid. This could have been more easily gained from the equation.



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Examiner Tip

If a candidate is very unsure how to proceed with a calculation then, rather than leave the space blank, they are always best advised to 'do what they can'. This is an example of that approach in (b) because the candidate clearly doesn't know how to calculate the mass of the salt required for the buffer but can determine the hydrogen ion concentration from the pH. This is worthy of credit and scored one mark.

(b) An acidic buffer solution can be made by mixing together a solution of ethanoic acid and solid sodium ethanoate.

(i) Calculate the mass of solid sodium ethanoate (molar mass = 82 g mol^{-1}) that would be added to 500 cm^3 of ethanoic acid, concentration 1.0 mol dm^{-3} , in order to make a buffer solution of $\text{pH} = 4.70$.

$$K_a = 1.7 \times 10^{-5} \quad [H^+] = K_a \times \frac{[HA]}{[A^-]} \quad (4)$$

$\xrightarrow{\text{acid}}$
 $\xrightarrow{\text{salt}}$

moles ethanoic acid: $(500 \times 10^{-3}) \times 1.0 = 0.5 \text{ moles}$.

$\text{pH} = 4.7$

$$\therefore [H^+] = 10^{-4.7} = 1.995 \times 10^{-5} \text{ mol dm}^{-3}$$

$$1.995 \times 10^{-5} = 1.7 \times 10^{-5} \times \frac{1}{[A^-]}$$

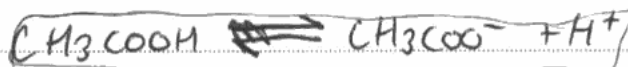
~~mass~~ moles = $\frac{\text{mass}}{M_r}$
 $\therefore \text{mass} = \text{moles} \times M_r$
 $= 0.426 \times 82$
 $= 34.9 \text{ g}$ (3sf)

$$[A^-] = \frac{1}{1.17368} = 0.852$$

$\text{conc} = \frac{\text{moles}}{\text{vol}}$ $0.852 = \frac{\text{moles}}{500 \times 10^{-3}}$
 moles = 0.426
 moles of sodium ethanoate

*(ii) Explain how this buffer solution resists a change in pH when a few drops of sodium hydroxide are added.

The buffer solution acts as a reservoir of ethanoic acid and CH_3COO^- ions in equilibrium. When NaOH is added, the OH^- ions react with the H^+ ions, forming water ($\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$). This means equilibrium shifts right (so more of the acid dissociates) to replace the reacted H^+ ions and to therefore keep pH constant.



(shifts \rightarrow)

(Total for Question 14 = 18 marks)



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 Examiner Comments

A high-scoring response with 4 marks for (i) and 2 marks for (ii). In part (ii) no reference is made to the ratios of ethanoic acid and ethanoate concentrations remaining (almost) unchanged but instead that the pH is constant which is in stem of the question.

(b) An acidic buffer solution can be made by mixing together a solution of ethanoic acid and solid sodium ethanoate.

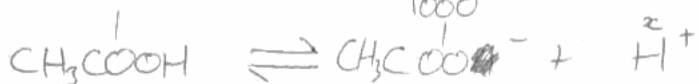
- (i) Calculate the mass of solid sodium ethanoate (molar mass = 82 g mol^{-1}) that would be added to 500 cm^3 of ethanoic acid, concentration 1.0 mol dm^{-3} , in order to make a buffer solution of $\text{pH} = 4.70$.

$$\text{pH} = 4.70 \quad [\text{H}^+] = 10^{-4.70} \quad (4)$$

$$= 1.995 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{moles of ethanoic acid} = \text{conc} \times \text{vol}$$

$$= \frac{500}{1000} \times 1 = 0.5 \text{ moles}$$



Solution has $2 \text{ CH}_3\text{COO}^-$ each of 0.5 moles .
 $= 1 \text{ mole}$

You need 82 grams

$$\frac{\text{mass}}{\text{Mr}} = \text{moles}$$

$$\text{mass} = \text{moles} \times \text{Mr}$$

$$\text{mass} = \boxed{82 \times 1}$$

$$= 82 \text{ g}$$

- *(ii) Explain how this buffer solution resists a change in pH when a few drops of sodium hydroxide are added.

(3)

When a few drops of NaOH is added, As ethanoic acid and sodium ethanoate are both in large ~~excess~~ ^{excess} when a small amount of OH^- ions are added: $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$
 H_2O concentration is negligible compared to acid and acid salt so pH remains almost constant. Addition of OH^- shifts equilibrium to the other side which causes OH^- to be removed.

(Total for Question 14 = 18 marks)



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Examiner Comments

Marks are always awarded wherever possible and one mark was given for arriving at a final mass of salt by multiplying by the given molar mass of 82 g mol^{-1} . One mark was also given for determining the hydrogen ion concentration from the pH value although sadly no use was made of it.



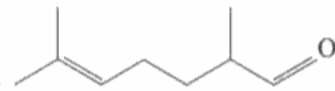
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Examiner Tip

In part (ii) reference is made to the shifting of an equilibrium but there is none shown in the answer. It is true that there is an equilibrium equation in part (i) but candidates are well advised to make sure in their answer exactly to what they are referring.

Question 15(a)

A challenging task and a good grade discriminator. Many candidates were able to correctly give the first part of the name relating to the two methyl groups but the designation of the carbon-carbon double bond was less well done.

15 The molecule  is sometimes known as melonal as it smells similar to watermelon.

(a) Give the systematic name for melonal. (2)

2-methyl 2,6-dimethylhept-2-enal



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Examiner Comments

Here is an example of the start of the name being given correctly "2,6-dimethyl" but the designation of "2-ene" is incorrect since the numbering starts from the aldehyde group.

