

Examiners' Report

June 2022

IAL Chemistry WCH14 01

Introduction

Overall, the paper seemed accessible to all candidates and there was little evidence that they ran out of time. Students were well prepared for rates and entropy topics and calculations were a particular strength too. The twenty multiple choice questions had a mean mark of 13.2. The easiest questions were 10a, 10b and 4 and the hardest question was 1c.

Question 16 (a)(i)-(iii)

This part of the question proved to have a range of marks. In part ai, the majority gave the correct K_p expression often including round brackets and pp instead of p but scored the mark. However, a minority included square brackets or omitted p so gained no credit.

Deducing the mole fractions from the % composition of ammonia proved to be quite challenging in aii. But despite calculating the wrong mole fractions, most were able to correctly multiply by 200 to get a transferred error mark for the partial pressures.

The calculation in aiii, proved to be quite accessible for most candidates, but common errors included, too many significant figures, the wrong units or no units.

16 This question is about ammonia and ammonium chloride.

(a) Ammonia is produced by reacting nitrogen and hydrogen as shown.



(i) Write the expression for the equilibrium constant, K_p .

(1)

$$K_p = \frac{p[\text{NH}_3]^2}{p[\text{N}_2] \times p[\text{H}_2]^3}$$

- (ii) An equilibrium was established by mixing nitrogen and hydrogen in a 1:3 ratio by volume, at a temperature of 450°C and pressure of 200 atm. The equilibrium mixture contained 28% of ammonia by volume.

Complete the table.

$$17:x = 0.28$$

$$17:0.28 = x$$

$$\text{total volume} = 216.8$$

(3)

Substance	Mole fraction	Partial pressure / atm
N ₂	0.0085 0.36	72
H ₂	0.0085	1.7
NH ₃	0.28	56

729

N₂
and
H₂

- (iii) Calculate the equilibrium constant.

Give your answer to an appropriate number of significant figures and include units, if required.

(3)

$$\frac{56^2}{72 \times 1.7^3} = K_{eqm}$$

$$K = 1844 \text{ } 8.87$$

$$\text{atm}^{-2}$$



ResultsPlus
Examiner Comments

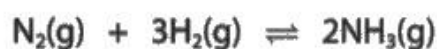
Although this candidate has the correct substances and powers in their K_p expression, they have used square brackets, which equate to concentration so do not score ai. They have got the wrong mole fractions in aii, but have successfully multiplied these values by 200 and so score 1 mark for the correct partial pressures. In aiii they have successfully used their values from aii to calculate the equilibrium constant with the correct units and 3 significant figures so score 3 marks.



Transfer error marks are available in calculations so it is important that intermediate working is shown so credit can be given.

16 This question is about ammonia and ammonium chloride.

(a) Ammonia is produced by reacting nitrogen and hydrogen as shown.



(i) Write the expression for the equilibrium constant, K_p .

(1)

$$K_p = \frac{p(\text{NH}_3)^2}{p(\text{N}_2)p(\text{H}_2)^3}$$

(ii) An equilibrium was established by mixing nitrogen and hydrogen in a 1:3 ratio by volume, at a temperature of 450 °C and pressure of 200 atm. The equilibrium mixture contained 28% of ammonia by volume.

Complete the table.

(3)

Substance	Mole fraction	Partial pressure / atm
N ₂	0.18	36
H ₂	0.54	108
NH ₃	0.28	56

(iii) Calculate the equilibrium constant.

Give your answer to an appropriate number of significant figures and include units, if required.

(3)

$$\begin{aligned} K_p &= \frac{56^2}{36 \times 108^3} \\ &= 6.92 \times 10^{-5} \text{ atm}^{-2} \end{aligned}$$



This candidate has correctly used p and round brackets in ai and successfully deduced the mole fraction and partial pressures in aii. In aiii they have calculated the equilibrium constant with the correct units and 3 significant figures, so full marks are scored.

Question 16 (a)(iv)

This question required the candidate to deduce the nature of the reaction when the yield increased as the temperature decreased. The majority appreciated the forward reaction was exothermic, but the explanation proved to be more difficult to answer successfully. A number also got confused between exothermic and endothermic or got the direction of equilibrium shift the wrong way round.

(iv) When the temperature was reduced to 400 °C at the same pressure, the equilibrium mixture contained 36 % of ammonia.

Explain what can be deduced about this reaction from this information.

(2)

Equilibrium will be shifted to the right
because decreasing temperature, ~~shifts~~ equilibrium
shifts to the ~~products~~ products side



ResultsPlus
Examiner Comments

This candidate understands the reaction shifts to the right, but they have not stated the reaction is exothermic so only 1 mark scored.

- (iv) When the temperature was reduced to 400°C at the same pressure, the equilibrium mixture contained 36% of ammonia.

Explain what can be deduced about this reaction from this information.

(2)

It suggests that the forward reaction is exothermic,
~~and that~~ as the amount of ammonia in the equilibrium
is increasing.



ResultsPlus
Examiner Comments

Here the candidate knows the reaction is exothermic, but they have just repeated the question by saying the amount of ammonia increases. Only 1 mark scored.

- (iv) When the temperature was reduced to 400°C at the same pressure, the equilibrium mixture contained 36% of ammonia.

Explain what can be deduced about this reaction from this information.

(2)

When temperature ~~is~~ decrease, the ammonia yield increase.
The forward reaction is exothermic. ~~Temperature increase~~
~~the~~ Equilibrium shifts to right.



ResultsPlus
Examiner Comments

The candidate has scored both marks by stating the reaction is exothermic and the equilibrium shifts to the right.

Question 16 (b)(ii)

The expression for the enthalpy change of solution was successfully done by the majority of candidates.

- (ii) Complete the expression for the enthalpy change of solution using the hydration enthalpies and lattice energy.

(1)

$$\Delta_{\text{sol}}H = -\Delta_{\text{hyd}}H + \text{Lattice Energy}$$



ResultsPlus
Examiner Comments

Although rarely seen this candidate has got the signs the wrong way round so no mark is scored.

- (ii) Complete the expression for the enthalpy change of solution using the hydration enthalpies and lattice energy.

(1)

$$\Delta_{\text{sol}}H = -\Delta H_{\text{LE}} + \Delta H_{\text{hyd}}$$



ResultsPlus
Examiner Comments

Here the candidate has given a correct answer. Although they have simplified lattice energy to LE this is allowed.

- (ii) Complete the expression for the enthalpy change of solution using the hydration enthalpies and lattice energy.

(1)



ResultsPlus
Examiner Comments

This candidate has broken down the hydration energies into the two parts, which is not essential to score. The important thing is to allocate the signs correctly which they have done so the mark is awarded.

Question 16 (b)(iii)

This straightforward calculation of the enthalpy change of solution using a Hess cycle was well done by most students and those who made one error were able to score 1 mark out of 2.

(iii) Calculate the enthalpy change of solution, using your expression in (b)(ii) and these data.

Enthalpy change of hydration of NH_4^+ = -307 kJ mol^{-1}

Enthalpy change of hydration of Cl^- = -378 kJ mol^{-1}

Lattice energy of NH_4Cl = -705 kJ mol^{-1}

(2)

~~Ans:~~

$$\begin{aligned}\Delta_{\text{sol}} H &= \Delta_{\text{hyd}} H - \text{lattice energy} \\ &= (-378 + 307) - (-705) \\ &= 634 \text{ kJ mol}^{-1}\end{aligned}$$



ResultsPlus
Examiner Comments

This is an example where the candidate has made one mistake. The calculation should be -307 , not $+307$. This mistake could have been avoided as the arrows were already on the Hess cycle so both hydration enthalpies should be negative. However, just one mistake scored 1 mark.

(iii) Calculate the enthalpy change of solution, using your expression in (b)(ii) and these data.

Enthalpy change of hydration of $\text{NH}_4^+ = -307 \text{ kJ mol}^{-1}$

Enthalpy change of hydration of $\text{Cl}^- = -378 \text{ kJ mol}^{-1}$

Lattice energy of $\text{NH}_4\text{Cl} = -705 \text{ kJ mol}^{-1}$

(2)

$$\begin{aligned}\therefore \Delta_{\text{soln}} H &= -(-705) + (-307 - 378) \\ &= 705 - 685 \\ &= 20 \text{ kJ mol}^{-1}\end{aligned}$$



ResultsPlus
Examiner Comments

Here the candidate has shown their working and produced a correct answer so scores 2 marks. Note that we do not need to see a + sign if the result is positive and the units are not required but are penalised only if wrong.

Question 16 (b)(iv)

This question proved very challenging for many. As well as having to explain how the size of the halide affected the hydration and lattice enthalpies, candidates also had to suggest how these changes would impact on the enthalpy of solution.

- (iv) A student suggested that the enthalpy change of solution of ammonium bromide would be of a similar magnitude to the enthalpy change of solution of ammonium chloride.

Comment on this suggestion in terms of the hydration enthalpies and lattice energies of these two compounds.

(3)

The atomic radii of Bromide ion is larger than chloride ion, which the lattice energy between ammonium ion and bromide ion is weaker than that ^{between} of chloride ion.



This candidate is confused between atomic and ionic radius, and it is not clear what the term weaker is referring to.



Make sure you are using the correct terminology when answering this type of question.

Do not confuse halogens and halides.

Also think carefully about what is changing and instead of saying larger or smaller refer to the values being more or less exothermic.

- (iv) A student suggested that the enthalpy change of solution of ammonium bromide would be of a similar magnitude to the enthalpy change of solution of ammonium chloride.

Comment on this suggestion in terms of the hydration enthalpies and lattice energies of these two compounds.

(3)

The enthalpy change of solution is equal to the sum of enthalpy of hydration and ^{negative} lattice energy. Since lattice energy refers to the ~~forming of bonds and~~ breaking of ~~to~~ the same type of bonds as the ~~formation of hydration~~ bonds formed during hydration, they cancel out leaving a similar magnitude of enthalpy change of solution overall.



ResultsPlus
Examiner Comments

This candidate has scored a mark for explaining the relationship between the lattice and hydration enthalpies on the enthalpy of solution. However, they have made no other comment about the trends and sizes of the ions so this is their only scoring point.

- (iv) A student suggested that the enthalpy change of solution of ammonium bromide would be of a similar magnitude to the enthalpy change of solution of ammonium chloride.

Comment on this suggestion in terms of the hydration enthalpies and lattice energies of these two compounds.

(3)

Ammonium bromide and ammonium chloride have same cation but different anion where chloride have smaller ionic radii than bromide and lattice energy of ammonium chloride is ~~is~~^{more} negative because the attraction between them is stronger and the hydration enthalpies for chloride is much more exothermic than bromide so the enthalpy change of solution of them is similar, because enthalpies



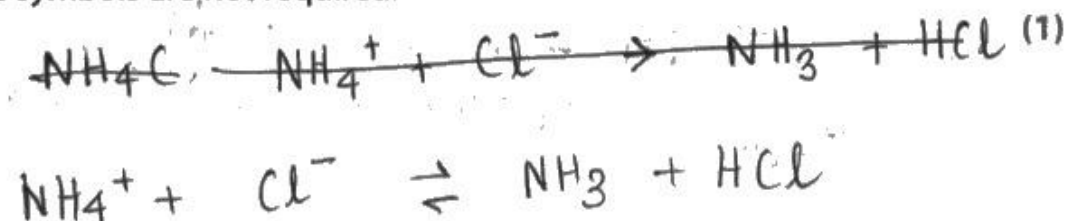
ResultsPlus
Examiner Comments

This is an excellent answer where the candidate has scored a mark for saying 'chloride is bigger than bromide', another for the 'lattice energy of ammonium chloride is more negative' and finally one for 'hydration of chloride is more exothermic than bromide'

Question 16 (c)

This ionic equation proved to be very challenging. Instead of using the ammonium ion, the majority used ammonium chloride and so found it difficult to score.

- (c) Write an **ionic** equation to show why aqueous solutions of ammonium chloride are acidic. State symbols are not required.



ResultsPlus
Examiner Comments

This was a common wrong answer where the candidate has incorrectly reacted the two ions together.

- (c) Write an **ionic** equation to show why aqueous solutions of ammonium chloride are acidic. State symbols are not required.

(1)



ResultsPlus
Examiner Comments

This correct answer was seen very infrequently.

(c) Write an **ionic** equation to show why aqueous solutions of ammonium chloride are acidic. State symbols are not required.

(1)



The presence of H_3O^+ make the solutions acidic.



ResultsPlus
Examiner Comments

This detailed answer that showed the ammonium ion reacting with water was an acceptable correct answer.

Question 17 (a)

This question tested the understanding of the reactions of carbonyl compounds. Whilst most candidates could correctly identify structure A, those of B and C proved to be more challenging. The quality of the drawings was also varied with missing hydrogens and pentavalent carbons occasionally seen. There were also several skeletal and structural formulae, despite displayed being emboldened in the question.

17 This question is about carbonyl compounds.

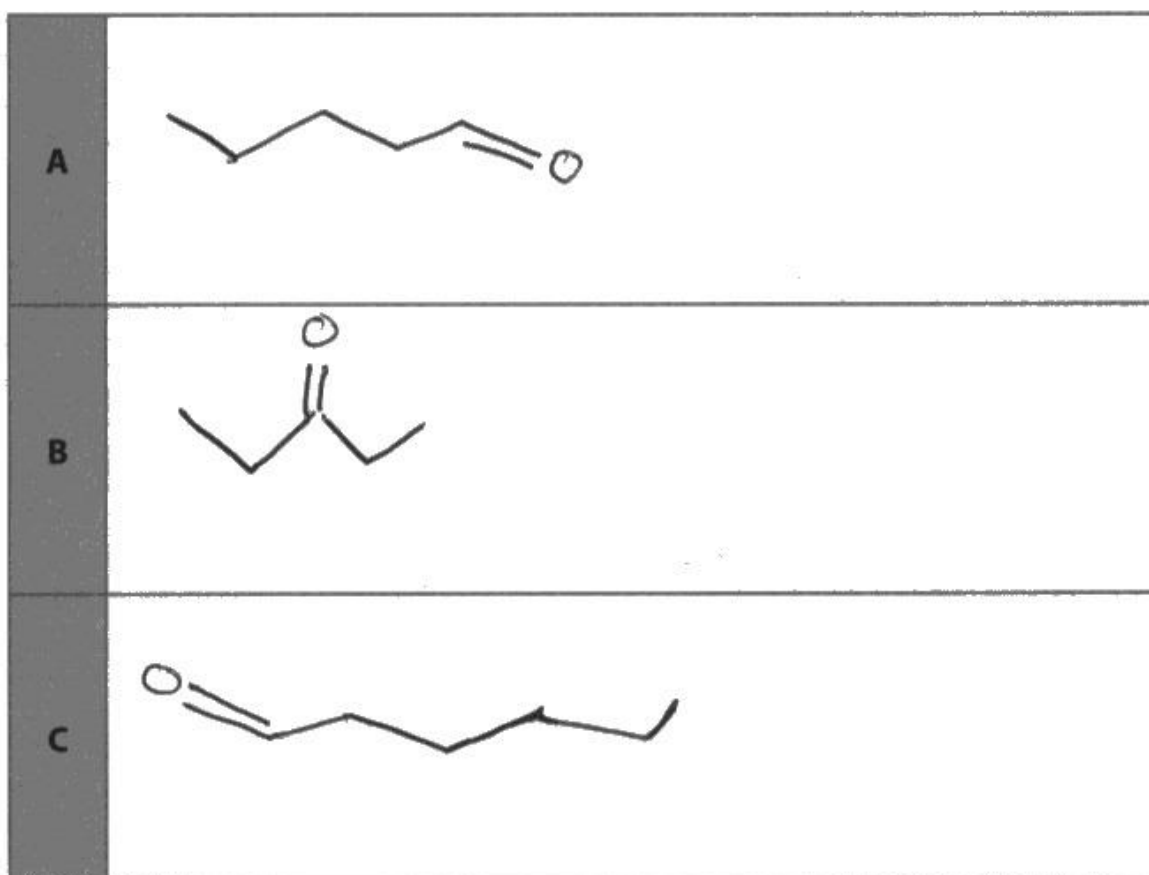
- (a) Three carbonyl compounds, **A**, **B** and **C**, are **straight-chain** structural isomers, with the formula $C_5H_{10}O$.