Question 15(b)(i)

Those candidates who used the skeletal formula from above were less likely to make errors in the structure than those who tried to write out the full displayed formula. Most realised that an alcohol was required but there were some carboxylic acids drawn which suggests that the question was misread.

The reagents were generally well-known although some 'short-cuts' were seen (see below) and occasionally HCl and KMnO_4 which were not allowed.

(b) (i) Melonal can be prepared by the oxidation of a compound, X. Suggest the formula of compound X and the names or formulae of the reagents needed to oxidize X. (3)

Compound X

$$\begin{array}{cccccccc} & & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \\ & & | & | & | & | & | & \\ \text{H} & - & \text{C} & = & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{OH} \\ & & | & & | & & | & & | & & | & & | & & \\ & & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \end{array}$$

Reagents needed for oxidation potassium dichromate (VI) and H
concentrated H_2SO_4



ResultsPlus Examiner Comments

If the oxidation number is given then it has to be correct. In this case the number is correct and both reagent marks were awarded.



ResultsPlus Examiner Tip

Candidates should double-check carefully any structure that they draw for such things as pentavalent carbons which will be penalised. This is the case here as one of the carbons in the double bond has too many hydrogens attached.

(b) (i) Melonal can be prepared by the oxidation of a compound, X. Suggest the formula of compound X and the names or formulae of the reagents needed to oxidize X. (3)

Compound X primary alcohol
heptanol $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

Reagents needed for oxidation acidified dichromate (VI)



ResultsPlus Examiner Comments

'Acidified dichromate' is a term often used as a short-cut but is insufficient on an examination paper to be given two marks. However, if the chemical symbols had been used namely: H^+ / $\text{Cr}_2\text{O}_7^{2-}$ then both reagent marks would have been awarded because a greater depth of understanding would have been shown.

Question 15(b)(ii)

The first marking point was frequently awarded, normally for 'distil' but the reason for its use was much less often seen. This is required by the question asking for a justification and candidates should be reminded to answer all aspects of the question set.

(ii) Briefly suggest a practical measure to maximise the yield of melonal in (b)(i).
Justify your answer.

(2)

Complete the oxidation under reflux, that way none of the reactants would boil off and escape, you would have to be careful that it didn't oxidise further into a carboxylic acid though.



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Examiner Comments

Marking points can be 'stand alone' and so candidates should always be advised to attempt both parts of the question since at least one of them may be awarded. In this example the reference to a wrong practical technique loses the first mark but the reason for use is appropriate and is awarded the second mark.

(ii) Briefly suggest a practical measure to maximise the yield of melonal in (b)(i).
Justify your answer.

(2)

- Distillation - method used
- Excess amount of $(K_2Cr_2O_7)$ and H_2SO_4



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Examiner Comments

Where contradictory statements are made for the same marking point then that point is lost. This student has correctly identified the practical technique of distillation but then referred to use of an excess of oxidising agent which negates the earlier correct point.

Question 15(c)

Candidates continue to be able to make effective use of the data booklet which reflects well on their learning. However, there are a significant minority that then undermine their answer by not completing the table correctly. For example the functional group column required the name of the bond type identified in the earlier columns of the table, but some candidates simply re-wrote the same answer in both the bond and functional group columns. This is unlikely to gain additional credit, especially on an A2 exam paper. In addition some identified the wrong bond for the stated wavenumber range for the alkene, e.g. giving 3095-3010 but then stating the bond responsible was C=C instead of C-C.

(c) Infrared spectra can be used to confirm the presence of functional groups in a molecule. Use page 5 of the data booklet to suggest the position of two absorptions and the identity of the bonds responsible which can confirm the presence of the two functional groups in melonal.

(2)

Wavenumber range / cm^{-1}	Bond	Functional group present in melonal
1740 - 1720	C=O	aldehyde Carbonyl group
1669 - 1645	C=C	alkene



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Examiner Comments

Note that the functional group identified is simply 'carbonyl' and this is not specific enough for this question.

Question 15(d)

Since molecular rearrangement is common in a mass spectrometer any order of atoms within the fragment was allowed. In addition any type of formula used was acceptable.

(d) The mass spectrum of melonal shows small peaks at $m/e = 57$ and $m/e = 83$.

Give the formula of each of the fragments most likely to have caused these peaks.

$m/e = 57$ $\text{CH}_2\text{CHCHO}^+$ (2)

$m/e = 83$ $\text{CH}_2(\text{CH}_2)\text{CHCH}_2\text{CH}_2^+$



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Examiner Comments

The positive charge could be written anywhere on the fragment to be awarded the mark. Although technically it should be on the CH of the $m/e = 57$ fragment, it is fine and quite common for the positive charge to be written at the end of the fragment formula as here.

(d) The mass spectrum of melonal shows small peaks at $m/e = 57$ and $m/e = 83$.

Give the formula of each of the fragments most likely to have caused these peaks.

$m/e = 57$ $\text{CH}_2\text{CHC}^{\oplus}\text{H}$ (2)

$m/e = 83$ $(\text{CH}_2)_2\text{C}=\text{CHCH}_2\text{CH}_2$



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Examiner Comments

The lack of a positive charge was only penalised once and so this response scored 1 out of the 2 marks available.



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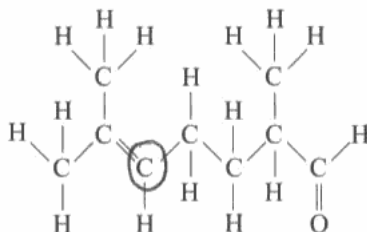
Examiner Tip

Candidates could be reminded of the stages in a mass spectrometer and that only positive ions are detected. In this way the formulae of any fragments will always be positively charged.