Only isomer **A** reacts with Tollens' reagent to give a silver mirror.

Only isomer **B** reacts with iodine in the presence of alkali to produce pale yellow crystals.

Draw the **displayed** structures of these three isomers.

(3)





This candidate clearly understood the chemistry for reaction A but did not follow the instructions and drew skeletal, instead of displayed structures.



When drawing organic compounds make sure you are giving the type of structure required in the question.

17 This question is about carbonyl compounds.

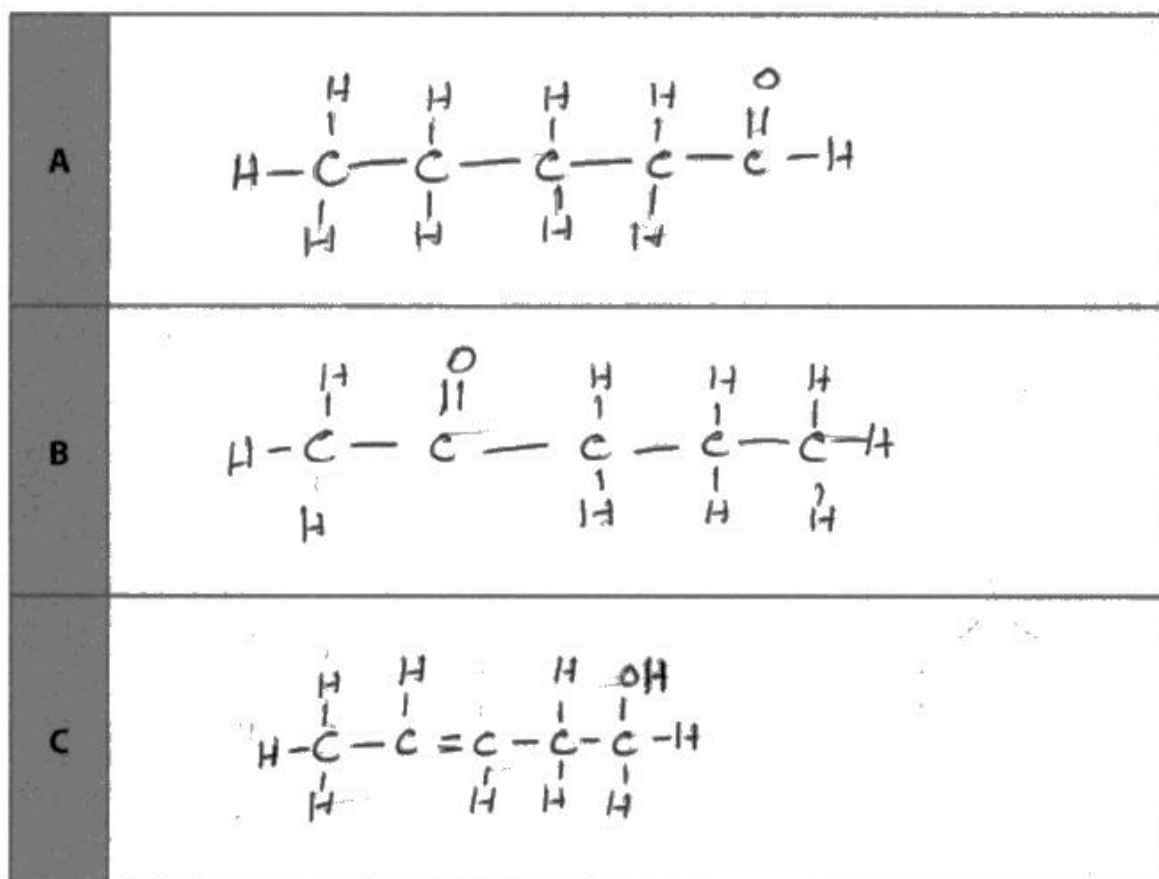
- (a) Three carbonyl compounds, **A**, **B** and **C**, are straight-chain structural isomers, with the formula $C_5H_{10}O$.

Only isomer **A** reacts with Tollens' reagent to give a silver mirror. *Aldehyde*

Only isomer **B** reacts with iodine in the presence of alkali to produce pale yellow crystals. *methyl ketone*

Draw the **displayed** structures of these three isomers.

(3)



ResultsPlus
Examiner Comments

Here there are two well drawn, correct, displayed structures for A and B. However, C proved to be the most challenging and many incorrect answers included alcohol or alkene functional groups.

Question 17 (b)(i)

The naming of this hydroxynitrile proved to be very challenging. Some candidates who correctly identified the two groups in the molecule chose the wrong stem and 2-hydroxypropanenitrile was occasionally seen. Others got confused with other nitrogen containing groups and amines and amides were also noted as incorrect answers.

(b) Another carbonyl compound, propanal, reacts with HCN in the presence of KCN to form a racemic mixture of two optical isomers of $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$.

(i) Give the IUPAC name for $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$.

(1)

1-hydroxypropenenitrile



ResultsPlus
Examiner Comments

This candidate has made two mistakes. The position of the hydroxy group is wrong as is the number of carbon atoms in the molecule.



ResultsPlus
Examiner Tip

Remember when naming nitriles, the stem includes the carbon attached to the N.

(b) Another carbonyl compound, propanal, reacts with HCN in the presence of KCN to form a racemic mixture of two optical isomers of $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$.

(i) Give the IUPAC name for $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$.

(1)

2-propanol-1-cyanide



ResultsPlus
Examiner Comments

Despite cyanides not being included in IUPAC nomenclature, this incorrect answer was seen regularly.

(b) Another carbonyl compound, propanal, reacts with HCN in the presence of KCN to form a racemic mixture of two optical isomers of $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$.

(i) Give the IUPAC name for $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$.

(1)

2-hydroxy butanenitrile



ResultsPlus
Examiner Comments

This correct name scored the mark.

Question 17 (b)(ii)

Whilst most candidates had a good understanding of how the isomers could be distinguished, a lack of precision prevented them from scoring marks.

- (ii) Describe how you could distinguish between pure samples of the two optical isomers.

(1)

Which direction they turn in, clockwise or anti-clockwise.



ResultsPlus
Examiner Comments

This candidate has the right idea, but they have not mentioned plane polarised light so no mark.

- (ii) Describe how you could distinguish between pure samples of the two optical isomers.

(1)

By rotation of plane polarised light.



ResultsPlus
Examiner Comments

Here the candidate has mentioned plane polarised light, but they have not talked about different rotation, so no mark awarded.

- (ii) Describe how you could distinguish between pure samples of the two optical isomers.

(1)

they would rotate the plane of plane polarised light ~~at~~ to equal degrees but in opposite directions



ResultsPlus
Examiner Comments

This is a fully correct answer.

Question 17 (b)(iii)

Many candidates gave an answer based on simple recall regarding nucleophilic substitution reactions, rather than the actual reaction taking place and the planar nature of a carbocation was a common wrong answer. Those who realised that the compound was planar did not always score the mark as they were not specific about its position. However, almost all candidates understood that the nucleophile could attack on either side.

(iii) Explain, with reference to the reaction mechanism, why this reaction produces a racemic mixture.

(2)

The carbocation formed by propanal is a trigonal planar. The nucleophile can attack the C with from either top or bottom, resulting in the formation of equal amounts of both isomers. Thus racemic mixture is formed.