Question 15(e)(i)

Although a simple task in itself this was a more challenging question and a range of atoms were selected.

- (e) (i) On the displayed formula below, circle the hydrogen atom that has a triplet peak in the proton nmr spectrum of melonal. (1)



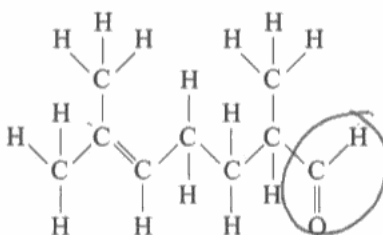
ResultsPlus Examiner Comments

Candidates should always double-check and even triple-check their answers if at all possible. This question asks for the "hydrogen atom" to be circled but this candidate has circled a carbon atom. It would be hoped that even a quick check-through would have spotted this and allowed it to be rectified.

Question 15(e)(ii)

A high-scoring question with the vast majority of candidates appreciating the correct part of the molecule to circle. However, as below, a sizeable minority of candidates were rather sloppy in their placement of the circle.

- (ii) On the displayed formula below, circle the atom that gives rise to a peak at a chemical shift of $\delta = 9.65$ ppm in the proton nmr spectrum of melonal. Refer to page 7 of the data booklet. (1)



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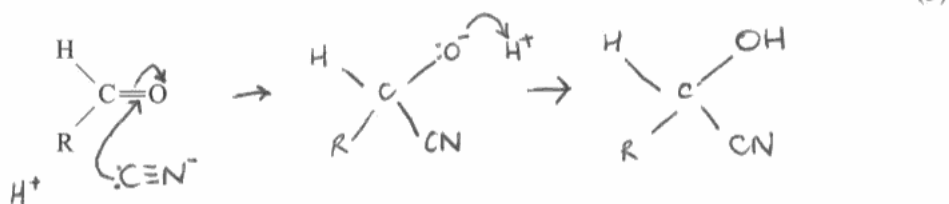
The question clearly asks for the 'atom', **singular**, to be circled but it was not uncommon for the whole aldehyde group to be circled as here. This was not awarded the mark.

Question 15(f)(i)

It is not uncommon for the cyanide ion to have the negative charge written by the nitrogen as in, CN^- . Hence the origin of the arrow coming from the cyanide ion in the first step was not viewed as crucial. However, the ending point of this arrow was important as evidenced below. The bond from the carbon to the CN group in the intermediate should be to the carbon and not the nitrogen. This was only penalised when a horizontal bond was drawn, for example, as $\text{CN}-\text{C}$. Occasionally the negative charge was missing from either the cyanide ion or the reaction intermediate.

(f) Aldehydes react with HCN in the presence of CN^- ions.

(i) Give the mechanism for this reaction, using the simplified displayed formula below.



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Although the placement of the arrows, in terms of where they go from, was not critical it is important to correctly identify the area that they are going to. In this example the cyanide ion arrow is clearly going to the carbonyl bond and this was penalised. The remainder of the mechanism is fine.

Question 15(f)(ii)

It was expected that candidates would begin with a 'Yes' or 'No' answer to the opening question and then give a suitable explanation. Some responses were confused because the answer 'Yes' was given but then the explanation was why there would be no rotation of plane-polarised light! All the marking points were 'stand alone' and full marks could be achieved from either a 'Yes' or 'No' answer. It was much more common to see a No answer with a good explanation. There were a small number of candidates who referred to the intermediate being planar rather than the carbonyl and so this did not score.

(ii) The product of this reaction has a chiral centre. Would you expect the reaction to produce a solution that rotates the plane of plane-polarized light? Explain your answer.

(3)

I would not expect the solution to rotate the plane of plane-polarised light because the CN^- ion can go in either above or below the carbon, producing equal amounts of both enantiomers. Therefore the light will be rotated equally in both directions so the solution will not rotate the plane of plane-polarised light.



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Examiner Comments

A reminder that three marks are available for this question and so three points need to be made. This answer clearly makes two such points but misses the planar nature of the carbonyl group.

Question 16(a)(i)

The majority of candidates got this correct but if the chemical formula is given then it has to be correct. There was some confusion evidenced with a small number of answers simply given as starch.

(a) (i) Suggest a suitable reagent with which you could titrate the iodine.

(1)

Sodium thiosulphate.



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Examiner Comments

Of course either spelling with an 'f' or a 'ph' as here was credited.

Question 16(a)(ii)

As previously mentioned, candidates need to answer all aspects of the question set. The answer must 'state and explain'. A reasonable number of candidates stated the use of sodium hydrogencarbonate (or sodium carbonate as a commonly acceptable alternative) but then failed to explain how it worked to quench the reaction.

Others did explain how quenching would be achieved but gave an incorrect base. If a reagent suggested was a "near-miss" then the second mark could be awarded.

(ii) State and explain how you would quench the reaction. (2)

Place the mixture in an ice bath
as it ~~pro~~ slows the reaction because
particles have less kinetic energy.



ResultsPlus

Examiner Comments

This reaction is normally carried out at room temperature and so use of an ice bath would really have a negligible effect but one mark out of the two was awarded for the generally acceptable principle.

(ii) State and explain how you would quench the reaction. (2)

Adding a base such as sodium hydroxide
would remove the acid catalyst.
This would make the reaction so slow
as to be non-existent.