ResultsPlus
Examiner Comments

Here the candidate is confused with nucleophilic substitution reactions and the formation of a carbocation being planar. This is incorrect so only 1 mark scored.

(iii) Explain, with reference to the reaction mechanism, why this reaction produces a racemic mixture.

(2)

Propanal is a planar compound, so the nucleophile CN^- can attack the carbonyl from both above and below. This will result in a racemic mixture as it does not rotate the plane of polarised light.



ResultsPlus
Examiner Comments

Here the candidate appreciates the propanal is planar but they do not say it about the $\text{C}=\text{O}$, so only 1 mark scored.

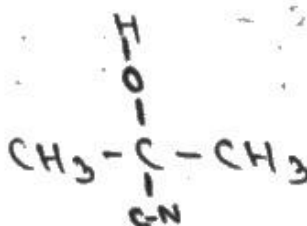
Question 17 (c)(i)

Most achieved this mark by drawing a correct skeletal or partial skeletal formula.

- (c) (i) Propanone, an isomer of propanal, also reacts with HCN in the presence of KCN.

Draw the **skeletal** formula of the product of this reaction.

(1)

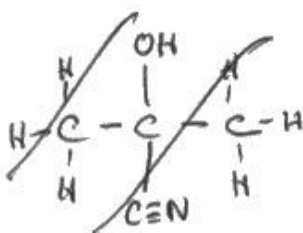


Despite skeletal being emboldened in the question some candidates drew a displayed formula and so did not score.

- (c) (i) Propanone, an isomer of propanal, also reacts with HCN in the presence of KCN.

Draw the **skeletal** formula of the product of this reaction.

(1)



This was the most common scoring answer that was an allow on the mark scheme. Note that many candidates who answered this question successfully drew the displayed structure first.

- (c) (i) Propanone, an isomer of propanal, also reacts with HCN in the presence of KCN.

Draw the **skeletal** formula of the product of this reaction.

(1)



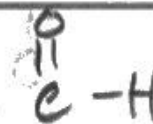
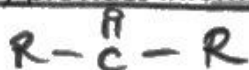
ResultsPlus
Examiner Comments

This fully correct skeletal formula was only rarely seen.

Question 17 (d)(i)

This was surprisingly poorly answered by most candidates. There was often confusion with IR spectra and proton NMR. Some of the carbonyl environments had multiple C atoms in the structures drawn, but the relevant C needed to be identified to score the mark. Often the quoted chemical shift was outside the permitted range too.

(d) ^{13}C NMR spectroscopy provides information about the structures of propanal and propanone.



(i) Identify the chemical shift range and carbon environment of **one** peak you would expect to see in **both** spectra.

(1)

Chemical shift range	Carbon environment
$1.8 - 2.9$ $198 - 222$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{C}-\text{C} \end{array}$



ResultsPlus
Examiner Comments

This candidate has got the correct chemical shift range but has not specified the carbon atom, so no mark was scored.



ResultsPlus
Examiner Tip

When using the data book make sure you are using the information accurately.

Question 18

Those candidates who had a good understanding of the reactions of ethanoyl chloride scored well on this question. Most gave fully correct equations for the three reactions scoring IP1, 4, 5 and 6. However, IP2 and IP3 were seen less frequently as candidates were often unable to note the similarities in the three reactions.

***18** Compare and contrast the reactions of ethanoyl chloride with water, with ethanol and with ammonia.
Refer to the structural features of the molecules that determine the type of reaction. Identify the products of the reactions. You may include equations in your answers.

(6)

Ethanoyl chloride with water would produce ethanoic acid. ~~Ethanoyl chloride with ethanol~~ ^{Ammonia} ~~would produce Ethanol with water~~ would produce an amine. All of these reactions take place at room temperature. Ethanoyl chloride with ethanol would produce an ester.



ResultsPlus
Examiner Comments

This candidate has only a limited understanding of the reactions of ethanoyl chloride and only scored a mark for the reaction with water to produce a carboxylic acid.



ResultsPlus
Examiner Tip

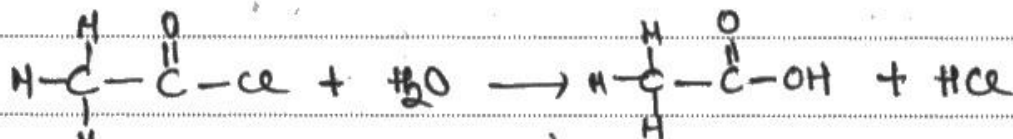
Learn the organic reactions as described in the specification.

- *18** Compare and contrast the reactions of ethanoyl chloride with water, with ethanol and with ammonia.
Refer to the structural features of the molecules that determine the type of reaction.
Identify the products of the reactions. You may include equations in your answers.

(6)

I Water :-

Equation :-



Carboxylic acid is formed as ^{main} products.

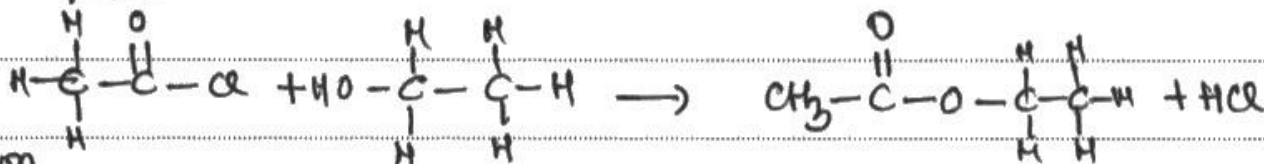
Conditions = rtp.
of reaction

type = ~~Condensation~~ Condensation.

II

I Ethanol :-

Equation :-



Reaction

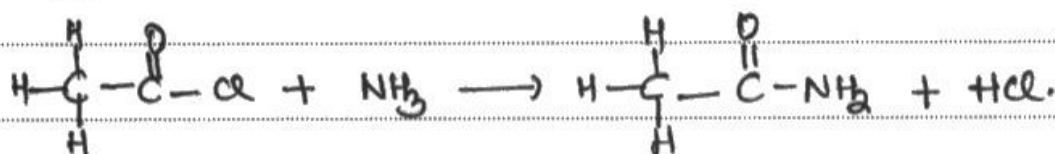
type = Esterification. Since C-Cl and O-H bond breaks and C-O and H-Cl bond forms

Condition = rtp

Product = ethyl ethanoate.

☐ With ammonia :-

Equation :-



of reaction Nucleophilic substitution

Type :- Condensation since a partially positively charged carbon atom of ethanoyl chloride attacked by lone pair on :NH_3 .

Product :- ethyl amide.

Condition :- rtp.

Similar

Similarity is 3 of the reaction :-
the reactions.

- All of these occur at rtp.
- HCl is always produced as common product.



ResultsPlus
Examiner Comments

This candidate has a good understanding of the reactions of ethanoyl chloride and scored IP1, 3, 4, 5, and 6.

Question 19 (a)

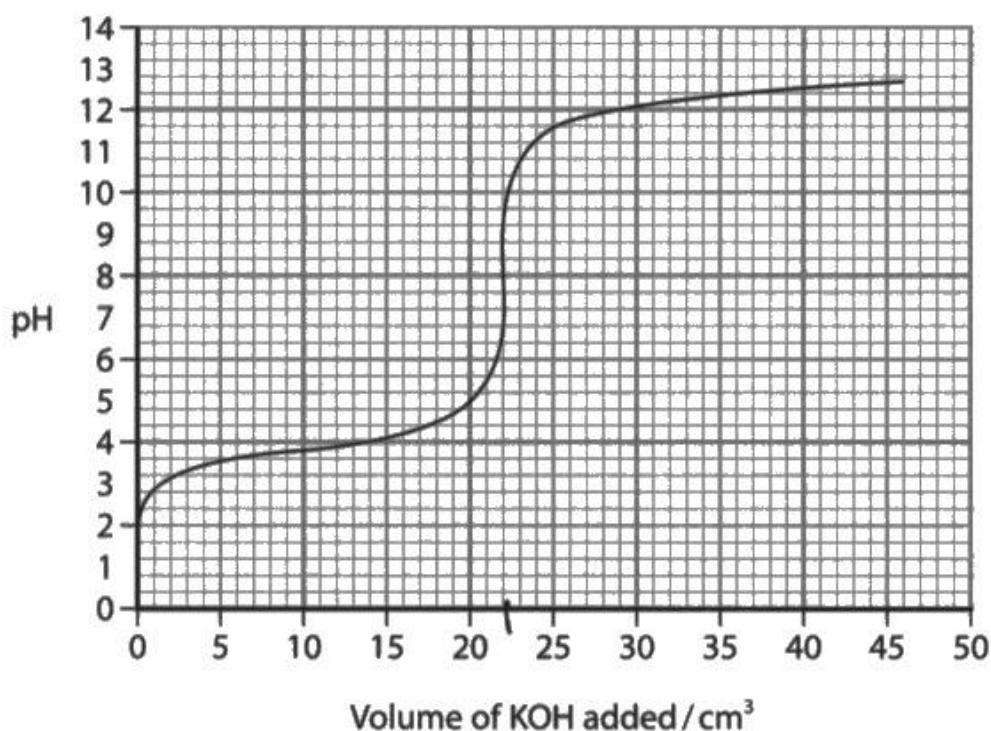
In ai, most candidates were able to give a correct equation, but the use of a titration curve to determine the concentration of a solution in aii was more challenging. Although 22cm^3 was often identified as the volume of KOH needed for neutralisation, many candidates used the final volume of 46cm^3 which indicated they did not understand the pH curve correctly.

In aiii all three possible routes seemed equally popular and most candidates were able to calculate the K_a correctly. Some quoted $\text{pH} = \text{p}K_a$ but picked an inappropriate pH such as 8 or 13 but managed to score transfer error marks without seeming to have a real grasp of what they were calculating.

19 This question is about methanoic acid and propanoic acid.

- (a) A student carried out a titration to find the concentration of an aqueous solution of potassium hydroxide.

25.00 cm³ of 0.150 mol dm⁻³ aqueous methanoic acid was pipetted into a conical flask. Potassium hydroxide was added from a burette while measuring the pH. The titration curve is shown.



- (i) Complete the equation for the reaction taking place in this titration. State symbols are not required.



(1)

- (ii) Calculate the concentration of the potassium hydroxide solution, using your equation in (i) and the titration curve.

ratio, 1:1, 22 cm³ needed.

(2)

Moles needed = ~~25 x 0.150~~ moles of the HCOOH
 $25 \times 0.150 \times 10^{-3} = 3.75 \times 10^{-3}$

conc $n = CV$ $C = \frac{n}{V} = \frac{3.75 \times 10^{-3}}{(22 / 1000)} = 0.17 \text{ mol dm}^{-3}$

(iii) Use the titration curve to determine a value for the acid dissociation constant, K_a , of methanoic acid.

(3)

~~$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$~~ 2 pH at 0 volume of KOH added.

~~$10^{-2} = 10^{-2} > 0.01 \text{ mol dm}^{-3} \text{ of } H_3O^+$~~

$[H_3O^+] = [HCOO^-]$

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = \frac{[H_3O^+]^2}{[HCOOH]}$$

$$K_a = \frac{(0.01)^2}{0.01} = 6.67 \times 10^{-4} \text{ mol dm}^{-3}$$



ResultsPlus
Examiner Comments

This is a fully correct answer where the candidate has used the alternative method 2 to calculate K_a .

Question 19 (b)

This type of buffer calculation was well understood by the majority and even those who found it more challenging were often able to score 1 mark for the calculation of hydrogen ion concentration. For some, the final answer was often quoted as ratio of salt: acid, rather than acid: salt as stated in the question, possibly as the version of Henderson-Hasselbach equation they used had the ratio of [salt]/[acid].

- (b) A student prepared a buffer by mixing together equimolar aqueous solutions of propanoic acid, CH₃CH₂COOH, and sodium propanoate, CH₃CH₂COONa.

The acid dissociation constant, K_a , for propanoic acid is $1.3 \times 10^{-5} \text{ mol dm}^{-3}$.

Calculate the volume ratio of propanoic acid to sodium propanoate needed to produce a buffer solution with a pH of 4.6

(2)

$$[H^+] = 10^{-4.6} = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[acid] = 4.25 \times 10^{-5}$$

$$[acid] = 4.25 \times 10^{-5} \text{ mol dm}^{-3}$$



ResultsPlus
Examiner Comments

Although unable to do the buffer calculation this candidate scored a mark for the calculation of the hydrogen ion concentration.

- (b) A student prepared a buffer by mixing together equimolar aqueous solutions of propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, and sodium propanoate, $\text{CH}_3\text{CH}_2\text{COONa}$.

The acid dissociation constant, K_a , for propanoic acid is $1.3 \times 10^{-5} \text{ mol dm}^{-3}$.

Calculate the volume ratio of propanoic acid to sodium propanoate needed to produce a buffer solution with a pH of 4.6

(2)

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$4.6 = 4.886 + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$-0.286 = \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\log_{10} \frac{[\text{salt}]}{[\text{acid}]} = -0.286$$

$$\frac{[\text{salt}]}{[\text{acid}]} = 10^{-0.286}$$

$$\frac{[\text{acid}]}{[\text{salt}]} = \frac{1}{0.5176} = 1.931968317$$

$$\begin{aligned} \frac{n}{V_a} \times \frac{n}{V_s} &= \frac{n}{V_a} \times \frac{V_s}{V} \\ &= \frac{V_s}{V_a} \end{aligned}$$

$$\frac{\frac{n}{V_a}}{\frac{n}{V_s}} = 1.931968317$$

$$\frac{V_s}{V_a} = 1.931968317$$

$$\frac{V_a}{V_s} = 0.517$$



ResultsPlus
Examiner Comments

Here the candidate has used the Henderson-Hasselbach equation, but they have got the ratio the wrong way round so only 1 mark is scored.



ResultsPlus
Examiner Tip

When performing any chemical calculation, always check the details required in the question.

- (b) A student prepared a buffer by mixing together equimolar aqueous solutions of propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, and sodium propanoate, $\text{CH}_3\text{CH}_2\text{COONa}$.

The acid dissociation constant, K_a , for propanoic acid is $1.3 \times 10^{-5} \text{ mol dm}^{-3}$.

Calculate the volume ratio of propanoic acid to sodium propanoate needed to produce a buffer solution with a pH of 4.6

(2)

$$\text{pH} = 4.6$$

$$[\text{H}^+] = 10^{-4.6} = 2.51 \times 10^{-5}$$

$$1.3 \times 10^{-5} = \frac{2.51 \times 10^{-5} \times [\text{CH}_3\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

$$\frac{[\text{CH}_3\text{CH}_2\text{COOH}]}{[\text{CH}_3\text{CH}_2\text{COO}^-]} = \frac{2.51 \times 10^{-5}}{1.3 \times 10^{-5}} = 1.93$$

The ratio of $\text{CH}_3\text{CH}_2\text{COOH}$ to $\text{CH}_3\text{CH}_2\text{COONa}$ is
1.93



ResultsPlus
Examiner Comments

Although they have not given the complete ratio an answer of just 1.93 is an allow on the mark scheme so 2 marks scored.

Question 20

Nearly all candidates could use the information in the question to deduce the correct orders of reaction, the rate equation and the units of k . Of those who got the orders wrong, many successfully carried this error forward to score to full marks for the rate equation and units of k . Occasionally k was omitted from the rate equation and there were some arithmetic errors, but these were rare.

However, in part b many candidates produced a S_N2 mechanisms even though their calculated rate equation did not include hydroxide ions. Furthermore, often the S_N2 mechanism showed no transition state, or an incorrect one. Those who did produce a S_N1 mechanism sometimes missed out the bromide leaving group so lost a mark and often the precision of the arrows was not good enough either.