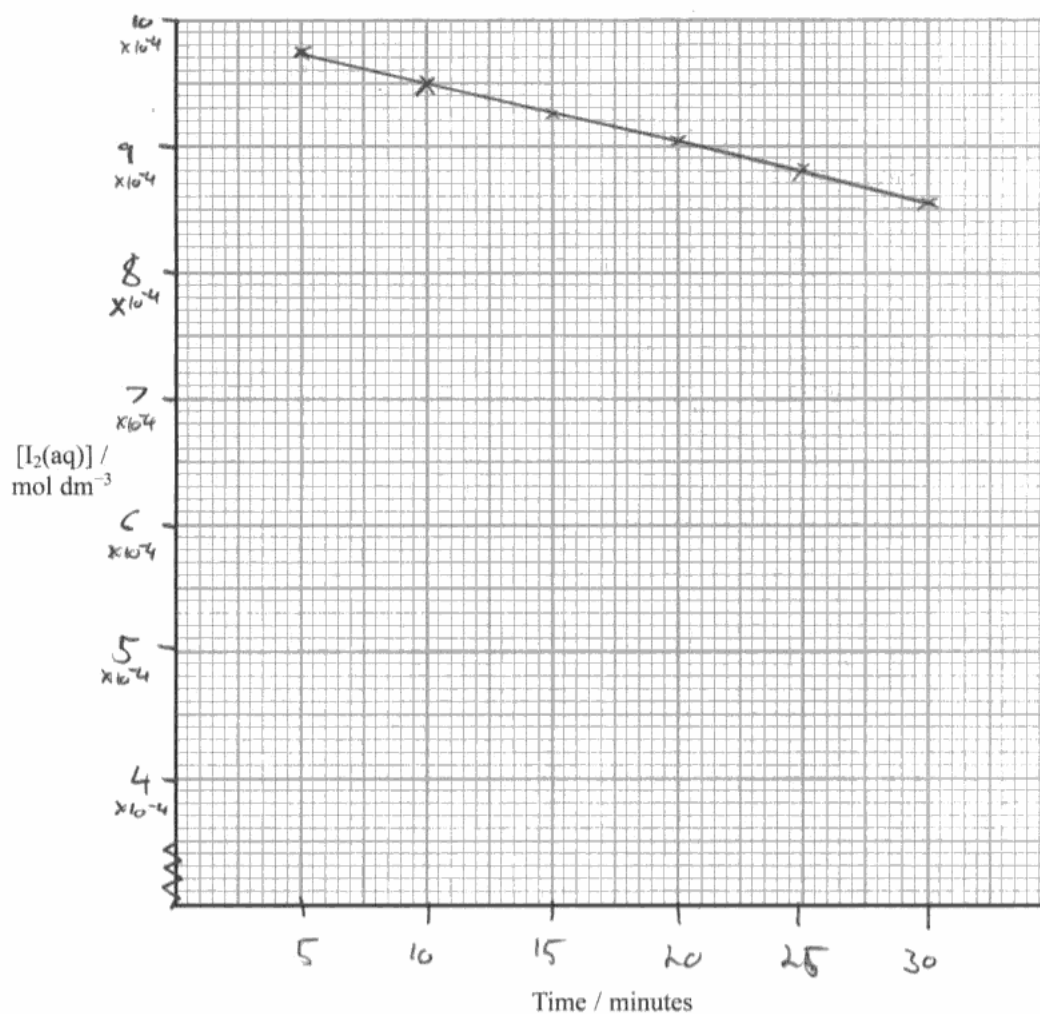
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Examiner Comments

The second mark was awarded for the neutralisation of the acid catalyst even though the use of sodium hydroxide is incorrect.

Question 16(b)(i)

The graph drawing seen in this summer session was vastly improved in comparison to that seen in the January session. Hopefully centres had stressed to their students the need for an appropriate scale that resulted in more than half of the graph paper being used. The vast majority of points were correctly plotted, a tolerance of one small square being applied. It is expected that the points would be joined by means of a straight line, made with the use of a ruler. This was not always evident. Also it was odd to see the wrong reaction order from a correct graph almost as if the expected answer was used rather than the one the graph suggested.



Order with respect to iodine 1st



ResultsPlus
Examiner Comments

A quick glance at this graph should suggest that something is wrong since only a very small part of the graph paper is used. One mark is lost for poor choice of scale as here.

The order stated is also incorrect.

Question 16(b)(ii)

The question requires reference to the graph and an explanation. It was not unusual to see a response that did one or the other but not always both. The more able candidates did tend to cover both points and so it was a useful grade discriminator.

(ii) Explain how you determined the order using your graph.

(2)

By looking at the gradient; as the gradient is constant throughout the reaction, it is a zero order of reaction



ResultsPlus

Examiner Comments

Two marks are available for the answer to this question and it's unlikely that a mark is to be given for something which has already been given credit. Hence in this example there is one mark for the reference to constant gradient but nothing for the order stated since that is awarded in (b)(i).

A comment that explains what a constant gradient means, namely that concentration has no effect on the rate, was required for the second mark.

Question 16(c)

Most candidates were awarded this mark. Although there were a number of responses which gave 'iodine clock' as their answer or referred to the simple use of starch, neither was given credit.

(c) State an alternative practical procedure that could be used to monitor the concentration of iodine.

(1)

colorimetry



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Examiner Comments

Candidates must be very careful if their writing is not the neatest or clearest in order to not be penalised due to confusion with terms. This example is OK for colorimetry but in others the first vowel looked very much like an 'a' and 'calorimetry' is completely wrong.

Question 17(a)(i)

Methy/methly were both allowed for methyl but the stem of the name had to be correct and normally was but care is needed (see below).

17 The ester $\text{CH}_3\text{CH}_2\text{COOCH}_3$ can be formed from the reaction between propanoic acid and methanol with an acid catalyst.



(a) (i) Name the ester.

(1)

methy/ Methyl propanoate



ResultsPlus

Examiner Comments

The inclusion or omission of an 'o' can make all the difference and so names should always be carefully checked.

This answer was not awarded the mark.

17 The ester $\text{CH}_3\text{CH}_2\text{COOCH}_3$ can be formed from the reaction between propanoic acid and methanol with an acid catalyst.



(a) (i) Name the ester.

(1)

ethyl ethanoate



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Examiner Comments

The most common ester that students come across but clearly incorrect in this instance.

Question 17(a)(ii)

The hazard associated with HCl(g) was commonly identified but more is required since it needs to be stated just why it is such a hazard, namely that it is toxic/corrosive etc. The second mark for the precaution was only awarded for a correct hazard or a 'near-miss' so that a simple reference to gloves/fume cupboard without a suitable hazard did not score.

- (ii) The same product can be made using propanoyl chloride instead of propanoic acid. Suggest an additional hazard that could occur using this reagent and describe how you would minimise this risk.

(2)

The reaction would produce HCl(g), but this risk can be minimised by performing the experiment in a fume cupboard as HCl(g) is harmful.



ResultsPlus

Examiner Comments

This type of response was very common where the HCl was identified as the hazard but not why so, and then the precaution of use of fume cupboard correctly given. Hence one mark out of the two awarded.

- (ii) The same product can be made using propanoyl chloride instead of propanoic acid. Suggest an additional hazard that could occur using this reagent and describe how you would minimise this risk.

(2)

Propanoyl chloride is toxic. Reaction should therefore be carried out in fume cupboard.



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Examiner Comments

Although most answers referred to the HCl it was possible to gain both marks from statements on propanoyl chloride, as seen here.

Question 17(b)

A full range of scores were seen for this question, with the majority scoring at least one mark. The equilibrium amount of water was the most common error. The K_c calculation was generally well-done but there were some transposition errors which resulted in a loss of marks, e.g. 1.14 used instead of 1.41 for the equilibrium amount of water. However, rounding errors were rarely seen. Strangely some candidates, even including the more able, only completed the table and did not attempt the K_c calculation. Presumably these were rushing through the paper and failed to read the requirements of the question since it was not a difficult calculation.

(b) Complete the table below to show the amounts of each substance present at equilibrium. Use your values to calculate the equilibrium constant, K_c , for the reaction. (3)

	CH ₃ CH ₂ COOH	CH ₃ OH	CH ₃ CH ₂ COOCH ₃	H ₂ O
Initial amounts / mol	0.52	0.37	0	1.2
Equilibrium amounts / mol	0.31	0.16	0.21	1.41



ResultsPlus Examiner Comments

Candidates need to always check that they have answered all parts of the question set and if there is a sizeable gap or space in the question, as shown here, then it is likely that something over-and-above completion of the table is required.

(b) Complete the table below to show the amounts of each substance present at equilibrium. Use your values to calculate the equilibrium constant, K_c , for the reaction. (3)

	CH ₃ CH ₂ COOH	CH ₃ OH	CH ₃ CH ₂ COOCH ₃	H ₂ O
Initial amounts / mol	0.52	0.37	0	1.2
Equilibrium amounts / mol	0.31	0.16	0.21	0.99

$$K_c = \frac{[\text{H}_2\text{O}][\text{CH}_3\text{CH}_2\text{COO}(\text{H}_2)]}{[\text{CH}_3\text{OH}][\text{CH}_3\text{CH}_2\text{COOH}]} = \frac{0.99 \times 0.21}{0.16 \times 0.31} = 4.19 (\text{no units})$$


ResultsPlus Examiner Comments

'Error-carried-forward' was applied here. The equilibrium amount of water is incorrect so only one mark out of two is gained for the table. However, the K_c calculation is correctly carried out for the candidate's values and so the mark for the calculation was awarded.

Question 18(a)

Definitions should be well-known and really ought to be relatively 'easy' marks to score. However, enthalpy of hydration proved to be more challenging. The second marking point which refers either to an infinitely dilute solution or that further dilution cause no further heat change, was the point seen least. Centres could practice further this definition with their students.

SECTION C

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

18 This question is about the solubility of some Group 1 halides.

- (a) Potassium fluoride is a soluble, white, crystalline solid used in etching glass. A Hess cycle can be used to calculate its enthalpy of solution, using data including enthalpies of hydration of ions.

Define the term **enthalpy of hydration** of an ion.

(2)

Is the energy needed to add
1 mole of ~~H⁺ ions~~^{H₂O} to a ~~comp. substance~~
1 mole of gaseous 1⁺ ions
$$X^+(g) + H_2O(l) \rightarrow X(aq)$$



ResultsPlus

Examiner Comments

Enthalpy of hydration is exothermic and reference to energy required or needed loses the first mark.



ResultsPlus

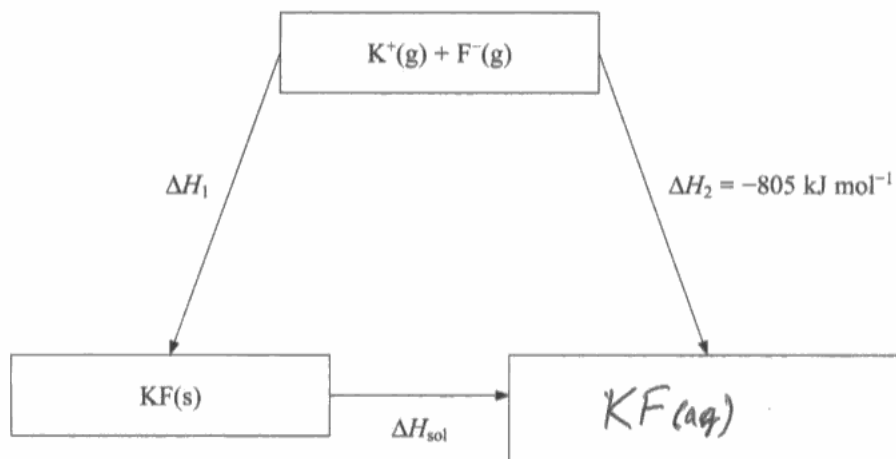
Examiner Tip

Enthalpy changes are usually with reference to one mole of a compound or ion but with hydration there is more than one mole of water molecules around each mole of aqueous ions.