- (iii) Calculate the rate constant for Experiment 1.
Include units in your answer.

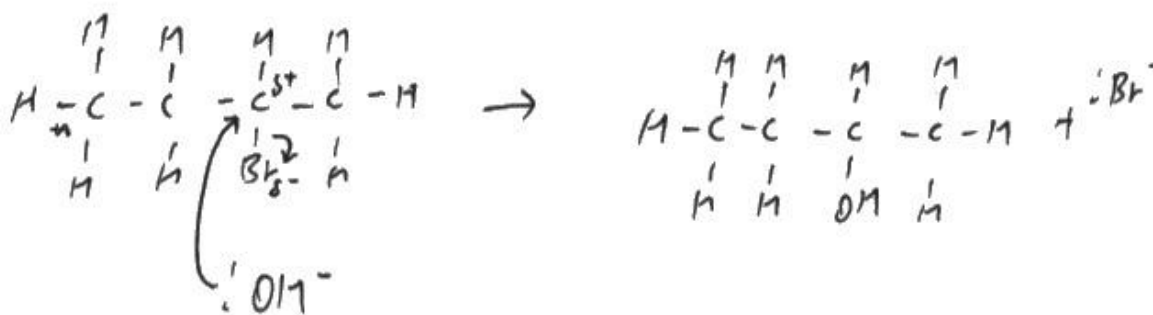
(2)

$$1.01 \times 10^{-3} = k \times 0.1$$

$$k = 0.0101 \text{ s}^{-1}$$

- (b) Draw the mechanism for this reaction that is consistent with your rate equation.
Include curly arrows, and any relevant dipoles and lone pairs of electrons.

(3)



ResultsPlus
Examiner Comments

Here the candidate has incorrectly drawn a S_N2 mechanism. The curly arrows are both correct, but they have missed out the transition state. Only 1 mark scored.

- (iii) Calculate the rate constant for Experiment 1.
Include units in your answer.

(2)

$$k = \frac{\text{Rate}}{[\text{CH}_3\text{CH}_2\text{CHBrCH}_3]}$$

$$k = \frac{1.01 \times 10^{-3}}{(0.100)} = 0.0101$$

Unit is

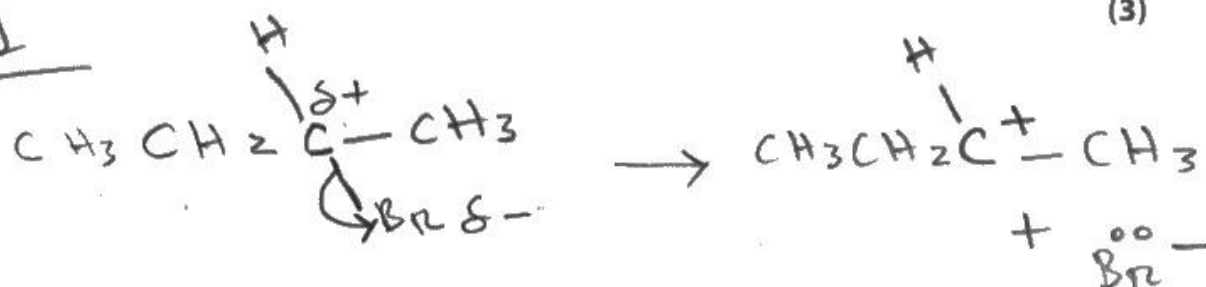
$$k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})}$$

$$\text{Unit is } \frac{1}{\text{s}} \text{ or } \text{s}^{-1}$$

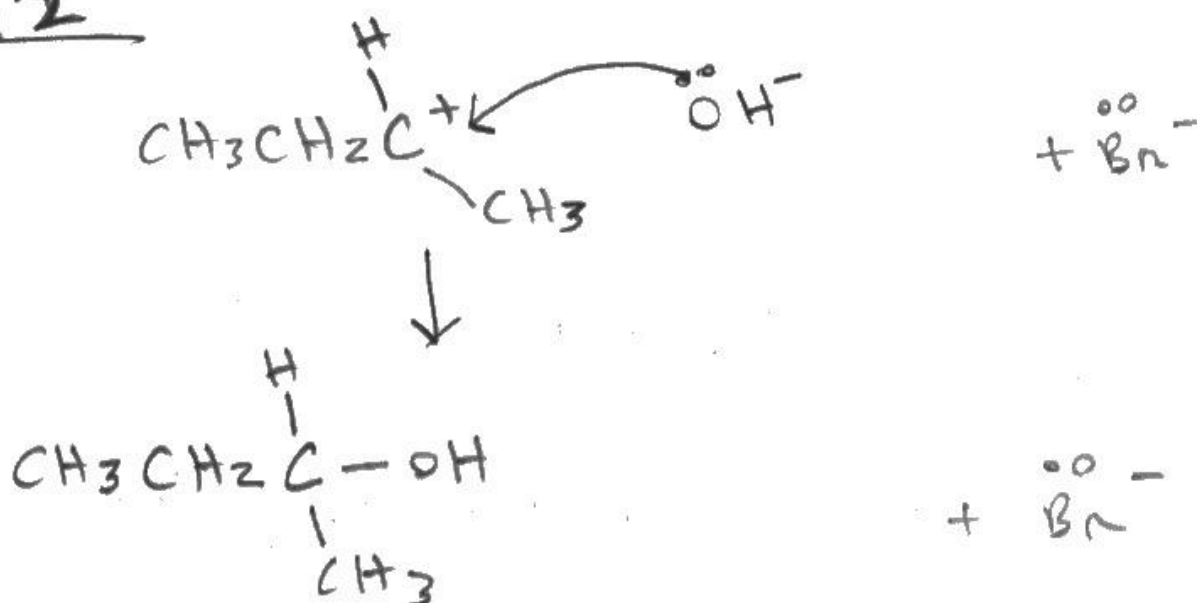
- (b) Draw the mechanism for this reaction that is consistent with your rate equation.
Include curly arrows, and any relevant dipoles and lone pairs of electrons.

(3)

Step 1



Step 2





This is a fully correct answer and scores full marks.

- (iii) Calculate the rate constant for Experiment 1.
Include units in your answer.