Question 18(b)(i)

A weird and wonderful array of chemical formulae were seen on occasion which did make the examiners wonder where on earth they came from! However, the majority did gain the mark and correct use of state symbols was not a problem.

(b) Consider the Hess cycle below.



(i) Complete the cycle by filling in the empty box.

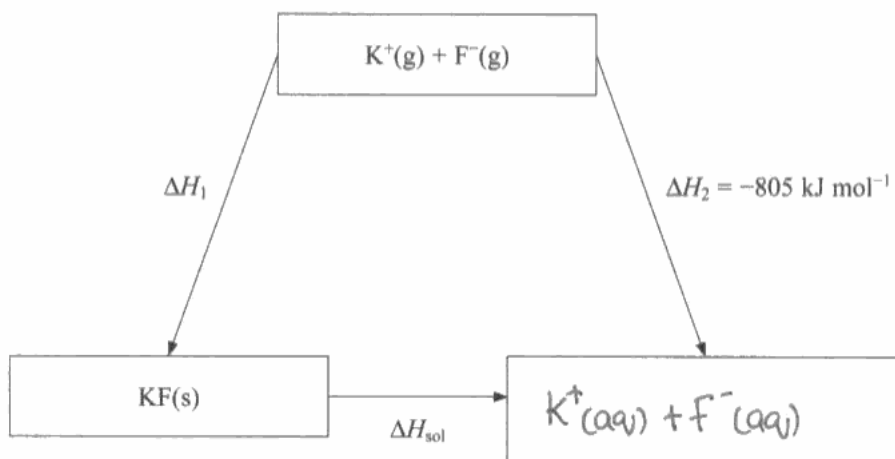


ResultsPlus

Examiner Comments

The aqueous ions needed to be clearly separated as they would be in solution.

(b) Consider the Hess cycle below.



(i) Complete the cycle by filling in the empty box.



ResultsPlus

Examiner Comments

A clearly written answer which is an example to many!

Question 18(b)(ii)

Despite clear instructions to answer in terms of ΔH_1 and ΔH_2 some candidates used other terms. This was disappointing. There was no evidence of working-out on the previous page.

(ii) Apply Hess's Law to obtain an expression for ΔH_{sol} in terms of ΔH_1 and ΔH_2 .

(1)

$$\Delta H_{\text{sol}} = \Delta H_2 - \Delta H_1$$



ResultsPlus
Examiner Comments

The expression was acceptable either 'way-round'. Here the expression begins in terms of delta ΔH_2 .

(ii) Apply Hess's Law to obtain an expression for ΔH_{sol} in terms of ΔH_1 and ΔH_2 .

(1)

$$\Delta H_{\text{sol}} = \Delta H_1 + \Delta H_2$$



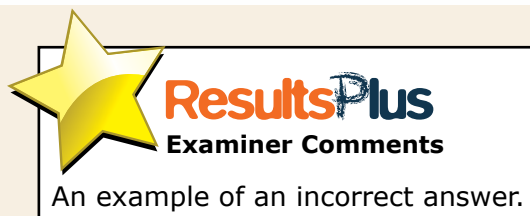
ResultsPlus
Examiner Comments

This expression is clearly incorrect but can still be used to gain full credit in part (iv)

Question 18(b)(iii)

A straight-forward question which was generally answered well. There was some confusion with formation, as evidenced below, and some tried to 'hedge-their-bets' by stating both. Neither was given credit.

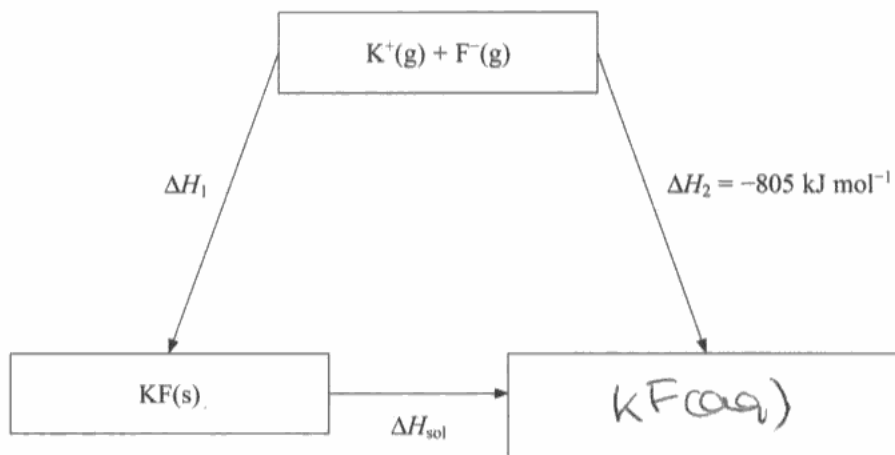
(iii) Give the name of the energy change ΔH_1 .	(1)
<i>ΔH formation</i>	



Question 18(b)(iv)

Most scored one mark for the use of the correct value of the lattice enthalpy. However, there was considerable confusion over the use of negative charges and when they 'cancel each other to make a plus'. Hence it was rare to award the second mark for a correct calculation. Since part (ii) could be seen credit was given to students for the correct use of their own expression in the calculation of part (iv).