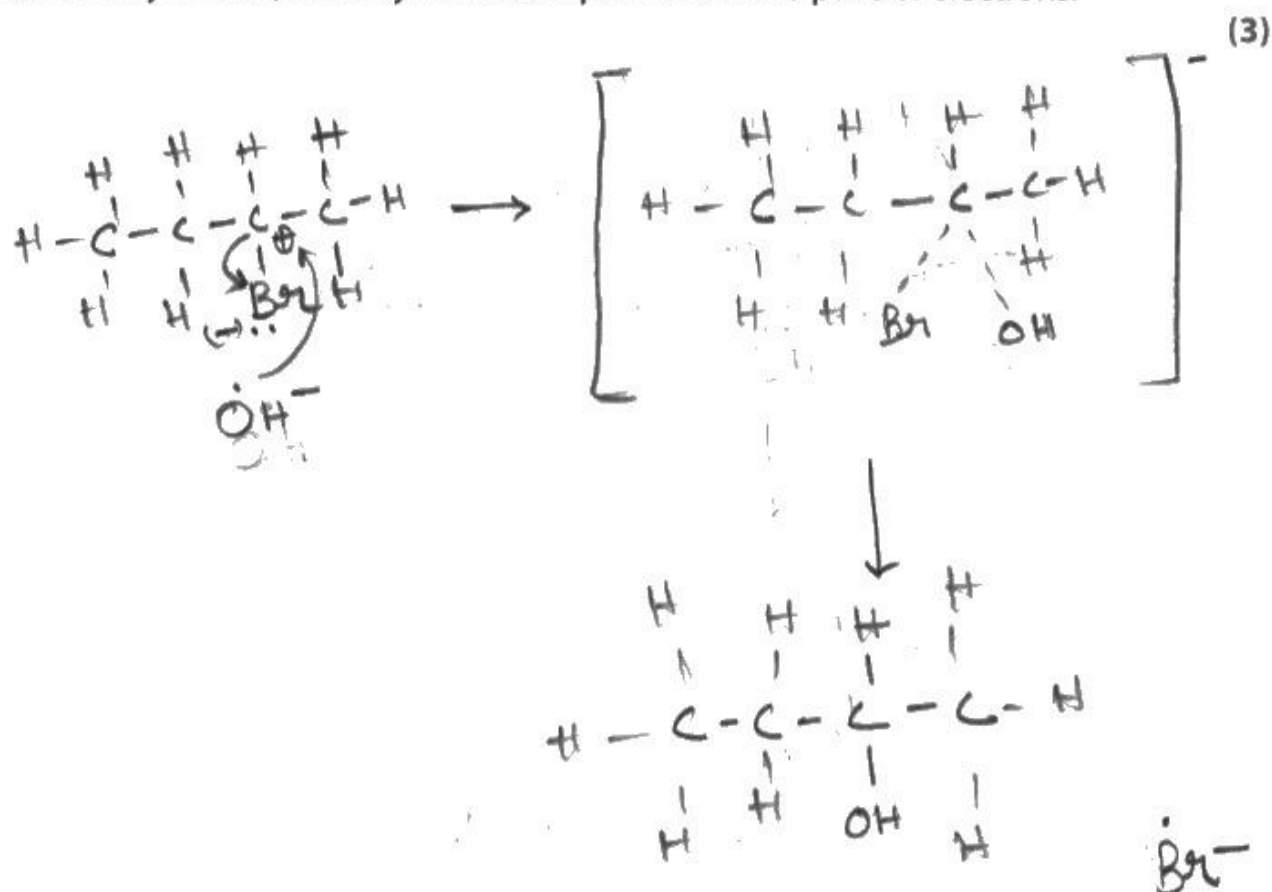
$$1.01 \times 10^{-3} = k [0.100] [0.100]^0$$

$$k = \frac{1.01 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}}{0.100 \text{ mol dm}^{-3}}$$

$k = 0.0101 \text{ s}^{-1}$

(2)

- (b) Draw the mechanism for this reaction that is consistent with your rate equation.
Include curly arrows, and any relevant dipoles and lone pairs of electrons.





Here the candidate has incorrectly drawn a S_N2 mechanism. The curly arrows are both wrong. The one from the OH does not come from a lone pair and the other should come from the bond, not the Br. However, the intermediate is correct.



Practise drawing mechanisms paying particular attention to the origin and direction of the curly arrows.

Question 21 (a)

Although there was a little confusion between enthalpy and entropy in (a)(i) and (a)(ii), most answers were correct or had one minor error. Common errors were not multiplying by 2 or 3 where necessary and mixing up negative signs. Some candidates also lost marks for incorrect units. In aiii, the majority calculated the temperature correctly, with the most common error not converting the entropy and enthalpy to the same energy unit.

(iii) Calculate the temperature at which this reaction becomes feasible, using your answers from (a)(i) and (a)(ii).

(3)

$$\begin{aligned}\Delta S_{\text{total}} &> 0 \\ \Delta S_{\text{sur}} + \Delta S_{\text{sys}} &> 0 \\ -\frac{\Delta H}{T} &> -\Delta S_{\text{sys}} \\ T &> \frac{\Delta H}{\Delta S_{\text{sys}}} \\ T &> \frac{+492.7}{542.9} = T > 0.91 \text{ K}\end{aligned}$$



ResultsPlus
Examiner Comments

This candidate failed to multiply the enthalpy change by 1000 to convert kJ to J. This was a common error and scored 2/3.

21 This question is about oxides of iron.

(a) The equation for the reduction of iron(III) oxide by carbon is shown.



Some data relating to this reaction are shown.

Substance	Fe_2O_3	C	Fe	CO
$\Delta_f H^\circ / \text{kJ mol}^{-1}$	-824.2	0	0	-110.5
$S^\circ / \text{JK}^{-1} \text{mol}^{-1}$	87.4	5.7	27.3	197.6

(i) Calculate the standard enthalpy change, $\Delta_r H^\circ$, for the reduction of iron(III) oxide by carbon.

$$\Delta_r H^\circ = \sum \Delta_f H^\circ - \Delta_r H^\circ \quad (2)$$

$$= (-824.2) + 3 \times 0 - (2 \times 0 - 3 \times 110.5)$$

$$= -492.7 \text{ kJ mol}^{-1}$$

$$\Delta_r H^\circ = \Delta_f H^\circ - \Delta_f H^\circ \quad \Delta_f H^\circ \text{ of p} - \Delta_f H^\circ \text{ of r}$$

$$= -824.2$$

$$= -(110.5 \times 3) - (-824.2)$$

$$\Delta_r H^\circ = (-110.5 \times 3) - (-824.2) = +492.7 \text{ kJ mol}^{-1}$$

(ii) Calculate the entropy change, ΔS_{system} , for this reaction.

$$\Delta S_{\text{sys}} = \sum S_p - \sum S_r \quad (3)$$

$$= (2 \times 27.3 + 3 \times 197.6) - (87.4 + 3 \times 5.7)$$

$$= +542.9 \text{ JK}^{-1} \text{mol}^{-1}$$

- (iii) Calculate the temperature at which this reaction becomes feasible, using your answers from (a)(i) and (a)(ii).

(3)

$$\begin{aligned}\Delta S_{\text{total}} &= 0 \\ 0 &= \Delta S_{\text{sys}} - \frac{\Delta H}{T} \\ -\frac{\Delta H}{T} &= -542.9 \\ T &= \frac{-(+492.73 \times 10^3)}{-542.9} = 908 \text{ K}\end{aligned}$$



ResultsPlus
Examiner Comments

This is a completely correct answer so scores full marks.

Question 21 (b)(i)

Despite being asked to explain why the reaction would be feasible at any temperature several candidates simply stated that the total entropy change would be positive so scored no marks. Some others only included information about the entropy change of surroundings but nothing about the entropy change of the system so also failed to score.

(b) The equation for the reduction of iron(III) oxide by carbon monoxide is shown.



The entropy change, $\Delta S^\ominus_{\text{system}}$, for this reaction is $+15.2 \text{ J mol}^{-1} \text{ K}^{-1}$.

(i) Explain why the reaction should be feasible at any temperature.

(2)

Since ΔH is exothermic so $\Delta S_{\text{surroundings}}$ is always positive. ΔS_{system} is also positive so ΔS_{total} at any temperature is positive, so reaction feasible.



This is an example of a fully correct answer as the candidate has explained clearly why the reaction is feasible at any temperature.

(b) The equation for the reduction of iron(III) oxide by carbon monoxide is shown.



The entropy change, $\Delta S_{\text{system}}^\ominus$, for this reaction is $+15.2 \text{ J mol}^{-1} \text{ K}^{-1}$.

(i) Explain why the reaction should be feasible at any temperature.

(2)

ΔS_{surr} is always positive as the reaction is exothermic. So ΔS_{total} is also always positive at all temperatures.



ResultsPlus
Examiner Comments

Here the candidate failed to mention the entropy change of the system so scored no marks. This was a common wrong answer.



ResultsPlus
Examiner Tip

When answering entropy questions candidates should comment on the contribution made by both the entropy of the system and the entropy of the surrounding to the total entropy change.

Question 21 (b)(ii)

The majority of candidate were familiar with this type of question and the answers seemed well rehearsed. The most common error was to miss out that the entropy change of the system hardly changes with temperature.

For this reaction ΔS_{total} will always be positive and the reaction will be feasible at any temperature.
(ii) Explain how an increase in temperature would affect ΔS_{total} of this reaction. *ΔS_{surr} will be positive for all values of temperature.*
No calculation is required.

(3)

Increase temperature would decrease the $\Delta S_{\text{surrounding}}$ as $\Delta S_{\text{surrounding}} = \frac{-\Delta H}{T}$

We know $\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$.

$\therefore \Delta S_{\text{total}}$ would decrease, but remain positive.



ResultsPlus
Examiner Comments

Here the candidate failed to mention the entropy change of the system hardly changes with temperature and so scored 2 marks.

- (ii) Explain how an increase in temperature would affect $\Delta S_{\text{total}}^{\ominus}$ of this reaction.
No calculation is required.

(3)

Ans: As temperature increases, $\Delta S_{\text{surroundings}}^{\ominus}$ decreases and become less positive.

$$\Delta S_{\text{surroundings}}^{\ominus} = - \frac{\Delta H}{T}$$

• $\Delta S_{\text{system}}^{\ominus}$ does not change significantly with temperature

• so $\Delta S_{\text{total}}^{\ominus}$ must decrease and be less positive.



ResultsPlus
Examiner Comments

Here the candidate has fully explained the effect of increasing the temperature on the total entropy change so scored 3 marks.

Question 21 (c)(iii)

Although there were some excellent answers, in general this question proved to be more challenging than expected. A number did not understand that there was repulsion between a negative ion and an incoming electron and there was also confusion with ionisation energies.

(iii) Suggest why the second electron affinity of oxygen is positive.

(2)

It needs energy that is ^{making it} ~~exothermic~~ endothermic in order to ^{completely} remove electrons from oxygen from a different energy level thus the second electron affinity of oxygen is positive.



ResultsPlus
Examiner Comments

This candidate is confusing electron affinity with ionisation, so no marks scored.

(iii) Suggest why the second electron affinity of oxygen is positive.

(2)

It will require more energy to overcome the repulsive forces between the electrons on the orbit and the added electron to be added.



ResultsPlus
Examiner Comments

Here the candidate appreciates there is repulsion between electrons, but they have not mentioned the negative ion so only 1 mark scored.

(iii) Suggest why the second electron affinity of oxygen is positive.

(2)

The second electron affinity of oxygen is endothermic. ~~As High~~ O^- is O^{2-} is more stable than O^- , so O^- loses an electron more readily. The reaction is thermodynamically unstable.



ResultsPlus
Examiner Comments

Just saying the electron affinity was endothermic was quite a common incorrect answer. No marks scored.

(iii) Suggest why the second electron affinity of oxygen is positive.

(2)

Energy is required to overcome the electrostatic repulsive forces between the negatively charged O^- ion and electron.



ResultsPlus
Examiner Comments

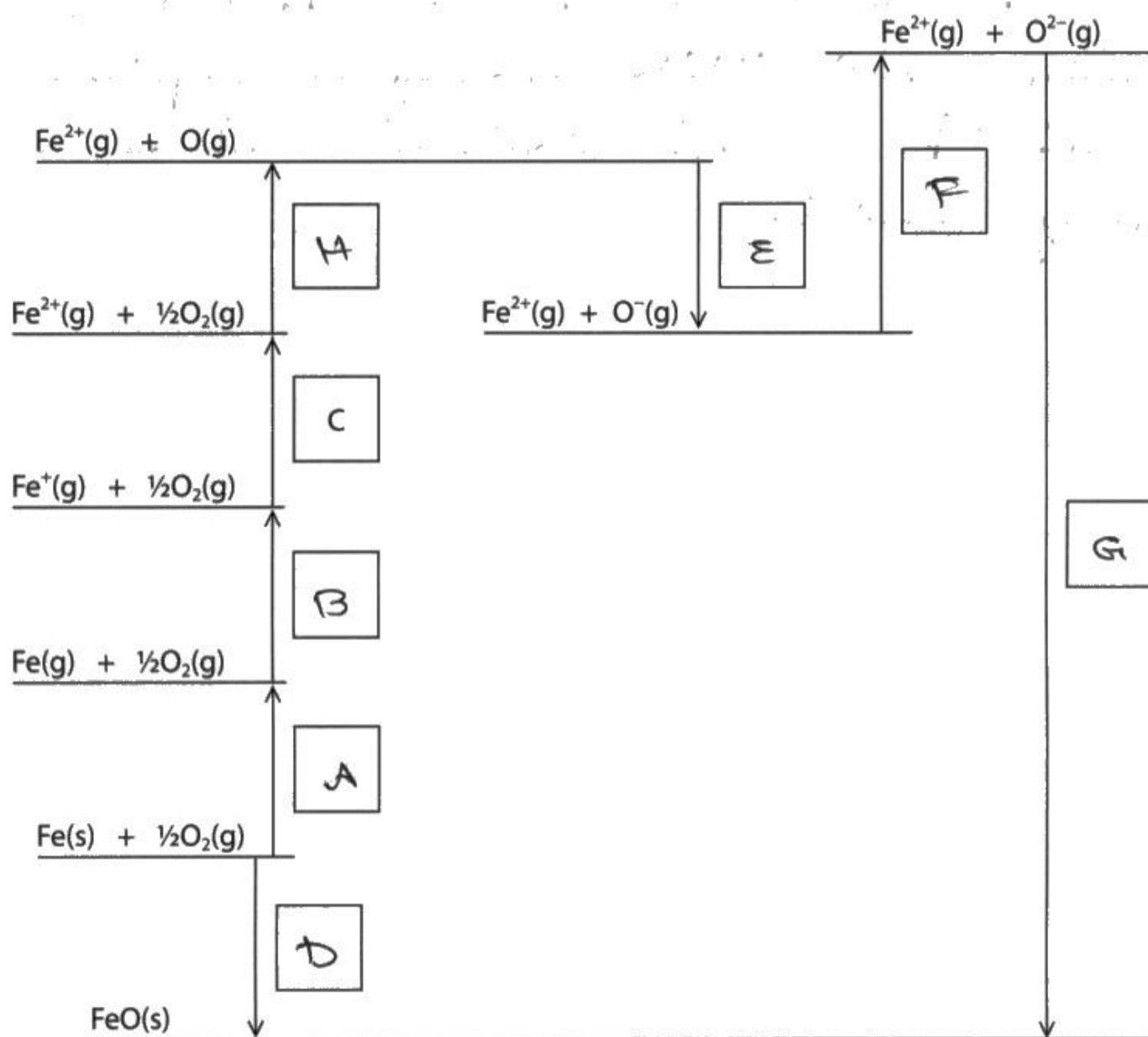
A fully correct answer as both scoring points are made.

Question 21 (c)(i)-(ii)

Candidates seemed very familiar with Born-Haber cycles, and most were able to correctly fill in the boxes. However, the calculation was less successful as many struggled to rearrange the data correctly. In addition, there were elementary arithmetic errors and miscopying of values which should have been avoided with careful checking.

- (i) Complete the Born-Haber cycle by putting letters in the boxes to label the energy changes.

(3)



- (ii) Calculate the value for second ionisation energy of iron, C.

(2)

$$\begin{aligned}
 G - F &= D - (A + B + C) \\
 -3920 - 498 &= -242 - (416 + 459 + C) \\
 -4418 &= -1444 - C \\
 \therefore C &= +3241 \text{ kJ mol}^{-1}
 \end{aligned}$$



This candidate has correctly filled in the boxes but has been unable to use the data to calculate the second ionisation energy. The candidate scored 3 for ci and 0 for part cii.



Practise using Born – Haber cycles to calculate any enthalpy change, not just lattice energies.

Paper Summary

Based on their performance in this paper, candidates should:

- read the question carefully and make sure they are answering the question that has been asked
- practise writing structural, displayed and skeletal formulae for a wide range of organic compounds
- practise organic mechanisms, paying particular attention to the origin and destination of the curly arrow
- check explanations carefully to ensure that they answer the points outlined in the question
- avoid using the terms 'bigger' or 'smaller' when answering questions involving enthalpy or entropy changes. Instead use phrases such as more exothermic
- revise exothermic and endothermic reactions relating them to the correct signs and temperature changes.