(b) Consider the Hess cycle below.



(i) Complete the cycle by filling in the empty box. ...

(ii) Apply Hess's Law to obtain an expression for ΔH_{sol} in terms of ΔH_1 and ΔH_2 . (1)

$$\Delta H_{\text{sol}} = -\Delta H_1 + \Delta H_2$$

(iii) Give the name of the energy change ΔH_1 . (1)

~~The enthalpy of atomisation~~ Lattice energy

(iv) Referring to page 12 of the data booklet and your answer to (ii), calculate the standard enthalpy of solution of potassium fluoride. (2)

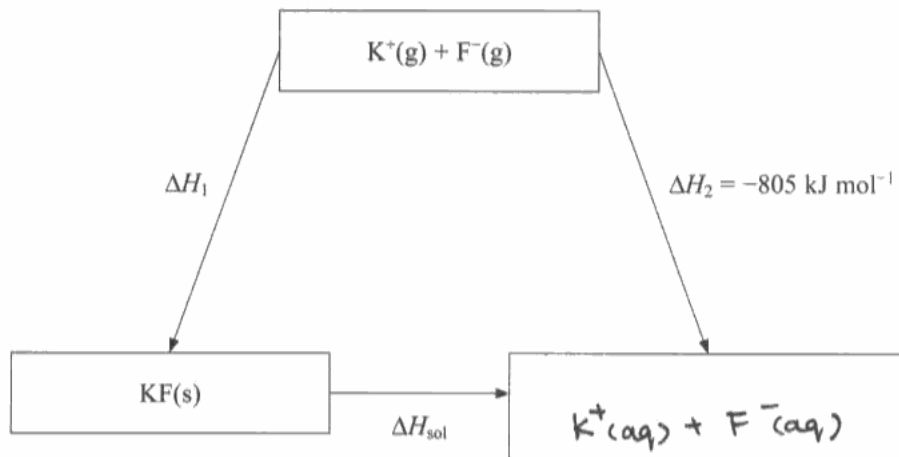
$$\Delta H_{\text{sol}} = -(-817) + 805 = +1622 \text{ kJ mol}^{-1}$$



ResultsPlus Examiner Comments

One mark for the use of 817. The value of ΔH_1 is correctly given two negative signs as per their expression in part (ii). However, ΔH_2 should be a negative value and so an incorrect final answer is given.

(b) Consider the Hess cycle below.



(i) Complete the cycle by filling in the empty box. ...

(ii) Apply Hess's Law to obtain an expression for ΔH_{sol} in terms of ΔH_1 and ΔH_2 . (1)

$$\Delta H_{sol} = \Delta H_2 - \Delta H_1$$

(iii) Give the name of the energy change ΔH_1 . (1)

LATTICE ENTHALPY

(iv) Referring to page 12 of the data booklet and your answer to (ii), calculate the standard enthalpy of solution of potassium fluoride. (2)

Lattice enthalpy of $K^+ + F^- \rightarrow$ ~~807~~ ⁸⁰⁷ (2)
~~experimental~~ theoretical value

$$\Delta H_{sol} = -805 - \cancel{(-805)} (-807)$$

$$= \cancel{-1622} + 2$$

$$+ 2 \text{ kJ mol}^{-1}$$
~~$$-1622 \text{ kJ mol}^{-1}$$~~
~~$$-1620 \text{ kJ mol}^{-1}$$~~



ResultsPlus

Examiner Comments

An incorrect value for the lattice enthalpy is used here but the calculation is otherwise correct and so the second mark can be awarded.

Question 18(c)(i)

Generally the very small value for the enthalpy of solution was not noticed nor the small mass of salt in the relatively large volume of water. In practice it is unlikely that there would have been any decrease in temperature observed but any statement of a temperature decrease was given credit because at least that part of the statement had been noted. Some candidates seemed to have no real concept of what was happening and suggested that the temperature would go down and then go up or vice versa.

It might be good for centres to get students to actually carry out this stated experiment in order for them to experience what does happen and to have some concept of the actual quantities involved.

(c) The standard enthalpy of solution of sodium chloride is $+3 \text{ kJ mol}^{-1}$. = 2000.

- (i) 1 g of sodium chloride was added to 250 cm³ of water in a beaker and stirred with a thermometer graduated in intervals of 1 °C. Describe and explain what would happen to the reading on the thermometer as the sodium chloride dissolves. No calculation is required.

(3)

AS the sodium chloride dissolves the temperature will decrease because it is an endothermic reaction so it takes in heat and cools down the surroundings.



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Examiner Comments

An example of the common response that the temperature would decrease and which was awarded one mark.

(c) The standard enthalpy of solution of sodium chloride is $+3 \text{ kJ mol}^{-1}$.

- (i) 1 g of sodium chloride was added to 250 cm^3 of water in a beaker and stirred with a thermometer graduated in intervals of 1°C . Describe and explain what would happen to the reading on the thermometer as the sodium chloride dissolves. No calculation is required.

(3)

As the sodium chloride dissolves, the reading on the thermometer would decrease as a small ^{positive} enthalpy of ~~soln~~ solution indicates ~~more~~ that energy is taken in from the surroundings and with the breaking of bonds, must be an endothermic reaction. (therefore decrease in temperature)

breaking bonds \Rightarrow endothermic.
dissolve solubility is usually.



ResultsPlus

Examiner Comments

Any reference to a small positive enthalpy change was given a mark and with the decrease in temperature suggested this response scores 2 marks.

(c) The standard enthalpy of solution of sodium chloride is $+3 \text{ kJ mol}^{-1}$.

- (i) 1 g of sodium chloride was added to 250 cm^3 of water in a beaker and stirred with a thermometer graduated in intervals of 1°C . Describe and explain what would happen to the reading on the thermometer as the sodium chloride dissolves. No calculation is required.

(3)

As the sodium chloride dissolves it takes in heat energy so it is an endothermic reaction. This means that the temperature on the thermometer would fall. However since only a gram of NaCl is being used and the thermometer has such large graduations it will be hard to measure the resulting temperature change as the reading will only change very little.



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Examiner Comments

This is one of the very rare responses to be given all 3 marks. There is reference to the temperature reading going down, the fact that only 1g of NaCl was used and that the thermometer had large graduations which would make the temperature change difficult to see.

Question 18(c)(ii)

This was a good question as a grade discriminator. The more able frequently scored maximum marks while the less able struggled to express entropy changes clearly and seemed to be confused between enthalpy and entropy. One point that centres could stress to their students is that they make abundantly clear even what might seem obvious to them. For example some candidates often stated that the increase in entropy of the system was greater than the entropy change of the surroundings but without necessarily stating that either the entropy change of the system was positive or that the entropy change of the surroundings was negative.

*(ii) Explain, in terms of entropy changes, why sodium chloride dissolves in water under standard conditions. No calculation is required.

(4)

$\Delta S_{\text{solution}}$ is ~~the addition of~~ ^{affected by} the lattice energy and $\Delta H_{\text{hydration}}$. $\Delta S_{\text{soln}} = \frac{-LE}{\Delta T_{\text{hyd}}} + \Delta H_{\text{hyd}}$.

The $\Delta S_{\text{solution}}$ of sodium chloride is positive meaning it will dissolve in solution as the lattice energy means it is exothermic, so favorable and the negative value of $\Delta H_{\text{hydration}}$ is smaller than the lattice energy. ^{more importantly} The ΔS_{total} of the reaction is positive as ~~the~~ sodium chloride is moving from a solid to a liquid so the entropy of the system increases as there is more disorder meaning ~~the~~ sodium chloride is favorable to dissolve.

*(d) Lithium iodide is generally much more soluble in organic solvents than lithium



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Examiner Comments

Many answers were similar to this one in that the majority of the response was not actually answering the question. Here the first mark is awarded for the total entropy change being positive in the 7th dotted line and then the second marking point in the last dotted line.

Question 18(d)

Candidates were expected to compare the theoretical lattice energy with the Born-Haber lattice energy for the same compound. However, the overwhelming majority compared the same 'type' of lattice energy between two different compounds. The differences between these two lattice energies for each individual compound reflects the degree of covalency due to the polarisation of the anion.

Candidates also seemed to ignore the statement that the solubility referred to organic solvents and attempted to answer their own question about solubility in water. This was not given credit.

* (d) Lithium iodide is generally much more soluble in organic solvents than lithium chloride. Explain this observation using values of lattice energies from your data booklet and your knowledge of the trend in ionic radii down Group 7.

(4)

~~Li~~ Lithium Iodide has ^{much} a less negative lattice energy than lithium chloride ~~that~~ because the iodide ion is larger than the chloride ion and thus its nucleus has a weaker pull on bonding electrons making the Li-I bond easier to break than Li-Cl. This also makes the $\Delta H^{\circ}_{\text{solution}}$ of lithium Iodide ~~more~~ ^{less} negative than lithium chloride so it is more soluble than lithium chloride.



ResultsPlus
Examiner Comments

This is an example of the type of response that only scored the 'increase in ionic radii down the group' mark.

* (d) Lithium iodide is generally much more soluble in organic solvents than lithium chloride. Explain this observation using values of lattice energies from your data booklet and your knowledge of the trend in ionic radii down Group 7.

(4)

The lattice enthalpy for Lithium iodide is +759 whereas lattice enthalpy of lithium chloride is +848. Therefore lattice enthalpy of LiCl is greater than LiI . This is because chloride and iodide ions have the same charge but a Iodide ion has a greater ionic radius as it has a greater number of electrons and electron shells which repel each other more and the distance between outer electron and nucleus is further. So less electrostatic force. Therefore Iodide ion has lower charge density and the electron cloud is more likely to be distorted by the Li^+ cation. This makes the electron act more as though they are shared, making the bond ~~more~~ covalent. So the ~~pro~~ LiI is more likely to ~~more~~ dissolve in ~~like~~ solvents like organic which have covalent bonds. (Total for Question 18 = 18 marks)



ResultsPlus Examiner Comments

Here is an example of one of the rare responses which scored more than one mark. There is reference to the polarisation of the larger iodide ion and as a consequence the increase in covalency.

Paper Summary

Questions such as Q15b)(ii), Q16(a)(ii) and others required not just a 'bald' answer but some justification or explanation. This was clearly asked for in the question and candidates should always endeavour to answer each question fully and to do that they need to read the question very carefully. In addition there was evidence that a simple double-check or read-through would have enabled some candidates to have remedied relatively simple errors such as in Q15(e)(i) and Q15(e)(ii).

Reminders to candidates to lay-out their workings in calculations in a neat and orderly fashion would be much appreciated. It is clearly not in the candidates best interest if an examiner has to struggle to find the marking points.

Examiners are always endeavouring to find new ways to ask the same type of question but the chemistry remains the same. As long as candidates fully understand the concepts then this should not present a problem. Centres should continue to stress the chemical grasp of topic areas rather than the learning by rote of some exam-style type of question.

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